LIFE CYCLE ASSESSMENT OF BIODIESEL FROM *CANNABIS SATIVA L.* FOR TRANSPORT FUEL IN THE UK

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Abstract

The climate change impact potential of biodiesel from hemp (*Cannabis Sativa L.*) has been investigated through life cycle assessment based on data collected from a case study farm in Essex, England. Hemp biodiesel was found to have a climate change impact potential of 0.137 kg CO_2-e MJ^{-1}. However, this result was significantly reduced to -0.684 kg CO_2-e MJ^{-1} when full accounting of CO_2 in the life cycle system, including absorption of carbon dioxide in the hemp straw, was used. The application of nitrogen fertilisers made the largest contribution (0.0678 kg CO_2-e MJ^{-1}) from a single process to the overall climate change impact potential. When the climate change impacts were allocated between the hemp biodiesel and its co-products (hemp straw, hemp seed presscake, glycerol, and potassium phosphate salts), the climate change impact of hemp biodiesel was inside the range of results from other studies (0.005–0.060 kg CO_2-e MJ^{-1}). The method of allocating impacts of a system according to the carbon contents of the co-products was found to generate similar results to the allocation methods which used mass and energy to apportion impacts between the products. Improvements in the hemp seed yield and oil content to 1200 kg ha^{-1} and 37.5 % respectively combine to reduce the climate change impact potential by 20.5 % to 0.117 kg CO_2-e MJ^{-1}. Experimental tests confirmed the similarity of methods of describing biodiesel-petroleum diesel blends by the mass, energy and volume proportions of biodiesel that they contain. This research extends the range of life cycle assessments of biodiesel produced from oilseeds to include hemp. In addition, this research shows that changes in emissions of greenhouse gases caused by the production of hemp biodiesel occur in the agricultural and industrial sectors, not in the road transport sector, and highlights the potential of hemp straw for the absorption and storage of carbon dioxide to mitigate climate change and its consequences.

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Chapter 1

Introduction

1.1 Rationale

The world is experiencing climate change which is very likely the result of human activities (IPCC, 2007). Evidence suggests that anthropogenic emissions of greenhouse gases have a net warming effect on the global temperature which, if sustained, could cause serious damage to human health and ecosystems, at a considerable cost to humans (Stern, 2007). In the United Kingdom, the majority of the greenhouse gases emissions are from the combustion of fossil fuels for energy purposes, including energy for transport.

The transport sector alone accounted for 24.2 % of carbon dioxide emissions in 2007 (National Atmospheric Emissions Inventory, 2009) and this sector is now the target of governmental policy and legislation to encourage the reduction of greenhouse gas emissions. One key instrument introduced by the European Parliament (European Commission, 2003) and acted upon by the UK government (HM Government, 2004), promotes the inclusion of fuels from plant matter, known as biofuels, to substitute for the familiar petroleum-based fuels petrol and diesel. Bioethanol, fermented from plant sugars, can be blended with petrol while biodiesel, produced through esterification of oils or fats, is blended with, or completely substitutes for, diesel.

The properties of blends of biodiesels and petroleum diesels have been tested for fuels which meet the American fuel specifications (Tat and Van Gerpen, 2000; Yuan et al., 2004) but less research has been published on blends of European specification fuels. In particular, there is scant research literature on the gross heat of combustion (energy per unit mass) and energy density (energy per unit volume) of biodiesel-petroleum diesel fuels. Given that the EU legislation concerning the promotion of biofuels (European Commission, 2003) prescribes the measurement of biodiesel content in blended fuels by their energy content, whereas research and commercial practice use volume and mass blends, research is required on the relationships between mass, volume and energy blend proportions to ensure reliable conversions, and hence reliable accounting for reporting progress against policy targets.

Concerns over the ultimate sustainability and net contribution to climate change of these biofuels (The Royal Society, 2008) gave rise to the introduction of sustainability reporting requirements for fuel suppliers which are based on accounting of emissions across the full life cycle of the biofuel production chain (Bauen et al., 2008). Life cycle assessments of the environmental impacts of producing biofuels have been published in the academic literature (for example, Bernesson et al. (2004); Casas and Rieradevall i Pons (2005); Stephenson et al. (2008)), based on or linked to the established and standardised procedures for such studies (ISO, 2006a). Most of the studies conducted in Europe concern rapeseed oil, with some research on sunflower and minority oils although very little research on biodiesel from hemp oil.

The hemp plant is mainly grown for the fibre in its straw, yet it also produces a useful oilseed which can be used as the feedstock for biodiesel (Yang et al., 2010). Rapeseed, on the other hand, is an oilseed crop which produces less substantial quantities of a straw which is inferior in quality to that of hemp. Hemp straw has been used as a raw material for building blocks in industrial and domestic buildings (Hemp Technology Ltd., 2010) and as such can act as a store for carbon for the lifetime of the building. However, as yet no published research is available on the carbon storage potential of the hemp plant. Casas and Rieradevall i Pons (2005) reported in brief on their life cycle assessment of the environmental impacts of hemp biodiesel compared with petroleum diesel. Turunen and van der Werf (2006) assessed the life cycle impacts of growing hemp for fibre, but no life cycle assessment of hemp oil has yet been published, and this will be addressed in this thesis.

1.2 Aims

The aims of this thesis are:

1. to determine how the densities and energy contents of blends of European-specification biodiesel and petroleum diesel change according to the blend proportions
2. to determine how closely the mass, volume and energy proportions of biodiesel in a biodiesel-petroleum diesel fuel blend compare
3. to document the cultivation and harvesting of a hemp crop grown for both straw and seed
4. to document the gross heat of combustion of the parts of the hemp plant
5. to estimate the potential of the hemp crop for carbon storage
6. to evaluate the net climate change impact potential of producing biodiesel from hemp biodiesel grown in the UK, in the context of the Renewable Transport Fuels Obligation.

1.3 Objectives

The objectives of the research presented in this thesis were:

- to test the densities and energy contents of blends of biodiesel and petroleum diesel fuels (Chapter 3), to fulfil Aim 1
- to calculate mass, volume and energy blends proportions of blends of biodiesel and petroleum-diesel fuels using experimental data (Chapter 3), to fulfil Aim 2
- to collect data from a case study farm on the cultivation and harvesting of a dual-purpose hemp crop, grown for both straw and seed (Chapter 5), to fulfil Aim 3
- to conduct or commission laboratory tests of the energy and carbon contents of parts of the hemp plant, with supplementary tests as required to improve the accuracy of the energy and

carbon content results (Chapter 5), to fulfil Aim 4

- to combine results obtained from the case study farm and laboratory tests in order to calculate the carbon content of the hemp crop, and hence its potential for carbon storage (Chapter 5), to fulfil Aim 5
- to conduct an attributional life cycle assessment of hemp biodiesel, using energy, mass and carbon content allocation methods (Chapter 6), to fulfil Aim 6.

1.4 Thesis structure

Chapter 2 situates this thesis in the context of the UK and of the existing research literature, and provides details of biodiesel production processes. In Chapter 3, the descriptors that are used commercially and scientifically to describe blend proportions are investigated, and the energy content of blended biodiesel-diesel fuels is determined for various blends of diesel fuels. Chapter 4 sets out the procedures for life cycle assessment methodology and reviews assessments of biodiesels. Chapter 5 presents the collection of data on hemp agriculture in the UK and laboratory analysis methods and results for the energy and carbon contents of parts of the hemp plant. The life cycle assessment of hemp as a biodiesel feedstock is detailed in Chapter 6. Finally, the conclusions of this thesis are summarised in Chapter 7.

Chapter 2

Background context

This chapter provides an overview of the context for this thesis. The mechanism of climate change and its effects are briefly explained (Section 2.1). The current greenhouse gas emissions situation in the UK is presented with particular reference to energy supply and consumption, and the transport sector in particular (Section 2.2). Strategies which may reduce emissions from the road transport sector are presented (Section 2.3), and the use of alternative fuels is discussed in greater detail (Section 2.4). International and national policies to encourage the substitution of biofuels into the petroleum-dominated road transport fuel supply are presented (Section 2.5). Assessment methods to ascertain the contribution of biofuels towards sustainability are presented (Section 2.6). Finally, biodiesel is discussed in greater detail, including the following aspects: its production process, a survey of suitable feedstocks, the basic chemistry underlying the conversion process from fats and oils to biodiesels, and a description of the conversion process (Section 2.7).

2.1 Climate change

Although the global climate has changed greatly over historical and geological timescales, recent changes in the global climate over and above what would be expected from the historical record have been observed. These changes have been attributed to high levels of anthropogenic emissions of the six greenhouse gases: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs) and sulphurhexafluoride (SF_6). According to the findings of the Intergovernmental Panel on Climate Change, (IPCC, 2007, p. 37): "there is very high confidence that the global average net effect of human activities since 1750 has been one of warming, with a radiative forcing of +1.6 [+0.6 to +2.4] W m^{-2}." Emissions of greenhouse gases are measured in terms of their radiative forcing effect which is compared to the equivalent radiative forcing effect of a mass of CO_2, giving rise to a metric based in units of kg CO_2-e. Other units include MtC, or million tonnes of carbon, which corresponds to 3.664 Mt CO_2-e.

Global climate change is already manifesting in many ways, including (IPCC, 2007): changing weather patterns, with more frequent incidence of storms and heavy rains, increased snowmelt and glacier lake formation; climate-related changes in animal behaviour including earlier breeding, changes in algal, plankton and fish abundance and earlier fish migrations in rivers, while for humans the effects include excess heat-related deaths and changes in vectors of infectious diseases in Europe. The future effects of climate change on the UK might include the loss of low-lying land as sea levels rise, storm damage and increased immigration as populations are displaced from other countries (DTI, 2007b), as well as changes in agricultural cycles and climate suitability for crops (IPCC, 2007). The recent review on the economic implications of climate change mitigation concluded that the costs of acting immediately to mitigate climate change might amount to approximately 1 % of global GDP, whereas the direct costs of unmitigated climate change may reach 5–20 % of global GDP (Stern, 2007).

Given that current scientific evidence and understanding links global, anthropogenic climate change to increasing levels of greenhouse gases in the atmosphere, and that the climate change mechanisms may slow or even reverse under conditions of reduced greenhouse gas emissions, international treaties to reduce greenhouse gas emissions have been drawn up and agreed to. The Kyoto protocol (UNFCCC, 1997), ratified by 161 countries at the time of writing, specifies emissions limits for signatories. In signing up to the Kyoto Protocol (UNFCCC, 1997), the government of the United Kingdom agreed to reduce total greenhouse gas emissions 8 % from 1990 levels by 2012: from 775.6 million tonnes CO_2-equivalent to 713.6 million tonnes CO_2-equivalent (DETR, 2000). The Kyoto protocol covers emissions from UK territory but excludes emissions from international aviation and shipping.

The Kyoto protocol includes a number of suggested measures that countries can adopt, including implementing polices and measures to research, develop and promote the use of new and renewable forms of energy, and to limit and/or reduce emissions of greenhouse gases in all sectors. The EU Emissions Trading Scheme (EU ETS), in operation since January 2005, is a Europe-wide mechanism to limit emissions from large-scale operations by the trading of emissions quotas. The transport sector, which accounts for 30 % of the total GHG emissions in the EU, is the largest single sector that is not currently within the scope of the EU ETS, and is therefore an obvious target for policies to complement the ETS.

Carbon dioxide has been identified as the "most important anthropogenic greenhouse gas" (IPCC, 2007, p. 36) and accounts for over 85 % of greenhouse gas emissions from the UK (Fig. 2.1). The combustion of fossil fuels (natural gas, coal and crude oil) is the primary cause of global increases in CO_2 concentration. The intensive use of fossil fuels developed during the 18th century with the advent of coal-powered stationary steam engines in textile mills and in coal mines for pumping water out of coal mines (Bagwell and Lyth, 2002). Later on steam trains were developed to run on coal-fired boilers and at the turn of the 20th century road vehicles using liquid fossil fuels were invented.

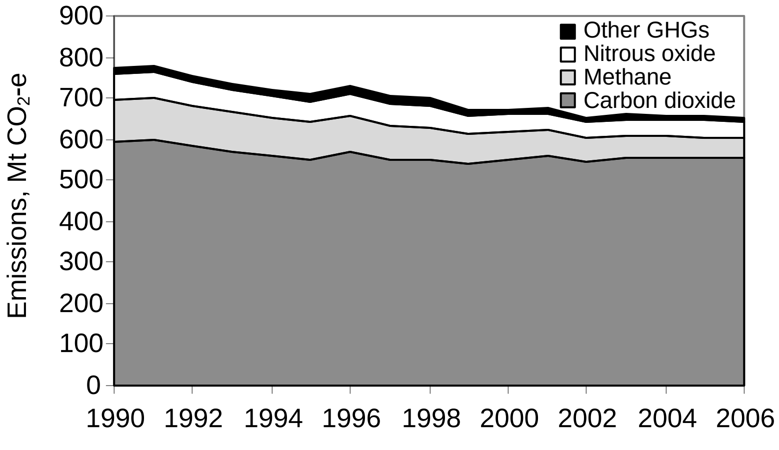


Figure 2.1: Greenhouse gas emissions from the UK, 1990–2006. Source: Department for the Environment, Food and Rural Affairs (2008).

Global emissions of carbon dioxide have increased over time while UK emissions of CO_2

have in fact decreased over that time (Fig 2.2). Most of the UK carbon dioxide emissions since 1970 have come from the electricity generation sector (38.3 % in 2007) while emissions from the transport sector have been increasing from 9.7 % of the total CO_2 emissions in 1970 to 24.2 % in 2007 (National Atmospheric Emissions Inventory, 2009). The CO_2 emissions from industrial energy sources, such as on-site combustion of fossil fuels to provide heat and power for iron and steel manufacturing, has decreased since 1970, reflecting the decline of industry in the UK. Emissions from static combustion plant in commercial, industrial, domestic and agricultural situations have remained approximately constant at 100–120 Mt CO_2, while emissions from all other sources combined are in the range 22–42 Mt CO_2 and from 1999–2007 have been at the lower end of this range, 22–28 Mt CO_2.

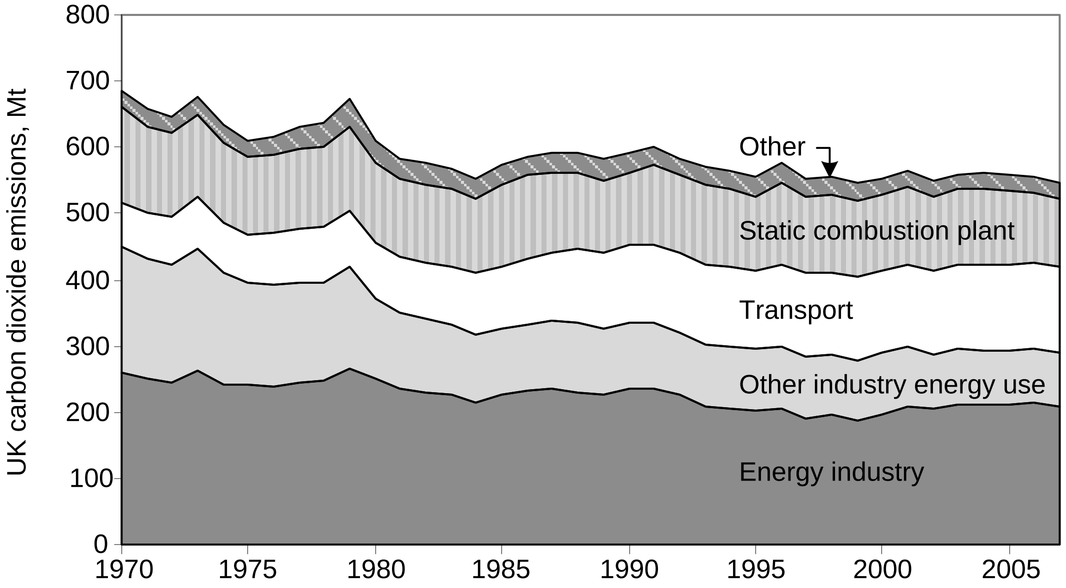


Figure 2.2: Carbon dioxide emissions in the UK, 1970–2007, by emission source.

The 1990 baseline in the Kyoto protocol is very favourable for the UK, since 1990 CO_2 emissions represent a peak in the historical trend, being at a time of relatively high coal used in electricity generation before the switch to gas in the following few years. The increasing emissions from the transport sector contrasts with the declining emissions in the industrial sector and the constant emissions from the domestic and other sectors. To ensure that the Kyoto targets are met, and further climate change mitigation is achieved, further reductions in emissions are required and the transport sector is the obvious target for government intervention to ensure reductions in emission, given the increasing emissions levels of that sector. Emissions from the transport sector are further described in Section 2.2, situated in the broader context of energy supply and consumption in all sectors in the UK, and possibilities for government intervention to reduce the emissions in the transport sector are discussed in Section 2.3.

2.2 Energy and emissions in the UK

The United Kingdom consists of the countries of England, Scotland, Wales and the province of Northern Ireland. As a member state of the European Union, the UK is subject to legislation passed in the European Parliament, as well as domestic legislation and international treaties to which it is a signatory. The Office for National Statistics (2005) provides the following data on the UK. The total land area is 24 094 thousand hectares, of which 19 % is agricultural land used for crops or lying fallow. A further 51 % of the total land area is given over to grasses and rough grazing, 16 % is urban and 11 % is forest or woodland. The climate is predominantly mild and temperate, with temperatures most usually in the range -10–32 °C. Annual rainfall varies from 550 mm in parts of East Anglia, to 1100 mm in western and upland areas, and over 2000 mm in the hilly and mountainous regions. Daylight and sunshine hours vary with latitude and the seasons, from 1–2 hours of sunshine in the darkest month of December, to 5–8 hours midsummer.

The UK's population, which comprises just over 60 million individuals (Office for National Statistics, 2008), representing just under 1 % of the global population (US Census Bureau, 2009), lives in 24.5 million households (The Scottish Government, 2005; NISRA, 2003; Office for National Statistics, 2003). Driving licenses, both full and provisional, are held by 41 million people, approximately 84 % of the driving-age population (DVLA, 2007a). The lower age limits for licenses are set at 17 and 16 years for passenger cars and motorcycles respectively. Over 80 % of adults live in a household with access to a car (Department for Transport, 2008). One million individuals hold heavy goods vehicle (HGV) licences, and 279 000 hold public service vehicle (PSV) licences (DVLA, 2007a). Foreign nationals driving in the UK are not included in these figures. The 33.5 million vehicles that are licensed for use on UK roads (DVLA, 2007a) and the fuel consumption of these vehicles are explored in the next subsection in the context of the overall trends for energy production and consumption in the UK.

The total energy supply in the UK in 2008, the latest year for which data are available, was 9393 PJ (Fig. 2.3), of which 33.2 % was supplied by petroleum products (Department of Energy and Climate Change, 2009). Conversion and transmissions losses account for 2908 PJ (31.0 % of the total supply) and of the original 9393 PJ only 6485 PJ is delivered to consumers. Fuels with the equivalent of a further 407 PJ energy were used in the UK for non-energy purposes in 2008. The total energy production has, after peaks and troughs in the 1970s, stabilised at 9000–10 000 PJ in the last 20 years.

The fossil fuels, coal, gas and petroleum, represent 91.4 % of the energy mix. The proportion of coal in the UK energy mix has decreased over the years, particularly since 1993 when gas power stations started to make more of a contribution to the electricity supply. The dip in coal consumption in 1984 corresponds to the miners' strikes in the UK and the corresponding increase in petroleum consumption reflects the switch from coal-fired electricity generation to oil-fired generation during that year. The quantity of gas used has increased as gas-powered electricity generation became more prevalent. The consumption of petroleum products has decreased since the 1970s level of 3500–4250 PJ to a relatively stable rate of 3200 PJ yr^{-1}. Hydroelectricity and other renewables, including energy recovery from waste incineration, supply 266 PJ (2.8 %) of the energy mix (Department of Energy and Climate Change, 2009).

Energy consumption by final user, is divided into four consumer groups: industry, transport, domestic and other, which comprise agriculture, public administration and commerce (Fig. 2.4). Energy used for industrial purposes has decreased over the last 40 years as larger manufacturing industries have closed down and more goods are imported, effectively exporting UK industry overseas. The domestic sector's energy consumption, currently standing at 1911 PJ, represents 29 % of the total energy consumption, slightly higher than the 1970 level of 25 %. Transport energy has steadily increased from 1180 PJ in 1970 to 2462 PJ in 2008, from 19 % to 38 % of the country's energy consumption, supplied mostly by petroleum products, petrol and DERV fuel.

Normalising the energy consumption by the population (Fig. 2.5) reveals that annual transport energy consumption has almost doubled, from 21 GJ per capita in 1970 to 41 GJ per capita in 2007, while energy consumption in the industrial sector has roughly halved and consumption in

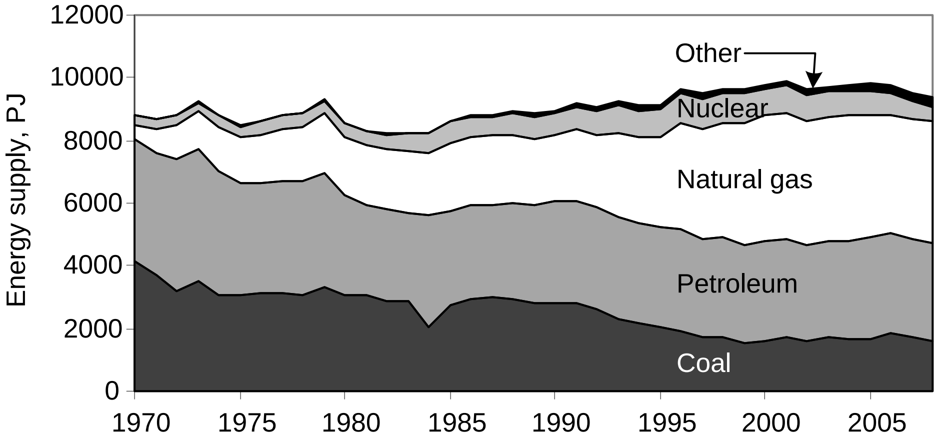


Figure 2.3: UK energy consumption by energy mode, 1970–2008 (Department of Energy and Climate Change, 2009). *Other* includes hydroelectricity, net imports and energy from renewables and waste.

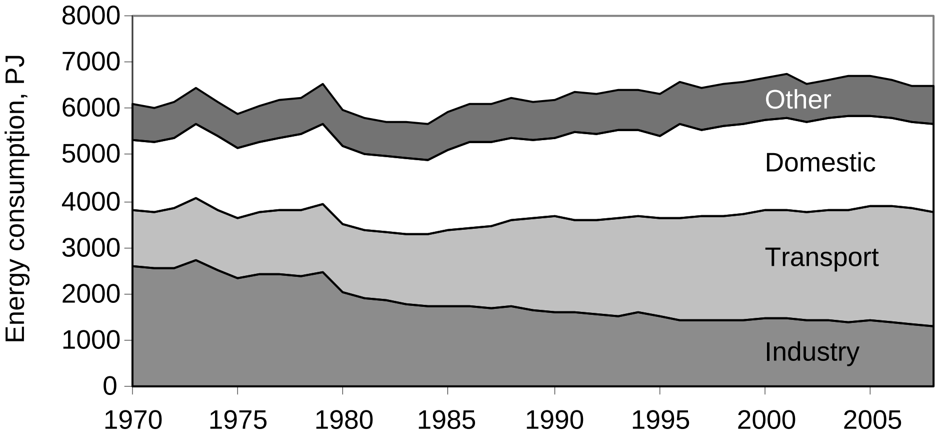


Figure 2.4: UK energy consumption by end user category

the domesticand other sectors has stayed level, within 10 % of the mean for 1970-2007. The average daily per capita consumption of energy for transport is 114 MJ, and 84.1 MJ energy for domestic purposes such as heating, cooking and lighting (BERR, 2007a). By way of comparison, the daily energy requirements for an adult, male or female, from food are around 8–10 MJ, not including the energy requirements of food production, preparation and transport.

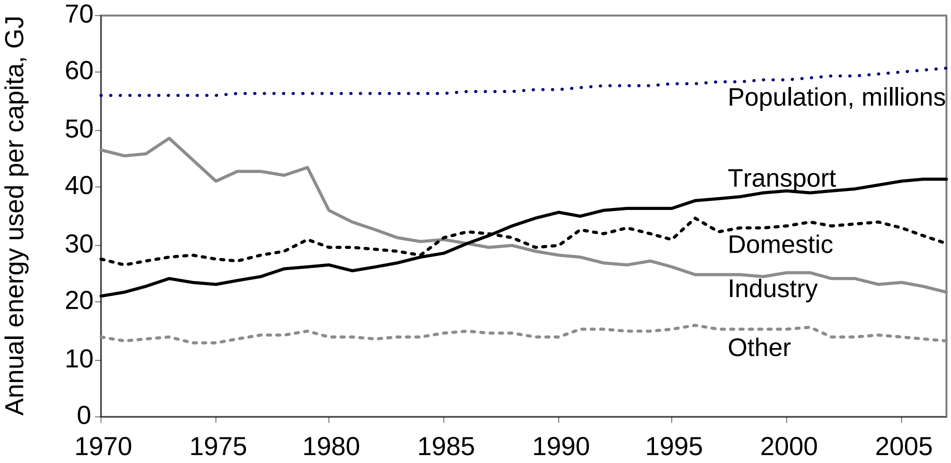


Figure 2.5: UK energy consumption per capita, 1970–2007 (BERR, 2008; Office for National Statistics, 2008).

Petroleum accounts for 3114 PJ, 33.1 %, of the UK's energy consumption, of which 264 PJ is lost in conversion and transmission, or in used in the energy industry (Department of Energy and Climate Change, 2009). An additional 8.483 million tonnes of petroleum products were used for non-energy purposes and the total energy content of these products is approximately 366 PJ (Department of Energy and Climate Change, 2009). Petroleum formed from ancient organic matter over millions of years and is known as crude oil in its raw state. Fractionation in refinieries separates out fractions of different densities, from the lightest, methane, to the heaviest, bitumen. Refinieries can also synthesise products through catalytic cracking and platinum-catalysed reforming in order to match market demands for various outputs. The transport fuels, petrol and DERV fuel, are at the lighter end of the spectrum. Some 8.483 million tonnes of petroleum products are also used for non-energy purposes, such as in the production of chemicals and plastics and for lubricating oils (Department of Energy and Climate Change, 2009).

The annual consumption of petroleum for energy purposes since 1989 (Fig. 2.6) has stayed roughly constant, to within ± 14 % of the mean, 2729 PJ. However, this disguises the increases and decreases in consumption in the different sectors. The share of industry in petroleum consumption has decreased in relative and absolute terms since 1970 to 266 PJ (9.3 %) in 2008, through switching electricity generation to using other fuels and de-industrialisation of the past few decades. Petroleum consumption by all transport modes has increased from 1160 PJ in 1970 to 2398 PJ (84.1 % of all petroleum for energy use) in 2008. From 1970 to 2008, road transport petroleum consumption increased by 93.1 % to 1730 PJ, representing 26.7 % of the country's total energy consumption, while air transport petroleum consumption increased by 274 % over the same time period. On the other hand, rail transport consumption of petroleum decreased slightly, from a peak of 52 PJ in 1970 to around 30 PJ per year during the years 2004–2008, while water transport petroleum consumption increased to around 70 PJ in 2006–2008, from around 50 PJ for 1970–2004. The domestic use of petroleum, predominantly for oil-fired space and water heating, has stayed fairly constant and in 2008 accounted for 127 PJ (4.5 %) of the energy use of petroleum products. Other uses of energy from petroleum in agricultural, public administration or commercial situations have been decreasing over time and in 2008 accounted for 59 PJ (2.1 %) of petroleum energy consumption.

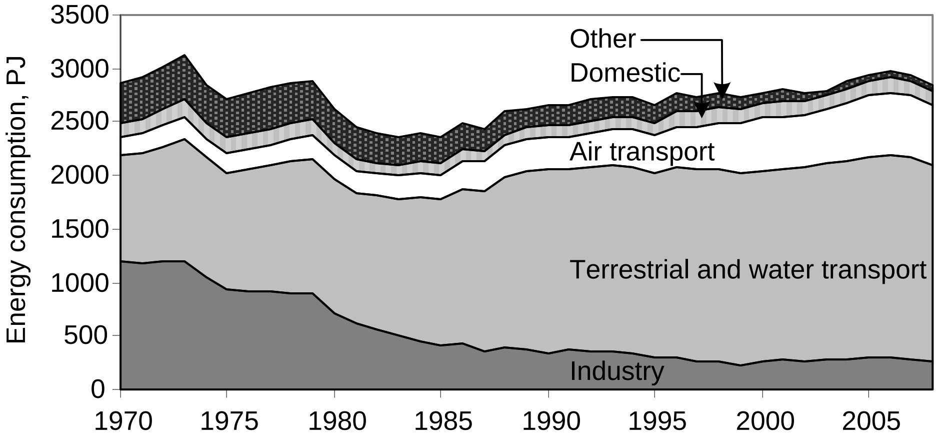


Figure 2.6: UK petroleum consumption 1970–2008, by mode of use. Source: Department of Energy and Climate Change (2009)

Petroleum products petrol and diesel (or DERV fuel - Diesel-engined road vehicle fuel) are used to power more than 99 % of the 33.5 million vehicles in the UK (Table 2.1). The main propulsion system in road transport is the internal combustion engine which runs on petrol, diesel or LPG. The fuel is pumped into airtight cylinders in the engine block, where it is ignited either by a spark, in the case of petrol or LPG, or by intense heat and pressure conditions for diesel fuel. The resultant explosion caused by the hot gases produced in combustion drives a piston in each cylinder. The pistons are connected to a cam shaft in such a way that the shaft rotates smoothly when the pistons fire in sequence. This cam shaft then drives the wheels by means of pulleys and system of gears. The kinetic energy released by the explosion of the fuel is much less than the chemical energy stored in the fuel, the gross heat of combustion, and the remaining heat energy is lost from the engine in the hot exhaust gases. Internal combustion engines have an upper limit to their thermodynamic efficiency, that is, the ratio between energy supplied to the engine and energy output by the engine in the form of useful motion to propel the vehicle. The benefits of petrol and diesel fuels include their high energy densities and that they can be stored on the vehicle and pumped into the engine without any intervention on the part of the human driver except for refuelling every few hundred miles.

Private cars	28 224 636
Light goods vehicles	1 474 238
Goods vehicles	503 216
Public service vehicles	107 214
Motorcycles	1 136 924
Other vehicles	2 075 878
Total vehicles licensed	33 522 106

Table 2.1: Licensed Vehicles in the UK, 2006 (DVLA, 2007b). Other vehicles includes, amongst others, service vehicles for fire, police and ambulance, minibuses, agricultural vehicles and vehicles for disabled persons.

Although the quantities of the individual components in the energy mix for road transport change over time, the total energy used in the sector has remained roughly level for the past ten years (Fig 2.7). The total energy used in cars and light goods vehicles has increased very slightly. A gradual reduction in petrol's share of the total road transport energy, while the share of diesel has increased, is evident. This correlates with vehicle registration data from the DVLA which reveals that an increasing proportion of new vehicles registered in the private cars and light goods vehicles categories are diesel (DVLA, 2007b). The changing composition of the road vehicle fleet (Fig. 2.8) has also contributed to an increase in the volume of diesel consumed, and consequently in the emissions of CO_2 from diesel. The number of vehicles on the road at the time of writing is a key factor in influencing policy decisions regarding emissions reductions strategies introduced by the government.

Road transport makes a significant, and increasing, contribution to the national CO_2 emissions in the UK. A number of options exist to reduce emissions from the transport sector and these are discussed in the following section, with particular attention given to biofuels as an alternative to petroleum fuels.

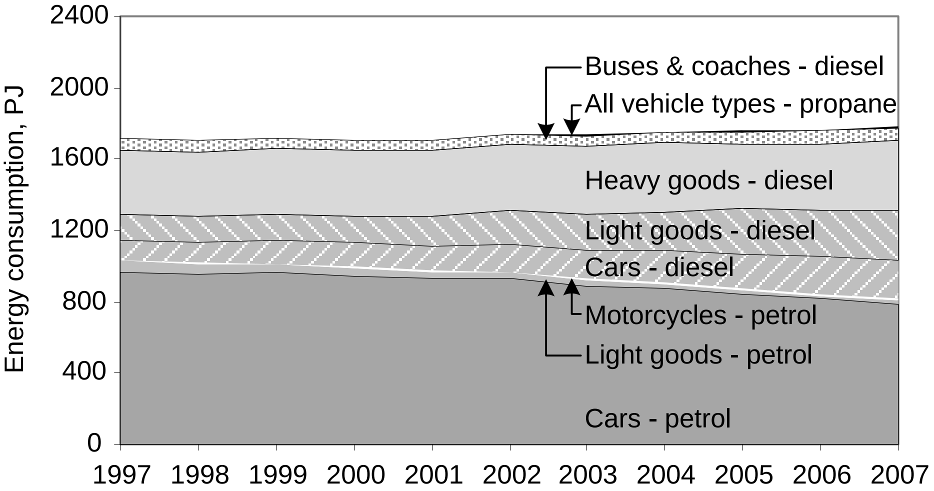


Figure 2.7: UK road transport energy consumption over time, by energy form and by vehicle category. Source data: Department for Transport (2009)

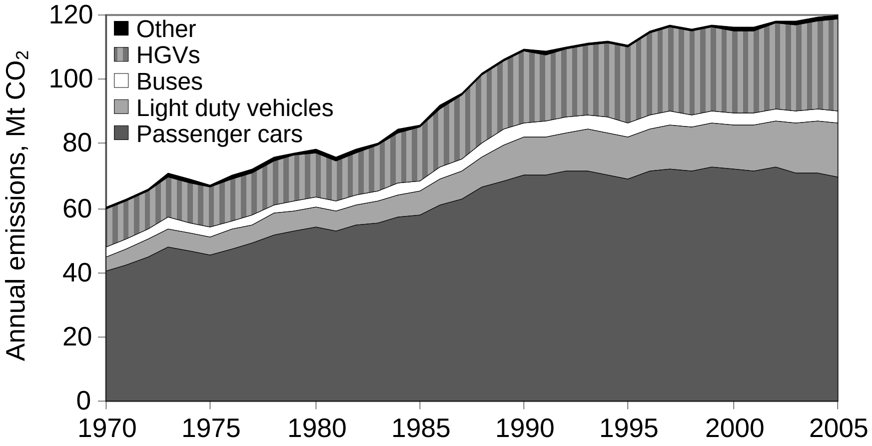


Figure 2.8: UK CO_2 emissions from the transport sector, by vehicle type, 1970–2006 (Department for Transport, 2009).

2.3 Options for reducing road transport emissions of greenhouse gases

Four broad categories can be used to describe the areas in the transport sector in which changes can be made that may result in reduced greenhouse gas emissions from vehicles:

- vehicle propulsion system
- vehicle efficiency of converting energy into motion, including driver behaviour
- fuels' intrinsic fossil carbon contents
- reduce demand for transport

Each of these areas is now explored in turn.

Current technologies for spark- and compression- ignition internal combustion engines have overall conversion efficiencies of around 20–25 $\%$ with the remaining energy content of the fuels lost as heat rather than being converted into useful work in moving the vehicle. Other technologies such as electric motors offer higher efficiencies at the point of use, but the conversion inefficiencies highlighted above in the discussion on the UK electricity supply lead to a similar overall loss in the system as in combustion engines. In light of the time pressures to reduce carbon dioxide emissions, and the technological lock-in of having 33.5 million vehicles in this country alone predominantly fuelled by liquid fossil fuels, with the supporting fuel distribution and supply infrastructure, and the fleet turnover time of around 14 years, changing the engine technology and its supporting services and infrastructure is a very big challenge and one that is not politically feasible in the current system.

The overall conversion efficiency of internal combustion engines is primarily governed by the thermodynamic relationship $(T_1 - T_2)/T_1$ where T_1 is the highest temperature in the engine and T_2 is the temperature of the cooling system. Both temperatures are in Kelvin and the relatively high value for T_2 at approximately 50 °C (323 K) and the relatively low T_1 are fundamental physical reasons for low efficiency. The efficiency is further influenced by external conditions, driver behaviour and the load that the vehicle is carrying. Engine designs have improved over the years but this has been countered by increases in vehicle kerbweight and the addition of auxiliary systems such as air conditioning units. The ActOnCO_2 campaign, run by the Department for Transport, encourages drivers to change their driving behaviour, for example through inflating tyres to the correct pressure, removing excess weight from the vehicle and as well as adopting a smoother driving style with longer periods of acceleration and braking.

The option of changing the carbon content of the fuel offers a way of reducing the CO_2 emissions from transport without relying on the co-operation of drivers with regard to their driving style, nor on developments or changes in propulsion systems. Biofuels have been promoted as a technical solution to the CO_2 emissions problem since the life cycle emissions of CO_2 are believed, though not necessarily yet shown, to be less than the life cycle CO_2 emissions from fossil fuels . In the simplest case, plants absorb CO_2 from the atmosphere during growth which they convert to biomass. The biomass is burned for human use as fuel which releases CO_2 back into the atmosphere, hence bioenergy is a carbon-neutral fuel. This is a gross simplification and requires further detail and more rigorous investigation to vouch for the carbon-neutrality of such fuels.

The fourth option for reducing carbon emissions in transport and travel requires far more actors to change their behaviour in reducing their travel or transport requirements, thereby reversing the trend of several decades. As explored above, the consumption of petroleum for travel and transport has increased steadily over the past 40 years. Fewer journeys are undertaken by foot or bicycle than in previous years (Department for Transport, 2009) and in general terms humans and goods are traveling further and in more vehicles. Some progress has been made towards reducing transport and travel, through carshare and freight consolidation schemes.

Of these four options, the third and fourth ones are most likely to succeed, however the political unpalatability of the fourth option, changing behaviours, leads to the third one being most likely. Indeed, the option of reducing the carbon content of fuels has already been acted upon by European and British governments (European Commission, 2003; Department for Transport, 2007b). Alternative fuels to petroleum-based petrol and diesel for road vehicles are discussed in the following section.

2.4 Alternative fuels for reduced fossil carbon content

The introduction of alternative fuels which have low fossil carbon contents, or low life-cycle carbon emissions, provides a route towards reducing emissions in the transport sector through changing the behaviour of a few key actors, the fuel supply companies, rather than requiring changes in millions of individuals' activities. King proposes several criteria that a good fuel will meet (King, 2007, p. 24):

- energy dense for maximum range and able to provide fast and convenient refueling of the vehicle,
- easily storable and transportable,
- stable over a wide range of temperatures,
- non-damaging to the car engine,
- inexpensive to produce and distribute,
- available from secure sources,
- not detrimental to local air quality,
- low fossil CO_2 over its life-cycle (in production, distribution and use).

Research and development has so far unveiled a number of alternative fuels, some of which come from renewable resources. In the case of transport, the available alternatives for internal combustion engines are:

- biodiesel
- (bio-)methanol
- (bio-)ethanol
- (bio-)butanol
- liquid petroleum gas (LPG)
- compressed natural gas (CNG)
- biogas
- hydrogen
- methanol

All of these fuels can be stored on board the vehicle and, with the exception of hydrogen, all are relatively mature and known to work in engines. The gaseous transport fuels, LPG, CNG and biogas, require modifications to the engine and extra fuel storage facilities. The vehicle and fuel-supply technology for LPG and CNG has been established since at least 1996 and 125 thousand tonnes of LPG (6.2 PJ) was supplied to the road transport sector in 2008 (Department of Energy and Climate Change, 2009).

A number of routes exist for the production of liquid and gaseous fuels from biomass (Fig 2.9). Fuels from biomass are categorised into those that can be used in diesel engines (biodiesel, BTL (biomass to liquids), pyrolysis oil and hydro-thermal upgrading diesel), those that can be used in petrol engines (the alcohols bioethanol and biomethanol), and gases (hydrogen and biogas).

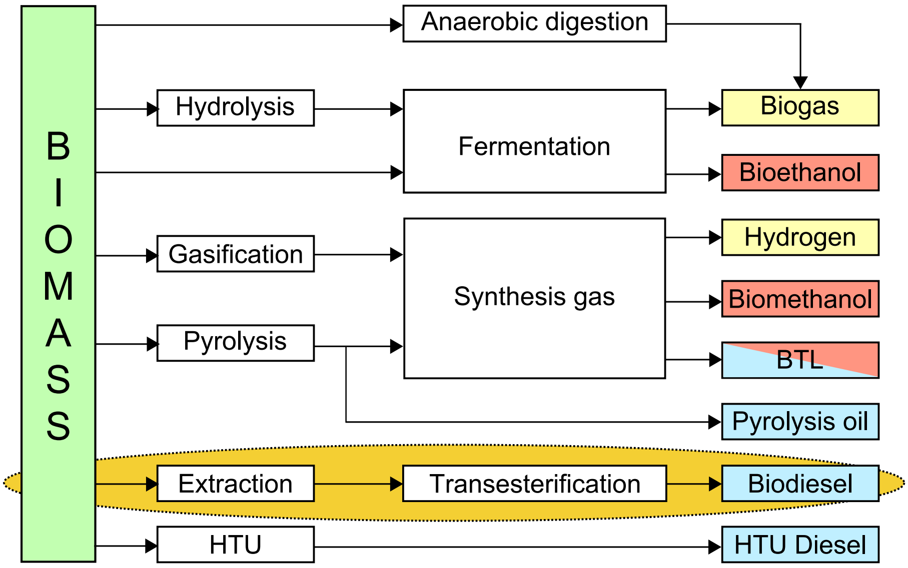


Figure 2.9: Production routes of liquid and gaseous biofuels. Fuels coded in yellow are gaseous, red fuels can be mixed into petrol and blue fuels are suitable for Diesel engines. The circled route in which biodiesels are produced via transesterification is the focus of this thesis. BTL: biomass-to-liquids; HTU: Hydro Thermal Upgrading.

Biodiesel, BTL (biomass-to-liquids), pyrolysis oil, and HTU Diesel (Hydro-Thermal Upgrading) can be used in Diesel engines. Of these four, biodiesel produced via transesterification of vegetable and animal fats and oils in the presence of an acid or alkaline catalyst is the most well-established technology, often referred to as a *first-generation* biofuel, whereas the others can be categorised as *second-generation* biofuels (Sims et al., 2008). BTL fuels are produced through Fischer-Tropsch synthesis which produces heavier hydrocarbon molecules from lighter compounds in synthesis gases (Demirbas, 2007). Oils produced via pyrolysis, which is a thermo-cracking process to break dry biomass into smaller molecules, can be cleaned and refined to obtain fuels suitable for Diesel engines (Demirbas, 2007). Similarly, HTU diesel is produced through a high-temperature process but with wet or sludge biomass (Zhong et al., 2002).

Bioethanol, biomethanol and some BTL fuels are suitable for use in spark-ignition engines as additives to petrol. The yeast-based fermentation process for producing bioethanol has been in use for centuries for the production of alcoholic beverages. Sugar beet, sugar cane and maize are used to produce bioethanol for transport, and second-generation feedstocks for ethanol production via lignocellulosis include woody biomass and straw. Biomethanol, which is produced from synthesis of gasifying biomass, can also be blended into petrol. Through refining processes, fuels that are suitable for petrol engines can also be obtained from BTL products.

Gaseous fuels can also be produced from biomass for use in transport. Biogas, which in its raw form consists of methane (CH_4) mixed with CO_2, is produced through the anaerobic digestion of biomass by bacteria (Sims, 2002). The biomass in an anaerobic digester can include domestic and commercial food and agricultural wastes. Biogas is also emitted during the decomposition of sewage and can be collected, cleaned of CO_2 and used for energy purposes. Thermal gasification of biomass can produce hydrogen for collection and use in fuel cell or combustion engines (Sims, 2002). Some biogas is also produced during the pyrolysis of biomass. However, the use of gaseous fuels for transport is limited by the lock-in from infrastructure which is primarily designed for delivery and use of liquid fuels, although limited penetration of gaseous fuels into the road transport fuel supply has been achieved in the UK and other countries.

At present, the production routes for first generation biofuels are well-established. However, barriers to further development of first generation biofuels include limits on land availability and competition with food, feed (for animals) and fibre crops. Current market prices for biofuels are only competitive with petroleum products through government subsidies. The sustainability of biofuels is under question owing to the lack of sufficient information regarding environmental impacts. This thesis aims to extend the current knowledge base of the environmental impacts of biodiesel through an investigation of the life cycle of biodiesel production from hemp seed oil, grown in the UK.

Production routes for second generation biofuels, for instance lignocellulosis of woody plant matter to produce a material that can be used as a feedstock for bioethanol, are as yet not commercially developed. It remains to be seen whether the production methods for first generation biofuels can smooth the transition to second generation fuels, or if the selection of biofuels that are suited to the current infrastructure will maintain the technological lock-in to liquid fuels for internal combustion engines.

The fuels based on biomass, namely biodiesel, bioethanol and biogas, have received particular attention on account of widespread perception of their environmentally-friendly credentials. Biofuels are widely promoted as environmentally benign fuels, based predominantly on the concept of a closed carbon cycle: next year's fuel crop will absorb the CO_2 released by the fuel from this year's fuel crop. This carbon cycle is more accurately described as the short-term carbon cycle: carbon is absorbed and released on a short timescale of a year or so, and is illustrated in Fig 2.10. In contrast with the short carbon cycle, the use of fossil fuels is part of an extremely long-term carbon cycle that lasts millions of years, illustrated in Fig 2.11. In the same way as today, in the distant past vegetation absorbed carbon from the atmosphere. When the vegetation died, it built up in layers and decayed, compressed by rock, forming oil, coal and natural gas deposits. These deposits lay virtually undisturbed with very low leakage rates from oil deposits for millions of years. In the last 300 or so years, humans have been releasing this long-sequestered carbon back into the atmosphere, and in the last 60 years the release of carbon from fossil reserves has increased many times over.

In times of emergency and fuel shortage, for example during periods of war, biofuels have been used as fuel. Neat vegetable oil can be blended directly with fossil diesel and used in diesel engines, but the oil damages the engine. The damage incurred includes coking and trumpet formation on the fuel injectors, partially or fully clogging the injectors, carbon deposits, oil ring sticking, and increasing the viscosity of the lubricating oil due to contamination by the vegetable oil, leading to thickening and gelling (Harwood, 1984). Most of these issues can be resolved by converting the vegetable oil to methyl esters: biodiesel. The potential of esterified vegetable oils as diesel fuels was first seen in 1937 in Belgium, where a patent was filed on the production of palm oil esters for fuel use (Mittelbach and Remschmidt, 2004). The most widely-used method of producing biodiesel is a straightforward reaction between vegetable oils and methanol, a type of alcohol, in the presence of a catalyst such as sodium hydroxide (caustic soda) or potassium hydroxide. This reaction is explored in more detail in Section 2.7.

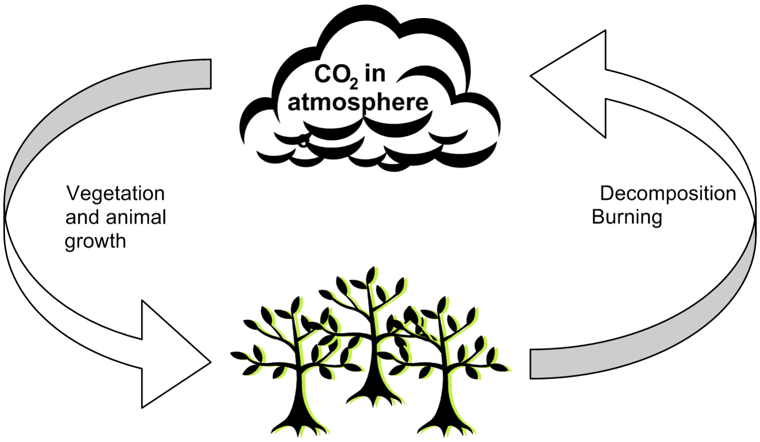


Figure 2.10: Short carbon cycle

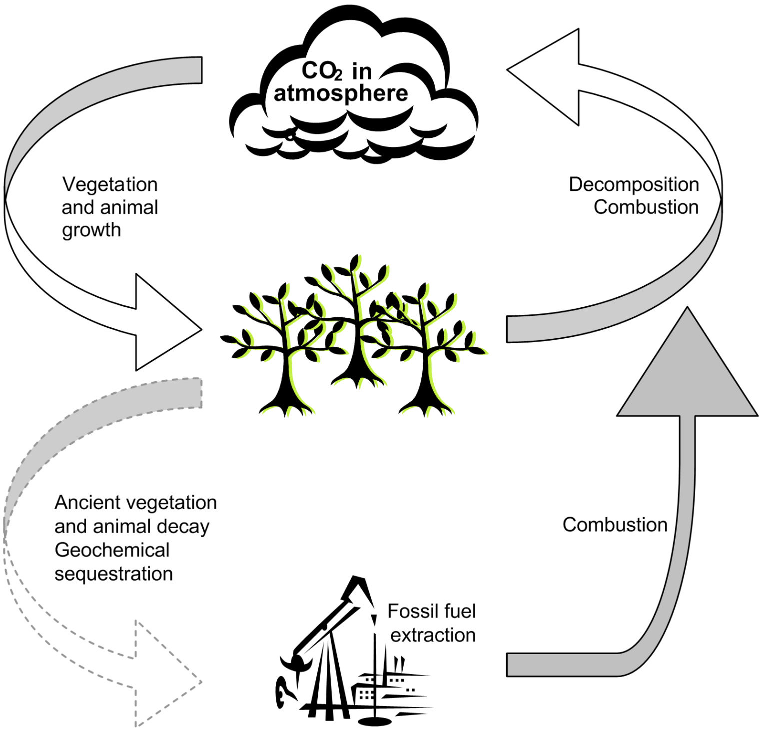


Figure 2.11: Long carbon cycle

In the immediate term, biofuels that can be used as direct substitutes or blends with existing fossil fuels are at a distinct advantage for penetrating the fuel market. Of the current biofuels available, only biodiesel can be handled by present-day engines as a direct substitute for fossil fuel with little or no engine modification. Biodiesel can react with and weaken natural rubber, therefore any natural rubber components in the engine, such as valve seals, must be replaced by synthetic rubber seals. At very high proportions of biodiesel at low temperatures, the biodiesel may begin to cloud as solid particles form in the fuel. Extra heating is needed to ensure that the biodiesel flows correctly in such conditions and some vehicles are modified to have two fuel tanks and fuel pipe systems: one for petroleum diesel, used to start the engine and to flush it through at the end of the journey, and one for biodiesel, used for the intermediate stage of the journey. Petrol engines in the UK can handle ethanol at a proportion of up to 5 %; in the United States, petrol-engined vehicles can use fuel with up to 10 % ethanol content, and in Brazil engines are legally required to be able to run on up to 25 % ethanol in the petrol. Flex-fuel vehicles have been developed by some manufacturers, for example the Ford Motor Company Ltd., to use petrol that contains up to 85 % ethanol.

2.5 Government policy on biofuels for transport

In recent years, governments around the world have been supportive of biofuels through policy measures such as fiscal incentives. The policy measures that are directly relevant to the UK situation are summarised in Table 2.2. In 2003, the EU Commission introduced the *Directive for promoting the use of biofuels or other renewable fuels for transport* (European Commission, 2003). Each European Union member state can implement its own policy to meet the objectives set in the Directive: the UK parliament created governmental powers to set an obligation on renewable transport fuels in the 2004 Energy Act - the Renewable Transport Fuels Obligation (RTFO) (HM Government, 2004). Subsequently, the EU Directive 2009/28/EC repealed and replaced the Directive 2003/30/EC and set a reduced target for the inclusion of renewable fuels in transport of 10 % by 2020.

The Energy Act 2004 grants the government powers to set a target for biofuel inclusion for transport fuels, and that penalties can be levied on those who fail to meet the obligation. The initial

1997	Kyoto Protocol
2002	20 pence per litre duty incentive on biodiesel introduced
2003	EU Directive on promoting the use of biofuels
2004	Energy Act 2004 included powers to introduce the renewable transport fuels obligation
2005	Government announced the first phase of the RTFO, 2008- 2010
2006	Budget Report contains details of the RTFO
2007	RTFO consultation document
2008	RTFO phase 1

Table 2.2: Political events leading to the introduction of the RTFO

formulation of the RTFO was modeled on the Renewables Obligation for electricity supply, which came into operation in 2002 with a policy lifetime of 25 years and recently extended to 35 years with the provision that no scheme can benefit from the initiative for more than 20 years. In the case of the RTFO, the government declared in 2006 that it would draw on the powers in the Energy Act 2004 from 2008 onwards. Targets for the inclusion of biofuels into the transport fuel supply were set for three financial years from April 2008: 2.5 % for 2008/09, 3.75 % for 2009/10 and 5 % for the year 2010/11 (HM Treasury, 2006). In November 2007, the RTFO received approval in the House of Commons and implementation of the RTFO began in April 2008.

The stated objective of the Renewable Transport Fuels Obligation is “to reduce carbon emissions from road transport by 2.6–3.0 million tonnes of CO_2 per annum” (Department for Transport, 2007a, Para. 4.2) through the inclusion of 2.5 billion litres of biofuel per year (Department for Transport, 2007a). This is in agreement with the underlying principles of the EU Directive which includes recognition that “greater use of biofuels for transport forms a part of the package of measures needed to comply with the Kyoto Protocol” (UNFCCC, 1997, Article (5)). A quick calculation shows that these objectives assume that biofuels cause carbon emissions that are 1.04–1.2 kg CO_2 eq. per litre lower than the emissions from petroleum fuels. The EU Directive also proposes that the “increased use of biofuels for transport...is one of the tools by which the community can reduce its dependence on imported energy and influence the fuel market for transport and hence the security of energy supply in the medium and long term" (European Commission, 2003, Para. 7).

The EU directive specified the biofuel proportion of the fuel supply by energy content, whereas the UK's RTFO uses a volumetric proportion. Bioethanol and biodiesel have lower energy contents than petrol and fossil diesel respectively, so in effect the UK's RTFO requires only a 3–4 % inclusion of biofuels in transport fuels when measured by energy content. The targets set in the RTFO thus fall short of the 5.75 % by energy content specified in the EU Directive 2003/30/EC. However, the medium-term target of 10 % of all transport energy to be supplied by renewable sources by 2020 may yet be achieved in the UK, depending on policy measure and social and technological changes that may occur in the coming decade.

Although the use of biofuels initially seems positive from the perspective of the long-term and short-term carbon cycles and the reductions in emissions of carbon dioxide from combustion of fossil fuels, concerns have been raised about the consequences of cultivating biofuels for transport in the following areas: overall sustainability of the biofuels supply chain (The Royal Society, 2008); competition for cropland between food and fuel crops and consequences for food prices (Renewable Fuels Agency, 2008); the effects of land use change (Upham et al., 2009); the cost-effectiveness of biofuels compared with other biomass uses (BERR, 2007b); effects on biodiversity (Koh and Ghazoul, 2008); the social impacts of cultivating biofuels, particularly in tropical regions (Koh and Ghazoul, 2008; Garcez and de Souza Vianna, 2009); and finally that the substitution of biofuels for petroleum-based fuels will have little or no effect on the demand for transport, or on the demand for transport fuels. In this thesis, the first of these concerns, regarding the overall sustainability of the biofuel supply chain, is assessed in part for the production of biodiesel from hemp seed oil, and sustainability assessments are the subject of the next section in the current chapter.

2.6 Sustainability assessment of biofuels

Sustainability concerns underpin the objectives of both EU and UK law regarding biofuels for road transport. The Brundtland Report set out a definition of sustainable development that has served as a benchmark in subsequent years: "meeting the needs of the present without compromising the ability of future generations to meet their own needs" (Brundtland, 1987, p. 8) and as current CO_2 emissions are very likely to directly affect the climate that will be experienced by future generations, reduction of such emissions is a fundamental part of sustainable practice. Despite the widespread use of the Brundtland definition of sustainability, it does not lend itself readily to quantitative assessment. Firstly, without further understanding in the natural sciences of the environmental interactions and consequences of system perturbations to those natural environments, the proximity or distance of the current state of affairs from a state of sustainability is unquantifiable. Secondly, the definition is unequivocally anthropocentric with its main concern being the meeting of human needs. Thirdly, needs are themselves not necessarily quantified or even agreed upon, and the impact of climate and technical changes to the capability of humans meeting their psychological and social needs is difficult to establish.

Putting aside these concerns with the concept and definition of sustainability, for the purposes of this thesis a narrower target is adopted, namely the reduction of carbon dioxide emissions from transport, and thereby reducing the contribution of the transport sector to anthropogenic climate change. As explored previously in Section 2.5, the Department for Transport's main environmental objective for the RTFO is exactly this target of reducing carbon dioxide emissions (Department for Transport, 2007a). The objectives of the EU Directive are to make a contribution to meeting climate change commitments and to promote an environmentally friendly security of supply through renewable energy sources (European Commission, 2003). The EU Directive also sets out requirements on the EU member states to report biennially on their implementation of the measures to fulfil the obligation in the Directive. In the years leading up to the establishment of the RTFO in UK law, concerns from the scientific community and the general public (Ponton, 2009; Boswell, 2007) regarding sustainability and other environmental impacts of growing crops to produce biofuels for transport have contributed to the inclusion of a sustainability reporting requirement in the RTFO. The reporting requirements for both the EU Directive and the RTFO are shown in Table 2.3 for comparison.

Category	EU Directive	UK RTFO
Environment	Environmental impact	Effects on the environment generally
Methodological approach	Life-cycle perspective of biofuels and other renewable fuels,	
Agriculture	Sustainability of crops used	Effects on agriculture
Climate change	Effects on climate change and their impact on CO_2 emissions reduction	Effects on carbon emissions
Sustainability		Effects on sustainable development
Economic matters		Effects on other economic activities
Other options	Review of further, longer-term options for energy efficiency measures in transport	

Table 2.3: EU and UK requirements for reporting on the environmental impact of transport biofuels. Sources: European Commission (2003, Article 4.2), (Department for Transport, 2007b, Para. 3.13.4).

The reporting commitments of both the EU Directive and the RTFO are predominantly concerned with assessing the extent to which the adoption of biofuels, and other renewable fuels in the case of the EU Directive, is sustainable. Both pieces of legislature mandate the assessment of the environmental impact of biofuels and the EU Directive specifies the life-cycle perspective approach for this purpose. The effects on agriculture are of interest in both sets of reporting requirements, with the EU explicitly requiring assessment of the sustainability of the crops used whereas the UK RTFO specifies more generally that the effect on agriculture is to be considered and reported on. With regard to climate change drivers, the EU directive takes a broader approach with "the effects on climate change" than the UK approach of "effect on carbon emissions". Strategies for emissions reductions in the transport sector, other than the use of lower emissions fuels, are also necessary for a comprehensive approach to achieving the targets set in the Kyoto Protocol. To this end, the EU also calls for the review of long-term options for energy efficiency as outlined earlier in this chapter. Finally, the UK RTFO's reporting requirements stipulates that the effects of biofuels on sustainable development should be included.

The RTFO also provides for the imposition of an assessment methodology on the fuel suppliers, by which they are to assess and report on the effects as detailed in Table 2.3. The Renewable Fuels Agency, the government body set up to administer the RTFO, stipulates that fuel suppliers should report on the net greenhouse gas saving and sustainability of the fuels that they supply (Renewable Fuels Agency, 2009a).

As discussed above, assessment and the reporting of that assessment is intrinsic to the EU Directive and to the RTFO on account of the intention to make measurable reductions to greenhouse gas emissions from road transport. The Kyoto Protocol sets the precedent for measurable indicators of progress by its quantitative targets for emissions reductions. For the purposes of UK and EU law, a reliable and accurate assessment method is therefore required. Further, the EU Directive implicitly categorises biofuels as renewable, yet to be a truly renewable fuel, the effect of producing and using such a fuel must have a net zero exchange with the environment such that the environment is in the same state after production and use of the fuel as it was before the production of the fuel. Therefore any assessment method must also be able to quantify the net changes in the environment as a measure of the renewability of the fuel under consideration.

In order to assess the sustainability of biofuels, an assessment methodology that can account for the impact of current activities on future generations is required. However, such assessment is almost impossible given that the impact of activities on future generations cannot be determined at the present time. The closest approximation that can be made to an accurate assessment of the impact on future generations is to develop a set of future scenarios and to assess the likely impact, given such scenarios, which is an approach widely adopted for projections of energy demand and supply (See, for example, Anderson et al. (2008)).

The first step in assessment is to determine the impact of activities on the environment at all stages of the product's production, use and disposal, from the extraction of raw materials, through processing to final disposal of the product or outputs, such as waste, from the process. This approach, known as the life cycle approach, is the foundation of the methodology specified by the RTFO reporting requirements, although the RFA methodology does not explicitly refer to "life cycle" at any point (Bauen et al., 2008). The EU Directive explicitly calls for a life-cycle perspective. A life cycle assessment methodology has been adopted in this thesis for the purpose of compliance with the EU Directive and the RTFO which both call, by name or by implication, for a life-cycle perspective. The more formalised life cycle assessment (LCA) method is also used in this thesis in order to allow a more ready comparison with other bioenergy and biofuel assessments conducted using the LCA framework. Life cycle assessment is a whole-system approach used to determine the environmental impact and effects of a technology or process, from its initiation and production, through its use to final disposal and recycling of component parts. The method draws on systems analysis through the consideration of all stages in the production system that gives rise to a product, as well as the use and final disposal stages of the product's life. Life cycle assessments of biodiesels are reviewed in Chapter 4.

A more detailed explanation of life cycle assessment methodology with particular reference to bioenergy life cycles is presented in Chapter 4 along with a survey of assessments of biodiesels that are relevant to this thesis. As biodiesel from hemp seed oil is the subject of the life cycle assessment in this thesis, the next section describes the production processes and chemistry of biodiesel production.

2.7 Biodiesel and its production

In this section, an overview of biodiesel, its properties and production are presented, including the chemistry of biodiesel production and the available methods for converting plant oils into biodiesel. The most-used method in the UK, alkali-catalysed transesterification, is discussed in detail.

Biodiesel is produced by breaking up triglycerides (fats or oils) from vegetable or animal origin into esters (biodiesel) and glycerol. The reaction that converts fats and oils into biodiesel is known as transesterification, and is the formation of esters and glycerol from the reaction of alcohol with fats or oils (Ma and Hanna, 1999). The reaction splits the triglyceride molecules into three long-chain esters, with the remainder of the triglyceride molecule forming glycerol, $CH_2OH-CHOH-CH_2OH$, also known as glycerine, as shown in Fig. 2.12. R represents a fatty acid chain, which may or may not include double bonds, branches, or other groups of atoms (moieties) with specific chemical functions.

The most frequent naturally-occurring fatty acids in plant and animal fats and oils are linoleic and linolenic acids, both with 18 carbon atoms; these have one and two double bonds respectively in the long chain of carbon atoms. Fats and oils from vegetable and animal sources can have as few as two carbon atoms in the R group, or as many as 26 carbon atoms with side groups or double bonds. The properties of biodiesel vary according to its fatty acid composition, which in turn depends on the source of the oils and fats that have been used as feedstock. Animal fats and vegetable oils contain varying proportions of fatty acids. Biodiesels that comprise methyl esters of

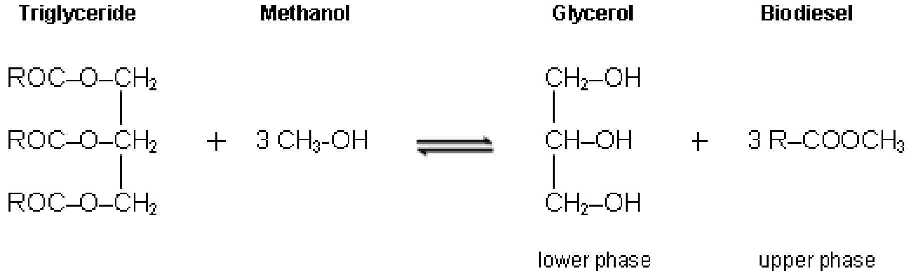


Figure 2.12: Transesterification reaction

fatty acids with around 12-18 carbon atoms in the long chain are of interest for transport biodiesel as these result in physico-chemical properties similar to those of petroleum diesel. The term *fatty acid methyl ester* refers to methyl esters of specific fatty acids (pure FAMEs) whereas *biodiesel* refers to mixtures of FAMEs, either mixed from pure FAMEs, or from the conversion of animal or vegetable fats to methyl esters.

Biodiesel is a yellow-orange liquid at room temperature and smells similar to, although slightly sharper than, the feedstock oil from which it is made. FAME densities vary from 848.8 kg m^{-3} (arachidate methyl ester, 40 °C) to 907.9 kg m^{-3} (acetate methyl ester, 40 °C) (Gouw and Vlugter, 1964) and densities of biodiesels investigated for fuel purposes have been observed in the range 857–885 kg m^{-3}, for rapeseed oil methyl ester and linseed oil methyl ester (Demirbas, 2008). Biodiesel density varies linearly with temperature, becoming denser at lower temperatures (Tat and Van Gerpen, 2000; Yuan et al., 2004; Baroutian et al., 2008; Yoon et al., 2008). The gross heats of combustion for FAMEs (laurate to stearate methyl esters, 12–18 carbon atom fatty acid chains) are reported to be in the range 36.99–40.23 MJ kg^{-1} (Klopfenstein and Walker, 1983) whereas gross heats of combustion for biodiesel have been reported in the range 40.84–41.98 MJ kg^{-1} for linseed and crambe biodiesels respectively (Demirbas, 2008). Biodiesel is miscible in all proportions with petroleum diesel, making it suitable for inclusion in blends with petroleum diesel (Tat and Van Gerpen, 2000).

Standardised specifications for biodiesel and petroleum diesel have been set out by the EU and are shown in Table 2.4. The EN 590 standard for fossil diesel fuel and the EN 14214 standard for biodiesel fuel apply to blends of up to 5 % biodiesel, or 100 % biodiesel respectively. Between 5 % and 100 % biodiesel, there is no official fuel quality standard. The behaviour of the blended fuel across the spectrum, from B0 to B100 has been the subject of a few research projects (See, for example, Romig and Spataru (1996); Tat and Van Gerpen (1999)), but as yet the research basis in this area is not complete. Researching the full range of blends is essential for the future of the biofuels industry, since it will enable vehicle engine manufacturers to design and test their engines on standardised fuel blends. This could also lead to the development of blended fuel standards across the entire spectrum from B0 to B100 which would free up the market for blend biodiesel-petroleum diesel fuels. Note that biodiesel according to the EN 14214 specification can contain up to 3.5 % w/w matter other than methyl esters and hence does not necessarily consist of pure methyl esters alone.

Fuel is injected into a diesel engine via nozzles which are designed to produce a fine spray of diesel particles in the cylinder. The droplet size in the spray is an important factor in governing the ignition and combustion characteristics of the fuel. The fuel's density and viscosity influence the droplet and spray characteristics and higher viscosity causes a poorer quality spray which increases carbon deposits around the nozzles, amongst other issues. The viscosity and density in particular are important parts of the EN specifications for this reason.

The ratio of C:H:O in biodiesel is around 228:38:32 with the exact ratio being dependent on the fatty acids present in the biodiesel. Therefore by mass biodiesel comprises 76.5 % carbon. When 1 kg of biodiesel is completely combusted to produce CO_2 and water, 0.765 kg carbon combusts to produce 2.81 kg CO_2. By comparison, the carbon dioxide emission factor for petroleum diesel is 3.16 kg CO_2 per kg of fuel (AEA Energy and Environment, 2008).

In soil, biodiesel is biodegraded by micro-organisms that use it as an energy source and it is less toxic than petroleum diesel (Lapinskienė et al., 2006). In the aquatic environment, biodiesel is degraded more readily than petroleum diesel since it comprises naturally-occurring molecules upon which naturally-occurring enzymes and organisms can act, whereas the aromatics and other hydrocarbons in petroleum diesel have fewer such matching enzymes or organisms (Zhang et al., 1998).

Property	Unit	DERV fuels		Biodiesels	
		min	max	min	max
Ester content	% (m/m)	-	-	96.5	-
	% (v/v)	-	5	-	-
Density at 15 °C	kg m^{-3}	820	845	860	900
Kinematic viscosity at 40 °C	mm^2 s^{-1}	2.00	4.50	3.5	5.0
Flash point	°C	55	-	101	-
Cetane number	-	51.0	-	51.0	-
Water content	mg kg^{-1}	-	200	-	500
Sulfur content	mg kg^{-1}		10.0	-	10
Carbon residue (at 10 % distillation remnant)	% (m/m)	-	0.30	-	0.3
Sulfated ash content	% (m/m)	-		-	0.02
Total contamination	mg kg^{-1}	-	24	-	24
Copper band corrosion (3 hours at 50 °C)	rating	Class 1		Class 1	
Oxidation stability	hours at 110 °C	-	-	6	-
	g m^{-3}	-	25	-	-
Acid value	mg KOH g^{-1}	-	-	-	0.5
Iodine value	g I_2 per 100 g	-	-	-	120
Linolenic Acid Methyl ester	% (m/m)	-	-	-	12
Polyunsaturated ($\geq$ 4 Double bonds) Methyl ester	% (m/m)	-	-	-	1

Table 2.4: EN 590 and EN 14214 fuel standards for diesel and biodiesel fuels. EN 14214 also contains additional criteria for the purity of biodiesel with regard to glyceride, methanol, alkali metals and phosphorus contamination, not shown in this table.

2.7.1 Feedstocks

Oils and fats for conversion to biodiesel via transesterification come from nuts, seeds, animal fats, algae, and used or waste oils. Oils from annual and perennial crops are the most widely used feedstocks for biodiesel. Annual crops, such as oil seed rape and soybean, are used in the European Union and the USA. Oils from perennial crops, including Jatropha curcas, a tree with oil-bearing fruits, and oil palms are used to produce biodiesel in India (Mohibbe Azam et al., 2005), some African countries and Malaysia. The choice of feedstock is affected by the relative availability and costs of the various oils and fats. In this thesis which is focused on the UK and its potential energy supply from biomass sources, only crops that can be grown on a commercial scale in the UK, namely oilseed rape and hemp, are considered in detail in this section.

Seed oils

Oilseed crops suited to the UK's climate include rape and linseed, and minority crops such as hemp, crambe, flax, soya bean and sunflower (Nix, 2008). Research into biodiesel from other feedstock crops includes castor bean oil (Conceicao et al., 2007), tomato seed oil (Giannelos et al., 2005), hazelnut oil (Xu and Hanna, 2009), Ethiopian mustard oil (Dorado et al., 2006), rubber seed oil (Ramadhas et al., 2005), linseed oil (Agarwal et al., 2008; Sangha et al., 2004), sunflower oil (Antolín et al., 2002; Bona et al., 1999; Sangha et al., 2004), tobacco seed oil (Veljković et al., 2006) and rice bran oil (Sangha et al., 2004; Zullaikah et al., 2005), amongst others.

The seeds are harvested using a combine harvester which separates the grain from the seedcase using a centrifuge. The straw can be either chopped up finely by the harvester and recombined into the soil, or dried, baled and collected for use as animal bedding or for bioenergy in power stations such as the straw-fired power station at Ely. The seed themselves are dried on the farm. The dried seeds are transported to a crushing facility where they are mechanically crushed to extract the oil. Solvent extraction methods may also be employed. The solid residue after the oil has been extracted from nuts or seeds is known as oil cake or press cake. Oil cakes can be used for animal or fish feed, or to provide substrates for bioprocesses (Ramachandran et al., 2007). Fig. 2.13 provides an overview of the processes involved in producing oils from nuts and seeds for making biodiesel.

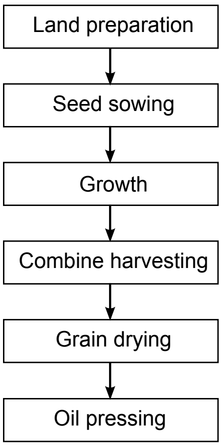


Figure 2.13: Oil production from plant seeds and nuts

Oilseed rape (*Brassica napus*) is the main oilseed crop currently grown in Europe (European Commission: Agriculture and Rural Development, 2009). An annual crop, oilseed rape is sown in late August or early September and is harvested the following year in late July or early August. The plant grows up to 170 cm tall and bears vivid yellow flowers in late spring. The fruits of the oilseed rape plant are 8-10 cm long slender pods in which the seeds themselves grow and mature. The seeds are small and black, around 4 mm in diameter. As the seeds mature, the plant dies and dries out. The seeds are harvested using a combine harvester and typical seed yields are 2.25–4.25 tonne ha^{-1} (Nix, 2008). Oilseed rape straw is fine and breaks easily and has little value so it is usually reincorporated into the soil although some rapeseed straw is baled and used in bioenergy stations.

Hemp (*Cannabis sativa L.*) was at one time a major crop in areas of the UK for fibre which was used in cloth, sail and rope making (Bradshaw et al., 1981) and is the main subject of investigation in this thesis. The hemp plant is an annual, wind-pollinated plant which grows in temperate climates. It has male and female varieties with the female bearing the seeds which are around 4 mm across and medium brown in colour. The fruit of the hemp plant are botanically nuts but commonly referred to as seeds, which is the term used in this thesis. The crop is sown in late April and grows quickly to its full height of around 2 m, being ready for harvest for fibre in late August, or for both seed and fibre in early October. At present in the UK, hemp is grown mainly for fibre, with a small proportion of dual-purpose hemp being grown. Seed from dual-purpose is combine harvested leaving the stems standing in the field. Seed yield from dual-purpose crops is around 0.35–0.50 tonne ha^{-1}. The stems are then mown with a triple-blade mower into 90 cm lengths which are left in the field to dry prior to baling. Hemp stems are sturdy and a source of fibre as well as being a potential source of biomass feedstock for electricity generation or CHP. The cultivation and properties of the hemp plant are investigated in Chapter 5.

Used and waste oils

Used cooking oils (UCO) can also be used a biodiesel feedstock and for this thesis the energy content and density properties of blends of biodiesel from tallow/UCO with petroleum diesel were investigated (Chapter 3). Such oils are collected from large and small-scale commercial caterers, ranging from crisp factories to fish and chip shops. In 2006, the UK's biodiesel production was estimated to comprise 56 200 tonnes per year from waste vegetable oils, and 12 300 tonnes per year from virgin rapeseed oil (Hilton, 2006). These figures do not include the small-scale production units operated by individuals, or small groups, for personal use.

In the UK, used oil collectors transport oils to rendering and refining facilities, where the oils are combined, heated, filtered and categorised into different qualities of oils. The used cooking oil that leaves the rendering and refining facilities rarely comes with a well-defined audit trail, since oils from many different sources are mixed together. The oil can vary widely from batch to batch, depending on the oils and fats that have been collected together in each batch. Some used cooking oils, for example from fish and chip shops, often contain a high proportion of animal fats, and these oils are combined at used oil rendering plants with other oils. Refined used cooking oils can contain a variety of contaminants, including margarines, animal fats, emulsifying agents, water, and free fatty acids. These contaminants affect the transesterification process. The refined product that is used for biodiesel meets a set of criteria specified by the biodiesel producer, and usually includes specification for maximum free fatty acid content and water content.

Cooking oils are subjected to high temperatures, of around 180 °C. High temperatures and the presence of water and food particles in the oil can catalyse the polymerisation of vegetable oils (Mittelbach and Enzelsberger, 1999). Mittelbach and Enzelsberger (1999) found that the polymer content of the oil is a good indicator of suitability for biodiesel production and correlates with the results of the Conradson carbon residue test in which the amount of carbon that remains after evaporation and pyrolysis of an oil is measured. Triglycerides can break down in high temperature conditions to di- or mono-glycerides, releasing free fatty acids into the oil and thereby increasing the free fatty acid content of the oil. The free fatty acid content of biodiesel feedstocks affects the conversion process when alkaline catalysts are used since fatty acids salts form, thereby rendering the catalyst ineffectual.

The meat industry produces waste animal fats at slaughtering and rendering facilities: 22.5 % of the slaughter products enter the rendering plants, and waste animal fat constitutes 24 % of the render products (Niederl and Narodoslawsky, 2004). Biodiesel produced from tallow, also known as tallow methyl esters or TME, contain higher proportions of saturated long-chain fatty acids than vegetable oils. This leads to increases in the pour point, cloud point and viscosity of the fuel, which characterise its low temperature behaviour. In engines, this can cause performance problems at low temperatures when waxes form from the long-chain molecules in the biodiesel.

Minority oils

In addition to the annual oilseed crops and large-scale waste oils from cooking and from the meat industry, minority crops and oil sources have been the subject of investigation in recent years. Such feedstocks include algae, wastewater and sewage sludge, fish oils and halophytic plants. Biomass can be pyrolysed to produce bio-oil, which has similar properties to biodiesel, but for the purposes of this thesis only fatty acid methyl esters are considered. At present, hemp seed oil is technically a minority oil, however as one of the main crops investigated in this thesis it has been discussed above in Section 2.7.1.

Algae have been the subject of investigation for the production of lipids suitable for conversion to biodiesel. As yet, the processes and technologies for growing algae to produce oils are not as well established as the vegetable and animal oil techniques. Miao and Wu (2006) investigated the production of biodiesel from microalgae, which develop a lipid content of up to 55 %. The lipid fraction was extracted and transesterified under acidic conditions and produced a biodiesel of comparable quality to vegetable oil biodiesel. In a review of microalgae for biodiesel, Chisti (2007) suggested that 50 % of the demand for diesel in the USA could be met by algae on as little as 1.1 % of the USA's total agricultural land area, growing microalgae with a 70 % lipid content in ponds or in photobioreactors. Although technically feasible, large-scale biodiesel production from algae is yet to become a practical reality.

Lipids from wastewater and sewage sludge have been investigated as potential sources of biodiesel feedstock. In addition to used cooking oils that are collected from large fryers, lipids collected from restaurant grease traps can be converted to biodiesel, subject to pre-treatment to deal with the free fatty acids (Canakci, 2007). Grease traps are located on the wastewater pipes from the restaurant and collect solid and liquid lipids referred to as brown grease. This brown grease provides a very low-cost biodiesel feedstock but has significant requirements for quality improvement prior to conversion to biodiesel. Lipids extracted from sewage sludge have been used to produce biodiesel in the laboratory and, if practical on a commercial scale in the USA, could be a source of up to 700 million litres of biodiesel (Dufreche et al., 2007).

Fish oils, extracted from the discarded parts of fish during processing for fish products, have been investigated and found to be suitable as a feedstock for biodiesel (Lin and Li, 2009; Reyes and Sepúlveda, 2006). The biodiesel produced from fish oils has viscosity, density and calorific content close to those of biodiesels from waste cooking oils.

The halophytic plant *Kosteletzkya virginica* has been grown experimentally in tidal land in China and investigated for its potential as an oilseed crop (Ruan et al., 2008). The plant tolerates salinity and yields seeds at a rate of 957kg ha^{-1} with an oil content of 16–18 % w/w.

2.7.2 Production methods

The production of fatty acid methyl esters, biodiesel, from vegetable oils via alkali-catalysed transesterification is a straightforward and well-established process (Figure 2.14), and has been widely used as a way of preparing fatty acids for analysis using gas chromatography (Christie, 1973).

Alkali-catalysed transesterification of vegetable oils in batches using methanol in the presence of sodium hydroxide or potassium hydroxide is the most widely used process commercially in the UK. At the start of the batch production process, oil, methanol and catalyst are combined

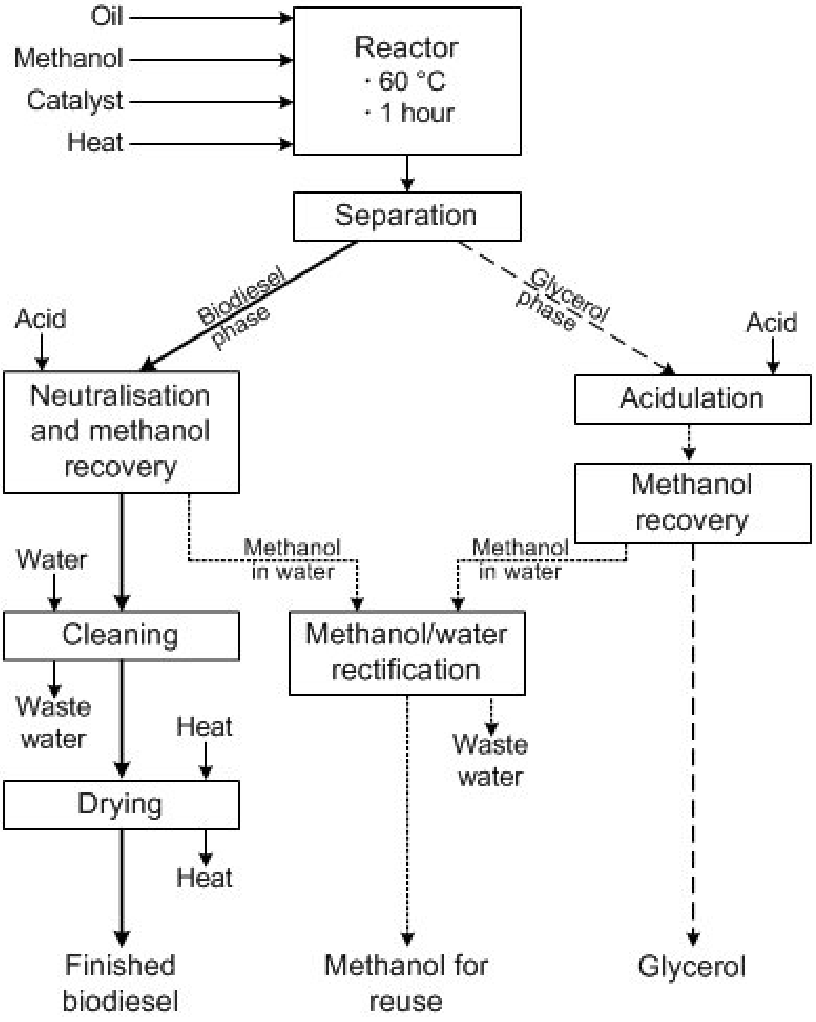


Figure 2.14: Biodiesel conversion process

in the reactor. Mixing is required initially to bring the reactants into contact with one another. Tetrahydrofuran has been used as a co-solvent to induce mixing of the methanol and oil phases (Mahajan et al., 2007). When the reaction is underway, the intermediate di- and mono-glycerides act as emulsifiers, and mixing is no longer required. The reaction vessel is typically maintained at a temperature of 60 °C, to bring the reaction to completion quickly. The reaction process takes around 90 minutes to reach 90 % completion (see, for example, Noureddini and Zhu (1997)) and in practice an excess of methanol is used, typically a 6:1 molar ratio of methanol to triglycerides, to drive the reaction towards completion (Freedman et al., 1986). The reaction mixture separates into two phases, a less-dense biodiesel phase and a more-dense glycerol phase, and the two can be separated by drawing out the glycerol phase from the bottom of the vessel, or using a centrifuge. The biodiesel phase is strongly alkaline, owing to the presence of the catalyst, and can also contain glycerol and methanol. Acid is added to the biodiesel phase to stop any further reaction. Methanol, catalyst, glycerol, soap and salts in the biodiesel phase are removed through washing the biodiesel with water. The maximum allowed methanol content of biodiesel is 0.2 % in the EN 14214 standard. As little as 1 % methanol in biodiesel can reduce the flash point from 170 °C to less than 40 °C (Van Gerpen and Knothe, 2005). The biodiesel is dried of any remaining water by heating it above 100 °C.

Methanol, ethanol, propanol, butanol and amyl alcohol can be used in the transesterification process. Methanol is generally the cheapest alcohol, and the European standard for biodiesel, EN 14214, specifies that the fuel should be 96.5 % methyl esters, enforcing the use of methanol in transesterification to produce fuels for use in Europe (British Standards Institution, 2004a).

Batch-production processes catalysed by acids or enzymes have also been developed. The acid-catalysed method is more suitable for processing feedstock oil that has a high free fatty acid content, because in a high acid-content blend of reactants, the alkaline catalyst is consumed by the free acids and is unavailable to catalyse the reaction. Canakci and Van Gerpen (2001) presented a two-step method for producing biodiesel from feedstocks with high free fatty acid contents. Acid-catalysed transesterification is used to pre-treat oils with high contents of free fatty acids, followed by the alkali-catalysed method once the free fatty acid content drops below 1 %. Both alkali and acid catalysts end up in the glycerol phase after the reaction, and removal of the catalyst for reuse was reported to be difficult (Canakci and Van Gerpen, 2001). Enzyme catalysts have reusability as a chief advantage, with less energy intensive reaction conditions required than for alkali or acid catalysed reactions

Alternatives to batch production are in development. Bournay et al. (2005) have proposed a continuous flow production process for biodiesel production using a mixed oxide of zinc and aluminium, with higher temperature and pressure conditions than the standard alkali-catalysed process. Both biodiesel and glycerol phases achieve high purity levels of 98.3 % and 98 % respectively, with fewer processing stages. In the absence of a dissolved catalyst, water washing is not required. Methanol recovery is achieved through partial evaporation and methanol vaporisation under vacuum conditions. Skelton et al. (2004) have developed a continuous flow biodiesel reactor using conventional alkali-catalysis and an Oscillatory Flow Reactor which is suited to long, two-phase reactions. The 20 litres per hour pilot unit produces a 99 % biodiesel yield at a residence time of 30 minutes, and 99.5 % yield at 40 minutes.

The process can be accelerated by changing the conditions, either by using alkali, acid or enzyme catalysts, or by using supercritical conditions to drive the reaction faster, with methanol (Saka and Kusdiana, 2001) or ethanol (Gui et al., 2009). Reaction conditions for a variety of catalysed transesterification reactions are summarised in Table 2.5.

Meher et al. (2006) reviewed the technical aspects of biodiesel production, including a survey of the alkaline catalysts used in the transesterification process. They highlight the disadvantages of alkaline catalysis: the high demands for energy; the difficulty of separating glycerol and the catalyst from biodiesel; the requirements for treating the alkaline waste water; and, the difficulty of excluding water and free fatty acids from the reaction mixture, and the detrimental effects that they have on the system.

Alternative methods of producing biodiesel have been reported, including the production of biodiesel from low quality, non-purified vegetable oils using a KF/MgO catalyst (Liang et al., 2009), in situ transesterification of soybean oil in soybean flakes (Haas et al., 2004), and the use of hybrid catalysts such as Ta_2O_5/SiO_2 - $[H_3PW_{12}O_{40}/R]$ where R is a methyl or phenyl moiety (Xu and Hanna, 2009).

Method	Catalyst	Temperature	Pressure	Time to completion	Yield (%)
Alkali	NaOH or KOH	60 °C	Atmospheric	1–2 hours	98
Acid	Concentrated sulphuric acid or sulphonic acid	70–180 °C, depending on the acid used	up to 80 bars	up to 27 hours	up to 99
Enzyme	Lipase	28–60 °C	Atmospheric	1–120 hours	up to 99
Supercritical methanol	(N/A)	350–400 °C	45–65 MPa	4 minutes	> 95
Mixed oxide	Zinc and aluminium mixed oxide	40–65 °C	4–6 MPa and 0.1–0.5 MPa		98.3
Continuous flow	NaOH		Atmospheric	20 litres per hour	99–99.5

Table 2.5: Catalysed transesterification reactions conditions. Sources: Mittelbach and Remschmidt (2004), Saka and Kusdiana (2001), Bournay et al. (2005), Skelton et al. (2004).

2.7.3 Co-products

The co-products of the biodiesel conversion process are glycerol, soapstock, salts, washwater, heat and methanol.

Glycerol's properties as a non-toxic humectant and lubricant result in it being widely used in the pharmaceutical, personal care and and food industries, and in some industrial processes. Glycerol for food, personal care and pharmaceutical products must be of 100 % vegetable origin. Only glycerol that has a complete and verifiable audit trail can be used in these products. This is a particularly important consideration for biodiesel production from used cooking oils, where an audit trail cannot be provided. Given the quantities of glycerol now being produced by the growing biodiesel industry, some researchers are investigating alternative uses for glycerol. For example, Karinen and Krause (2006) report on the production of branched oxygen-containing components from glycerol, for use in fuels or as solvents.

Methanol, recovered from the glycerol, biodiesel and washwater, can be reused in further transesterification processes. In the glycerol phase, methanol is removed by a vacuum flash process, or by evaporation (Van Gerpen and Knothe, 2005). Methanol can be recovered from the wash water. Some methanol is lost from the reaction process through evaporation or trace quantities may remain dissolved in the glycerol, biodiesel or wash water.

Other co-products, which perhaps might elsewhere be considered as waste products, include soap, salts and wash water. Soap, potassium or sodium salts of fatty acids, may persist to the final product stage of the transesterification process, if it is not broken down into free fatty acids and salts in the acidulation stage. Potassium sulphate is formed when potassium hydroxide is used as the catalyst and neutralisation is carried out with sulphuric acid. Such salts are suitable for use as fertiliser. The post-processing stages of washing the biodiesel give rise to wash water which contains dissolved catalyst, acid, methanol and salts.

Typically, only material co-products are considered. However, given that life cycle assessment in this project is closely concerned with the energetic inputs and outputs, it is important to include heat in the co-products. Heat can be recycled in the biodiesel production process, for example the heat extracted when the final biodiesel product is cooled down could be used to preheat the feedstock oil going into the process by simple heat transfer, for example via a contraflow shell and tube heat exchanger.

Chapter 3

Densities and energy contents of biodiesel-petroleum diesel blends

The promotion of biofuels in transport is measured by two different metrics: volumetric proportions in the UK's Renewable Transport Fuels Obligation (Department for Transport, 2007b) and energetic proportions in the EU's Directive on biofuels (European Commission, 2003). In this chapter, the differences between the two metrics are explored and the implications for reporting policy results are outlined. These metrics are closely related to the density and gross heat of combustion (energy content) of the fuels and these two properties are investigated experimentally in order to test relations between blend proportions. These relations are then applied to data concerning the overall diesel fuel supply to the UK in 2008/09 in order to assess the differences between the RTFO and EU Directive's modes of reporting biofuel proportions in the road transport fuel supply.

The calculations of the proportions of fossil diesel and biodiesel components in diesel fuel blends are undertaken in three ways:

- volumetrically (UK RTFO and fuel suppliers)
- gravimetrically (peer-reviewed research)
- by energy content proportions (European Directive 2003/30/EC).

These three ways of describing fuel blend proportions are not always exactly equivalent, given that different diesel fuels have different densities and different gross heats of combustion. The differences between these proportions are explored in this chapter through experimental and theoretical investigation of diesel fuel blends.

Transport fuels are dispensed volumetrically in the UK, as in many other countries, in legislation enforced by UK Trading Standards. This volumetric approach is used in the RTFO to specify the required proportion of biofuels to be sold in the UK as a volume percentage of the total fossil fuel sales (Department for Transport, 2007b). The volumetric proportion of biodiesel in a diesel fuel is denoted by fuel suppliers by the use of the B-number. For example, a fuel blend which contains 5 % biodiesel by volume is denoted by B5, whereas a fuel blend which contains 25 % biodiesel by volume is labelled B25.

Following this standard commercial practice of volumetric blending, several researchers have adopted the volume proportions approach in their work (Albuquerque et al., 2009; Alptekin and Canakci, 2008, 2009; Benjumea et al., 2008; Yoon et al., 2008). Benjumea et al. (2008) justified their selection of volumetric blending by referring to the common practice of volumetric blending at ambient temperature in the fuel industry. Alptekin and Canakci (2008) used volumetric blend proportions of petroleum diesel-biodiesel blends and found that the volumetric proportions predicted the blend viscosity more accurately than the mass proportions did. They subsequently used the volumetric approach in further work (Alptekin and Canakci, 2009).

Some researchers working on the densities of blended diesel fuels have used the gravimetric method of calculating blend proportions. Tat and Van Gerpen (2000) investigated the specific gravity of blends of petroleum diesel and biodiesel fuels using mass proportions to describe the blends. The approach that they used was adopted by others researching the specific gravity of other petroleum diesel-biodiesel fuel blends (Yuan et al., 2004). Tat and Van Gerpen (2000) provided no justification for their selection of mass proportions over volume proportions but a simple statement that “owing to differences in density between the biodiesel and No. 2 diesel fuel, blends prepared by volume would be somewhat different” (p. 115). Therefore, when comparing data on the properties of petroleum diesel-biodiesel blends, attention is needed on the type of blending that has been used, in order to assess the comparability of the data.

In contrast to the established commercial and research practices for describing fuel blends, the EU Directive on promoting the use of biofuels in transport fuels (European Commission, 2003) specifies targets in terms of the proportion of energy in the fuel mix that comes from biofuels. Although the UK government specifies an average gross heat of combustion for petroleum diesel fuel of 45.5 MJ kg^{-1} (Department of Energy and Climate Change, 2009), no official indication of the range of gross heats of combustion is given for diesel fuels. As of 2008, no gross heat of combustion is given by the UK government for biodiesel. Therefore, calculation of progress towards the EU target may be hampered by the lack of accurate information regarding the gross heats of combustion of both petroleum diesel and biodiesel fuels.

The energy content and density combined give an indication of the energy per unit volume of fuel, referred to herein as the energy density, which is an important parameter for engines. Information on the properties of blended diesel fuels is important for verifying the compatibility of fuels with current vehicles and infrastructure, through compliance with the EN specifications for diesel fuels as set out in Table 2.4 on page 34. When fuel is delivered to engines, it is measured by volume. Therefore, fuels with a lower energy density provide the engine with less energy per delivered volume than fuels with higher energy densities. This reduction in delivered energy can result in reduced engine performance for a given volume of fuel.

The relation between the density and energy contents of blended diesel fuels and their significance for the energy density was investigated experimentally and theoretically. This chapter comprises a survey of the literature, laboratory techniques and the current research basis (Section 3.1), experimental methods and results for the density and energy content of blended diesel fuels (Sections 3.2 and 3.4). The significance of the differences in the energy densities of petroleum diesels, biodiesels and blended diesel fuels is explored through combining results from energy content and fuel density tests. A set of samples from twelve commercial fuel retailers was obtained and each sample tested for its energy content to provide information on the variability of diesel fuel energy contents. Finally the results from these sections are synthesised and areas for further consideration are outlined in Section 3.6.

3.1 Background

3.1.1 Density

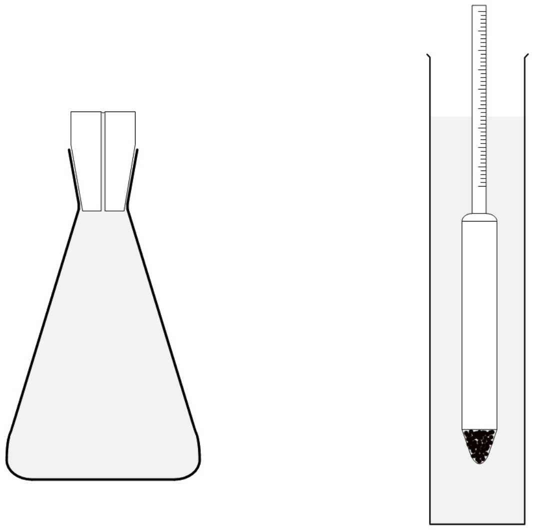
Density is the mass of a substance per unit volume and in SI units density is measured in kg m^{-3}. Experimentally, the density of a liquid can be determined using a pycnometer, a hydrometer, an oscillating U-tube or with a digital density meter. A pycnometer, or density bottle, is a small glass bottle with a capillary tube in its stopper, as shown in Fig. 3.1(a). When the stopper is put into the bottle, the liquid fills it to the top of the capillary tube, permitting an accurate volumetric sample. The volume of the bottle is calibrated with measurements of distilled water.

Simpler equipment such as volumetric flasks could be used in place of the pycnometer. However, volumetric flasks have higher variability in their volume than the pycnometer and accurately positioning the meniscus is more difficult in a volumetric flask than in a pycnometer. To reduce errors a much larger quantity of sample, for example 500 ml, is required for the volumetric flask method than the c. 160 ml required for three tests of each sample in the pycnometer.

A hydrometer is a calibrated tube which floats in a sample of the liquid to be measured, as shown in Fig 3.1(b). The weighted tip ensures that the hydrometer floats vertically in the sample. The depth to which the hydrometer sinks reveals the specific gravity of the liquid, which is measured from a scale on the neck of the hydrometer. The hydrometer can be used to measure the density of samples at controlled temperatures by placing the sample with the hydrometer in it into a constant temperature water bath (Fig. 3.2). The specific gravity of a liquid sample, SG_{sample}, is the ratio of its density, ρ_{sample}, to the density of water, ρ_{water}, at a specific temperature, usually 15.6 °C, as shown in Eqn. 3.1:

$$SG_{sample} = \frac{\rho_{sample}}{\rho_{15.6\ ^{\circ}C,water}} \tag{3.1}$$

The standard procedures for measuring density of biodiesels, according to the EN ISO standards, involve the use of either a standardised glass hydrometer (EN ISO 3675) or an oscillating U-tube (EN ISO 12185) at the prescribed temperature of 15.6 °C (Mittelbach and Remschmidt,



(a) Pycnometer (density bottle)

(b) Hydrometer

Figure 3.1: Apparatus for measuring the density of liquid samples

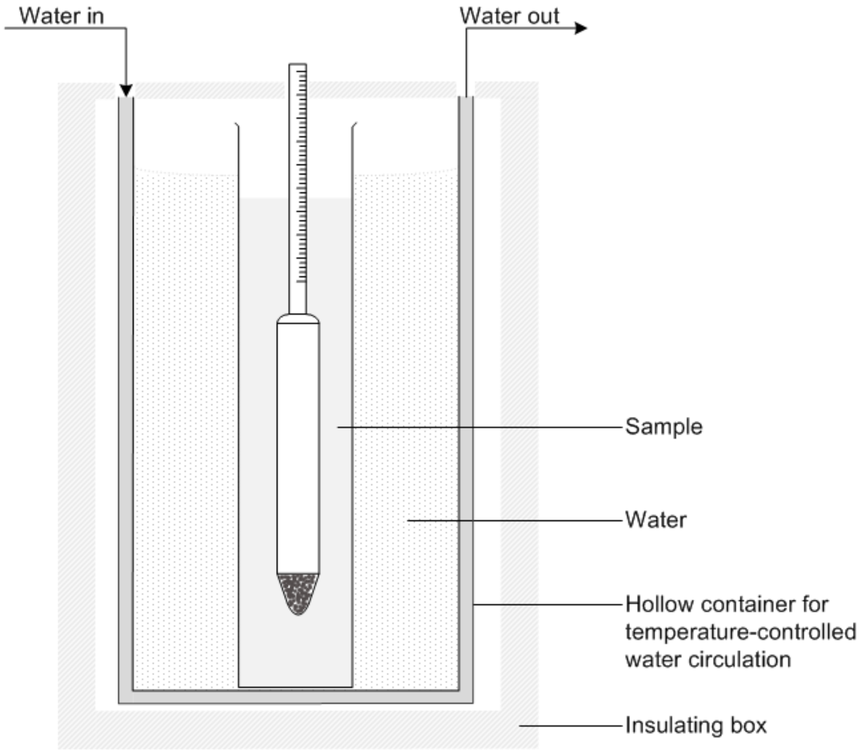


Figure 3.2: Hydrometer in insulated water bath

2004). The oscillating U-tube method employs a tube to contain the liquid sample between oscillation points that are separated by a known distance. A mechanical oscillation is established in the sample and from this oscillation the mass of sample between the points, and hence the sample's density, can be calculated.

Provided that no interactions occur between blend components upon mixing, the density of the blend, ρ_{Blend}, is expected to follow the relation given in Eqn 3.2 (Clements, 1996):

$$\rho_{Blend} = \sum_{i} \rho_i v_i \tag{3.2}$$

where ρ_i is the density of the ith component and v_i is the volume fraction of the ith component. For example, a 50:50 blend by mass proportions of a dense fuel and a less dense fuel would contain a volumetric proportion of the denser fuel of less than 50 %, and volumetric proportion of the less dense fuel of more than 50 %.

The EN 14214 specification gives a range of 860–900 kg m^{-3} for the permitted density of biodiesels which is in agreement with much of the literature on the properties of biodiesels (Alptekin and Canakci, 2008; Gouw and Vlugter, 1964; Mittelbach and Remschmidt, 2004). Gouw and Vlugter (1964) showed that the density of fatty acid methyl esters (FAMEs) with chain lengths between 12 and 22 carbon atoms at 20 °C varied in the range 866.3–897.9 kg m^{-3}. This agrees with the summary of results in the literature presented by Mittelbach and Remschmidt (2004) that gave a range of 873–904 kg m^{-3} for similar FAMEs. Density decreases with increasing chain length and increases as the number of double bonds in the carbon chain increases. Alptekin and Canakci (2008) reported on six biodiesels produced in the laboratory from commercially available vegetable oils (sunflower, canola, soybean, cottonseed and corn oils and waste palm oil) with their densities in the range 874.6–884.5 kg m^{-3} at 15 °C. The lowest density biodiesel came from waste palm oil and the most dense biodiesel from soybean oil.

The density range in the EN 590 specification for DERV fuel (British Standards Institution, 2004b) is 820–845 kg m^{-3}. Guidance from the UK's National Weights and Measures Laboratory gives figures from BERR for the densities of different types of diesel (National Measurement Office, 2009). Diesel with less than 0.005 % sulphur has an average density of 833.7 kg m^{-3}, sulphur-free diesel density is 840 kg m^{-3} and B5 diesel which contains 5 % biodiesel by volume has a density of 842.5 kg m^{-3} (National Measurement Office, 2009). The average density for DERV fuel (less than 0.005 % sulphur) is 834.7 kg m^{-3} according to the UK Petroleum Industry Association data cited in the Digest of UK Energy Statistics 2009 (Department of Energy and Climate Change, 2009). In a Department for Transport report on the costs of introducing biofuels, a density of biodiesels of 840 kg m^{-3} was given (Department for Transport, 2006). However, this value lies significantly below the lower limit for biodiesels in the EN 14214 specification (British Standards Institution, 2004a).

Research on the properties of petroleum diesel-biodiesel blends has generally been conducted using fuel that meets the American standards, reflecting the location of the researchers (Tat and Van Gerpen, 2000; Benjumea et al., 2008; Yuan et al., 2004). The ASTM D 6751 standard for biodiesels has no upper limit on density and therefore denser biodiesels can be sold within the standards than in the European Union, according to the European specification. Ways of reducing the density of the densest biodiesels have been investigated, for example Albuquerque et al. (2009) blended castor, soybean, cotton seed and canola (rape seed) biodiesels and investigated the specific gravity of their blends according to ASTM method D4052 with a view to producing an EN 14214 compliant biodiesel. Alptekin and Canakci (2009), working in Turkey, prove to be the exception having based their study on fuels that are, for the most part, EN 590 and EN 14214 compliant. They tested five biodiesels, from sunflower, soybean, canola, corn and cottonseed oils, and of these the canola methyl ester was outside the EN 14214 specification for the flash point, at 107 °C, 13 °C below the lower limit of 120 °C. The work presented in this chapter uses fuels which meet the European specifications and therefore it complements the research on fuels which meet the American specifications (Tat and Van Gerpen, 2000; Benjumea et al., 2008; Yuan et al., 2004).

Albuquerque et al. (2009) demonstrated linear relations between the density of petroleum diesel-biodiesel blends and the proportion of biodiesel in the blend. These relations agree with Eqn 3.2. Yuan et al. (2004) found that the specific gravity of blends of yellow grease biodiesel with number 2 diesel fuel also behaves in accordance with Eqn. 3.2. Benjumea et al. (2008) also demonstrated a linear relation between biodiesel proportion and the density of the blended fuel for blends of palm oil biodiesel and commercial grade Number 2 diesel fuel, as classified by the ASTM. Alptekin and Canakci (2008) produced biodiesels from six different vegetable oils (sunflower, canola, soybean, cottonseed and corn oils and waste palm oil) and blended them with petroleum diesels from two different retailers, Shell and Petrol Office. The blend densities were tested at 15 °C using an Anton Parr density meter. Their analysis of the results showed a good fit between a linear relation and the experimental results with R^2 regression coefficients ranging from 0.9984 to 0.9999. The relation that they used was of the form

$$D = Ax + B \tag{3.3}$$

where D is density, A and B are coefficients and x is the biodiesel fraction.

The evidence reported thus far generally portrays a simple relation between biodiesel blend proportions and the density of these blends. Benjumea et al. (2008, p. 2072) state:

> “When the components of a mixture have similar chemical structure it is expected that they do not interact with each other and consequently the interaction parameter [used to describe the effect of such an interaction] can be neglected. Biodiesel-diesel fuel blends can be assumed to behave this way because both liquids are non-polar, completely miscible, and when blended their volumes are practically additive.”

The density of liquids varies with temperature and the rates of change of density with temperature may, if different for petroleum diesel and biodiesels, affect the volumetric proportions of blended diesel fuels. The influence of temperature on volumetric proportions is investigated in this chapter. Linear relations were found between the densities of petroleum diesel-biodiesel blends and temperature (Tat and Van Gerpen, 2000; Yuan et al., 2004; Noureddini et al., 1992). Commercially, Standard Temperature Accounting (STA) is being introduced in the UK to compensate the dispensed volumes of fuel for changes due to deviations in temperature from the standard temperature of 15 °C (National Measurement Office, 2009). Tat and Van Gerpen (2000) studied the specific gravity of soybean oil biodiesel and its blends with diesel fuels that met the ASTM standards for diesel: number 1 diesel and number 2 diesel (ASTM D975, 2010). They surveyed gravimetrically blended diesel fuels across a range of temperatures, from the crystallisation point to 100 °C using a specific gravity balance and a small water bath for temperature control. They found that the relation between temperature and the specific gravity was linear, and that the blends with higher proportions of fossil diesel had lower specific gravity across the temperature range. The densities of biodiesel and number 2 diesel fuel are such that at higher blend proportions, a

75 % biodiesel blend by volume would be a 74.93 % blend by weight proportions. The specific gravities were compared with the ASTM D1250 corrections for fossil diesel, and were found to be within 0.30 % of those values. Yuan et al. (2004) undertook a similar study of the specific gravity of soybean and yellow grease biodiesel fuels and biodiesel/diesel fuel blends, using a glass hydrometer instead of the specific gravity balance used by Tat and Van Gerpen (2000). The results of Yuan et al. (2004) for soybean biodiesel concurred with those of Tat and Van Gerpen (2000) and the results are summarised in Table 3.1. The relation between the specific gravity of the fuels and the temperature is given in Eqn. 3.4:

$$SG = A + BT \tag{3.4}$$

where A and B are parameters specific to each fuel.

Analysis of data in Gouw and Vlugter (1964) for the densities of fatty acid methyl esters shows that most of the fatty acid methyl ester densities at 15.6 °C are in the range 860–900 kg m^{-3}. Gouw and Vlugter (1964) provided a data table for densities of pure fatty acid methyl esters at 20 and 40 °C. The densities at 15.6 °C were extrapolated from the values in the data table using the assumption that a linear relation between temperature and density is valid, as found elsewhere (Tat and Van Gerpen, 2000). Gouw and Vlugter (1964) did not provide data on the densities of palmitate, heptadecanoate, stearate, nonadecanoate or arachidate methyl esters. For these methyl esters, the rate of change of density with temperature was estimated by comparing the carbon chain length and structure with the rates of density change with temperature for other methyl esters, and from these the densities at 15.6 °C and 20 °C were estimated.

The results of this analysis are shown in Figure 3.3. Four fatty acid methyl esters fall outside the EN 14214 specification at 15.6 °C, namely acetate, proprionate, butyrate and linoleate. The first three of these do not occur widely in fats and oils. Linoleate methyl ester occurs in low concentrations in biodiesels made from vegetable oils and in such cases the lower densities of the other methyl esters in the biodiesel lowers the overall biodiesel density to within the EN 14214 limits.

Biodiesel feedstock	A	B
Soybean oil[1]	0.8976	-6.6200×10^{-4}
Soybean oil A[2]	0.89468	-6.90148×10^{-4}
Soybean oil B[2]	0.89753	-7.01565×10^{-4}
Yellow grease[2]	0.88607	-6.82948×10^{-4}

Table 3.1: Specific gravity response to temperature for various biodiesels, in the form $SG = A + BT$ where T is in °C. Data are given to the degree of accuracy presented in the original sources. [1] Tat and Van Gerpen (2000). [2] Yuan et al. (2004)

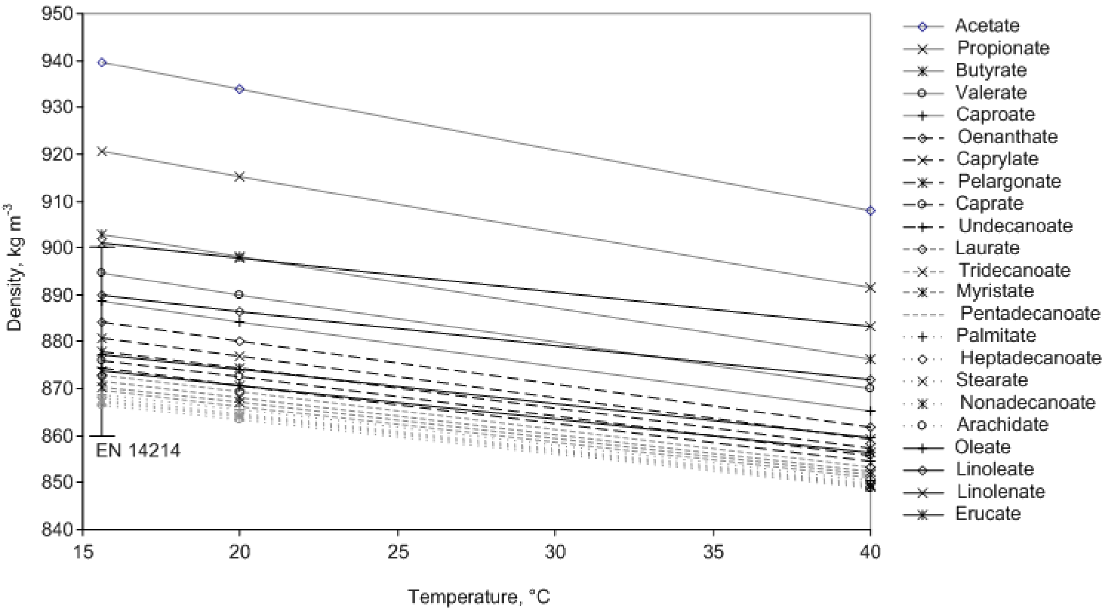


Figure 3.3: Densities of FAMEs compared with the EN 14214 specification. Data from Gouw and Vlugter (1964). Density at 15.6 °C is extrapolated from data at 20 °C and 40 °C.

3.1.2 Energy contents of blended diesel fuels

The energy content of biodiesel must be at least approximately equivalent to DERV fuels in terms of their energy content, so that vehicle engines can run on biodiesel fuels, or blends of biodiesel fuels with DERV fuels, as effectively as they can on DERV fuels. As mentioned in the introduction to this chapter, the UK government uses and publishes only an average gross heat of combustion for petroleum diesel fuel (45.5 MJ kg^{-1} Department of Energy and Climate Change (2009)) without any indication of the range, nor an official value for the gross heat of combustion of biodiesel. The Department for Transport does include a value of 40.128 GJ tonne^{-1} (40.128 MJ kg^{-1}) for the energy content of biodiesel in its report on the costs of biofuels (Department for Transport, 2006). Furthermore, the fuel specifications for petroleum diesel and biodiesel (EN 590 and EN 14214 respectively) make no mention of requirement for the fuels' gross heats of combustion. By contrast, the EN 14213 specification for biodiesel for heating purposes does include a gross heat of combustion specification.

The gross heat of combustion of a material is governed by the energy required to break bonds between atoms in the material, and the energy released when these atoms are then oxidised. When two fuels are blended together, the combined gross heat of combustion per unit mass will therefore be the sum of the parts, unless the fuels react with one another during blending. The expected relation between blend proportions and heat of combustion per unit mass is therefore given by

$$GHC_{blend} = \sum_i x_i GHC_i \tag{3.5}$$

for blends that contain mass fraction x_i of the ith component, which has gross heat of combustion per unit mass GHC.

The gross heats of combustion of biodiesels from vegetable seed oils have been reported in the ranges 40.84–41.98 MJ kg^{-1} (Demirbas, 2008). Klopfenstein and Walker (1983) also tested the gross heats of combustion of individual fatty acid methyl esters and their results were 36.99–40.23 MJ kg^{-1}. The lowest value, 36.99 MJ kg^{-1}, reported by Klopfenstein and Walker (1983) is for laurate methyl ester, which occurs is small concentrations in vegetable oils that are typically used for biodiesel production (Shu et al., 2007). The lowest value of the majority components of vegetable oils is 38.72 MJ kg^{-1} for linoleate methyl ester (Klopfenstein and Walker, 1983). A value of 40.128 GJ tonne^{-1} (40.128 MJ kg^{-1}) is used in UK government documentation (Department for Transport, 2006).

3.1.3 Energy density

The energy density, ED, of a substance is its energy content per unit volume (Eqn. 3.6)

$$ED = \frac{energy\ content}{volume} \tag{3.6}$$

and is related to the gross heat of combustion, GHC (Section 3.1.2), and density, ρ, by Eqn. 3.7.

$$ED = GHC \times \rho \tag{3.7}$$

Sims (2002) reports energy densities of 38.6 MJ litre^{-1} and 33.3 MJ litre^{-1} for automotive diesel and biodiesel respectively.

3.2 Methods

For the experimental work for the research, blended diesel fuels were made from pure petroleum diesel and biodiesel. The density of the blended fuels was tested using a pycnometer and the energy contents were tested using a bomb calorimeter. For comparison purposes and an indication of the variability of diesel fuels in the UK supply, twelve samples of commercially-sold diesel fuel were obtained and tested for their energy contents. The energy densities were calculated from the density and energy content results. Further, the temperature response of density of fuel blends was measured using a hydrometer with the sample held in a temperature-controlled water bath.

3.2.1 Sources of fuel samples

For the experimental testing of the relationships commercially available biodiesels and DERV fuels were purchased for use in this study. Two separate suppliers of biodiesel were used:

- Argent Energy Ltd for TME
- ADM GmbH for RME

Pure petroleum diesel fuel for making blends with biodiesels was obtained from a local supplier, CPS Fuels Ltd. Further, six samples were purchased from retailers around England in order to obtain an indicative range of the energy contents and densities of DERV fuels generally available in the UK. Six additional samples were purchased in Norwich to test the similarity of fuels from a small geographical area. All fuels used in this study meet the relevant EU specification, EN 14214 for biodiesels, EN 590 for fuels sold as DERV fuel. DERV fuels can contain up to 5 % biodiesel and only fuel referred to in this thesis as petroleum diesel is devoid of biodiesel content.

Sample	Location	Supplier type
UK-A	Skipton	Supermarket
UK-B	Stafford	Motorway service station
UK-C	Cheltenham	Oil-company owned
UK-D	Sleaford	Oil-company owned
UK-E	Cromwell	Oil-company owned
UK-F	Norwich	Supermarket
N-1	Norwich	Oil-company owned
N-2	Norwich	Supermarket
N-3	Norwich	Supermarket
N-4	Norwich	Supermarket
N-5	Norwich	Oil-company owned
N-6	Norwich	Oil-company owned

Table 3.2: DERV fuel samples from commercial sources

3.2.2 Making fuel blends

The blends selected for these experiments varied from B0 to B100, with more blends at lower B numbers chosen (B5 and B10) since this is the range of interest according to the EU Directive and RTFO policies on biofuels. The selected blends for investigation were: B0, B5, B10, B25, B50, B75, B90 and B100 with the B number calculated by volumetric proportions.

Samples were blended in 250–500 ml quantities from the separate fuel components. This was sufficient for use in the density and energy content tests which require 160 ml and 1–2 ml respectively for each sample. Initially, a volumetric method was used to make blends of biodiesel and DERV fuel since volumetric blend proportions are used in the RTFO. However, errors were incurred when measuring fuels volumetrically due to the fuel adhering to the internal surfaces of the measuring vessel and to errors in the volumetric containers themselves. After a few initial experiments, the volumetric method of measuring blends was abandoned in favour of a gravimetric method of measuring the blend components. Pure biodiesel and DERV fuel densities were determined using a pycnometer. These densities were then used to calculate the quantities of fuel required to make up blends of the fuels at particular volumetric proportions of the fuel components. The required masses of the fuels were weighed out using a mass balance.

3.2.3 Density measurements

The densities of blends of biodiesel and DERV fuel from CPS Fuels Ltd, sampled on 5th March and blended on 20–21 March 2007, were measured. A nominally 50 ml pycnometer was used to determine the densities of the blended fuels. The pycnometer was calibrated using distilled water at a temperature of 21.4 °C and toluene at 23.8 °C. The temperature of the fuels at the time of measurement was just over 22 °C, varying slightly. The pycnometer was cleaned with propan-2-ol between samples and dried with a clean air flow. The pycnometer was weighed to determine the degree of cleanliness and dryness achieved and, if found to have retained traces of sample, cleaned again and dried with a pumped air supply.

Pycnometer calibration

The true volume of the pycnometer was established using distilled water. The dry pycnometer weighed was and then filled with water. A digital temperature probe was used to record the water temperature inside the bottle. The stopper was inserted into the neck of the pycnometer and excess water was dried off the outside of the bottle using absorbent tissue. Finally any water droplets on top of the stopper were removed by swiftly dabbing the stopper top with filter paper so that water was not drawn up from inside the capillary tube. The prepared bottle was weighed and the water content was calculated from the difference between the initial and final weights. Two further distilled water samples were measured in this way before drying the pycnometer and weighing it again to check its dry mass. This procedure was repeated on three occasions. Data on the density of distilled water at various temperatures was used to calculate the volume of water present in each test.

To test the accuracy of the density bottle method of determining density against a liquid of a similar density to diesel and biodiesel, measurements of the density of toluene were carried out. Toluene, $C_6H_5CH_3$, has a density of 866.8 kg m^{-3} at 20.0 °C (Lide, 2005), in the middle of the range of interest for diesel and biodiesel, 825–890 kg m^{-3}. Furthermore, since toluene comprises a single molecule form as shown in Fig 3.4, the composition of toluene does not vary, therefore the density of toluene is a known and specific characteristic of the liquid.

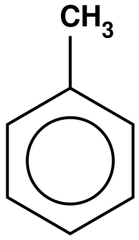


Figure 3.4: Toluene, $C_6H_5CH_3$.

3.2.4 Temperature response of density

The response of fuel density to changes in temperature was determined for DERV fuel, RME, TME, and B50 using a Cole Palmer EW-08292-10 hydrometer in c. 220 ml of fuel sample, held at temperature by a temperature-controlled water bath as shown in Fig. 3.2. The temperature control unit circulates water through the hollow container, made of metal for good thermal conductivity.

The hydrometer is calibrated in units of specific gravity, relative to the density of water at 60.0 °F (15.6 °C) i.e. 999.007 kg m^{-3}, and marked with intervals of 0.5 units SG. The readings were converted to density using Eqn. 3.1. The apparatus was allowed to equilibrate for at least 10 minutes after the circulating temperature-controlled water had reached the required temperature, as shown on the control unit. The temperature of the sample was measured using a BS 1365:1990 certified thermometer with 0.5 °C intervals. The water in the water bath was stirred manually, as was the fuel sample, to ensure a uniform temperature. Such agitation was particularly important when cooling the apparatus below room temperature, to avoid thermal stratification in the fluids.

3.2.5 Energy content measurements

The bomb calorimeter, shown in Fig. 3.5, enables determination of the gross heat of combustion through the contained combustion of the sample in the oxygen-rich environment of the metal bomb, which causes a rise in the temperature of the water in the calorimeter's containing bucket. The temperature rise is measured accurately with a calibrated thermometer, graduated to 0.01 °C, allowing readings to be taken to 0.002 °C. The weighed sample is placed in the dish and the fuse wire inserted into the electrodes such that it is in contact with the surface of the sample. The bomb is charged with oxygen to 30–35 atm. When the ignition unit is triggered, a high current flows through the fuse wire which becomes hot and then ignites, igniting the sample. In a successful run, the sample oxidises completely and the heat of combustion is transferred through the bomb and into the containing bucket of water. From the heat of combustion of the sample, and the mass of the sample before its combustion, the energy density (gross heat of combustion per unit mass) of the sample can be determined.

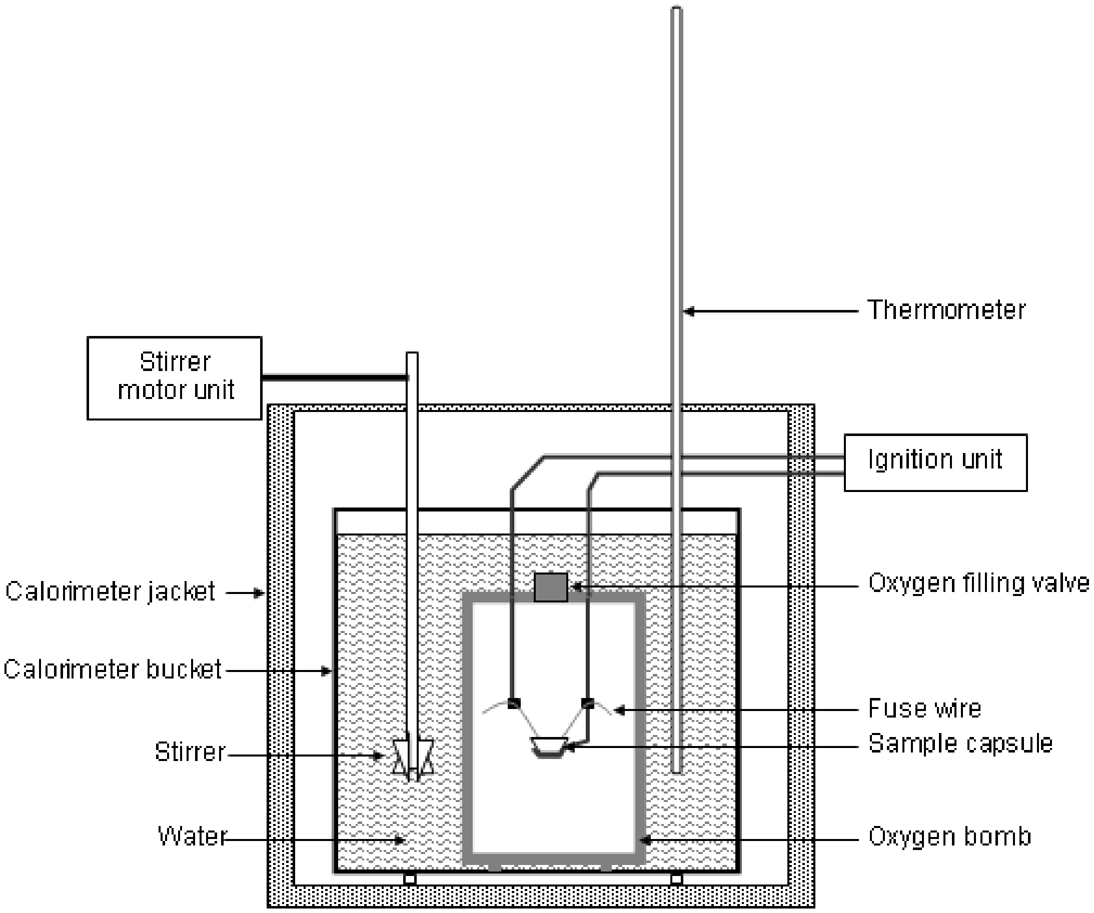


Figure 3.5: Plain jacket bomb calorimeter

Tests were conducted with the oxygen bomb charged to a pressure of 32 atm, in the upper-middle region of the advised range of oxygen pressures of 25–35 atm. This pressure was selected on the basis that a slightly high pressure would provide more than sufficient oxygen to ensure a good combustion of the carbon and hydrogen rich DERV and biodiesel fuels.

Measuring the temperature change

The temperature response of the calorimeter during an experiment is shown in Fig. 3.6. Before ignition, the water temperature equilibrates with the surroundings, aided by the mechanical stirrer which circulates water around the bucket (see Fig. 3.5). After ignition, the water temperature increases slowly at first, then more rapidly as combustion of the sample is completed and the energy of combustion is conducted via the metal bomb to the water. The rate of temperature increase then falls until a peak is reached, provided that the surroundings are at a lower temperatures than the calorimetry assembly. After the heat of combustion has been transferred to the water, the calorimetry assembly moves towards thermal equilibrium with the surroundings, observed by a steady decrease in the water temperature. If sulphur or nitrogen are present in the calorimeter bomb, sulphuric or nitric acid may form. The heats of formation of these acids affects the calculation of the heat content of the sample, as discussed further in Section 3.2.5.

When the calorimeter is at a different temperature to that of its surroundings, heat will be transferred to or from the calorimeter, according to the temperature difference and this heat transfer must be corrected for in the observed temperature rise. The standard procedure for this radiation correction is based on research that showed that the heat loss and gain can be approximated by assuming that the calorimeter is heated by its surroundings during the first 63 % of the temperature rise at a rate equal to that measured during the five minute pre-period (Parr Instrument Company, 2006). The heat transfer rate for the remaining 37 % of the temperature rise period is assumed to be the same rate as the cooling, or heating, rate during the five minute post-period, when a steady rate of temperature change is established. For the purposes of this instrument, the time at which the temperature has risen by 60 % of the final rise is used to calculate the corrections for the heat transfer to and from the surroundings during the overall temperature rise; this time is t_{60}.

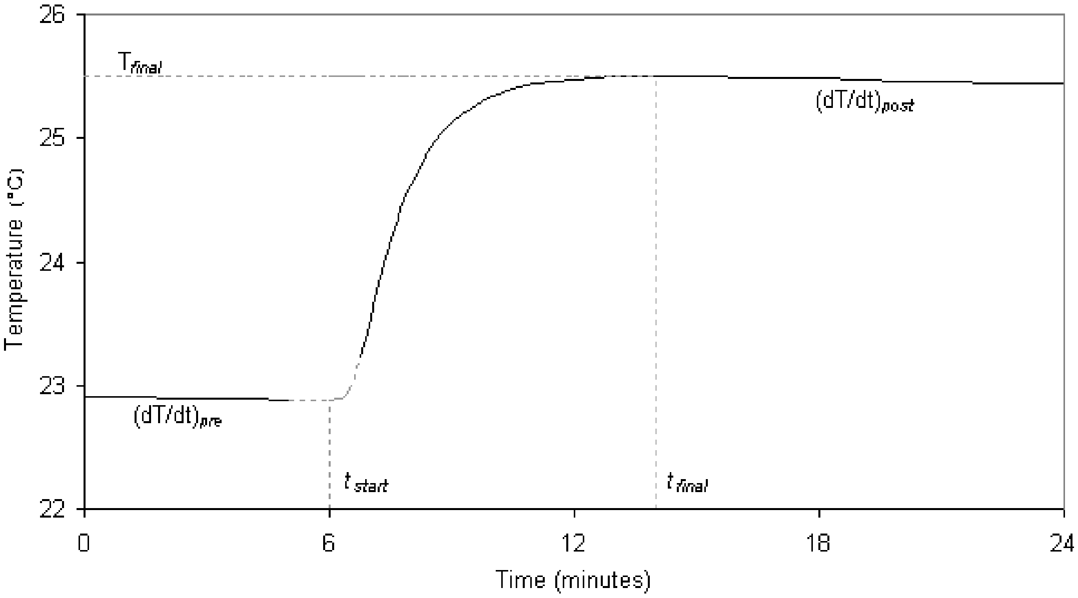


Figure 3.6: Typical temperature profile of a calorimetry run. The pre-period and post-period rates of temperature change are indicated by (dT/dt)$_{pre}$ and (dT/dt)$_{post}$ respectively.

The corrected temperature rise is given by

$$T_{corrected} = T_{final} - T_{start} - \left.\frac{dT}{dt}\right|_{pre} (t_{60} - t_{start}) - \left.\frac{dT}{dt}\right|_{post} (t_{end} - t_{60}) \tag{3.8}$$

where T represents the temperature of the calorimetry assembly and t is time, measured from the start of the pre-period. Pre and $Post$ denote the pre-period and post-period for the rates of temperature change.

The calorimeter assembly, that is the sample holder, the bomb, the containing bucket and water, has a total specific heat capacity, W, also known as the energy equivalent value of the calorimeter. The calorimeter was standardised using nominally 1 g pellets of benzoic acid (Fig. 3.7). The known energy content of the benzoic acid pellets, 26.435 MJ kg^{-1} (Parr Instrument Company, 2006), was used to determine W. Five standardisation tests were conducted, yielding a value of 2421.6 cal °C^{-1}, or 10.132 kJ K^{-1}, for W. At this value of W, the measured energy content of the benzoic acid varied by ± 0.4 %.

A set of seven tests of rapeseed methyl ester was carried out to establish the repeatability of

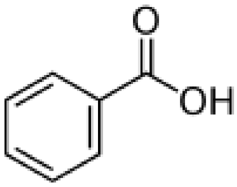


Figure 3.7: Benzoic acid, C_6H_5COOH.

the tests. The average gross heat of combustion was 39.78 MJ kg^{-1} and the standard deviation was 0.12 MJ kg^{-1}. The total range of the results was 0.32 MJ kg^{-1}.

Corrections to the calculation

In addition to the corrections to the temperature change to account for the pre-period and post-period exchange of heat with the surroundings, corrections are also calculated and applied to compensate for heat emitted in the combustion of fuse wire, and heat absorbed in the formation of nitric acid when N_2 is present in the bomb, and the heat of formation of H_2SO_4 when the sample contains significant proportions of sulphur.

The heat of combustion of the fuse wire is accounted for by calculating the energy released by the combusted part of the fuse wire. Any unburned wire in the bomb after combustion has taken place is removed, straightened and measured against a ruler with a millimetre scale. The heat of combustion of the fuse wire is 2.3 calories cm^{-1}, 9.6 J cm^{-1} (Parr Instrument Company, 2007). Approximately 8 cm of fuse wire is burned in each combustion experiment.

Nitric acid can be formed during combustion from nitrogen present in the bomb in the form of N_2 which comes from the atmosphere. During the formation of nitric acid, heat is absorbed from the calorimeter and such heat loss results in a slight reduction in the overall temperature rise. The energy that is absorbed in the formation of nitric acid is calculated from the results of a titration of dilute $NaCO_3$ against the bomb washings. This titration quantifies the amount of acid present and an energy equivalent is calculated according to methods provided by the bomb calorimeter manufacturers (Parr Instrument Company, 2007). The presence of nitrogen in the bomb can be eliminated through purging the bomb prior to pressurisation with O_2. However, this technique is not suitable for partially volatile substances such as DERV fuel which may be lost from the bomb during such a purging operation.

Similarly, sulphur present in a calorimetry sample is converted to sulphuric acid, H_2SO_4, in the high temperatures inside the oxygen bomb. The heat of formation of the sulphuric acid is absorbed from the heat of combustion of the rest of the sample. By measuring the amount of sulphur in the washings after combusting the sample, a correction can be calculated to account for the heat lost to the formation of sulphuric acid. Alternatively, the sulphur content of the sample can be measured using X-Ray Fluorescence. The calculation to correct for the heat of formation of H_2SO_4 (e_2) in the calorimeter is:

$$e_2 = 13.7 \times c_2 \times m$$

where c_2 is the proportion of sulphur in the sample as a percentage by weight and m is the mass of the sample (Parr Instrument Company, 2006).

Calculation of energy density from experimental data

The experimental data collected comprises the temperature readings as shown in the example in Fig 3.6, the length of fuse wire remaining in the bomb after combustion, the titration to determine the quantity of HNO_3 produced and a measurement of the sulphur content of the sample. These data are used in Eqn 3.9 to calculate the gross heat of combustion of the sample.

$$GHC = \frac{\Delta T \times W - c}{m} \tag{3.9}$$

where:

GHC is the gross heat of combustion of the sample per unit mass

ΔT is the corrected change in temperature of the calorimetry assembly

W is the specific heat capacity of the calorimetry assembly

c represents the corrections.

The standard calculation procedure for the calorimeter (Parr Instrument Company, 2006) delivers a result in calories per gram. The standard conversion factor of 0.004184 is used to convert the result from calories per gram to megajoules per kilogram.

3.3 Calculation of differences between blend proportion descriptions

The blend numbers by volume, B$_v$, and by mass, B$_m$, proportions are related by Eqn. 3.10 where ρ_B and ρ_P are the biodiesel and petroleum diesel densities.

$$B_m = \frac{\rho_\mathrm{B} B_v}{\rho_\mathrm{B} B_v + \rho_\mathrm{P}(1 - B_v)} \tag{3.10}$$

The theoretical volume and mass proportions of blended petroleum diesel and biodiesel fuels were calculated using Eqn 3.10. The combinations of fuel densities used in these calculations are shown in Table 3.3 and the results of the calculations are in Fig. 3.8. The density data for blend G were obtained from Department of Energy and Climate Change (2009) for petroleum diesel and Department for Transport (2006) for biodiesel. However, the biodiesel density value in Department for Transport (2006) is outside the limits specified in EN 14214 (British Standards Institution, 2004a).

	Biodiesel density	Petroleum diesel density	Note
A	900.0	820.0	EN 14214 max, EN 590 min
B	900.0	845.0	EN 14214 max, EN 590 max
C	860.0	820.0	EN 14214 min, EN 590 min
D	860.0	845.0	EN 14214 min, EN 590 max
G	840.0	834.7	Government data

Table 3.3: Densities of fuels used to compare B$_v$ and B$_m$.

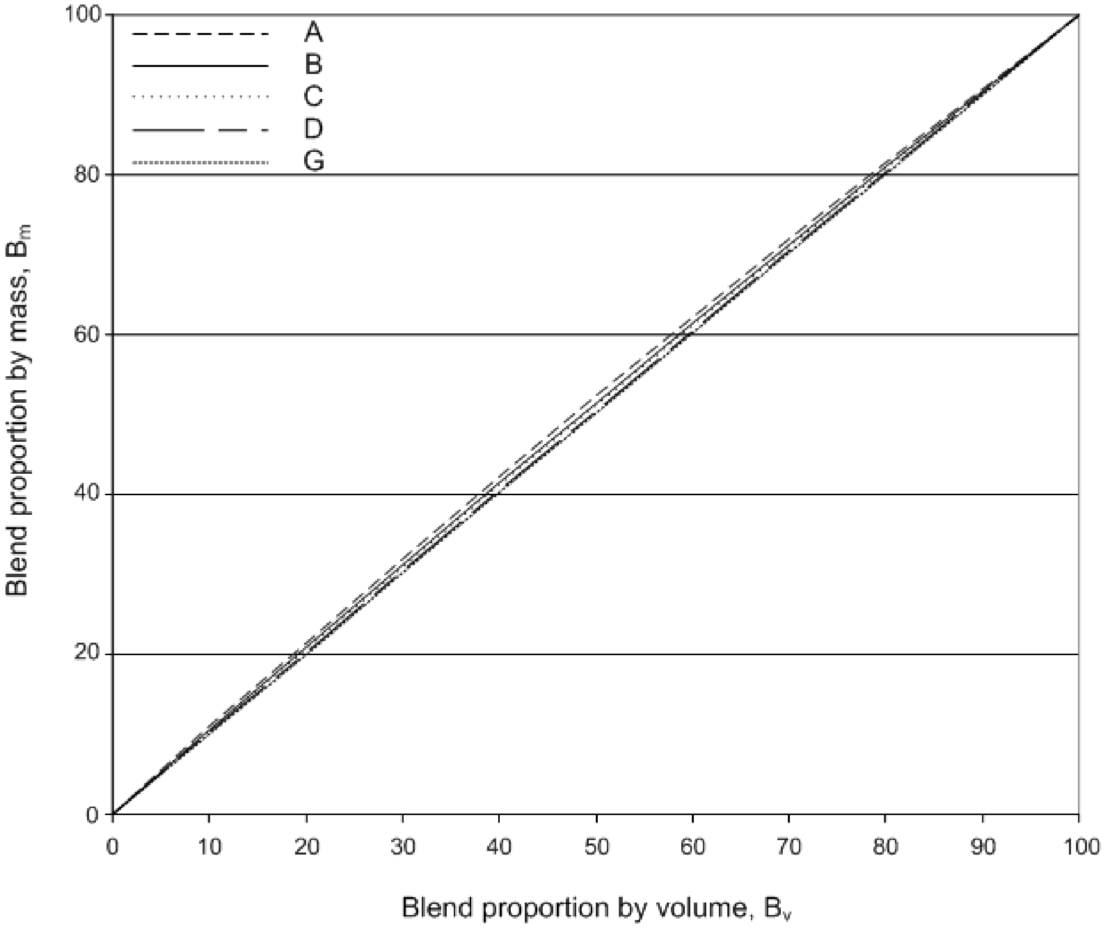


Figure 3.8: Blend proportions in terms of volume and mass calculations. Refer to Table 3.3 for the densities of the fuel components used in the calculations.

The results are very close together and below 5 % v/v the weight proportions are in the range 5.03–5.46 %. The lowest line is for data set G, in which the biodiesel value is outside the EN specification. The maximum differences between the weight proportions for blends which meet the EN specifications occur for blends of 50 % v/v with weight proportions of 50.4–52.3 % w/w.

The relations between the energy proportions and volume proportions were calculated in a similar way, using Eqn 3.11.

$$B_e = \frac{\varepsilon_{\mathrm{B}}\rho_{\mathrm{B}}B_v}{\varepsilon_{\mathrm{B}}\rho_{\mathrm{B}}B_v + (1 - B_v)\varepsilon_{\mathrm{P}}\rho_{\mathrm{P}}} \tag{3.11}$$

where ε is the gross heat of combustion (energy per per unit mass) for each component in the blend, and e and ε are related by Eqn. 3.12:

$$e = \rho\varepsilon \tag{3.12}$$

Recalling Eqn. 3.7, Eqn. 3.11 can be written in terms of the energy densities of the two fuel components in the blend, Eqn. 3.13

$$B_e = \frac{B_v ED_{\mathrm{B}}}{B_v ED_{\mathrm{B}} + (1 - B_v) ED_{\mathrm{P}}} \tag{3.13}$$

From the gross heats of combustion and densities of fuel components, the energy densities were calculated (Table 3.4). Energy proportions for combinations of the calculated energy densities (Table 3.5) for biodiesel and petroleum diesel were calculated from volumetric blend numbers using Eqn. 3.13. The results are shown in Fig. 3.9.

For all bar one of the fuel combinations, the energy proportion of biodiesel in the blend is less than the volume proportion. The exception is case A which assumes a maximum density and gross heat of combustion for the biodiesel component, while using a low density for the petroleum diesel component. The greatest difference between the energy and volume proportions for biodiesel in any blend occurs at 50 % v/v for the blend which contains a low density, low gross heat of combustion biodiesel with a high density petroleum diesel, case H. The maximum calculated difference is 3.6 % at 50 % v/v which corresponds to 46.4 % e/e biodiesel. The results calculated for the blends which uses government data for the densities and gross heats of combustion is one of the lower sets of results and this is due to the low density of biodiesel put forward in Department for Transport (2006). For blends at 5 % v/v, the energy proportions of biodiesel are 4.4–5.1 %.

	GHC, MJ kg^{-1}	Density, kg m^{-3}	
BD-1	41.98	900.0	Max GHC, max EN 14214 density
BD-2	41.98	860.0	Max GHC, min EN 14214 density
BD-3	38.72	900.0	Min GHC, max EN 14214 density
BD-4	38.72	860.0	Min GHC, min EN 14214 density
BD-5	40.128	840.0	Government data
PD-1	45.5	820.0	Government average, min EN 590 density
PD-2	45.5	845.0	Government average, max EN 590 density
PD-3	45.5	834.7	Government data

Table 3.4: Energy contents and densities of fuels used to compare B_v and B_m. GHC values from Demirbas (2008); Klopfenstein and Walker (1983); Department for Transport (2006); Department of Energy and Climate Change (2009). Densities from EN 14214, EN 590 and Department of Energy and Climate Change (2009).

	Biodiesel	Petroleum diesel
A	BD-1	PD-1
B	BD-1	PD-2
C	BD-2	PD-1
D	BD-2	PD-2
E	BD-3	PD-1
F	BD-3	PD-2
G	BD-4	PD-1
H	BD-4	PD-2
Gvt	BD-5	PD-3

Table 3.5: Fuel combinations for energy blend proportion calculations

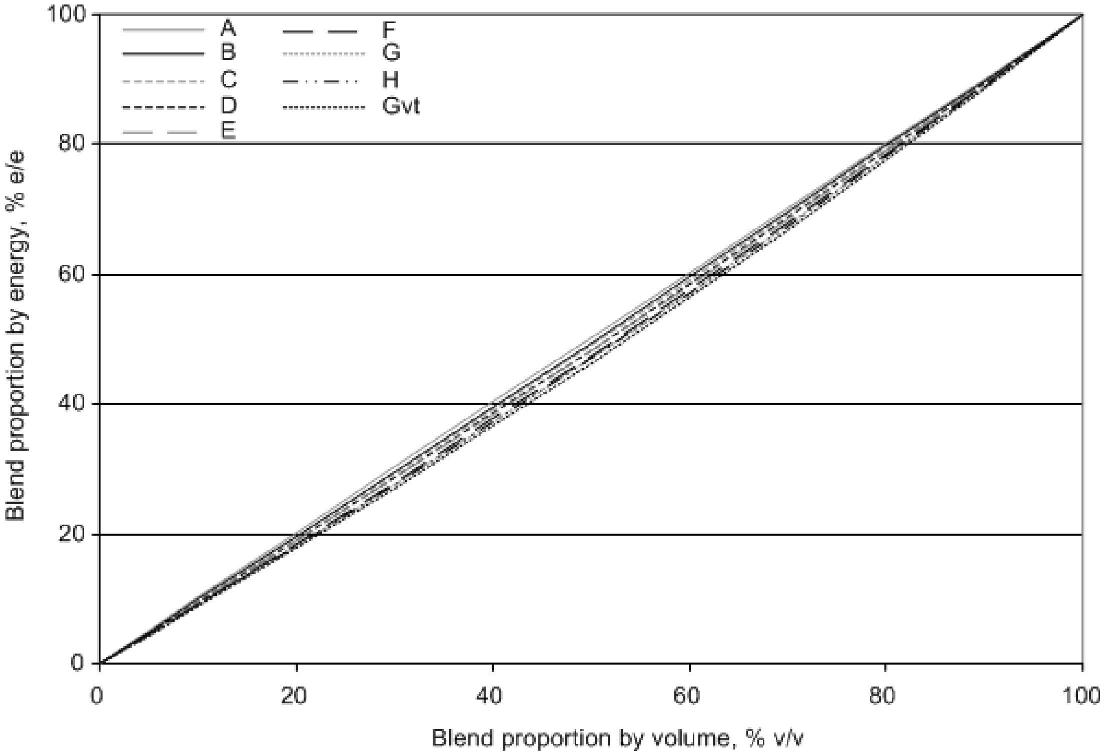


Figure 3.9: Blend proportions in terms of volume and energy calculations. Refer to Tables 3.4 and 3.5 for details of the fuel components used in the calculations.

3.4 Experimental results

3.4.1 Density variation with blend proportion

The pycnometer's volume was determined to be 49.828 cm^3 and the standard deviation in the results was 0.006 cm^3. The density of the toluene, used for calibration (Section 3.2.3), was measured at 863.3 kg m^{-3} at a temperature of 23.8 °C, averaged from three sets of measurements of weight and temperature. The experimental results using the pycnometer are very close to the value presented in the literature for toluene at this temperature (863.27 kg m^{-3}, Harris (2000)). The pycnometer method for determining the density of a liquid is therefore reliable to within 0.1 kg m^{-3}.

Toluene is different to diesel and biodiesel in two aspects. Firstly, as noted above, the liquid comprises molecules of a single type, therefore the properties of the liquid are singular and exact, not spread over a range as is the case for diesel fuels. Secondly, toluene is much more volatile than diesel fuels. Traces of toluene that spread over the outside of the density bottle when the stopper is inserted vaporise readily, leaving the bottle's exterior surface free of traces. Biodiesel and DERV traces are greasy and need to be removed with solvent, such as propan-2-ol. The error in the measurements of biodiesel densities may therefore be greater than the error in the toluene results.

The measured densities of blends of pure petroleum diesel with the two different biodiesels, rapeseed methyl ester (RME) and tallow/UCO methyl ester (TME), are shown in Fig. 3.10. A 50:50 RME-TME blend is blended with DERV in the DERV-RME-TME blend. The biodiesel densities (RME: 872.9 kg m^{-3}, TME: 877.7 kg m^{-3}) are both higher than the DERV fuel density (839.0 kg m^{-3}) The densities of intermediate blends of biodiesel and petroleum diesel show good correlation with the theoretical predictions that were calculated using Eqn 3.2.

The range of densities specified in the EN standards for DERV fuel and biodiesel is approximately 5 % of the density value of DERV fuel and biodiesel. The experimental measurement of the fuels' densities must therefore be more accurate than this ± 5 % range.

Four sources of error in the density bottle method were identified and analysed as follows:

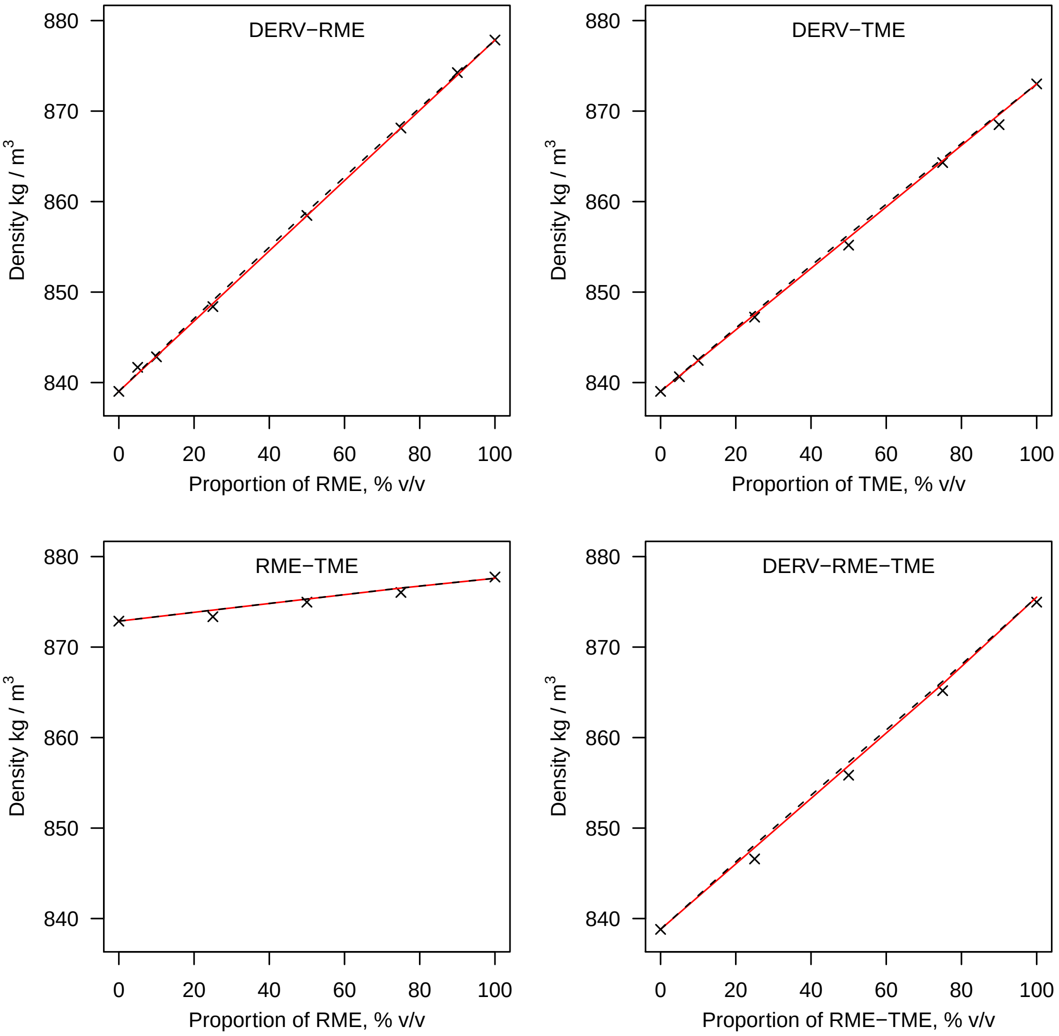


Figure 3.10: Density variation with blend proportion for blends of biodiesels and DERV fuel. Predicted densities are shown by dashed black and solid red lines for mass and volume proportion predictions respectively.

- The density bottle volume is notionally 50 ml. The bottle was calibrated using distilled water at temperatures in the range 20.2–23.7 °C. Its volume was determined to be 49.828 ±0.006 mL.
- The balance used to weigh the bottle and sample gives readings to 0.00001 g for weights up to 40 g, and to 0.00001 g for weights above 40 g. A non-volatile object was weighed several times to determine the repeatability of measurements using the mass balance; it was found to be consistent to 0.001 g, or 0.0025 % of the typical fuel sample masses, 41–46 g.
- The range in the measurements of the filled density bottle was 0.02–0.09 % of the mean average sample mass and the standard deviation of repeat measurements is 0.01–0.04 %.
- The laboratory temperature is stable to ± 1°C. Using the linear relation found by Tat and Van Gerpen (2000) for soybean biodiesel, as detailed in Table 3.1, to determine the mass of a 50 mL sample at temperatures from 14–25 °C, it can be deduced that the change in sample mass with temperature for this volume is -0.033 g $°C^{-1}$. The biodiesel samples under investigation may be subject to a ± 0.016 g error caused by variation in the laboratory temperature, representing a proportional error of 0.04 %.

Combining the percentage errors from these sources gives a root mean squared error of 0.07 % for the density bottle method of calculating density, which corresponds to an absolute error of 0.6 kg m^{-3} for a sample with a density of 850 kg m^{-3}.

In preliminary tests, the difference in sample mass dependent on the sample blend number was of the order of 0.015 g per % B number. When the full range of blends are tested, the interval between blends is a minimum of 5 %, therefore the smallest expected difference between sample masses is 0.075 g. An interval of 10 % corresponds to a difference in sample mass of 0.150 g, which is five times the difference caused by a ± 0.5 °C change in temperature.

3.4.2 Density variation with temperature

The variation in the density of biodiesels with temperature is shown in Fig. 3.11 for RME, TME, a 50:50 blend by volume of RME and TME, and data from the literature. The corresponding variation in the density of DERV fuels, including the data from six of the samples from around the UK, and also data from the literature is shown in Fig. 3.12 for In the experiments, the thermometer was read to 0.1 °C, leading to an estimated error of ±0.2 °C as a result of variation in the temperature of the sample. The hydrometer was read to 0.1 units SG, with an estimated error of ±0.2 units SG, in large part due to the difficulty of identifying the exact level of the lowest part of the meniscus on the hydrometer's scale.

The fuels all demonstrate a linear relationship between density and temperature which can be defined as $\rho = a + bT$ with r^2 values of 0.998 or higher in all cases. The coefficients for this relation are shown in Table 3.6. For comparison, the density ranges at the EN specification test temperature, 15.6 °C are also shown and the results confirm that all fuels comply with the EN specification. With the exception of the data from the UK National Weights and Measures organisation (NWML), the rate of change of density with temperature, i.e. the parameter b, is almost the same in all cases, varying by ± 0.024 kg m^{-3} $^\circ\text{C}^{-1}$, or ±3 % of the mean gradient, -0.7120 kg m^{-3} $^\circ\text{C}^{-1}$.

The NWML data, compiled by NWML from data supplied by the Department for Energy and Climate Change and the UK Petroleum Industry Association National Measurement Office (2009), also show a linear relationship between density and temperature. However, the NWML data show a significantly different rate of change of density with temperature that can be clearly observed by the difference in angle between the dashed and solid lines in Fig 3.12 representing the NWML and the experimental data respectively. The magnitude of b for the NWML data, is of the order of 20 % greater than the values determined experimentally for DERV fuels. Furthermore, the NWML data do not fit with the ASTM diesel fuel tested in Yoon et al. (2008).

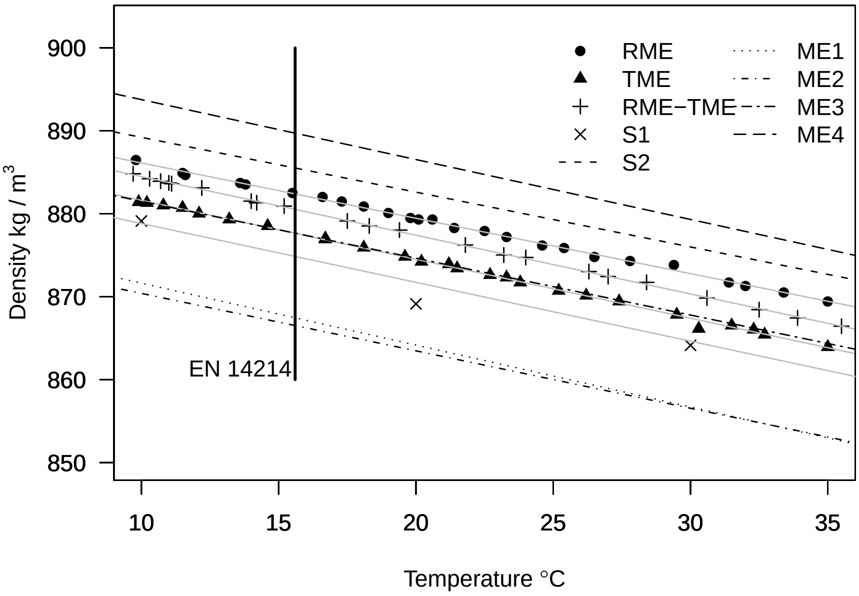


Figure 3.11: Densities of biodiesels (RME, TME, RME-TME, S1, S2) and pure methyl esters (ME1–4) with temperature. Experimental data are shown by points with linear regression lines drawn through. Dashed lines without points show data from the literature which was presented in the form $\rho = a + bT$. The range of allowed densities in the EN 14214 specification is indicated at 15.6 °C. Literature data are as follows: S1: Soybean methyl ester Yoon et al. (2008); S2: Soybean methyl ester Tat and Van Gerpen (2000); ME1: Methyl palmitate, ME2: Methyl stearate, ME3: Methyl oleate, ME4: Methyl linoleate Clements (1996). Note that the lines for TME and ME3 are almost coincident.

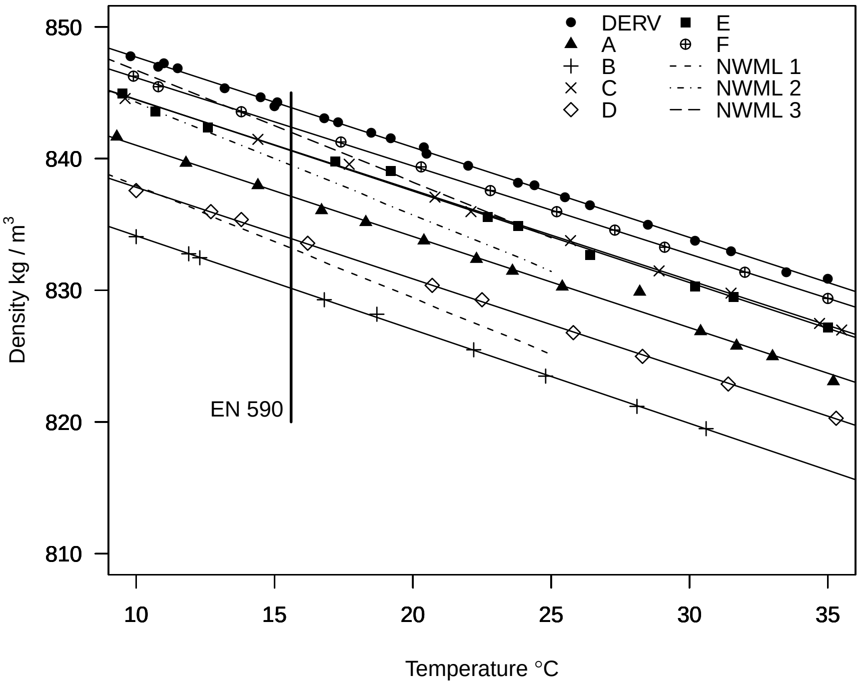


Figure 3.12: Densities of petroleum diesels with temperature. Experimental data are shown by points with linear regression lines drawn through. The broken lines show NWML fuel data and the range of allowed densities in the EN 590 specification is indicated by the vertical line at 15.6 °C. Refer to Table 3.2 for source information for the DERV fuels A–F.

Fuel	a (kg m^{-3})	b (kg m^{-3} °C^{-1})	Density at 15.6 °C (kg m^{-3})
Experimental data			
RME	892.74	-0.6637	882.39
TME	888.73	-0.7107	877.64
RME/TME	891.70	-0.7106	880.62
DERV fuel	854.55	-0.6846	843.87
UK-A	847.94	-0.6925	837.13
UK-B	841.26	-0.7124	830.15
UK-C	851.32	-0.6854	840.63
UK-D	844.77	-0.6950	833.92
UK-E	851.47	-0.6971	840.60
UK-F	852.84	-0.6699	842.39
Data from other sources			
DERV $<$ 0.005% sulphur National Measurement Office (2009)	846.52	-0.8550	833.18
Sulphur free (National Measurement Office, 2009)	852.78	-0.8523	839.49
B5 (National Measurement Office, 2009)	855.22	-0.8488	841.97
ULSD (ASTM D 975) (Yoon et al., 2008)	836.99	-0.628	
Soybean methyl ester (Yoon et al., 2008)	884.47	-0.626	
Methyl palmitate (Clements, 1996)	879.094	-0.74608	867.46
Methyl stearate (Clements, 1996)	877.325	-0.69247	866.52
Methyl oleate (Clements, 1996)	888.357	-0.68563	877.66
Methyl linoleate (Clements, 1996)	900.981	-0.72226	889.71
Average biodiesel	888.80	-0.6909	878.02
Average DERV fuel	848.70	-0.7292	837.32

Table 3.6: Density changes with temperature of biodiesels and DERV fuels, according to the relation $\rho = a + bT$. The values for a show the densities of the fuels at 0 °C which can be compared with the densities that are shown for 15.6 °C. Experimental data precision is determined by estimated experimental error as shown by the number of significant figures. Data from the literature is given to the precision specified in the original sources.

3.4.3 Blend proportion variation with temperature

The linear relations obtained for the densities of biodiesel and diesel fuels with temperature (Table 3.6) were used to investigate the variation in B_v with temperature. The average values for the a and b co-efficients in Table 3.6 for biodiesel and petroleum diesel were used in the calculation. The masses of fuel components required to make volumetric blends in the range 0–100 %, at 10 % intervals, were calculated for fuels at 15.6 °C. B5 blends were also considered, given the present commercial conditions for sales of DERV fuels with up to 5% biodiesel by volume. From these masses, the co-efficients in Table 3.6 were used to calculate the volumes of each blend component at intervals of 5 °C across the range -5–30 °C which is representative of average outside air temperatures in the UK. The B_v number was then calculated at each temperature for the blends and the differences between the B_v number at the reference temperature, 15.6 °C and the B_v number at other temperatures were determined.

Fig 3.13 shows the change in B_v with temperature, using the B_v number at 15.6 °C as the reference, using the average values for a and b for the biodiesels and the DERV fuels in Table 3.6. The blend that exhibits the greatest change in B_v number is the B_v50 blend. The magnitude of the deviation in B_v from B_v at the standard temperature is proportional to the difference in temperature from the standard temperature. B_v5 blends show a change in B_v of ± 0.01; a B_v5 blend made volumetrically at 15.6 °C will be just under a B_v5.01 blend at -5 °C and almost B_v4.99 at 35 °C.

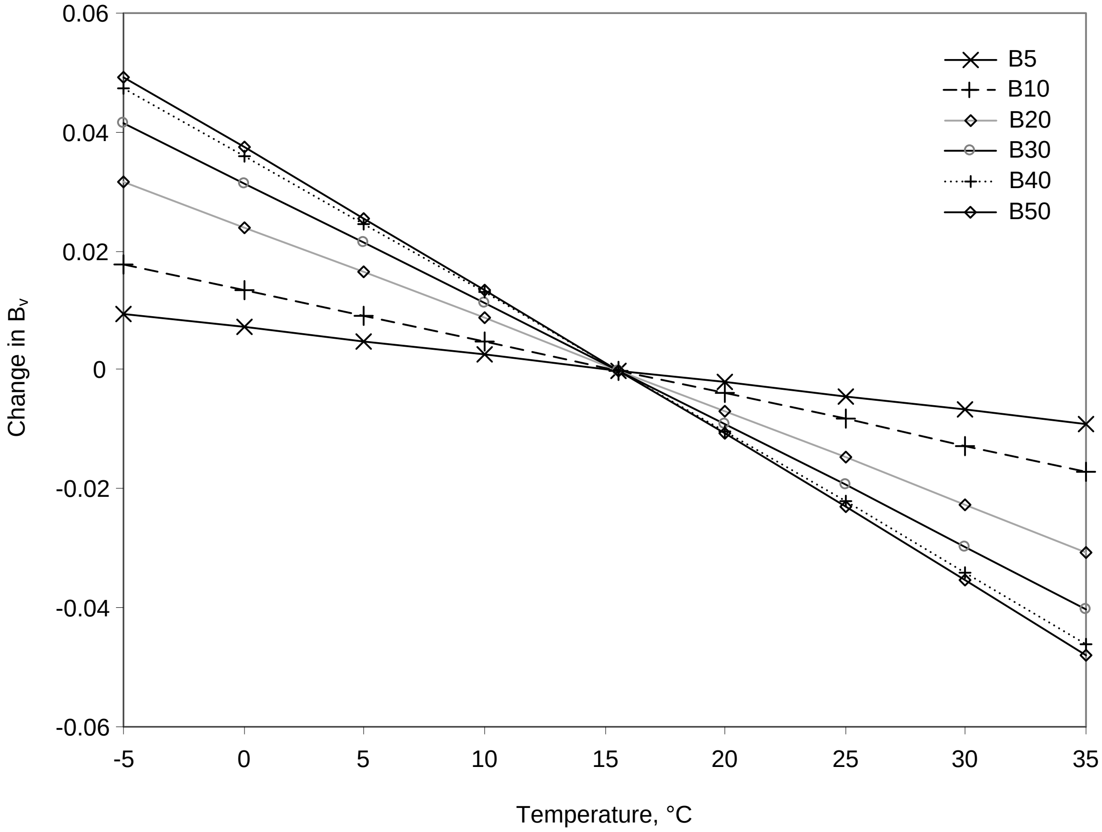


Figure 3.13: Change in B_v with temperature relative to B_v at 15.6 °C. The results for B60–B90 are almost coincident with the results for B40–B10 and therefore not shown explicitly here.

3.4.4 Energy content tests

The experimental results of energy content tests are shown in Fig 3.14 for blends of DERV fuel with rapeseed methyl ester (RME), tallow/UCO methyl ester (TME) and with a 50:50 blend of RME and TME. All four sets of data show that the experimental results agree with the theoretical predictions that were calculated from the volumetric proportions and individual energy contents of the blend components. The gross heat of combustion of a blend can therefore be calculated from the weighted sum of the gross heats of combustion of the blend components. The gross heat of combustion of biodiesels is found to be around 12 % lower than the gross heat of combustion of DERV fuel.

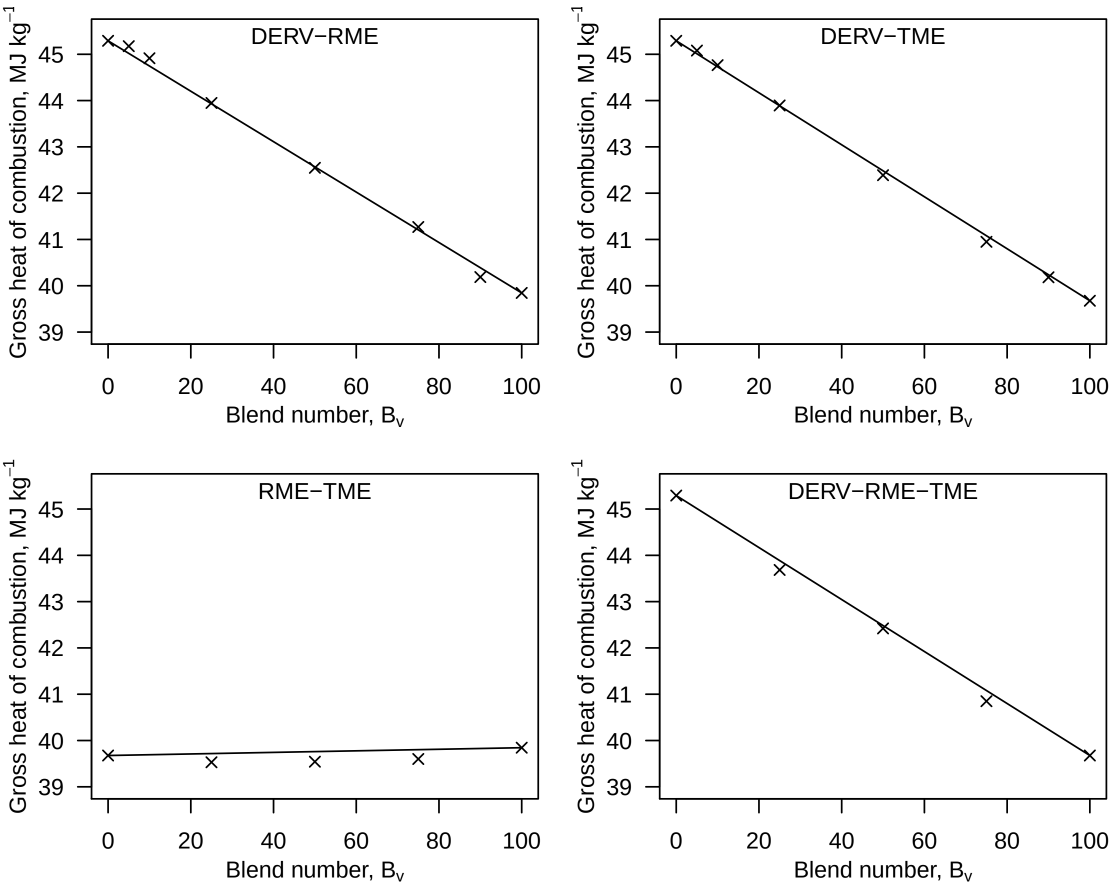


Figure 3.14: Energy contents of blends of DERV fuel with rapeseed methyl ester (RME) and tallow/UCO methyl ester (TME). DERV-RME-TME represents a blend of DERV fuel in varying proportions with a 50:50 blend of RME and TME.

Fig 3.15 shows the gross heats of combustion of six DERV fuels from various locations in the UK and six samples from around Norwich. The UK samples were collected during Spring 2009 and the Norwich samples in August 2009. The gross heats of combustion ranged from 44.9–45.7 MJ kg^{-1} with an overall average of 45.3 MJ kg^{-1}. The gross heats of combustion of the six UK samples, with an average of 45.0 MJ kg^{-1}, are lower than those of the samples that were collected in Norwich which have an average of 45.6 MJ kg^{-1}. This difference persists even when the standard error in the calorimetry procedure is taken into account.

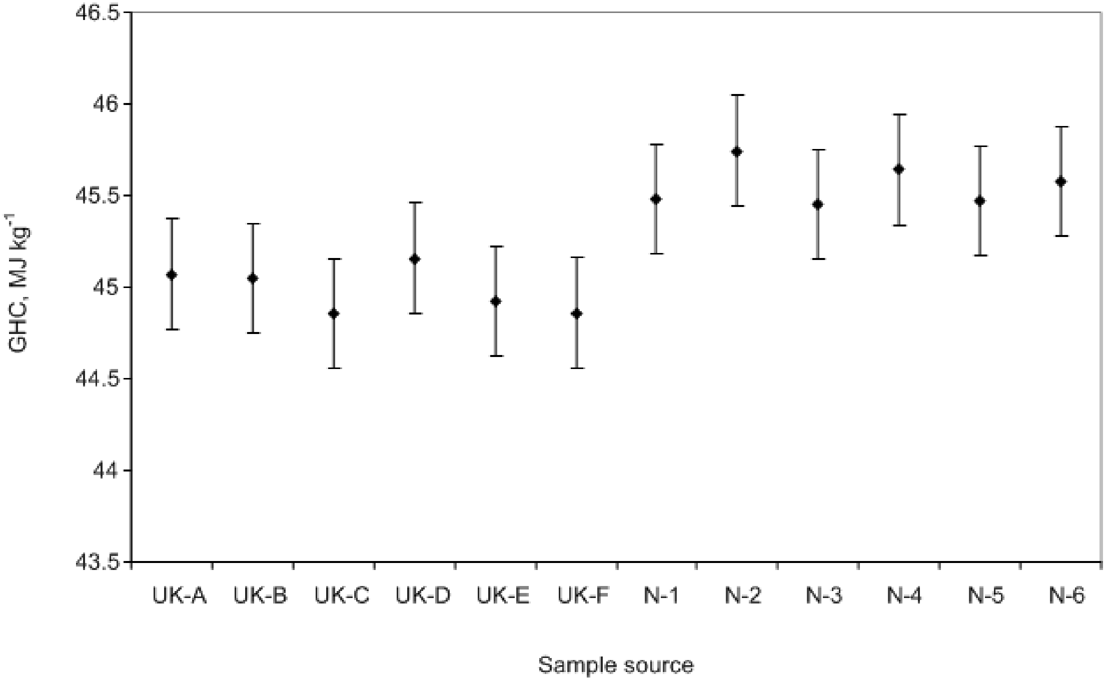


Figure 3.15: Gross heats of combustion for DERV fuels in UK and Norwich sample sets. The error bars represent ±0.3 MJ kg^{-1}

The accuracy of the calorimetry procedure was determined by calculating the RMS error from sources of errors in the readings, the results of the repeatability test and corrections for residual carbon that had not combusted during the test. The likely errors in the readings were estimated and these are tabulated in Table 3.7. These estimated errors were combined using a root-mean-squared calculation to determine the overall error that may occur in the calculated gross heat of combustion due to errors in taking measurements and this overall error was found to be 2.3 % (0.92 MJ kg^{-1}

for a sample with a gross heat of combustion of 40.0 MJ kg^{-1}).

The standard deviation of results for a set of seven tests of rapeseed methyl ester is 0.12 MJ kg^{-1} with a range of 0.32 MJ kg^{-1}. This is less than the estimated errors due to observational errors as calculated from Table 3.7.

Some samples did not undergo complete combustion and left traces of carbon in the sample capsule. The carbon residue in the combustion capsule was weighed by measuring the change in capsule weight. The change was assumed to be due only to the carbon residue and not to any other issue. No unburned sample was observed in the combustion capsules and condensed water was air-dried before weighing the capsule. The mass of the carbon residue varied from 0.0002—0.004 g. This corresponds to a change in the measured gross heat of combustion of the sample of up to 0.2 MJ kg^{-1} which is approximately the same as the variability of the results from the calorimeter. Taking into consideration the RMS error calculated from errors in the readings, the results of the repeatability test and corrections for the carbon residues, a total error of ± 0.3 MJ kg^{-1} is assumed in the results from the calorimeter.

The sulphur content of the biodiesel and diesel samples, and therefore the correction to the calorimetry results, was negligible. The maximum sulphur content of ultra-low sulphur DERV fuel, according to the BS EN 590:2004 standard is 50 mg kg^{-1}, or 50 ppm. "In the UK biodiesel is defined for taxation purposes as diesel quality liquid fuel produced from biomass or waste cooking oil, the ester content of which is not less than 96.5 per cent by weight and the sulphur content of which does not exceed 0.005 per cent by weight or is nil" (DTI, 2007a, p. 181). The presence of sulphur at a proportion of 50 mg kg^{-1} in the diesel fuel sample would correspond to a 0.0003 MJ kg^{-1} reduction in the measured gross heat of combustion of around 40.000 MJ kg^{-1}. This 0.0007 % change is imperceptible. Provided that the sulphur content of the biodiesel sample does not exceed the EN 14214 specification, the influence of the heat of formation of sulphur in the oxygen bomb is negligible when measuring the gross heat of combustion of the sample. The sample must contain 3.3 % sulphur by weight to affect the gross heat of combustion by 0.5 %, and this sulphur content is well above the allowed maximum. The sulphur contents of four DERV samples, UK-A–D, and three commercial biodiesels were tested using XRF and were all less than 19 ppm. On the strength of the UK fuel standards and this experimental evidence, the sulphur

	Baseline scenario values, v	Δv	$(\Delta v)/v$
Calorimeter equivalent (calories)	2400	30	0.0123
Firing time (hh:mm:ss)	00:06:00	1 s	0.003
60 % rise time (hh:mm:ss)	00:07:45	2 s	0.004
Start time of const. temp change (hh:mm:ss)	00:14:00	1 s	0.001
Temperature at ignition (°C)	19.002	0.004	0.0002
Final temperature, T_{Final} (°C)	23.006	0.004	0.002
Rate of temp change in pre-period (°C/min)			0.007
Rate of temp change in post-period (°C/min)	-0.004	0.002	0.006
Standard alkali solution used in acid titration (ml)	12.0	0.1	0.008
Sulphur in sample (% m/m)			
Wire consumed in firing (cm)	8.0	0.1	0.01
Sample mass (g)	0.6000	0.001	0.002

Table 3.7: Estimated errors used to calculate the overall error likely in calculated gross heats of combustion using the Parr 1341 oxygen bomb calorimeter. Δv is the estimated error in the measured values through reading error.

content is therefore neglible in all of the calorimetry experiments on biodiesels and DERV fuels in this investigation.

3.4.5 Energy density variation with blend proportion

The densities and gross heats of combustion for RME-DERV, TME-DERV and RME-TME-DERV blends from B0 to B100 were used to calculate the energy density for each blend using Eqn. 3.7 (Fig.3.16). The energy density of the petroleum diesel-biodiesel blends decreases from 38 MJ litre^{-1} at B0 to 35.0 MJ litre^{-1} at B100. The energy densities are in agreement with the expected results, allowing for errors of up to ±0.3 MJ litre^{-1}.

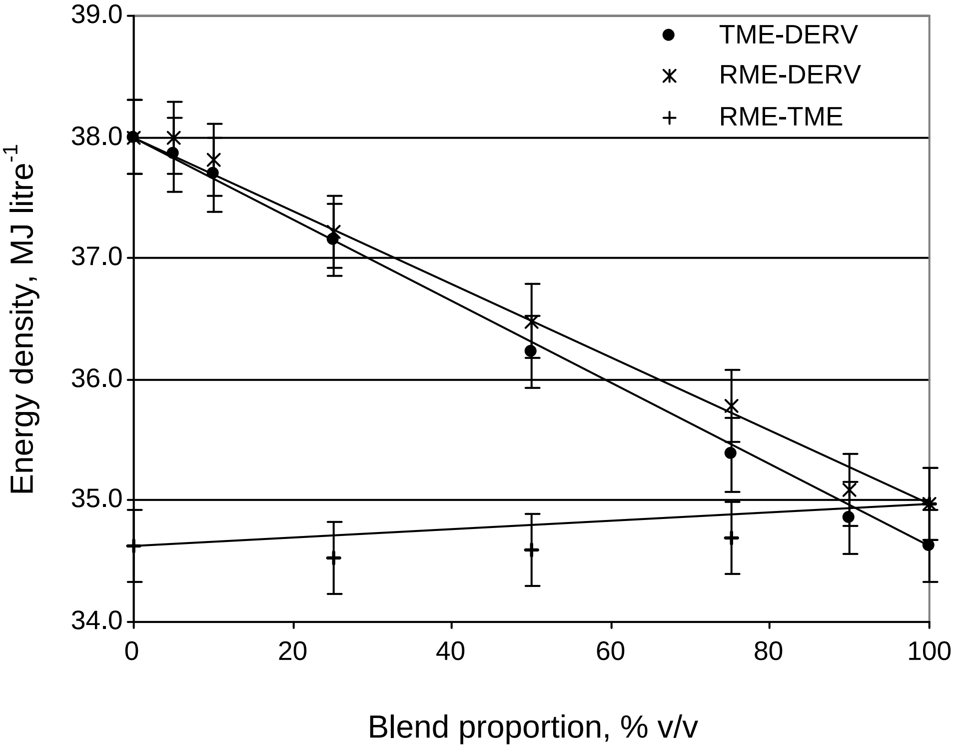


Figure 3.16: Energy densities for blends of biodiesels with petroleum diesel

3.5 Discussion

3.5.1 Samples

The timing of this study coincided with the introduction of the Renewable Transport Fuels Obligation and commercial fuel suppliers were quick to include biodiesel in their fuels, although some suppliers had been including biodiesel as an additive before the obligation took effect (Renewable Fuels Agency, 2009b). One single sample of petroleum diesel without any biodiesel content was obtained just before the RTFO was enforced. Small samples of petroleum diesel could not be obtained for this study from wholesale fuel suppliers since they provide fuels in quantities of 100 litres or more. The petroleum diesel fuel used meets the EN 590 specification and therefore this work contributes to the existing knowledge base which predominantly uses American standard fuels (ASTM specifications).

Two commercial biodiesels were obtained for this study, one produced from rapeseed oil and the other from used cooking oils and tallow. These biodiesels were both produced on an industrial scale in Europe; the rapeseed biodiesel in Germany and the UCO/tallow biodiesel in Scotland. Again, the use of fuels produced in Europe which meet the European specification EN 14214 contributes to the expansion of the knowledge base and complements the work already undertaken by Alptekin and Canakci (2009) using European specification fuels.

The small sample sets of commercially-sold diesel fuels from around the UK and from retailers in Norwich were collected during two periods of the year: the UK samples were collected in Spring/early Summer while the Norwich samples were collected in late August. The fuel properties and selection of additives added to the fuel changes through the year to respond to the seasonal variations in temperature and therefore in performance conditions. A useful extension of the work in this chapter would be the collection of samples throughout the year to assess the annual variability of the energy content and density of diesel fuel. Further, the collection and analysis of samples from a greater number of fuel retailers would provide a more robust indication of the variation in fuel properties geographically.

3.5.2 Energy contents and densities of diesel fuel samples

The sample sets of DERV fuels had gross heats of combustion ranging from 44.9–45.7 MJ kg^{-1} with an average of 45.3 MJ kg^{-1} which is 0.2 MJ kg^{-1} lower than the UK government figure (Department of Energy and Climate Change, 2009). Conducting tests on a much bigger set of DERV fuel samples would provide a more reliable assessment of the range of DERV fuel energy contents, which in turn could be used for calculation of progress towards the EU Renewable Energy Directive (European Parliament and the Council of the European Union, 2009).

The energy contents of the two biodiesels tested (39.7 and 39.8 MJ kg^{-1}) were below the range reported in the literature (40.84–41.98 MJ kg^{-1}, Demirbas (2008)) and also below the value presented by Department for Transport (2006) (40.128 MJ kg^{-1}). Further tests on the gross heats of combustion of biodiesels supplied in the UK would improve the accuracy and reliability of the government's values. Such test results would be a useful contribution to the community of diesel fuel researchers.

The low experimental values for energy contents compared to the literature and government data may indicate that the experimental procedure is systematically producing low results. However, the calorimeter was calibrated with more than ten tests of benzoic acid. Further, a colleague using the same equipment has his results verified by a professional laboratory and the results agreed to 0.1 MJ kg^{-1}. Operator error may be a factor. Unfortunately, a test to compare the calorimetry results of the two operators using samples from the same source was not conducted during the study period.

3.5.3 Comparison of blend proportions by volume, mass and energy

The calculations in Section 3.3 showed that the difference between volume and mass blend proportions is less than 2.3 % for blends from 0–100 % v/v biodiesel which are made from fuel components that meet the EN 14214 and EN 590 specifications. For B5 blends which meet the current EN 590 specification, the maximum expected difference between the volume proportion and mass proportion of biodiesel is 0.46 % for a blend which consists of 5 % v/v (5.46 % w/w) biodiesel with a density of 900 kg m^{-3} and petroleum diesel with a density of 820 kg m^{-3}.

The experimental results for the variation of density with volumetric blend proportion confirmed the relation in Eqn. 3.2 for the European fuels selected in this study. The energy content proportions of a blend are the same as the blend's energy density proportions (Eqn. 3.13). The energy proportions are generally lower than the volumetric proportions owing to the lower gross heats of combustion of biodiesel compared to those of petroleum diesel (Fig. 3.9). However, a very high biodiesel density can compensate for the low gross heat of combustion of biodiesel, as shown for case A in Fig. 3.9.

In both comparisons, of volume and mass proportions, and of volume and energy proportions, the differences between the blend proportions are most significant when difference in the properties of the individual blend components is greatest. The blend proportion which shows the greatest variation between the different methods is B50.

3.5.4 Diesel fuel density response to temperature

All of the diesel fuels tested behaved in accordance with Eqn. 3.4. Results from the literature also fit this relation (Table 3.6) with the exception of the data used by the UK Trading Standards body to correct their test equipment for the temperature of the fuel under test (National Measurement Office, 2009). Six commercially-obtained DERV fuels were tested in this thesis and are in close agreement. Performing tests to determine the density response to temperature of a wider sample of DERV fuels would increase the dataset and thereby allow a more critical and robust assessment of the likely accuracy of the corrections in National Measurement Office (2009).

The variation with temperature changes of the volume proportions of biodiesel in blended diesel fuels was calculated from the results for the individual fuels in Table 3.6 and shown to be at most 0.002 $^{\circ}\mathrm{C}^{-1}$. The most noticeable variation in blend proportion with temperature was observed in the B50 blend. The change in blend number was approximately linear for all blends with the greatest changes in the blend number at the largest temperature difference from the reference temperature, 15.6 °C. However, the relatively small change in the blend proportion means that the effects are negligible. For example, in commercial operations situated in the UK, differences in temperature are unlikely to exceed 10 °C; temperature-dependent changes in B_v in such conditions for B_v5 blends will stay within ± 0.015 of the standard temperature B_v number.

3.5.5 Energy densities

Energy density, along with energy content (gross heat of combustion) itself is not included in the specification for diesel for road transport vehicles. The energy density of biodiesel is less than the energy density of petroleum diesel since the higher density of biodiesel compensates a little for the lower gross heat of combustion than that of petroleum diesel.

3.6 Conclusions

In this chapter, the mass, volume and energy proportions of biodiesel fuel in blends of biodiesel and petroleum diesel were investigated theoretically and experimentally. The main findings of this chapter are:

- The relation describing the density of a blend to the densities of its component parts was confirmed.
- The energy content of a blended diesel fuel is the sum of the energy contents of its parts.
- The densities of diesel fuels change linearly with temperature.
- The data obtained in this thesis on the density response to temperature agrees with data from the literature, but not with data from the UK Trading Standards body (National Measurement Office, 2009).
- The mass and volume proportions for describing biodiesel-petroleum diesel blends agree to within 2.3 % when the blend components are compliant with the EN specifications 14214 and 590.
- The mass proportion of biodiesel in a biodiesel-petroleum diesel blend is usually greater than the volume proportion describing the same blend.
- The volume and energy proportions for describing biodiesel-petroleum diesel blends agree to within 3.6 %.
- The energy density of a blend can be predicted from the energy densities of the blend components.
- The energy densities of the biodiesels and petroleum diesel measured experimentally in this thesis differ by 3 MJ litre^{-1}, less than the difference reported by Sims (2002).

Chapter 4

Life cycle assessments of biodiesel: literature review

In this chapter, life cycle assessment methodology is explored and in particular its application to agricultural and bioenergy systems is described. The development of the methodological approach used in this thesis to compare the production of biodiesel from hemp oil, with biodiesel from rapeseed oil and diesel from petroleum sources is presented.

Life cycle assessment methods were first developed in a study by Coca-Cola in 1969 (Baumann and Tillman, 2004), as a tool to establish whether glass or plastic bottles were environmentally preferable. In the following twenty years, more companies carried out their own studies of products, for example in manufacturing companies who wished to reduce the cost of production, or to eliminate waste. Life cycle assessment subsequently came to the fore as a tool for assessing the environmental impact of a process or of a product. During the 1990s, the life cycle assessment methodology was further refined, leading to the development of ISO standards 14040 to 14044, which set out the internationally recognised protocols for conducting LCAs. Life cycle assessment is still a young discipline, and continually developing (Finnveden et al., 2009).

Life cycle assessment has four phases, according to the ISO standards (ISO, 2006a):

- Goal and scope definitions
- Inventory analysis
- Impact assessment
- Interpretation

These phases provide a framework for conducting the life cycle assessment. The goal and scope definitions determine the depth and breadth of the other three phases, since it is in the initial definition of the LCA that the research questions that are to be addressed are defined. In turn, these questions inform and define the entire LCA process. The scope of the LCA governs the extent of the inventory analysis, and the LCA goal determines the impact categories that are to be assessed in the third stage of the LCA. Finally, the interpretation of the LCA is framed by the goal. The interplay between the different stages of the LCA is illustrated in Fig.4.1.

At the outset of an LCA study, the goal and scope of the study are specified in some detail. The particular questions that the study is intended to address are set out. Example questions include "what is the product stage which causes the largest environmental impact?" and "what is the likely improvement in environmental impacts that will be observed if certain changes are made to the process?"

At the heart of the life cycle assessment is the product flow under consideration. A representative unit of this flow, the functional unit, provides the basis for calculating and assessing the life cycle impacts, which are subsequently expressed per functional unit, for example a reference flow of transport fuel can deliver passenger-kilometres traveled, therefore the functional unit can be defined as a certain number of passenger-km. Life cycle assessment is based on systems analysis, therefore adequate definition of the system that produces the product flow is essential. At first glance, defining the system might appear to be a straightforward task, but when the complex web of sub-systems associated with the inputs and outputs from the system is explored, the definition of system boundaries becomes a much more intricate procedure. When agricultural systems are under assessment, the use of tractors and other capital equipment can be considered, but then if a factory exclusively manufactures tractors, the LCA may be extended to include a proportion of the LCA of the tractor factory. The question in LCA can start as "what shall we include?" but can

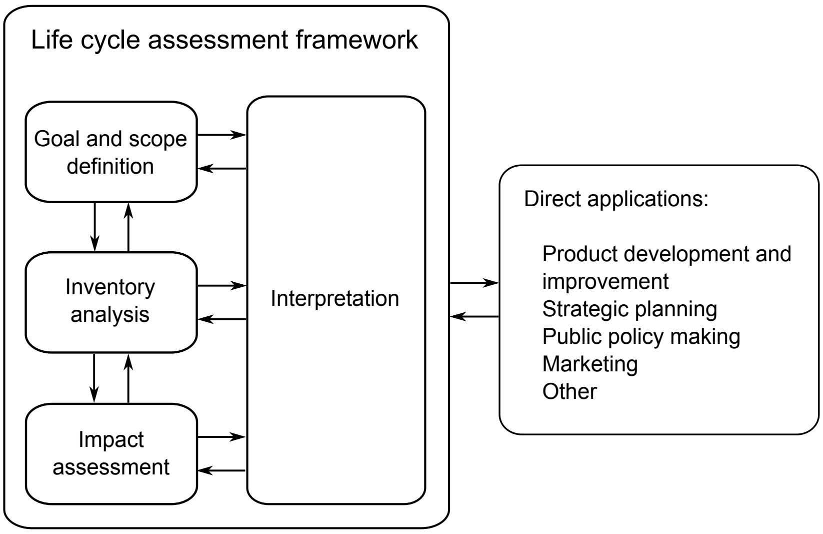


Figure 4.1: Phases of an LCA (ISO, 2006a)

rapidly become “what can we leave out?” while maintaining system integrity and a sufficient level of detail. In the case of a comparative LCA, a reference system is required to provide a baseline, or a measure of the status quo against which the product system is to be assessed.

Following the definition of the functional unit, system boundaries and reference system, a detailed inventory is compiled of the inputs and outputs to the system. During this stage missing pieces of information may become obvious by their absence, and can be noted and included. This can sometimes lead to modification of the focus or direction of the LCA’s original goal and scope. LCA can therefore be an iterative process starting with goal and scope definition which lead to collection of inventory data, which can lead back to refinement of the goal and scope before assessing the impacts of the items identified in the inventory.

The impacts of the product life cycle are calculated from the data compiled in the inventory. A number of impact assessment methods exist to determine the impacts across categories such as the global warming potential, abiotic (and therefore non-renewable)resource consumption and the ozone depletion potential. Specific emissions over the life cycle can also be determined, for example the emissions of carbon dioxide and other greenhouse gases. Integrated impact assessment methods exist that aim to present results from a number of impact categories in a single indicator, for example the ecological footprint of a product which converts the LCA results to an area of land that is required to support the production of the product.

The final phase of life cycle assessment involves interpretation of the results from the inventory and impact assessment phases, addressing the objectives set out in the initial goal and scope definition. The interpretation places the quantitative and qualitative results of the LCA into context, providing a fuller understanding of the implications of the results. The outcomes from this section of the assessment are highly dependent on the assumptions, both explicit and implicit, that the first phase of setting the goal and scope contains.

Selected life cycle assessments of biodiesels are reviewed in this chapter in terms of the framework provided by ISO (2006a). The ISO framework 2006a was selected for this review and for the subsequent LCA in Chapter 6 as through applying a framework to a case study one can explore the strengths and weaknesses of the framework itself. The studies reviewed in this chapter are relevant to the UK and to the feedstocks (hemp seed oil and rapeseed oil) under investigation in this thesis. Mortimer et al. (2003) surveyed a number of assessments of biodiesels for use in the UK, with regard to their social, economic and life cycle environmental costs. The impacts of biodiesel production from tallow and used cooking oils in a Scottish situation were evaluated and reported on by Niederl and Narodoslawsky (2004). A later study by Stephenson et al. (2008) compared large and small scale production methods. These studies are described in more detail in Section 4.1 and provide the context for the following sections in which the methodology options for biodiesel life cycle assessment are evaluated. The methods surveyed and evaluated in this chapter are used to inform the methodology chosen in this thesis.

The review of life cycle assessment methodologies is separated into four sections with each section corresponding to a phase of the LCA process as described by ISO (ISO, 2006a,b), namely the goal and scope, inventory, impact assessment and interpretation (Fig. 4.1). Section 4.2 describes the goal and scope phase in which the key questions that the LCA is to answer are formulated and definitions of the functional unit and system boundaries are investigated and evaluated. The goal and scope phase largely determines the processes and procedures that are to be used in the following three phases. In Section 4.3, the methods for data collection in the inventory phase are discussed, including the calculation of the full inventory of impacts on the environment and the estimation of values for missing data. Section 4.4 provides a review of the methods that are used in the impact assessment phase concerning the calculation of the potential impacts of the product system on the environment. The final interpretation phase of LCA is discussed in Section 4.5, putting the methods that are used to establish significance of the outcomes and results of the first three phases into the context that was originally specified in the initial goal and scope phase.

4.1 Biodiesel assessments

In this section, biodiesel life cycle assessments and current reporting methodologies are introduced. Firstly, a number of research papers and commercial reports are introduced, selected on the basis of their geographical relevance to the UK or to Europe. The majority of the literature surveyed here is on the subject of oilseed rape since oilseed rape is the most well-established biodiesel crop in European countries and therefore it provides a useful benchmark against which other crops can be assessed. The notable exceptions to this are the works of Casas and Rieradevall i Pons (2005) as it is directly concerned with hemp as a biodiesel feedstock, and of Niederl and Narodoslawsky (2004) which was included because of its relevance to the work in Chapter 3 of this thesis in which some properties of blends of biodiesels and petroleum diesel are investigated. Secondly, the Renewable Transport Fuel Obligation carbon reporting guidelines (Bauen et al., 2008) and the EU Renewable Energy Directive *Rules for calculating the greenhouse gas impacts of biofuels, bioliquids and their fossil fuel comparators* (European Parliament and the Council of the European Union, 2009) are summarised.

The ecoinvent team (Frischknecht and Jungbluth, 2007) conducted an extensive set of life cycle assessments on biodiesel in selected European situations and one US site to build the processes that they include in the ecoinvent database. This database can be used to build other LCAs, and the processes that it contains can be modified and supplemented to generate LCAs that are more specific to a site or system that is subsequently under investigation by other parties, such as the LCAs undertaken in this thesis. The data provided in the ecoinvent database are from LCAs conducted in accordance with the ISO guidance (ISO, 2006a) and therefore include capital goods of contributory processes, of which more is said in Section 4.2.8.

Stephenson et al. (2008) conducted a life cycle assessment of biodiesel from oilseed rape crops based on data for East Anglia, comparing large-scale production in a batch transesterification process with a small-scale continuous flow reactor. The environmental impacts quantified in this study were the total energy requirements of the process (MJ) and the global warming potential (GWP, measured in kg CO_2-equivalent). They found that the energy requirements in the production of biodiesel were over 50 % lower than those for fossil diesel and that the GWPs of biodiesel produced in large and small scale plant were 26 % and 32 % lower than the GWP of ultra-low suplur diesel.

In Spain, the energy use and greenhouse gas emissions reductions that are associated with the replacement of petroleum fuels by biofuels are assessed for the cases of biodiesel, produced from mixtures of soybean, rapeseed, palm and sunflower oils, and bioethanol, obtained through the fermentation of wheat and barley grains (Lechón et al., 2009). The scenarios which included combined heat and power (CHP) units, to make use of the agricultural co-products for energy use, used less energy than the equivalent scenarios without CHP units. The paper was situated in the Spanish policy context which is affected by the same EU policies as the UK.

Also in Spain, Casas and Rieradevall i Pons (2005) conducted a comparative assessment of biodiesel from hemp seed oil and petroleum diesel including the fuel production and use processes. Their results indicated that hemp biodiesel could have a negative global warming potential since they included the CO_2 that is fixed in plant parts other than the seeds from which the oil is extracted. Casas and Rieradevall i Pons (2005) suggest that hemp cultivation should be promoted and that biodiesel from hemp would be economically viable if the other plant parts were also used. This current thesis extends this work by evaluating the life cycle impacts of hemp grown in the UK, and considers both the seed oil and other plant parts in the evaluation.

Reijnders and Huijbregts (2008) surveyed the literature to assess the likely levels of greenhouse gas emissions that are produced in cultivating oilseed rape and soybean oil for biodiesel production. They considered oilseed rape that was grown in European conditions, and they compared it with producing oil from American-grown soybeans. The emissions associated with land-use change were included and found to dominate the results, with the life cycle emissions of both soybean biodiesel and rapeseed biodiesel higher than those of petroleum diesel by 1–31.6 kg CO_2-e kg^{-1}_{fuel} (approximately 37–808 g CO_2-e MJ^{-1}_{fuel}), depending on the crop type.

Niederl and Narodoslawsky (2004) quantified the environmental impact of biodiesel produced from tallow and used vegetable oil at a processing plant in the UK, using an ecological footprint method in which all impacts were converted into a measure of land. The goal and scope and inventory phases of this study are of interest in the current thesis. However, the use of a single impact assessment indicator such as the ecological footprint has no scientific basis (ISO, 2006b) and therefore such indicators are avoided in this thesis. Both tallow biodiesel and used vegetable oil biodiesel were found to have lower ecological footprints than fossil diesel or other biodiesel measured by the Sustainable Process Index with values varying from -1.2 m^2 MJ^{-1} to 8.3 m^2 MJ^{-1} compared with 26.1 m^2 MJ^{-1} for fossil diesel depending on the boundary definitions and whether substitutions procedures were used.

One of the most comprehensive and transparent reviews of research on biofuels in the UK (Mortimer et al., 2003) surveyed the comparative energy, global warming and socio-economic costs and benefits of biodiesel produced on a large scale from virgin vegetable oils and compared with conventional fossil diesel. In this report eleven other studies were analysed and the carbon dioxide reduction effectiveness of using biofuels in transport was compared with other emissions reductions strategies in the UK context, such as generating electricity from short rotation coppice biomass fuels. These studies, dated between 1996 and 2002, were conducted for a mixture of commercial, government interest and academic research purposes. The methods on the assessment of greenhouse gas emissions used in the studies surveyed by Mortimer et al. (2003) were used to inform the methodology decisions in the RTFO carbon reporting guidelines (Bauen et al., 2008).

Following the introduction of legislation to permit the introduction of the RTFO (HM Government, 2004) guidelines for reporting on the fuels' sustainability were drawn up, including the carbon reporting methodology (Bauen et al., 2008). This is particularly relevant to and significantly informs the purpose of this thesis. This method was developed in order to bring some uniformity and comparability to reports, since LCA methods as specified by ISO (2006a) are open to interpretation and therefore results do vary as a consequence of practitioners selecting differing methods and boundaries. The reporting methodology is concerned only with "all direct and indirect emissions, or avoided emissions, that are a result of the production of a biofuel" (Bauen et al., 2008, p. 6) that contribute to the carbon intensity of the fuel as expressed terms of the mass of CO_2 equivalents per unit energy in the fuel, using units of g CO_2e MJ^{-1}_{fuel}. The carbon reporting guidelines explicitly exclude greenhouse gases that are typically insignificant in the production of biofuels and therefore only emissions of CO_2, N_2O and CH_4 are accounted for. Similarly, the EU RED (European Parliament and the Council of the European Union, 2009) limits the greenhouse gas calculations for biofuels to these three gases.

However, the calculation specification in the EU RED (European Parliament and the Council of the European Union, 2009) is more tightly defined than that of the RTFO carbon reporting guidelines and specific categories of emissions are listed for inclusion in the calculation and this is discussed further in Section 4.3. The EU RED also uses units of carbon intensity expressed in terms of g CO_2e MJ^{-1}_{fuel} which is in agreement with the methodology specified by Bauen et al. (2008).

These studies and the reporting methodologies set out for the RTFO and EU RED are examined in closer detail in the following sections which are organised according to the LCA structure as set out in the ISO guidelines (ISO, 2006a). The methodology used in this thesis is developed from the literature surveyed in this chapter and is set out in Chapter 6 in which the life cycle assessment conducted in this thesis is detailed.

4.2 Goal and scope definitions

The purpose of an LCA is set out in the goal and scope definition, with reference to the broader circumstances on conditions in which the LCA is conducted. The general requirements of the goal and scope definition specified by ISO (2006a) are listed in Table 4.1. The four elements of the goal define the context and purpose of the LCA with explicit mention of the reasons for carrying out the study, the intended types of results from the study and the audience for the results. The scope defines the breadth, depth and detail of the study to ensure that the study is compatible with and sufficient to address the goal of the LCA. The product system and its functions are specified and from that information the functional unit, which provides the reference flow for the system, is defined. The breadth and depth of the product system is systematically defined with the setting of the system boundaries and assessment methodologies that will fulfil the goal of the LCA are selected. Requirements for the data collection phase are specified in order to obtain sufficient data to adequately satisfy the goal of the LCA. The underlying assumptions and limitations of the study are detailed explicitly. Finally, the reporting requirements are specified, which have implications for the presentation of the LCA results. The scope therefore sets out the plan of work for the LCA. The definitions of the goal and scope specify the approach and extent of the assessment and can therefore influence the final interpretation of the assessment (von Blottnitz and Curran, 2007). Each of the elements of the goal and scope is explored in turn in the following subsections.

Section	Definition
Goal	• the intended application • the reasons for carrying out the study • the intended audience of the study's results • any intentions to disclose the results of comparative assertions to the public
Scope	• the product system to be studied • the functions of the product system or, in the case of comparative studies, the systems • the functional unit • the system boundary • allocation procedures • the impact categories selected and methodology of impact assessment, and subsequent interpretation to be used • data requirements • assumptions • limitations • initial data quality requirements • type of critical review, if any • type and format of the report required for the study

Table 4.1: The ISO definition of LCA goal and scope components (ISO, 2006a, p. 11).

4.2.1 Intended application

Life cycle assessment methods were originally developed in a commercial context and in such a context the goal of the LCA is determined largely by the agencies that commission or that are undertaking the assessment. LCAs can be commissioned in-house for product assessment in manufacturing industries (Niederl and Narodoslawsky, 2004) or retailers (Tesco plc., 2010), by non-governmental organisations such as environmental campaign groups to assess the comparative benefits and disadvantages of products, or by policy-makers to assess the implementation of a project retrospectively and to map out the potential future impacts of a policy decision (Bauen et al., 2008; European Parliament and the Council of the European Union, 2009; Lechón et al., 2009). Prospective life cycle assessments are also undertaken to assess the likely impacts of decisions, in either policy or industrial practice, commissioned by the decision makers themselves or by third parties who are interested in exploring such potential impacts (Spirinckx and Ceuterick, 1996; Talens-Peiró et al., 2010; Stephenson et al., 2008). LCAs conducted by academics may or may not be commissioned by external clients and the intended applications, other than extending and developing the knowledge base, are not always explicit and in such cases the intended applications have therefore been inferred from the presentation of the studies.

Baumann and Tillman (2004) identified four types of LCA that can be used in order to fulfil the intended application of the LCA:

- a preliminary life-cycle approach method
- stand-alone or descriptive LCA
- accounting or attributional LCA
- change-oriented, consequential LCA

Life cycle approaches, rather than full life cycle assessment, can be applied to inform decisions on supply-chain management, product development or design and construction methods. A stand-alone, descriptive LCA can highlight the hotspots: the production subprocesses which have the greatest impact on the overall process. Accounting, or attributional, LCA quantifies the environmental impacts of a product while consequential, or change-oriented, LCA quantifies the likely or potential impacts of a change in the output of a product. The four types of LCA set out by Baumann and Tillman (2004) can be reduced to two, attributional and consequential, since the life-cycle approach is not a full LCA, and the stand-alone LCAs is an attributional LCA without the stage of the product under study being compared with another product process. Neither the RTFO carbon reporting method (Bauen et al., 2008) nor the EU greenhouse gas calculations (European Parliament and the Council of the European Union, 2009) constitute a full LCA, but both take a life cycle approach in the development of their methods.

In an attributional LCA, the impacts of the processes that are involved in the production, consumption and disposal of a product are quantified. Attributional LCA can answer questions such as “What are the emissions associated with producing a defined quantity of a product?”. They can be used to identify key processes in a product life cycle, known as hotspots, which contribute most to the overall environmental impacts of the product (Brander et al., 2008). Average values for the environmental impacts from the processes in the product system are used to determine the impact of the product system as it stands at the time of the LCA. Attributional LCA uses allocation to apportion environmental impacts to products and co-products of the product system (Finnveden et al., 2009).

However, attributional LCAs do not account for the indirect effects that arise from changes in the quantity of a product that is produced, whereas this is exactly the purpose of consequential LCA. Consequential LCA addresses questions that are concerned with marginal changes in environmental impact associated with changes in production of the product under consideration, expanding the product system to include the effects caused by implementing a proposed, future change. The key difference between the two methods is that the results of attributional LCAs will ultimately sum to the overall impacts globally, whereas consequential LCA results may include double-counting of emissions and impacts since the scope of separate LCAs may overlap. Brander et al. (2008) suggests that each method is to be used separately and with internal consistency so that an LCA uses either an exclusively attributional or an exclusively consequential method in order to produce meaningful results.

For decision- or policy-making, both attributional and consequential perspectives ought to be used in order to balance the reliable but limited results of an attributional LCA with the more complete yet less accurate results of a consequential LCA that accounts for changes in land use elsewhere as a result of crop displacement (Schmidt, 2008).

4.2.2 Reasons for conducting biofuel studies

The main concerns described in Section 2, of climate change, sustainability and the need to move away from dependency on petroleum fuels all contribute to the motivation for the studies of biofuels. In the research literature, for example, Stephenson et al. (2008) indicated that the reason for their study was to "study the sustainability of ... manufacturing routes" (op. cit. p. 427), while legislation on the use of biofuels in both EU and UK contexts stipulate the use of sustainability assessments to evaluate the appropriateness of the technology for meeting the aims of the policies. Assessments of individual biofuels from different feedstocks provide a scientific basis for judging which biofuels are more conducive to meeting the aims of the policies than others.

4.2.3 Intended audience for the studies' results

The audiences for studies published in the research literature are most usually the peer community of LCA practitioners and biofuels researchers. Research findings can also be published in report format for consideration by commercial and governmental agencies. Defra, who commissioned the report by Mortimer et al. (2003) to evaluate the social and economic implications of biofuel use, used the findings to inform the debate on the fuel duty derogation which reduced the diesel fuel duty payable on biodiesel fuels. In the commercial sector, LCAs can be undertaken by biofuel suppliers in order to comply with the reporting obligations of the RTFO in the UK, or the EU RED and other national policies in countries in the rest of Europe.

The purposes of LCAs through the past four decades were often to inform the technical development of industrial processes. For example, the work of Niederl and Narodoslawsky (2004) was intended to be "the base for an informed dialogue with important stakeholders" and specifically mentioned the commercial importance of the results for "decision making during [the] planning phase of new technology installation" (Niederl and Narodoslawsky, 2004, p. 5).

4.2.4 Intentions for public disclosure of comparative assertions from the studies

The results of LCAs conducted commercially are used in-house to inform decisions on process improvement, or prospectively to indicate the optimum pathways for production. More recently, LCAs have been used to communicate the environmental impacts of a product to consumers (for example, Tesco plc. (2010)) and to compare products between producers. In such applications, the results of an LCA must be sufficiently robust and the LCA process itself adequately consistent across producers in order to provide meaningful comparisons to consumers. If the results of an LCA are to be communicated publicly, the LCA must therefore undergo a process of critical review prior to its release to the public.

In the academic context, a critical review process is undertaken by the peer-reviewers when the results are submitted to a journal for publication. Therefore, in LCAs for journal publication, both the public disclosure and critical review procedures can be assumed to follow this route.

The scope of the LCA, which defines the breadth, depth and detail of the study (ISO, 2006a) and decisions regarding the scope of LCA studies on biodiesel product systems, and on subprocesses of those systems, is discussed in the following subsections.

4.2.5 Product system

A simple representation of the biodiesel product system is illustrated in Fig 4.2 Each box represents a phase in the life cycle, starting with the cultivation of oilseeds and the production of the feedstock from virgin or used oils and fats, or waste products, which is then converted to biodiesel, distributed in the fuel supply and finally used in road vehicles. Each of these life cycle processes can be examined in detail and the results from studies of phases earlier in the chain can be carried forward into the later phases.

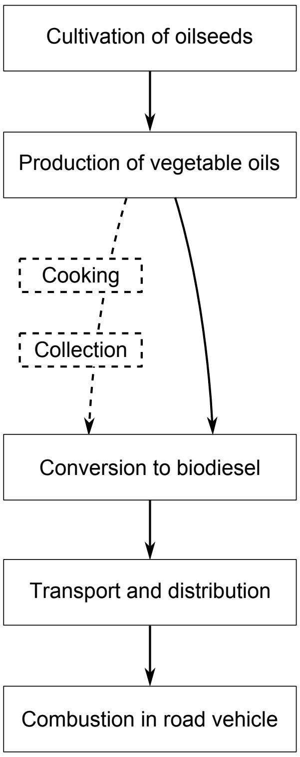


Figure 4.2: Simplified life cycle of biodiesel production and use phases. For completeness, the additional life cycle processes that are involved in the case of used cooking oils are indicated by dashed lines. While the products of the biodiesel conversion process are invariant, the coproducts that arise from the production of biodiesel feedstock oils vary between feedstocks.

4.2.6 Functions of the product system

The primary function of the final product in the biodiesel product system is the supply of energy in liquid form to vehicle engines. The vehicle engine converts the stored chemical energy into heat and kinetic energy which then drives the engine's pistons and hence the crankshaft and from there the wheels, resulting in forward or reverse motion of the vehicle.

The fuel provides energy for functions other than locomotion in the vehicle and some of these uses of energy affect the rate of fuel consumption. These other uses include, for example:

- auxiliary driving equipment
    - power-assisted steering
    - power-assisted braking
    - headlights, rear lights and indicators
    - window demisting by heated ventilation or direct heating
    - windscreen wipers
- driver and passenger comfort
    - space heating
    - air-conditioning
    - ventilation fans
    - stereo or other entertainment equipment
- other onboard equipment
    - refrigeration units (for temperature-controlled freight transport)
    - mobile phone charger
    - SatNav devices

All of these, with the exception of *driver and passenger comfort*, refer to technological functionalities of the system. However, the underlying functions all relate to the fulfilment of human needs and wants. For example, the requirement for vehicle motion comes, in the first instance, from the desire of human individuals for mobility which enables them to fulfil various purposes such as commuting to work to earn a living to support the family, traveling to see family members and friends, transporting food around the country so that it is accessible in shops and markets, and so forth. These underlying purposes drive the demand for the function of the fuel, namely its energy content, and yet these underlying purposes are not the explicitly the subject of LCAs.

4.2.7 Functional unit

The functional unit, the key flow in the system, is chosen on the basis of the function of the product system under assessment and all other flows are related to the functional unit. The functional unit must be quantitative so that the assessment can be referenced to a defined quantity. Central to the LCA process is the identification of causal relationships between the production and function of a particular product, defined by the functional unit, and the exchanges in the environment that occur as a direct result of this product (Baumann and Tillman, 2004).

Four categories of functional unit were identified in a survey of 67 biofuel life cycle assessments (van der Voet et al., 2010):

- mass/volume oriented
- energy oriented
- service oriented
- land-area oriented

Each of these categories of functional unit addresses a different question posed in the goal of the LCA. Mass/volume functional units allow for direct comparison of alternative fuels. Energy functional units provide information and how to best use bioenergy products. Service-oriented functional units compare fuel performance in a vehicle, and land-area oriented functional units serve to compare the efficacy of different land uses.

Mortimer et al. (2003) selected a functional unit of “one tonne of biodiesel from oilseed rape and distributed to relevant sales points for subsequent use in road transport vehicles in the UK” (p. 8) although subsequently they propose that “the main comparison with conventional diesel, other energy sources and energy efficiency measures is by the unit of energy delivered or saved (MJ)” (ibid.). In practice, both energy and mass functional units are used by Mortimer et al. (2003)

to compare the results of the studies that they surveyed. A mass-based functional unit was also selected by Stephenson et al. (2008) in their specification of "one tonne of biodiesel, blended to a given fractional volume with conventional, fossil-derived diesel, and delivered to a filling station in East Anglia."

Defining the functional unit as a quantity of fuel, or of delivered energy, circumvents the issue of the characteristics of the final vehicle in which the fuel is used and this approach has been widely used (Kaltschmitt et al. (1997); Mortimer et al. (2003); Bernesson et al. (2004); Niederl and Narodoslawsky (2004); Stephenson et al. (2008)). Bernesson et al. (2004) used a functional unit of 1.0 MJ energy in the fuel delivered to the vehicle, measured by the fuel's lower heating value (net heat of combustion). The net heat of combustion quantifies the amount of energy that is directly available to the engine whereas the gross heat of combustion also includes the energy that escapes from the engine in the heat of the steam. Conversely, Niederl and Narodoslawsky (2004) used 1 MJ of combustion energy (gross heat of combustion) as the functional unit in their study of biodiesel from tallow and used vegetable oils. The energy contents of fuels can be expressed in terms of the gross and net heats of combustion, and both are used in different LCAs, according to the practitioners' choices. In LCA of energy products, the net heat of combustion represents the usable energy, but the gross heat of combustion more accurately reflects the total energy that would be available to an engine were it possible to harness such energy through the use of condenser stages such as are used in domestic central and water heating systems. The gross heat of combustion also accounts for the total loss of energy from its stored chemical form, i.e. petroleum diesel or biodiesel, when it is combusted. The RTFO carbon reporting methodology (Bauen et al., 2008) does not specify whether the net or gross heat of combustion is to be used. Conventionally, published data tables give the gross heats of combustions of fuels (Department of Energy and Climate Change, 2009). Furthermore, were biodiesel to be used in static plant, such as domestic heating boilers with a condensing function, the full energy of the fuel, including the energy in the steam exhaust, would be available to the boiler. Therefore a functional unit of the gross heat of combustion is more widely applicable to other contexts than the net heat of combustion.

However, such an energy-based functional unit is based on the assumption that 1 MJ biodiesel can directly displace 1 MJ petroleum diesel and that the energy in the fuel is available to, and used in, the engine and auxiliary vehicle systems in the same way (Kaltschmitt et al., 1997). The average energy content of fossil diesel in the UK, measured by the gross heat of combustion, is 45.5 MJ kg^{-1} (Department of Energy and Climate Change, 2009) whereas the biodiesel energy content is of the order of 40.8–42.0 MJ kg^{-1} (Demirbas, 2008). Furthermore, biodiesel may have greater lubricity than petroleum diesel, and therefore vehicles using blends of biodiesel/petroleum diesel may use less fuel (Knothe, 2006).

The functional unit can include the performance of a vehicle. For example, Lechón et al. (2009) used a functional unit that depends on a vehicle's performance, based on units of MJ per km driven in a diesel or flex-fuel Ford vehicle. Similarly, Zhou et al. (2007) used a functional unit of 200 000 km driven in a vehicle, taking vehicle fuel consumption data from third-party sources. Functional units of this kind do not specify the driving conditions (traffic jams, urban cycle or motorway cruising), or driver behaviour (Barkenbus, 2010), or variations in weather conditions (Tovey, 2008). Each of these sets of conditions can have a significant impact (c. 10 %) on the quantity of fuel used over a given distance and therefore the functional unit could be made more robust by specifying exact driving conditions. In their comparative study of hemp biodiesel and petroleum diesel, Casas and Rieradevall i Pons (2005) took account of some of these factors by specifying a functional unit of an 18 ton refuse collection lorry in a defined urban cicuit of 50 km, equivalent to a consumption of 44.80 litres of petroleum diesel or 47.04 litres of biodiesel. Bearing in mind the comments above on the driving conditions, weather conditions and driver behaviour, these consumption figures appear to be over-precise. A comparison of rapeseed biodiesel with fossil diesel used a function of 100 km in a particular, unspecified vehicle to determine the quantities of fossil diesel and biodiesel to be compared to be 0.9 kg and 1 kg respectively (Spirinckx and Ceuterick, 1996). A further complication can arise when a functional unit is defined by a number of passenger-kilometres travelled, in which case the vehicle's carrying-capacity and occupancy must also be considered since a vehicle which carries four passengers provides four times the passenger-kilometres of the same vehicle carrying one passenger at the expense of small increases in the rate of fuel consumption.

In a significant departure from the standard method of defining a functional unit according to the product's function, Kim and Dale (2005) used an area of land, the hectare, as the functional unit or, strictly speaking, as the reference unit in their comparative study of biofuel cropping systems. The hectare was recommended by Cherubini et al. (2009) for use as functional unit in bioenergy systems after their review of relevant LCAs that considered solid, liquid and gaseous biofuels. This choice was made on the grounds that the main constraint on bioenergy production is the availability of land for growing crops. For bioenergy resources from residues and wastes, they propose a functional unit of delivered energy as land is not required in such systems. However, their recommendation appears to undermine the critical definition of a functional unit, that it ought to describe the service provided by the system that is under consideration. If an LCA is carried out with a functional unit defined as a service or product, the land requirements per functional unit can be derived and the results of the LCA re-expressed in terms of the land area requirements. This approach was followed by Kim and Dale (2005) in their life cycle assessment on biodiesel from soybean oil and bioethanol from the wet milling of corn and chemical treatment of corn straw (stover). The purpose of their work was to compare the environmental impacts of a specified cropping area, which is a very different approach to the ISO-specified method (ISO, 2006a) which focuses on a functional unit rather than on a system constraint.

In the current global circumstances of anthropogenically-induced climate change, one constraining factor on fuel systems is the emission of greenhouse gases. The functional unit could therefore be the "reduction of 1 kg of CO_2 equivalent emissions" (van der Voet et al., 2010, p. 438). From a constraint-oriented perspective similar to that of Cherubini et al. (2009) and using greenhouse gas emission or energy-based constraints, other reference units can be considered:

- passenger-km per kg CO_2
- tonne-km per kg CO_2
- MJ per kg CO_2
- litres of fuel per kg CO_2
- km travel per MJ fossil fuel energy

These functional units are simply the reciprocals of LCA results from studies using purpose-driven functional units, such as passenger-km or MJ, their use appears to provide no great advantage in conducting LCA studies. However, if a carbon-constrained society were to become reality through domestic tradable quotas of carbon emissions (Starkey and Anderson, 2005), the reference unit of the kg CO_2 would be very useful for making direct comparisons between modes of transport. The use of reciprocal units is demonstrated in the car industry by the common use of miles per gallon in the UK which contrasts with the use of units of litres per 100 km in continental Europe. This latter unit of measurement provides the information relative to the function of the fuel, whereas the UK custom provides the information relative to the quantity of fuel.

Baumann and Tillman (2004) recommend that for products or processes that fulfil more than one function, a single function must be chosen and represented by the functional unit. However, in systems with more than one product which satisfy more than one purpose, defining the functional unit is a more difficult task as all products can be considered. For example, hemp is grown commercially for fibre products which can have functional units of weights of fibre of specified strength, diameter and other characteristics (van der Werf and Turunen, 2008). Furthermore, in the present study, hemp is considered primarily for its oilseed whereas in commercial agriculture the hemp is predominantly grown for its fibre. To specify a functional unit based on either the purpose of the oilseed, or the purpose of the fibre, would be to overlook the dual purpose of the crop and various alternatives are explored in Section 6.2.2. The land-constrained reference unit proposed by Cherubini et al. (2009) could be of use in conducting LCA for multi-function crops by giving a common metric to assess against. As stated earlier this approach is not concerned with the function of the crops but rather with the availability of the land and such an approach would be of more use in assessments of the effectiveness of using land for particular purposes than in product-oriented life cycle assessment.

In applying LCA to the quantification of policy impacts, the policy lifetime and extent can be considered. In the case of the RTFO, the policy has a defined lifetime of 3 years, from April 2008 to April 2011. A functional unit that is more completely representative of the policy could be defined as the volume of biodiesel that is required to satisfy the policy targets over the policy lifetime. At current rates of fuel consumption and with the stepped targets from 2.5 % to 5 % over the three years applied to all road fuel types separately, this amounts to 2.8 billion litres of biodiesel. Such a functional unit would be more typical of a consequential LCA than an attributional LCA as it considers the question of the total potential environmental impact that may be brought about by a change from the status quo to another state. Reinhard and Zah (2009) took a consequential LCA approach in their assessment of the indirect consequences of importing biodiesel that would satisfy 1 % of Switzerland's diesel consumption, yet used a functional unit of "1 MJ fuel at the regional storage in Switzerland" (p. 549) rather than a reference flow of the total quantity of biodiesel required to meet 1 % of the diesel supply. The consumption of diesel in Switzerland was 2 Mt in 2007, and this rose to 2.2 Mt in 2008 (Erdoel Vereinigung Union Petroliere, 2009), therefore Reinhard and Zah (2009) were calculating the impacts from 0.020–0.022 Mt diesel entering the Swiss road transport sector fuel market.

The above discussion of functional units illustrates the wealth of approaches that can be taken in a life cycle assessment, depending on the purpose of the LCA. The selection of a functional unit is the selection of the most appropriate reference flow which will enable the answering of the question posed at the outset of an LCA (van der Voet et al., 2010).

4.2.8 System boundary

The system boundaries define the processes that are included in the system, and therefore the processes that are included in the life cycle assessment (ISO, 2006a). The ISO standard (2006a) leaves the exact boundary decisions to the discretion of the LCA practitioner, whereas the EU RED (European Parliament and the Council of the European Union, 2009) and RTFO carbon reporting guidelines (Bauen et al., 2008) specify the boundaries that are to be adopted studies which follow the policy guidelines.

The three major types of system boundary, which consequently define the extent of the life cycle inventory (Section 4.3), are (Guinee et al., 2002):

- between the technical system and the environment
- between the technological system under study and other technological systems, and
- between significant and insignificant processes.

These three categories of boundaries are explored in the following subsections.

Boundary between the system and the environment

The boundary between the system and the environment, also referred to as the boundary between the system and nature (Baumann and Tillman, 2004) is conventionally set at the point at which raw materials are extracted at source. The cut-off points for the system are those at which elementary flows enter or leave the system, with elementary flows defined as those of "material or energy entering the system being studies that has been drawn from the environment without previous human transformation, or material or energy leaving the system being studied that is released into the environment without subsequent human transformation" (ISO, 2006a, p. 3).

The boundary with nature defines the extent of the system in the context of the natural environment. In an agricultural LCA, the soil is usually defined as being part of nature, even though it is heavily manipulated by human activities with the additions of fertilising agents and organic matter. This boundary is of particular importance in establishing what the inputs from nature are, in contradistinction to input from the technosphere, and the endpoint of the life cycle, at which point the product, or its waste products, returns to nature. The distinction between nature and everything else is somewhat artificial, since in the broadest sense nature includes everything, including humans and human-made artefacts, machines, chemicals and so forth.

The exclusion of biogenic CO_2 emissions from the inventory data, in either CO_2 extraction from the atmosphere or biogenic CO_2 emission, is a "special convention" (Rabl et al., 2007) which can give rise to anomalous results in life cycle assessment of bioenergy systems. Luo et al. (2009) found that the impacts associated with extraction and emissions of biogenic CO_2 are significant in systems with co-products. Both Rabl et al. (2007) and van der Voet et al. (2010) recommend dispensing with the special convention and accounting for biogenic CO_2 extraction and emission as per any other environmental extraction or emission.

Typically, CO_2 absorption in plant growth is not considered in biodiesel LCAs as it is assumed to be fully combusted when used as a fuel and therefore results in no net change in atmospheric CO_2 levels. This assumption is sound provided that no other CO_2 absorptions occur at the time of seed growing. The carbon stored in the seeds themselves is in both the oil and the presscake. The carbon in the oil is assumed to be released in combustion. The presscake, formed when the oil is extracted, is assumed to be disposed of into composting, or burned, or digested by animals. In all of these cases, the CO_2 is released back into the atmosphere. In addition, the production of most oilseed crops, and particularly in the case of hemp, also results in significant production of other biomass, and hence carbon storage, in the form of straw. The carbon absorption in the straw is also assumed to be re-released into the atmosphere when the straw is ploughed back into the earth, as happens for rape straw. However, if the straw has commercial uses which do not involve combustion or decomposition, the carbon stored cannot be assumed to be re-released into the atmosphere. Casas and Rieradevall i Pons (2005) included CO_2 absorption in their LCA of hemp biodiesel without specifying exactly which processes and quantities they included, therefore their final results cannot be used directly in comparison with those of other biodiesel LCAs.

Boundaries between the system and other technical systems

The start and end points of the life cycle under assessment must be clearly defined and either cradle-to-grave or cradle-to-gate (Stephenson et al., 2008) system boundaries are typically used. The well-to-wheels system boundary is also used in biodiesel LCAs van der Voet et al. (2010). A cradle-to-grave boundary starts at the first point in the production process and ends at final disposal of the product. For biodiesel from purpose-grown vegetable oils, the cradle of the process is the preparation of the land for crop growth and the grave is the final use of biodiesel in a vehicle. An alternative to the cradle-to-gate and cradle-to-grave LCA system definitions is available, although not widely used, in the form of a cradle-to-cradle system definition (McDonough and Braungart, 2002). This represents a cyclical approach which could be used to assess the impacts of the process right up to the point at which the process can begin again.

The system under assessment is always embedded in a wider context which is referred to here as the background. For instance, the LCA system may draw a certain quantity of energy from the electricity supply, and (Talens-Peiró et al., 2010) found that the transesterification stage of the biodiesel production process from used cooking oils was “highly influenced” by the environmental impacts of the electricity supply. However, that electricity supply can and does alter its composition as the energy mix varies over time – in some years more coal may be used than in other years, or the contribution of renewable or hydropower electricity may be proportionally greater. However, a distinction can be drawn between the LCA system and the wider background, and subsequently a sensitivity analysis can be conducted to determine the likely impacts of change to the background system on the LCA results (Talens-Peiró et al., 2010). In some cases, the impacts of changes in the background situation may sometimes be greater than the marginal changes in the life cycle of the product or process itself.

In the case of biodiesel, fossil fuel use is frequently assumed in the transport stages in the life cycle. Furuholt (1995) identified transportation of oil between the source of the oil and the refineries, as well as transport between the refinery and the point of use, as producing the main contributions to the NOx and SO_2 emissions in the diesel life cycle. This is largely due to the high level of NOx and SO_2 emissions from the diesel engines that power both oil tankers on the sea and distribution lorries on the road. Replacing this fossil fuel with biodiesel alters the system to reflect a possible future energy system that includes less fossil fuel, if any at all.

In the real world of products and processes, no completely closed systems exist. It is therefore impossible to clearly delimit a single product's production and usage processes from the background context in which it is situated: “A product system never exists in isolation, and the way in which a service is provided generally always has an alternative” (Wenzel, 1998, p. 550). Pehnt (2006) first develops a static life cycle assessment of renewable energy technologies, using a status-quo approach when considering the background impacts. Secondly, he conducts a life cycle assessment using a dynamic approach, in which a future energy scenario is used to provide the background: that is, a more predominantly renewable electricity supply and improved production processes are proposed. The consequences and impacts of this future scenario are used in the assessment. Pehnt (2006) raises two questions regarding the time dimension of the life cycle assessment:

- How fast will the background system change?
- How fast will the improvement potentials be made accessible?

A sensitivity analysis can contribute to addressing these questions, thereby making the LCA results more robust and reliable into the future.

In the case of feedstocks from wastes such as tallow and used cooking oils, the start point of the life cycle is defined as the raw waste stream (Niederl and Narodoslawsky, 2004; Talens-Peiró et al., 2010). The upstream environmental impacts of the raw waste streams may be allocated in part to the upstream processes, for example industrial food frying processes or meat production, and in part to the downstream biodiesel production (Niederl and Narodoslawsky, 2004), or ignored

(Talens-Peiró et al., 2010). In the latter study, the environmental impacts of producing the oils were allocated entirely to the previous use phase, cooking, and the used cooking oil was considered to be a resource devoid of previous environmental impact.

Various start and end boundaries for biofuel systems are observed in the literature and these are determined in part by the selection of biofuel feedstock. For example, Niederl and Narodoslawsky (2004) defined three starting points for their assessments: the starting point of the beef production process, the point at which render materials are transported to the rendering plant and finally the point at which the render products are transported to the biodiesel production facility. The end point that they used is the combustion of the fuel, without regard to a specific engine or boiler.

The manufacturing of capital goods that are involved in system processes, for example the production of agricultural vehicles that are subsequently used in field operations for tending biodiesel crops, can be included or excluded from the life cycle product system. In the case of a factory that is purpose-built to produce a given product, the LCI (life cycle inventory) of the factory, which is a capital good, can be causally attributed to the product. However, a farm rarely comes into being in the UK as a direct result of the demand for a product, moreover it is an established business with associated premises and machinery that is used to produce crops or livestock according the the farmer's decisions in light of market information. Therefore the capital goods of a farm cannot be causally attributed to the farm's products in the same fashion that a factory's capital goods can be attributed to its products.

Not only are the inputs to a process complex, but also the process output may have more than one component. The main product flow can be accompanied by the production of co-products which may initially be designated as waste since they have no perceived value. However, the co-product of biodiesel conversion, glycerol, is a valuable product, as are agricultural residues such as straw or the presscake that remains after oil has been extracted from seeds (Section 2.7.3). System expansion, which involves the inclusion of avoided impacts from products that would have been produced had the co-product not been produced, is one method for dealing with co-products, and is recommended as the preferred approach for carbon reporting for the Renewable Transport Fuels Obligation (Bauen et al., 2008).

In cases where system expansion is not selected to handle the influence of co-products on the product system, the environmental impacts are allocated between the product and co-products of a system according to an allocation ratio derived from intrinsic (for example physical or chemical properties) or extrinsic (such as monetary value) parameters. Allocation is described in more detail in Section 4.2.9.

Significant and insignificant processes

A great deal of data is required to satisfy such system boundaries and in practice cut-off criteria are used to eliminate material and energy flows from the system that have little significance to the results of the assessment (Mortimer et al., 2003). Bauen et al. (2008) recommend the exclusion of four categories of processes which "always make a small absolute contribution to the chain emissions" (p. 6):

- emissions from cultivating seed for sowing
- emissions from the manufacture and maintenance of machinery and equipment (capital goods)
- emissions of perfluorocarbons, hydrofluorocarbons and sulphur hexafluoride which are of little relevance to biofuel production
- emissions associated with the production of chemicals used in conversion plants that would contribute less than 1 % of the total biofuel life cycle emissions.

However, Stephenson et al. (2008) included both seed for sowing and capital goods in their analysis.

As noted previously, CO_2 absorption during plant growth and emissions in final fuel combustion in a vehicle are conventionally assumed to cancel one another out in a biodiesel life cycle assessment. This assumption is tested in the life cycle assessment in this thesis (Chapter 6).

Boundaries of time and geography

Temporal and geographical boundaries are considered to be special cases of boundaries between the system and the environment, and between the system and other technical systems (Finnveden et al., 2009).

The need for temporal context and boundaries arises in four aspects of the life cycle: to situate the system under investigation in time, to specify the time period over which emissions and other exchanges with the environment may have an effect, to specify the start and end points of the system in time, and finally to attribute the effects from prior and subsequent product systems - a key issue of this type is land use change (Searchinger et al., 2008). However, at present there is “no agreement on how these impacts should be included in an LCA” (Finnveden et al., 2009, p. 11).

The time period in which the emissions have an impact must also be specified, bearing in mind that this time period may influence the outcome of the LCA. For example, if the effects of a persistent pollutant were assessed only for a short period of time for the purposes of the LCA, its effects would undervalue the true effects of the pollutant in the earth, waters and atmosphere. When reporting the results of the LCA, such assumptions must be explicitly declared so that the LCA results can be appropriately used in subsequent studies and applications.

Temporal boundaries can also define the start and end points of the system itself. In agricultural systems, crops are typically grown in a rotation system over a number of years. For example, a field rotation that is frequently used in the UK consists of two crops of wheat, one rapeseed crop, two further years of wheat and finally a crop of legumes, such as peas or beans (Squier, 2008). The start point of the crop in the field is conventionally taken to be the first activity after the previous crop has been fully harvested and the end point is harvested (Nemecek and Kägi, 2007).

The effects of the process under assessment on the environment are themselves either implicitly or explicitly temporally bounded by decisions regarding the timeframe over which the effect is considered. Such boundaries occur in the third phase of LCA, when indicators are calculated from the inventory results. Some LCA methods include a specific time period over which the effects are distributed. For example, the IPCC GWP 2007 method for indicator calculations uses timeframes of 20, 50 and 100 years (Solomon et al., 2007). The effects of changing the timeframes used by the indicator methods can be assessed by using different timeframes and comparing the results. With regard to emissions timescales, Finnveden et al. (2009) pose the question, “should the emissions of the country ... be corrected for ... time-lags between production and emissions, as in electrical equipment that will be discarded only 20 years afterwards?" (p. 13).

When considering temporal boundaries in the context of a sustainability assessment, the meaning of sustainability as described by Brundtland (1987) implies that truly sustainable systems will stand the test of many generations of humans, not just of one or two human life spans. In the case of fossil fuels, any use at all of these substances results in an increased scarcity of such resources for future generations and this raises an interesting issue of how to weight or to normalise resource depletion.

The subject of geographical boundaries can be separated into two aspects. Firstly, the geographical boundaries defined for the system govern the applicability of the LCA results to other similar systems inside that geographically bounded region, or to geographically similar regions. Secondly, the environmental impacts of the system can spread over a wide area and these effects can be included, or excluded, from the analysis.

In LCA, the practitioner can decide how to handle environmental exchanges that happen remotely, for example in different countries or continents. If fertilisers produced in another country are used to fertilise crops here in the UK, the impacts of fertiliser production can be allocated to the process of crop production, or not included, according to the practitioner's choice of geographical boundaries. Internationally, emissions of greenhouse gases, which are of key concern in this thesis with regard to the consequences for climate change, are allocated to the country in which the emissions are produced. However, Druckman et al. (2008) argue for the adoption of a consumption perspective when calculating emissions totals, in order to achieve a dataset which is more representative of causation, and this is in agreement with a comprehensive LCA which includes all impacts, regardless of their source or effect location.

4.2.9 Allocation procedures

When a system has two or more products, the impacts of the system are not necessarily attributable to the main reference flow and could therefore be distributed between the products, as touched upon briefly in discussions of system start and end points. A generalised life cycle is shown in Fig 4.3 which illustrates the possible points in the life cycle at which other output streams may be produced.

The ISO (2006a) guidance on life cycle assessment encourages the use of system subdivision or, alternatively, expansion in order to avoid the need for allocation. System subdivision is the process of dividing the unit process into subprocesses for which input and output data can be collected separately. System expansion, also known as substitution (van der Voet et al., 2010), is the process of adding elements to the reference system such that the co-products of the system in question are matched with alternative products, or avoided products. The environmental impacts caused or avoided by the co-products are accounted for by expanding the system to include avoided or additional impacts associated with the co-products. System expansion thereby takes into account the different functions that co-products can fulfil in addition to the main function of the functional unit itself. For example, the major co-product in the case of biodiesel is glycerol and the impacts of biodiesel production can include the avoided impacts of the glycerol production process by an alternative production route. Where co-products can be used for different purposes, multiple LCAs can be conducted on different scenarios of co-product use and from these an industry-average style of LCA may be calculated based on the proportions of the co-products that go into different uses. However, system expansion can become unwieldy when many co-products are produced in the system, and when each co-product has complex avoided impacts.

However, displacement of products, as assumed by system expansion, is not always causal. For example, although electricity might be produced from the co-products, or indeed from the principal products of the system under consideration, this would not directly cause the displacement of

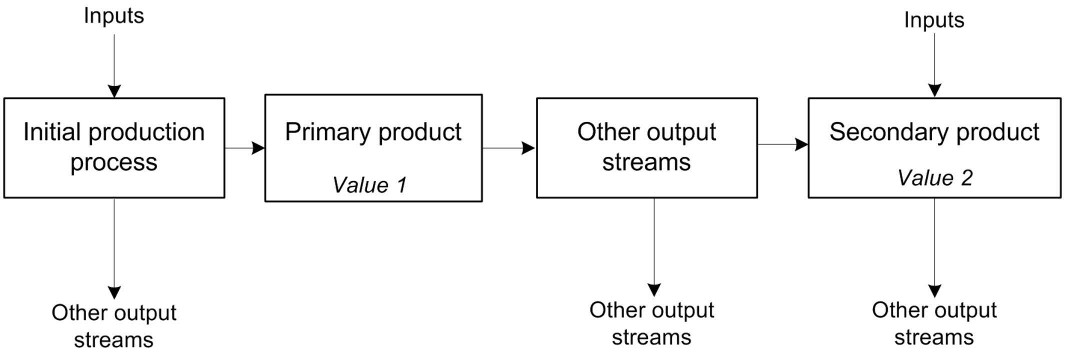


Figure 4.3: Schematic system with co-products from other output streams as raw material

electricity from other sources across the National Grid. More likely, it would marginally change the electricity mix. Weidema et al. (1999) put forward a five-step procedure for identifying the marginal technologies that are affected by a change in the output of a product.

For cases in which system expansion is unfeasible within the constraints of the project, allocation should be used according to a method that can be justified according to the process and functional unit definitions (Finnveden et al., 2009). For example, if the functional unit in Fig 4.3 concerns a quantity of product that has Value 1, and the co-product similarly has Value 2, the impacts are allocated in the ratio of the values of the products. Such values are necessarily quantitative and can be represented by product masses, financial values and, of interest for this LCA with its focus on a bioenergy system, energy values.

ISO 2006b recommend the use of the following bases for allocation procedures, in order:

1. physical properties (e.g. mass)
2. economic value
3. number of subsequent uses (in the case of recycled materials)

In the cases of oilseed and biodiesel production, and their co-products straw and glycerol respectively, either mass or energy allocation methods are appropriate. In the case of agricultural products, the mass of the product and co-products is relative to their uptake of agricultural inputs. For biodiesel and glycerol, either mass-based allocation could be applied with the same reasoning as for agricultural products, or energy allocation. Niederl and Narodoslawsky (2004) used both mass and financial allocation approaches in their work on biodiesel production from tallow and used cooking oils, while the EU Renewable Energy Directive (European Parliament and the Council of the European Union, 2009) recommends that energy-based allocation be used, thereby considering glycerol as an energy carrier. However, energy allocation can also be applied to agricultural products and co-products and this is especially relevant for cases in which both the product and co-product(s) are intended to be used as fuels. Straw can be combusted in co-firing or in dedicated bioenergy plants, or smaller-scale biomass boilers, and as such its energy content is the most appropriate property with which to calculate input/outputs allocations.

Allocations of inputs, outputs and the related environmental impacts are carried out in proportion to the components' physical properties, as far as is possible. If allocation in this way is not possible, or justifiable, allocations can be made according to the financial value of the products. However, the variability of financial values limits the usefulness of monetary valuation as a decision-making tool (Hall and Scrase, 1998).

The calculation of ratios ($Allocation_i$) to allocate impacts between co-products weights each co-product according to the selected allocation parameter as shown in Eqn. 4.1:

$$Allocation_i = \frac{Parameter_i \times Proportion_i}{\sum_j Parameter_j \times Proportion_j} \tag{4.1}$$

where the proportions of, in this case, two co-products i and j in the life cycle assessment are given by $Proportion_i$ and $Proportion_j$, while the values of the selected allocation parameter for each co-product are $Parameter_i$ and $Parameter_j$.

Rape straw is, in some studies, ignored as a co-product because its uses are limited when it is produced on a small scale (Bernesson et al., 2004; Reinhard and Zah, 2009) and in such cases the environmental impacts are not allocated to rape straw, but wholly allocated to the seed, with $Parameter_{rapestraw}$ set to zero in Eqn. 4.1. The selection of the properties with which the allocation parameters and ratios are calculated can have a significant impact on the LCA results (Bernesson et al., 2004).

4.2.10 Impact categories, methods and interpretation

The selection of impact categories, or areas of protection, for which results are required in an LCA, is largely determined by the goal and scope of the LCA, since this governs the direction of enquiry in the LCA. In defining the categories, Baumann and Tillman (2004) outline six areas for consideration: completeness of the category, the practicality of assessing the category as defined, the relevance of the category to the purpose (the goal and scope) of the LCA, the independence of the categories so as to avoid double counting of impacts, the availability of applicable scientific methods for calculating the impacts in each category and the suitability of the category for linking to available characterisation methods. The considerations of completeness and practicality may require a compromise in some circumstances for example when a fully complete assessment of the impacts in the category is too impractical to carry out. There exist established methods for classifying inventory items into categories. Processes that are compatible with LCA software have been developed and these have been widely used in biodiesel life cycle assessments (Casas and Rieradevall i Pons, 2005; Talens-Peiró et al., 2010; Chiaramonti and Recchia, 2010).

Three over-arching impact categories, or areas of protection, have been identified (Consoli et al., 1993; ISO, 2006a) into which all other impact categories can be grouped, that is resource use, human health and ecological consequences. A fourth category, consequences on manmade environment, can also be considered but approaches and methods to quantify such consequences are as yet not developed (Jolliet et al., 2004).

The environmental extractions and emissions identified in the inventory of an LCA are classified into these areas of protection, or into intermediate categories such as the potential for greenhouse gas emissions, eutrophication or the potential for acidification of waterways. Jolliet et al. (2004) give a set of intermediate, or midpoint, categories and indicate the impact pathways that classify each midpoint category into one or more damage categories (areas of protection), shown in Fig 4.4. The inventory data, once classified, are combined to calculate quantitative indicators for each category (Section 4.4).

4.2.11 Data requirements

The data required to carry out an LCA depend on the goal and scope of the LCA. For a cradle-to-gate or cradle-to-grave LCA of biodiesel, data are required on the cultivation or collection of the feedstocks, any preparatory processes of the feedstocks, for example oil extraction from oilseeds or refining of used oils, the esterification process and transport and distribution of the final product, depending on where the system boundaries are drawn.

Furthermore, the data required also depend on the impact categories selected in the scope of the LCA. In the case of an LCA which focuses on the climate change impact potential of a system,

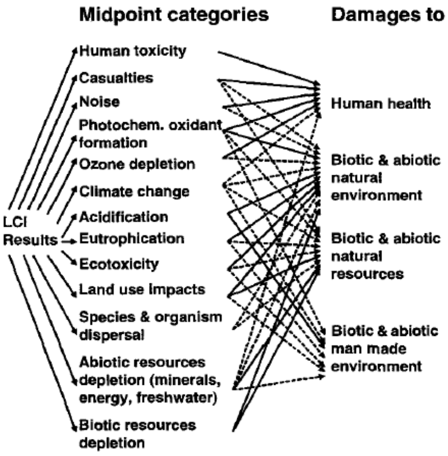


Figure 4.4: Midpoint and endpoint impact categories, reproduced from Jolliet et al. (2004), p. 395.

data on direct greenhouse gas emissions, and on processes which lead to indirect greenhouse gas emissions, are required.

4.2.12 Assumptions

The underlying assumptions on which an LCA study is founded must be made explicit in order to enable future comparisons between systems. The assumptions can include aspects of the system description, for example the origins of components for the system processes, the methods that are used in the impact category indicator calculations, and assumptions regarding unknown or uncertain data (Lechón et al., 2009). The effect, if any, of these assumptions can, where appropriate, be subsequently tested by sensitivity analysis in the interpretation phase (Section 4.5).

A reference system can be defined for a comparative LCA and usually the reference system represents business as usual (BAU), thus providing a baseline case for comparison. In the case of biodiesel, the reference system is most often fossil diesel and the co-products are accounted for through expansion of the reference system, as described above. The substituted products in system expansion are declared in the reference system, whilst noting that the LCA may generate different results if alternative substituted products were used in the LCA. In the case of a consequential LCA, the marginal differences from the BAU scenario are assessed for the proposed system change. The results of a consequential LCA are always relative, not absolute, and therefore care is required when comparing LCAs to ensure that they are of the same type, attributional or consequential, and in the case of consequential LCAs to ensure that the BAU scenario is the same for both LCAs.

Avoided products can be included in system expansion. For example, the straw co-product of the oilseed crop can be used to provide heat and power to the biodiesel conversion process, thereby avoiding the use of petroleum diesel. The environmental impacts of using petroleum diesel that have been avoided can therefore be credited to the biodiesel production system. The selection of avoided products can have a significant impact on the final results of the LCA (Gnansounou et al., 2009)

Brander et al. (2008) reviewed the RTFO and EU RED methodologies for the calculations of emissions from the production of biofuels and suggests that the methods are not only different in their scope and approach, but also that the RTFO method is, in fact, internally inconsistent. They argue that the methodologies do not strictly adhere to either attributional or consequential modes of life cycle assessment and therefore the results of both the RTFO and the EU RED methodologies are likely to be incomparable with other studies. They suggest that even studies carried out according to the RTFO methodology will not be directly comparable with one another because the method still leaves room for differences in its interpretation and application.

4.2.13 Limitations

The limitations of an LCA in regard to its geographical and temporal relevance must be specified (Baumann and Tillman, 2004), along with an indication of the limitations encountered in conducting the LCA, for example in cases of unavailable data.

4.2.14 Initial data quality requirements

The quality of the data that is collected in the life cycle assessment has a strong influence on the reliability of the assessment. The data must be as accurate and relevant as possible in geographical location and system size, and not obsolete (Baumann and Tillman, 2004). In the scope of the LCA, the required quality of the data for the purposes of the LCA is defined.

The time period in which the process is situated may impact the LCA results. The changing nature of the energy mix for electricity provides a simple example of time-context dependency. When undertaking an attributional LCA of a process that occurred in the past, or which is occurring at present, the energy mix of that time must be used, or else the environmental emissions are inaccurately reported as the energy mix changes. Furthermore, for prospective LCAs that are designed to handle the consequences of process changes, future energy mix scenarios must be modeled in order to account for changes in electricity emissions factors, and hence changes in environmental impact.

4.2.15 Critical review

Results that are to be used as the basis for communication with the public must undergo critical review to ensure that the method that has been used, and the results of the study, are sufficiently robust for release into the public domain. In this section, any requirement for critical review must be declared, as well the the type of review required and the criteria for selecting a reviewer (Baumann and Tillman, 2004).

4.2.16 Study report type and format

The intended application of an LCA governs the type and format of the report, or reports, produced from the LCA findings. The four client-types outlined by Baumann and Tillman (2004), public policy makers or authorities, industry, environmental NGOs and consumers, may receive the results presented in different modes according to the preference of the agent, whether company, governmental body or academic, and the purpose of the communication.

The results of LCAs can be used to inform customers of the environmental impact of products in order to persuade customers to purchase one product over another (Baumann and Tillman, 2004) and in such cases the findings of the LCA may be reduced to an information label on the product itself at the point of sale. Environmental labeling of products has been undertaken for many years and one notable example is the energy rating system for household appliances on the scale A+–G that was introduced following European Council legislation 1992. A similar A–G rating scheme has now been applied to buildings in the UK (HM Government, 2008). Carbon footprint labeling is used to communicate the life-cycle CO_2 emissions of products in supermarkets to customers (Tesco plc., 2010), and in that particular case the life cycle study was reviewed by an external reviewer, the Carbon Trust. This highly aggregated representation of results is useful for some contexts and less useful for others. For example, the results of the comparative LCA of fossil diesel and rapeseed biodiesel by Spirinckx and Ceuterick (1996) were presented in a highly aggregated fashion which disguises some of the subtleties of the system and the LCA assumptions and results.

4.3 Inventory analysis methods

Compiling the inventory includes three main activities (Baumann and Tillman, 2004, p. 97):

1. Construction of the flowchart according to the system boundaries decided on in the goal and scope definition.
2. Data collection for all the activities in the product system followed by documentation of collected data.
3. Calculation of the environmental loads (resource use and pollutant emissions) of the system in relation to the functional unit.

These activities are supplemented by more detailed modeling procedures:

- allocation
- accounting for recycling rates
- accounting for energy

The activities and modeling procedures listed above can be carried out with the assistance of software packages that have been specifically designed for conducting LCAs. The inventory analysis activities and procedures, and the software tools that assist the process, are described in greater detail in the following subsections.

4.3.1 System flowchart construction

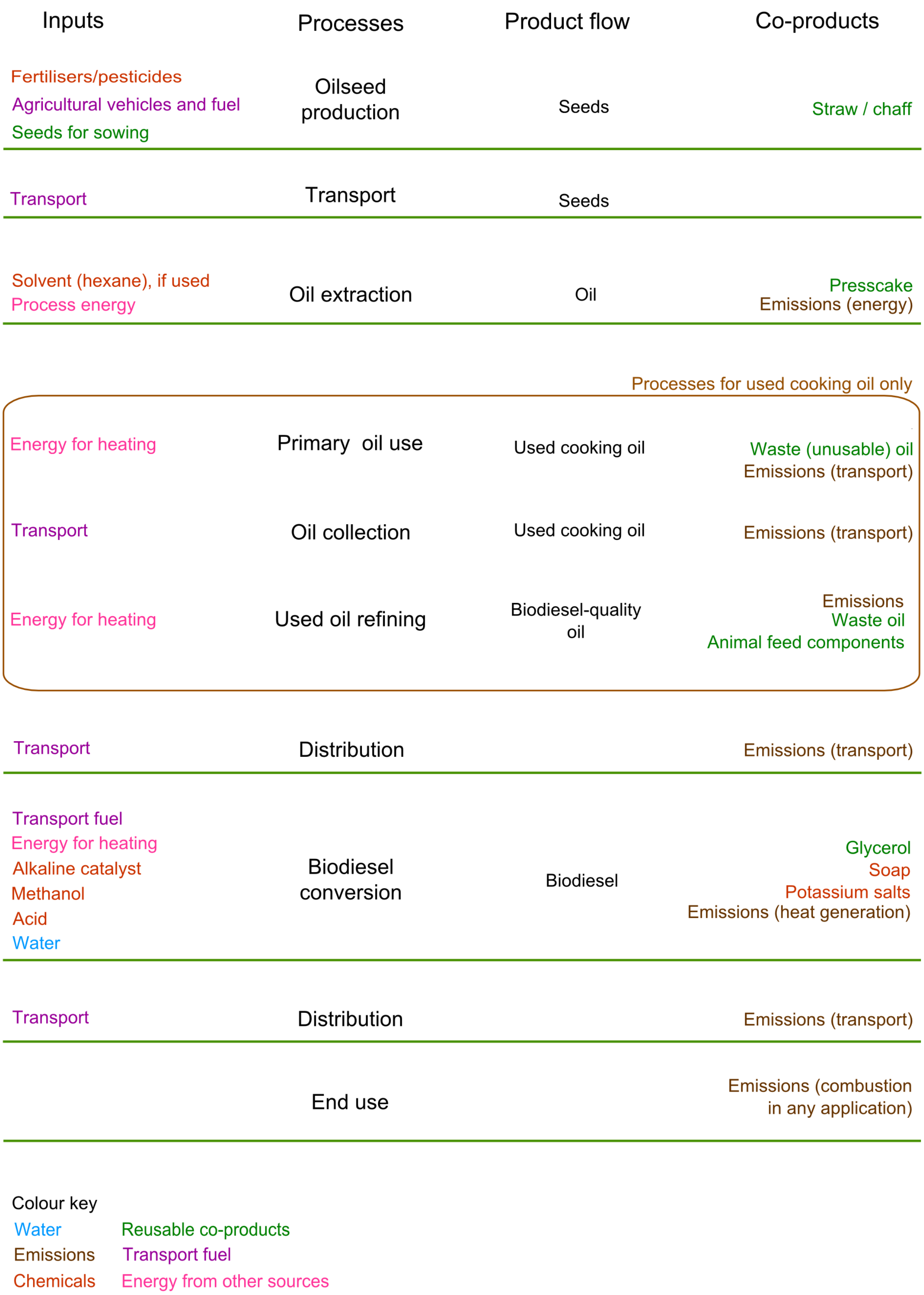
In practice, the construction of the system flowchart is, like most of the LCA procedure, iterative in nature. As more data is collected, more elements and connections become known and are incorporated, or excluded, from the system flowchart depending on the criteria in the goal and scope, the criteria themselves being also subject to iteration as appropriate.

Fig. 4.5 shows the various stages in the production of biodiesel and the inputs, product flows and co-products that are associated with each stage, based on the information set out in Section 2.7. The production stages are named in the central column, with the inputs on the left and the outputs, including the product flow of interest and the co-products, on the right hand side. Life cycle assessment for biodiesel typically includes some or all of these stages, inputs and outputs, depending on the boundaries that are drawn up for the system under assessment and these boundaries are explored further in Section 4.2.8. In the case of used cooking oil feedstock, extra processes are involved for the primary use phase of the oil for cooking and these are indicated in the box in the middle of Fig. 4.5.

4.3.2 Data collection

The initial data collection process results in the construction of the system flowchart, as shown above in Fig. 4.5. These data concern the overall nature of the system and general information regarding the processes that are to be included in the assessment. The next step is to obtain more detailed and quantitative data on the inputs and outputs of the processes, and on the connections between the product flows. For example the oil content of the seeds is the piece of information that connects the seed product with the oil product, and similarly the conversion factors from vegetable oil to biodiesel connects the oil product with the final biodiesel product output.

Depending on the scope of the LCA, the detailed data can be collected from the literature, from established databases, or from primary data collection through interviews and observations at places of production. In this LCA, the primary data required concerns the processes on the farm and the specific inputs and outputs from the cultivation processes. Such data can be collected through interviews, either in person or via telephone or email. Stephenson et al. (2008) collected



Inputs	Processes	Product flow	Co-products
Fertilisers/pesticides Agricultural vehicles and fuel Seeds for sowing	Oilseed production	Seeds	Straw / chaff
Transport	Transport	Seeds	
Solvent (hexane), if used Process energy	Oil extraction	Oil	Presscake Emissions (energy)
			Processes for used cooking oil only
Energy for heating	Primary oil use	Used cooking oil	Waste (unusable) oil Emissions (transport)
Transport	Oil collection	Used cooking oil	Emissions (transport)
Energy for heating	Used oil refining	Biodiesel-quality oil	Emissions Waste oil Animal feed components
Transport	Distribution		Emissions (transport)
Transport fuel Energy for heating Alkaline catalyst Methanol Acid Water	Biodiesel conversion	Biodiesel	Glycerol Soap Potassium salts Emissions (heat generation)
Transport	Distribution		Emissions (transport)
	End use		Emissions (combustion in any application)

Colour key

Water	Reusable co-products
Emissions	Transport fuel
Chemicals	Energy from other sources

Figure 4.5: Selected elements of the lifecycle of biodiesel produced from vegetable oils or used cooking oils

data on farm inputs and on vegetable oil to biodiesel conversion processes through communication with the commercial partners involved and this method is also employed in this thesis.

Inventory data for background processes can be obtained from international databases, such as the ecoinvent database (ecoinvent Centre, 2009). Where appropriate, the ecoinvent database entries can be modified to better reflect the specific details of the life cycle under assessment. For example, in assessing sunflower and oilseed rape for biodiesel production in Chile, Iriarte et al. (2010) modified data to take account of the conditions in Chile, rather than use the data in their original state for European conditions.

4.3.3 Calculation of resource use and pollutant emissions

From the inventory data, the overall quantities of individual substances consumed or emitted in the life cycle system under consideration are calculated. However, in practice this stage of the calculation is used only as a precursor to the impact assessment calculation which is discussed in the following section.

4.4 Impact assessment methods

The impact assessment phase of the LCA, referred to as LCIA - Life Cycle Impact Assessment, comprises the aggregation of the inventory data on emissions and resource consumption into impact categories, also known as areas of protection, which are defined according to the goal and scope of the LCA. When the data are collated, the meaning and implications of the data are easier to grasp and processes can be readily compared when presented in a small number of impact categories.

The process of LCIA has three core phases and four supplementary phases which are carried out if the goal and scope call for it (Baumann and Tillman, 2004). The core phases comprise the definition of the impact categories, followed by classification of inventory data into the categories and finally the quantitative characterisation of the impacts through calculating the category indicators. These core phases are based firmly in the natural sciences and as such are more objective in nature than the supplementary phases. The four supplementary phases are contextually defined and include quantification of a more subjective nature. Normalisation of the characterisation data against reference data can be done to ascertain the relative impact of the process when compared to, for example, overall national emissions or consumption. Secondly, the impact categories results can be grouped into indicators through sorting or ranking. Thirdly, the impacts can be weighted to enable aggregation of the results across impact categories. Fourthly, data quality analysis, using methods of sensitivity analysis and uncertainty analysis, can be applied to the results to obtain a measure of the robustness and reliability of the impacts as calculated (Baumann and Tillman, 2004).

The complexity of interactions in environmental systems, and the resultant web-like chains of causes, effects and feedback loops, leads to quantification of impacts in terms of their maximum potential impact, rather than the actual impact of specific emissions or resource consumption. For this reason, LCA handles global impacts more effectively than it does local impacts as the methods avoid assessing specific localised effects of emissions.

The development of an indicator includes consideration of the system boundaries, observations of characteristics and parameters in the system, and prior knowledge of the interactions of the system (Bell and Morse, 1999). Methods to calculate indicators for commonly investigated categories in LCA, such as climate change potential, resource depletion and ozone depletion potential, have been developed (see, for example, Goedkoop and Spriensma (2001); Goedkoop et al. (2008)). These methods are available ready-made for use in LCA software tools such as SimaPro (Pre Consultants, 2007) and GaBi (PE International, 2010). The practical advantage of these methods is that the LCA practitioner does not need to develop their own methods from scratch for each resource used or emission produced throughout the life cycle. LCAs conducted using these methods are also easier to replicate.

4.4.1 Impact category definition

Inventory data and impact categories are linked by indicators which can be of two types: midpoint or endpoint, shown in Fig. 4.6, (Jolliet et al., 2004). Midpoint indicators quantify the change in an aspect of the environmental system, for example the ozone depletion potential or global warming potential. Endpoint indicators assess the likely damage to an area of protection, such as human health or natural resource depletion, and include both quantitative and qualitative assessments (Jolliet et al., 2004). The midpoint and endpoint indicators are linked by impact pathways, illustrated in Fig. 4.6. The radiative forcing midpoint indicator, measured by the level of greenhouse gas emissions, is linked to the endpoint indicator, damage to human health, measured in Disability-Affected Life Years (DALYs) by an impact pathway which includes rises in temperature, changes in rainfall patterns and extreme weather events, and changes in ocean currents, which may consequently affect human health via increases in water stress and reductions in food availability (IPCC, 2007).

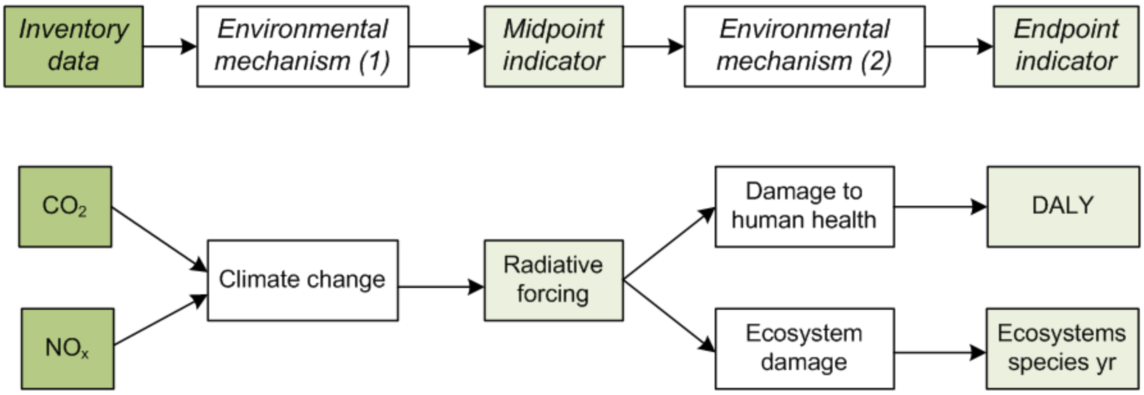


Figure 4.6: Connections between midpoint and endpoint indicators. The DALY is the unit used to interpret the impact on human health and life: Disability-affected life years.

The term *midpoint* indicates that the indicator is calculated at an intermediate position between the inventory results and the ultimate environmental damage (Jolliet et al., 2004). Midpoint indicators are defined “at the place where mechanisms common to a variety of substances come into play” (Goedkoop et al., 2008, p. 6), beyond which further modeling is considered to become too uncertain (Jolliet et al., 2004). The calculations of midpoint indicator values are rooted in the natural sciences, often at the limits of current knowledge.

Beyond the midpoint, the damage contribution to damage to ecosystem health and human health by radiative forcing is calculated in the category endpoint indicators. Endpoint indicator calculations involve greater levels of uncertainty than calculations of midpoint indicators as a result of the complexity of the impact pathway. An endpoint indicator, also known as a damage indicator, is “always a simplified model of a very complex reality, giving only an approximation of the quality status of the damaged entity” (Jolliet et al., 2004, p. 395). Midpoint indicators have standalone meanings in a midpoint-oriented LCA and can also be integrated into endpoint indicators. Because midpoint indicator methods are based on simpler, and better understood, environmental mechanisms than the endpoint indicators, the midpoint indicators usually have a lower uncertainty than the endpoint indicators (Jolliet et al., 2004). ReCiPe (**?**), a ready-made set of life cycle impact assessment calculations which can be applied to life cycle inventory data, generates both midpoint and endpoint indicators.

The assessment and reporting requirements of the EU Directive and the RTFO combine to provide the following set of criteria for an assessment methodology of biofuels for transport:

1. life-cycle environmental impact
    (a) carbon emissions compared with those from petroleum fuels
    (b) depletion of natural resources
    (c) emissions to air, water and land
2. agriculture
    (a) sustainability of crops used for the production of biofuels
    (b) impact of land use
    (c) impact of intense cultivation
    (d) effect of crop rotation
    (e) use of pesticides
3. other economic activities

Carolan (2009) surveyed 15 articles on bioethanol from four journals published in the period 2006–2008 and summarised the impact categories used as follows:

- Biodiversity,
- Global warming,
- Carbon dioxide (net)
- Carbon dioxide (tailpipe)
- Sulphur oxides

- Nitrogen oxides
- Carbon monoxide
- Ecological toxicity
- Hydrocarbons
- Water security
- Net energy
- Food displacement
- Soil erosion
- Volatile organic compounds

Further to this, he commented on what he described as ’Dimensions Often Missed in “Scientific Technical Reports”’, that is, the social costs of biofuels such as displacement of peoples as a result of land use change, or the working conditions that people experience in growing and harvesting raw materials for biofuels. In the ethanol studies surveyed by Carolan (2009), the raw material was supplied by sugar cane, with significant costs to the workforce in terms of the duration and conditions of their harvesting work.

4.4.2 Classification

Classification is the procedure of assigning inventory results to the categories as defined. In this phase the importance of the independence of categories is highlighted as it is here that double-counting of inventory results and their impacts can occur if categories have been defined such that an impact can be included in more than one category. When ready-made LCIA methods are used via LCA software, this stage is controlled by the selected LCIA method. The differentiation of classification and characterisation, the following step in LCIA, are explained by Spirinckx and Ceuterick (1996) as follows (p. 129, emphases in original), “The *qualitative* relation between inventory data and impact categories is called **classification**; the *quantification* of this relationship is called **characterisation**.”

4.4.3 Characterisation

The quantitative assessment of the impacts involves the calculation of category indicators from the inventory data which have been assigned to the various impact categories. Typically such calculations use equivalence factors (also known as potentials, equivalents, category indicators or characterisation factors) to scale the impacts in terms of a single quantity. For example, in considering the impact of greenhouse gas emissions, the equivalence factor is the tonne of carbon dioxide equivalent, calculated for each greenhouse gas by comparing its potency to that of carbon dioxide.

The value for each category indicator (CI) is calculated:

$$CI = \sum_i F_i I_i \tag{4.2}$$

where F_i is the equivalence factor for item i in the inventory and I_i is the quantity of i in the inventory (Pennington et al., 2004).

Impact assessment characterisation typically delivers the maximum potential impact of the process rather than the actual impact of the process.

In the characterisation phase, the following difficulties may be encountered:

- Inventory values for the indicator calculation are missing
- Useful methods do not (yet) exist for particular factors
- The result parameter represents a flow to another system, such as recycling

Some possible resolutions of these difficulties include:

- development of *ad hoc* characterisation methods for the LCA
- use characterisation methods that are not yet fully developed
- present results qualitatively as a supplement to the main analysis

4.4.4 Normalisation

In the normalisation phase, the characterised inputs are referenced against external values. For example, the total CO_2 emissions of the product or process can be normalised against the total CO_2 emissions nationwide. This enables a comparison of the magnitude of the impact with respect to the wider context in which the process operates or the product is produced and used.

4.4.5 Grouping

The impact categories can be grouped according to broader fields of interest, or according to their relative importance or significance. Grouping can occur on a geographical basis by assigning the impacts to global, regional or local levels of impact. Emissions categories can be grouped according to the compartment to which the emission is made, whether that be air, water or land.

4.4.6 Weighting

Weighting is the process of quantitatively scaling the impacts according to qualitative assessment of their relative importance to allow more direct comparison of the weighted categories. In particular, applying weighting to the impact category results can enable a single index to be calculated for the process or product, leading to extremely simple comparisons of single index numbers for each product or process. Weighting factors are predominantly determined by social science methods, including comparison to authorised (policy) targets (known as the distance-to-target approach), ranking by importance of the impacts as perceived by an expert or authoritative panel or using a proxy measure such as energy consumption to represent the overall environmental impact (Baumann and Tillman, 2004). Further weighting methods include the comparison of the inventory and characterisation results to technological abatement potential (known as the distance-to-technically-feasible-target approach) or monetarisation through the financial valuation of the impacts (or of willingness-to-pay for avoiding the impacts) (Powell et al., 1997).

In the determination of weighting factors, ethical, political and ideological values are involved and consensus may be difficult to achieve (Finnveden, 1997). A sound scientific (i.e. natural science) foundation of the weighting method may be absent from these subjective evaluations of relative importance or significance of impacts which cannot be empirically verified. Furthermore, different expert panels may produce different weighting factors and rankings for the LCA categories (Kim and Dale, 2005), making long term trends in LCA results for particular products or services difficult to track objectively unless the component parts of the assessment are clearly identifiable. As with other aspects of LCA, the practicability and completeness of weighting vary inversely with one another since "the more that is covered in the study, the more difficult it becomes to conduct" (Powell et al., 1997, p. 13). The procedures for weighting remain controversial, not only for choosing weighting values, but also when choosing the weighting method and even in the decision to apply weightings to the LCA at all (Finnveden et al., 2009).

Cultural paradigms, invoked in some methods (Goedkoop and Spriensma, 2001; Goedkoop et al., 2008), are used to calculate and distribute impacts across time and space. These paradigms are Individualist, Egalitarian, and Hierarchical and are based on the five ways of life set out by Thompson et al. (1990), the missing two being Hermit (autonomy) and Fatalist. A summary is shown in Table 4.2. Thompson et al. (1990) describe a way of life as a viable combination of cultural bias (shared beliefs and values) and social relations (the patterns of interpersonal relations). The three cultural value sets, obtained using panels comprising members of a Swiss LCA interest group, in the LCIA methods give rise to three sets of weighting. The Individualist perspective is shorter term than the Egalitarian or Hierarchical perspectives and only proven cause-effect relations are counted as environmental impacts. The Egalitarian perspective is at the other end of the spectrum and applies the precautionary principle consistently so that, in principle, nothing is left out. Of course, unknown impacts cannot be accounted for even in the Egalitarian perspective. The Hierarchical perspective takes the middle ground between these two extremes and uses both the established findings of natural sciences and facts proposed and supported by political and scientific bodies of sufficient standing in the environmental community (Baumann and Tillman, 2004).

The omission of two culture theories from the ReCiPe method leads to the question of what the implementation of LCA with such paradigms would look like. A fatalist view would be that there is nothing one can do to change the environmental impacts and therefore they are unlikely to perform LCA in the first place. The hermit seeks to minimize their impact and exploitative interaction with nature, and in 'becoming one with nature' they would see no distinction between

Way of life	View of nature
Individualist	Nature is a skill-controlled cornucopia of raw materials.
Hierarchist	Nature's rich differentiation should ensure that it is forthcoming when approached in the right way by the right people but retributive when pushed beyond these carefully learned bounds. Carefully planned frameworks for resource development and allocation are required.
Egalitarian	Nature is a strictly accountable source of natural resources. Mankind is trapped in a downward spiral of resource depletion.
Fatalist	Nature's cornucopia is controlled, in the fatalists' vision, not by skill, but by a *lottery*. Nothing the fatalists do seems to them to make much difference.
Hermit	Their aim is neither to manage nature, nor to exploit it, nor to accommodate themselves to its stern limits, but seek to become one with nature. They do this, not in a misery of self-imposed privation, but in joyous participation in nature's fruitfulness. For them, nature's cornucopia is *freely available*.

Table 4.2: Cultural paradigms underpinning the ReCiPe methodology (Thompson et al., 1990)

impact upon themselves or upon nature. That being the case, a hermit would not distribute impacts according to any method, but rather would see the total impact on the whole of nature.

4.4.7 Data quality analysis

The final stage in the impact assessment phase of the LCA, data quality analysis, adds to and clarifies the understanding of the inventory and impact analysis results and leads directly into the fourth LCA stage, interpretation. Components of the data quality analysis include:

- identifying the most polluting activities in the life cycle
- identifying the activities that consume the greatest resources in the life cycle
- identify the most crucial pieces of inventory data for which small changes in values can lead to large changes in calculated impacts (sensitivity analysis)
- evaluation of the significance of methodological choices and assumptions (sensitivity analysis)
- uncertainty analysis of the results

These elements contribute to greater understanding of the significance, uncertainty and sensitivity of the impact assessment results. However, the results of an impact assessment cannot specify which product is ‘better’ in any meaningful terms: the raw results and analysed impacts of the products’ life cycles must be assessed against criteria, set in the initial goal and scope phase, and fundamental to the interpretation phase of the LCA. Furthermore, it is human values that determine the relative merits of compared products and the underlying value judgements made in carrying out an LCA need to be explored and made explicit for a full interpretation of the results. As can be seen from these seven phases, impact assessment has both natural science and philosophical or ethical components, some of which blend into the fourth and final LCA phase, interpretation.

4.5 Interpretation methods

The interpretation phase of the LCA comprises the analysis and presentation of the results of the LCA. Although the analysis method may have been set out in the goal and scope, and criteria for the presentation of results, the interpretation phase may also include other analysis and presentation of the results according to what the results in fact are. The iterative nature of LCA allows for amendment of the goal and scope according to the outcomes of the process itself and this is of particular importance when an LCA generates results that are surprising and outside the original goal and scope.

4.5.1 Sensitivity analysis

Data quality

The very nature of life cycle assessments and the broad range of data with varying degrees of robustness means that LCAs have an inherent uncertainty which derives from both the data quality and the scope and definition of the system. The elements of a life cycle assessment can contribute a degree of uncertainty which can be classified in four ways, shown in Fig 4.7. Each element can be known or unknown in two different ways. Firstly, the existence of a element of the LCA may be known or unknown. Secondly, the quantitative contribution and its uncertainty of the element may be known or unknown. The elements of the LCA which are known about may be known, in which case they are quantified where possible and included in the LCA (the known knowns), or unknown, in which case an informed estimate with a degree of uncertainty is used in calculating the LCA results (the known unknowns). Elements of the system which are not known about, through ignorance or overlooking by the LCA practitioner also fall into two categories. The unknown unknowns are those elements about which the LCA practitioner is not aware, and even if the practitioner were aware of them, those elements would not be robustly quantifiable. The unknown knowns are those elements which are relevant to the LCA and quantifiable, yet overlooked by the practitioner.

The most difficult aspects to account for in an LCA are those that are not known of at the time of the assessment. From the perspective of the current time, historical advances can be viewed more accurately in light of present-day information about the impacts of such developments. For example, the persistence of CFCs could have been determined from the available knowledge regarding the unreactivity of such compounds, yet their effect on ozone in the upper atmosphere were not known of, nor anticipated, at the time of their inception and promotion as refrigerants and aerosol propellants (O’Riordan and Jordan, 2000). In the current day perspective of the LCA

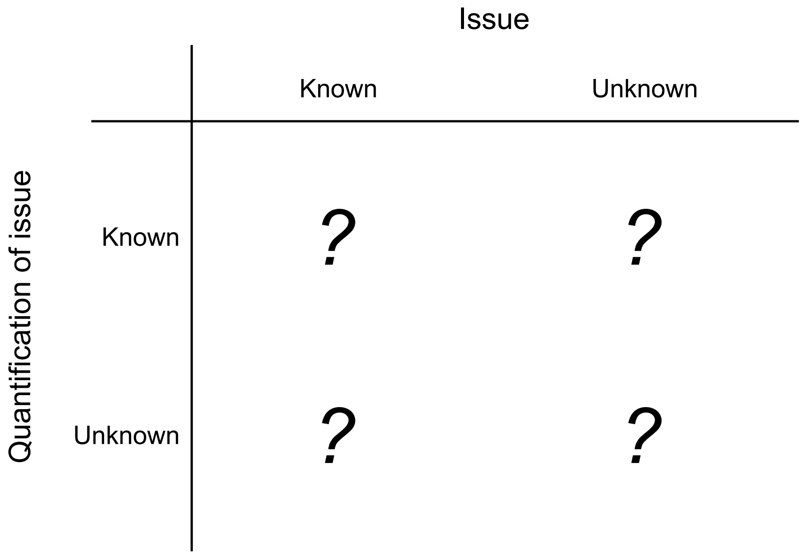


Figure 4.7: Classification of sources of uncertainty in life cycle assessments

or EA practitioner, there are undoubtedly effects that are neither known nor anticipated. The recent history of biofuel LCA studies shows the effect of an unknown becoming more known, with the publication of Crutzen et al. (2007) in which the probable contribution of NOx from agriculture was suggested to be much more than previously anticipated.

Typically, an estimate for the likely uncertainty in the results can be determined via a sensitivity analysis, in which key inputs are varied and the effect of the variation on the final results is ascertained. In the case of the known knowns, sensitivity analysis can be used to quantify the effects of the known uncertainty in the data which is used in the LCA on the results of that LCA. In the case of the known unknowns, the missing data points that are known by the practitioner, an estimate of the likely inventory contributions of the known element can be made by drawing on the literature and using that estimate to calculate the LCA inventory and indicators. An estimate may be determined by using an approximation which is based on a similar element from a different production process. The influence of the estimate on the overall LCA results can be assessed using sensitivity analysis. For example, in the case of an agricultural operation with an unknown fuel input for a specific tractor, an estimate can be made using data on tractors of similar sizes, conducting similar field operations. Comparison of the LCA results with and without the approximated data can provide an indication of the relative significance of the missing data point and from this the practitioner can decide whether or not further investigation of this element is necessary.

There is little that a practitioner can do to directly address the issue of unknown elements in the life cycle. However, thorough documentation of the life cycle system and the processes that are accounted for in the LCA allow for future revisions of the LCA results as further data or system elements become known. Sensitivity analysis is also used to assess the significance of variability in the input data.

4.5.2 Presentation of results

The inventory and impact assessment stages can both generate large quantities of data and the role of the interpretation phase is to select and present key results that address the issues set out in the goal and scope. The presentation of the results is very often graphical and in many cases the results are normalised, either against one particular results, or against a reference set of results, and presented in this normalised form. Normalised presentation of data is especially useful for preserving commercial confidentiality, as well as for quick, visual interpretation of the results. However, the relative importance of individual results for particularly key impacts or emissions can be missed when results are presented in this way. Results are therefore often presented in different ways to provide a fuller understanding of the LCA data (Baumann and Tillman, 2004).

In addition to normalisation, LCA results in different categories can be combined into a single indicator such as the ecological footprint or Sustainable Process Index (Niederl and Narodoslawsky, 2004). Single indicators, while easily and directly comparable between product systems, do obscure the different aspects of the results. Further, the weighting factors that are used to convert from multiple to single indicators may change over time, or in different locations, or when set by different expert panels or focus groups. Multi-dimensional results are more useful to convey the breadth and depth of the results and to provide transparency for future users of the LCA outputs, as emphasised by Mortimer et al. (2003). In this thesis, multiple indicators are used in order to preserve as much useful information as possible, while keeping the number of indicators manageable so that the results are straightforward to interpret and compare.

The presentation of complex multivariate data is a challenge in a variety of contexts, not just LCA. Ten Brink et al. (1991) proposed the AMOEBA method for illustrating multivariate, quantitative data on what is presently known as a radar diagram. This approach has subsequently been adopted in the presentation of sustainability progress indicators (Sun et al., 2010) and even for the evaluation of service provision by the police force (Police Standards Unit, 2004). The advantages of this approach are that the radar diagram simplifies the presentation of the multi-dimensional results such that they are easy to understand in a quick glance. These diagrams are easy to modify, for instance to allow for changes in aspects such as the weighting factors. However, the same simplification of the presentation can lead to obscuration of important details and simplistic results, in the same way that single indicators do.

4.6 Published results

LCA studies can vary in their methodology, particularly in the choices of the functional unit, the system boundaries and how to allocate to co-products, which can have significant impacts on the final results (van der Voet et al., 2010). Direct comparisons between LCAs are therefore difficult. To bring some uniformity and therefore comparability to the reports provided by transport fuels suppliers on the greenhouse gas emissions associated with biofuels, the Renewable Fuels Agency (RFA) set out a detailed methodology (Bauen et al., 2008) for suppliers to use in reporting on the sustainability of their renewable fuel products. A standardised methodology is also presented in the EU Renewable Energy Directive (European Parliament and the Council of the European Union, 2009) for calculating greenhouse gas emissions.

Bearing in mind the difficulty in comparing LCA results directly, results for the global warming potential, also referred to as the climate change impact potential, from the literature are presented for biodiesels (Fig. 4.8) and for petroleum diesels (Fig. 4.9). Where the original results for biodiesels are presented in terms of volume or mass, conversion factors of 39.6 MJ kg^{-1} and 882 kg m^{-3} have been applied to obtain results in terms of the energy content of the fuels. A gross heat of combustion of 45.5 MJ kg^{-1} (Department of Energy and Climate Change, 2009) was assumed for petroleum diesel fuels, where necessary.

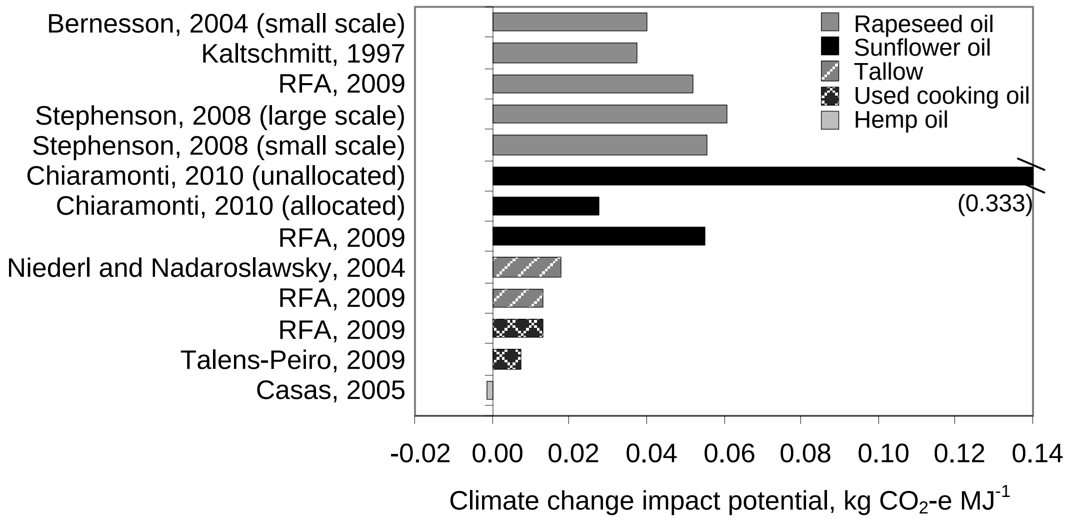


Figure 4.8: Climate change impact potential of biodiesels from different feedstocks, calculated in different ways

The climate change impact potentials associated with the production of biodiesels in the literature surveyed (Fig. 4.8) are all positive, with the exception of Casas and Rieradevall i Pons (2005), and hence have a negative effect on the global climate from an anthropocentric perspective. The life cycle assessment carried out by Casas and Rieradevall i Pons (2005) included the absorption of CO_2 during the growth of the hemp plant, whereas conventionally this is excluded from LCAs of biodiesels under the assumption that the CO_2 absorption will be balanced out by the corresponding CO_2 emissions during combustion of the fuel.

The rapeseed biodiesels have climate change impact potentials in the range 0.0375–0.0610 kg CO_2-e MJ^{-1} with a factor of just under 2 between the smallest and highest results. The two results from Stephenson et al. (2008) illustrate their conclusions that differences in the scale of rapeseed cultivation and biodiesel production are insignificant when viewed in the context of the overall accuracy of the results.

Two of the results for sunflower seed oil biodiesel from the work of Chiaramonti and Recchia (2010) show how significantly the allocation method selected affects the results, while the result from Renewable Fuels Agency (2009b), which is based on data from the Ukraine, lies between the extremes of the results from Chiaramonti and Recchia (2010) and is comparable to the results from Stephenson et al. (2008) for rapeseed oil biodiesel.

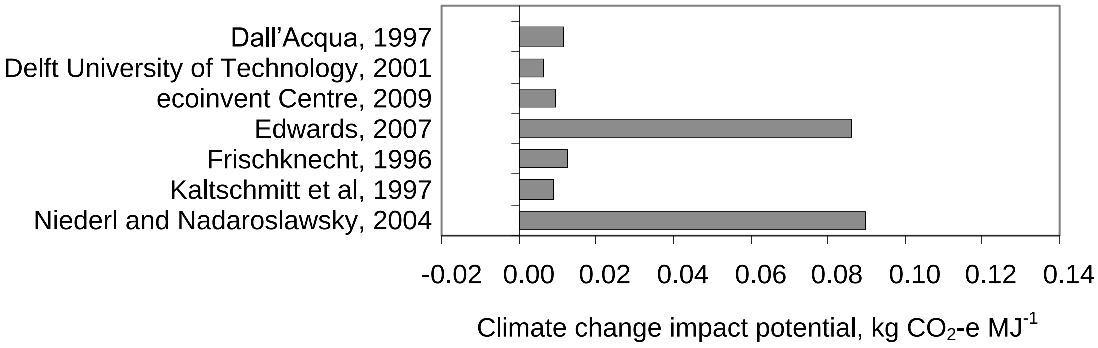


Figure 4.9: Climate change impact potential of petroleum diesels, calculated in different ways

The climate change impact potentials from the production of biodiesels from tallow and used cooking oils, in the range 0.007–0.018 kg CO_2-e MJ^{-1}, are markedly lower than those for oilseed biodiesels. The production impacts of the tallow and used cooking oil feedstocks are attributed to other upstream product systems from which they are emitted as wastes.

The petroleum diesel results are in the range 0.006–0.0126 kg CO_2-e MJ^{-1}, except for the results of Edwards et al. (2007) and Niederl and Narodoslawsky (2004). Focusing initially on the lower results, there is a factor of approximately two between the lowest and highest results, as found for the biodiesel results too.

With regard to the two outlying data points, Edwards et al. (2007) explicitly mention that both production and combustion emissions of petroleum diesels are included in their calculation of climate change impact potentials and this accounts for the 0.07 kg CO_2-e MJ^{-1} difference. However, while Niederl and Narodoslawsky (2004) present their result with neither methodology nor source data, their result is so close to that of Edwards et al. (2007) that it can be inferred that the combustion emissions are included as well. In fact, the data point that Niederl and Narodoslawsky (2004) use may come from an earlier version of the report by Edwards et al. (2007) which was published in 2003.

Over time, the climate change impact potential of the extraction of crude oils, and hence the production of petroleum diesels, may increase as the extraction of the remaining oil reserves becomes more difficult and hence more energy intensive. On the other hand, as bioenergy becomes more widely used, the greenhouse gas emissions of biodiesel production may reduce through the replacement of fossil fuels with bioenergy.

Although the production of petroleum diesels gives rise to lower greenhouse gas emissions than the production of biodiesels, the biodiesel combustion emissions balance with the CO_2 absorbed during growth of the oilseed plants, whereas the petroleum diesel combustion emissions cannot be balanced out directly in anything less than geological timescales, as discussed in Chapter 2. The results presented by Casas and Rieradevall i Pons (2005) indicate the possibility of a negative climate change impact potential, and hence a beneficial effect to the atmospheric greenhouse gas concentrations, as viewed from the human perspective. This is particularly the case for the hemp plant, *Cannabis sativa L.* since it produces significant quantities of useful straw co-product which could act as temporary CO_2 storage; this is explored further in Chapters 5 and 6.

4.7 Limitations and omissions in biodiesel LCAs

Cherubini et al. (2009) reviewed the literature concerning the application of LCA to bioenergy systems and found a number of issues with the method, or with the application of the method. LCA is, by its very nature, site and time specific, therefore the results are not readily generalisable. In agricultural systems in particular, soil type and climate can have significant impact on the overall LCA results: for the purposes of the UK's biofuels strategy for road transport fuels LCA must be undertaken for each biofuel production system and the results compiled to obtain data on the overall environmental impact of the biofuel policy. Crop yields vary depending on the weather; this too cannot be easily incorporated into an LCA.

Further issues noted by Cherubini et al. included the methods by which the biomass carbon cycle, N_2O and CH_4 emissions were represented in the system, and the varied choices in separate LCAs of different reference systems, methods of allocation to co-products, input parameters and the consideration of future trends. In summary, they report that these, and other, issues "prevent an exact quantification of the GHG emissions savings of fossil energy consumption avoided through the use of bioenergy, because too many variables are involved" (Cherubini et al., 2009, p. 445). The very nature of the LCA approach means that exact results are neither achievable nor desirable:

an exact LCA would require huge amounts of data to calculate, and yet it would not be applicable to other systems.

The growth of oilseed crops for biodiesel has the potential to change the UK landscape and soil quality. The environmental impact of potential changes in land use can be quantified and evaluated and a set of impact categories has been proposed by Mattsson et al. (2000) which include soil erosion, hydrology, soil organic matter, soil structure, soil pH, accumulation of heavy metals and the soil content of phosphorous and potassium.

Impacts from changes in land use can be included in biofuel LCAs (Panichelli et al., 2009) but is often omitted owing to the difficult and controversial nature of land use change assessment methods (van der Voet et al., 2010). The conversion of land from tropical rainforest or Cerrado to palm oil plantations or arable land for soybean cultivation results in severe and localised environmental degradation in terms of soil erosion and habitat destruction (Reijnders and Huijbregts, 2008). Emissions and environmental impacts caused by such changes in land use may or may not be attributed to the biofuel production processes. In considering the impacts of land use change, the causal relationship between biofuel demand and land use change must be established. These considerations tend towards the consequential mode of life cycle assessment in which the direct causal links are hard to establish (Ekvall and Weidema, 2004).

In their survey of biofuel LCAs, which included both biodiesel and bioethanol fuels, van der Voet et al. (2010) noted that the environmental impacts of water use are also neglected in the current literature. Finnveden et al. (2009) also cites the area of water use impacts as critical for the further development of LCA methods since water stress may well become a significant issue under climatic changes (IPCC, 2007).

The literature and policy documents surveyed in this chapter are used to inform the life cycle assessment of hemp biodiesel in this thesis (Chapter 6), which also draws on data presented in Chapter 5 on the cultivation, harvesting and energetic properties of hemp.

Chapter 5

Hemp: agronomy and analysis of products

5.1 Introduction

The hemp plant, briefly introduced in Section 2.7.1, is investigated further in this chapter. The aims of this chapter are to:

- collect and present data on the agronomy of dual-purpose hemp in UK conditions
- quantify the energy content of the hemp plant and its products
- quantify the carbon content, and hence CO_2 absorption and temporary storage potential, of hemp.

General information about the plant is provided (Section 5.2). The agronomy of hemp cultivation and harvesting is investigated (Section 5.3). Finally, selected physical and chemical properties of hemp plant products are tested and the results presented (Section 5.4).

The life cycle assessment of hemp biodiesel in this thesis (Chapter 6) requires data on the inputs and outputs associated with the cultivation and harvesting of dual-purpose hemp. To this end, data were collected from a case study of a farm in Essex, south-east England and are reported in this chapter (Section 5.3). The data were compared with information from the literature on hemp agronomy in the UK and other countries.

The key purpose of the analytical tests in this chapter is to determine the energy contents of the separate parts of the hemp plant. Analytical tests were conducted on samples of hemp plant parts collected from the case study farm and other sources (Section 5.4.2). In addition to testing the plant parts, hemp oil was transesterified to hemp methyl ester (biodiesel) and its energy content tested. Moisture and energy contents, and elemental compositions of hemp plant parts were undertaken. In addition, the fatty acid profile of hemp oil was determined for comparison with the literature to establish the representativeness of this sample with other hemp oils. The methods are detailed in Section 5.4.2 and the results are presented in Section 5.4.3.

Furthermore, the energy content and carbon content data collected in this chapter are used in the allocation stages of the hemp oil biodiesel life cycle assessment, while the results of the elemental analysis are used to calculate the uptake of carbon into the various plant parts, which informs the calculations of the CO_2 flows in the life cycle of hemp biodiesel (Chapter 6).

5.2 The hemp plant and its products

Hemp (*Cannabis sativa* L.) is an annual, wind-pollinated plant which grows in temperate climates. Originally native to central Asia, it was subsequently cultivated in much of Europe, including the UK (Bradshaw et al., 1981), for its fibre and seeds. Hemp fibre has been used historically for rope, canvas and paper making. More recently, the fibre has been used to produce insulation panels for vehicles and construction materials (Hobson, 2007). Hemp should not be confused with deccan hemp, also known as jute, which has the botanical name *Hibiscus cannabinus*.

Various cultivars of hemp have been selectively bred for three main characteristics, namely high fibre content, high seed yield or high narcotic content. Cultivars tend to be good in any one of these three categories. For industrial purposes, hemp varieties have been developed for the production of straw and fibre and are therefore not optimised for oil production (Matthäus and Brühl, 2008). Narcotic and non-narcotic hemp varieties cannot be identified visually and so hemp stands which are grown for fibre or seed and are therefore non-narcotic can be mistaken for plants with psychoactive components. For this reason, farmers in the UK are discouraged from growing hemp in fields which offer easy access from busy public roads, that are in close proximity to housing estates, or that are close to schools or leisure areas (Hobson, 2007).

In this thesis, the hemp cultivars under consideration are non-narcotic and the crop is referred to as hemp in order to distinguish it from the names commonly given to the narcotic cultivars of the species, that is cannabis, or its products hashish or marijuana. The compound in hemp that is responsible for its narcotic effects is tetrahydrocannabinol, THC, and it is present in the resin, known as hashish, that is excreted by the stigma of the female flowers. Marijuana is the name given to the harvested flowers.

The hemp plant (Fig 5.1), is mostly grown commercially for its straw, with some crops grown for seed for sowing or for both straw and seed (Bócsa and Karus, 1998). Hemp straw comprises fibres on the outside, and a woody core, known as shiv or hurds. The fibres and shiv perform different roles for the plant, with the outer fibres serving as transport pathways for nutrients and water while the inner shiv provides structural strength (Bócsa and Karus, 1998). The fibre content of the straw varies from 15.8-24.0 % depending on the ratio of stalk length to thickness; the greater the length and the smaller the diameter of the stalk, the higher its fibre content (Bócsa and Karus, 1998). Hemp straw can grow up to 4 m tall (Bócsa and Karus, 1998). The fibres are the more valuable component and are used for making insulation panels, cloth and rope, while the shiv is used for horse bedding, and lime-hemp blocks for construction (Braham and Low, 2008).

Hemp has male and female varieties (Fig. 5.1). The female plant bears clusters of seeds and seed yields of up to 2000 kg ha^{-1} have been reported from plants which are bred and grown for seed production only (Kriese et al., 2004). However, yields of this magnitude are not considered in the present thesis since only dual purpose crops are under study here for which yields are more usually up to 1000 kg ha^{-1} (Bócsa and Karus, 1998). The seeds contain 26.25–37.50 % oil by weight with the exact proportion depending on the variety (Kriese et al., 2004) as well as the year of cultivation, the climatic conditions and the location (Matthäus and Brühl, 2008). Oil is extracted from the seed using a press or solvent extraction methods. The remaining seed matter, presscake, can be used as animal feed.

Following the League of Nations ruling to control Indian hemp in 1925 (Kendell, 2003), and the subsequent prohibition orders on growing hemp in the UK and USA, cultivation and research

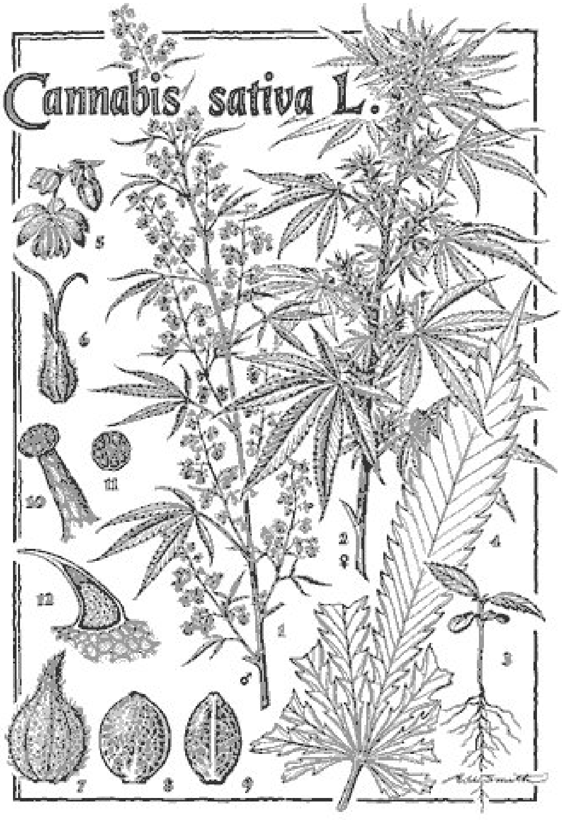


Figure 5.1: Composite plate of *Cannabis sativa L.* by Elmer Smith. “1. Flowering branch of male plant. 2. Flowering branch of female plant. 3. Seedling. 4. Leaflet. 5. Cluster of male flowers. 6. Female flower, enclosed by perigonal bract. 7. Mature fruit enclosed in perigonal bract. 8. Seed (achene), showing wide face. 9. Seed, showing narrow face. 10. Stalked secretory gland. 11. Top of sessile secretory gland. 12. Long section of cystolith hair (note calcium carbonate concretion at base)”. Reproduced from Small and Marcus (2002), p. 287.

into hemp has been limited. However, hemp cultivation in Eastern European countries continued through the 20th century, predominantly for fibre (Bócsa and Karus, 1998). Hemp is currently grown under licence in the UK to produce horse bedding and fibre for the paper, automotive and insulation industries (Hobson, 2007). In Europe, farms in France, Germany, Hungary and Finland are also cultivating hemp crops for research and industrial use (Bócsa and Karus, 1998). Canada introduced industrial hemp regulations in 1998, permitting growth of low THC content hemp under licence (Moes et al., 1999).

Interest in hemp as a bioenergy crop has been slight, with few studies produced so far which most likely reflects its status as an illegal crop in the USA, and a licence-only crop in the EU. A very early mention of hemp oil as a fuel for engines was made by (Walton, 1938) in his survey of the use of straight vegetable oils in diesel engines. Casas and Rieradevall i Pons (2005) conducted a light-touch LCA of hemp seed oil biodiesel for municipal waste vehicles while Yang et al. (2010) investigated various catalysts for the simultaneous transesterification and hydrogenation of hemp oil to produce a biodiesel with an iodine value that is lower than the EN 14214 (2004a) limit of 120 g / 100 g. Deeley (2000) questioned the possibility of using hemp for climate change mitigation as a bioenergy crop and carbon storage method, and the current thesis takes his questions further through the application of a life cycle assessment (Section 6).

The direct use of hemp oil in diesel engines was tested and results indicated that admixtures of hemp oil with rapeseed oil were preferable for their lower rates of injector coking (Carus et al., 2007). However, little technical or scientific assessment of biodiesel from hemp oil was found in the literature. Given that much of the recent research on hemp has been undertaken in Eastern Europe, there may exist research in, for example, German, Hungarian or other languages and these have not been surveyed for this thesis owing to constraints on translation.

Hersener and Meier (1999) indicated its potential for the use of hemp for electricity generation. Jungbluth et al. (2007), in the LCIA database ecoinvent, also refers to hemp as a bioenergy crop, citing the work by Hersener and Meier (1999) but the ecoinvent database itself does not, at the time of writing, include hemp production processes. Tuck et al. (2006) considered hemp as a potential bioenergy crop in European countries in their modeling of the potential geographical distribution of bioenergy crops if the climate changes in accordance with current climate change models. Similarly, Scholz and Ellerbrock (2002) included hemp in their study of the environmental impacts of bioenergy crops. Dornburg et al. (2005) estimated the likely greenhouse gas emissions and financial costings of hemp as a bioenergy crop alongside wheat and poplar crops. In that study, Dornburg et al. looked at the effect of allocating greenhouse gas emissions and costs to products from crops with co-products and found that crop products that were sold for material purposes could, in effect, subsidise the production of bioenergy products. Dornburg et al. (2005) also found that the greenhouse gas emissions of the bioenergy products changed in response to allocation of the emissions across all products and from the same crop. This issue of allocation is significant in this thesis, as is explored in greater detail in Chapters 4 and 6.

Straw from various crops, including hemp, can be co-fired with coal or gas in power stations. Straw is used as the main fuel in bioenergy power stations such as the Elean Power Station near Ely, Cambridgeshire (EPR, 2010). The ash from bioenergy power stations contains high levels of P and K which can serve as a source of phosphate and potassium for agricultural fertilisers.

Hemp dust produced during the mechanical processing of hemp stems to separate the fibres from the hurds is compacted into logs for burning in domestic woodburners and stoves (Squier, 2008). Approximately 15 % w/w of the straw disintegrates into dust in the separation process. The compacted logs have an energy content of 15 MJ kg^{-1} (Hemp Technology Ltd., 2010).

The potential of production of sugars for fermentation to ethanol from the digestion of hemp straw has been investigated (Sipos et al., 2010). Hemp has also been considered as an additive to anaerobic digestate for the production of biogas but was found to be unsuitable for such purposes (Mallik et al., 1990).

5.3 Hemp farming

As discussed previously, most of the current research basis on hemp farming comes from eastern and southern Europe, notably the countries of Hungary and Germany (Bócsa and Karus, 1998). Furthermore, the focus of research has, until recently, been the single purpose straw crops for hemp shiv and fibre. Bócsa and Karus's review of hemp agriculture (1998) provides data on both single and dual purpose hemp crops, with an emphasis on straw crops. Turunen and van der Werf (2006) provided comprehensive data on growing hemp for straw in France and subsequently presented a life cycle assessment from that data (van der Werf and Turunen, 2008), while Ranalli (2004) has identified several areas for improvements in hemp breeding, including reduced lignin content for better paper production and improvements in the fatty acid profile of the seed oil.

In this section of the thesis, data has been collected on hemp growing in the UK. Since one of the aims of this thesis is to compare the climate change impact potential of producing biodiesel from hemp seed oil with the impact potential of biodiesel from the more widely used rapeseed oil, some data has also been collected on rape seed cultivation and harvesting practices. However, the emphasis in this section is on hemp agriculture, since rape seed agriculture has been reported on elsewhere (see, for example, Stephenson et al. (2008)).

5.3.1 Data collection methods

Data on the cultivation and harvesting of hemp products was obtained through interviews in person and over the telephone with the farmer and the agronomist associated with the case study farm. Further data specific to the case study were collected through email exchanges. Additional data were found in the literature and in commercial information packs (Bócsa and Karus, 1998; Hanfaes Research Centre, 2004; Hobson, 2007) for verification of and comparison with the data from the case study farm.

5.3.2 Results

Case study farm The farm in this case study is located in south east England in the county of Essex. The soil is London clay across most of the farm and naturally high in potassium. The farm comprises predominantly established arable land, growing crops that include wheat, oilseed rape, peas, beans and flax as well as industrial hemp.

Rotation systems The case study farm grows hemp in a four-year rotation (Table 5.1), in contrast to the more widely used six-year rotation cycle which includes four years of growing wheat (Squier, 2008). An alternative six year rotation, with three years of wheat, two of hemp and one of oilseed rape, was proposed by Squier (2008) but this has not yet been implemented.

Year	Standard six-year	With hemp, four year	Alternative six year
1	Wheat (1st)	Wheat	Wheat
2	Wheat (2nd)	Oilseed rape	Hemp
3	Oilseed rape	Wheat	Wheat
4	Wheat (1st)	Hemp	Hemp
5	Wheat (2nd)	-	Wheat
6	Peas or beans	-	Oilseed rape

Table 5.1: Cereal rotation schemes with and without hemp. Wheat crops that are grown in succession are referred to as first and second wheat.

Calendar of hemp cultivation and harvesting The sequence of field operations involved in the cultivation and harvesting of single and dual purpose hemp crops is shown in Table 5.2.

For the cultivation of hemp, the land is prepared for the crop after overwintering by spraying a general purpose herbicide to clear the ground and lightly tilling the soil to give a good, loose seedbed. The plant has a short growing season with sowing in late April or May and harvesting during August, September or October (Bócsa and Karus, 1998).

Single purpose crops are cut once flowering begins, towards the end of July or beginning of August. At this stage, no mature seeds have yet developed on the plant. A triple-bar mower cuts the hemp stems into standard lengths. The chopped stems are spread in the field for 3 to 7 days to dry. Hemp straw is very quick drying and less affected by rain than wheat or rape straw are (Squier, 2008). Baling follows the drying period and the baled straw is moved into storage.

Dual-purpose crops are harvested in late September in two passes. The first pass combines the seed using a high level combine harvester that skims the tops of the plants. The straw is harvested separately to preserve the long fibres, which would be cut short if the combine harvester also

Time of year	Operations
August–November	Spread with biosolids, if available
	Deep cultivation or plough
November–February	Overwintered stubble from previous crop
February–March	Spray with Round-Up
	Light cultivation pre-sowing
Late April	Drill hemp seed
	Roll
Mid August	Straw-only crops
	Mow straw
	Drying straw in the field, 3–4 weeks
	Rake and bale straw
	Transport to store
	Drying, if necessary
Mid September	Dual-purpose crop
	Combine harvest seed
	Dry and store seed
	Mow straw
	Dry straw in the field, 2–3 weeks
	Rake and bale straw
	Transport to store
	Drying, if necessary

Table 5.2: Processes in the cultivation of hemp (Squier, 2008).

harvested the straw. The second pass mows the stems as previously described for the straw-only crop and the straw is left to dry in the field, baled and moved into storage (Squier, 2008).

The inputs and outputs associated with these processes are discussed in the following subsections.

Agricultural machinery Tractors are used in field operations of seed-sowing and rolling, herbicide and pesticide applications, mowing, turning mown straw in the field and baling. A combine harvester is used to harvest the seed from the field. Specialised tractor attachments that are used include the seed drill, roller, plough, spring tine harrow, sprayer, bar mower, baler, bale-loader and trailers for transporting harvested seed and baled straw to storage. Squier (2008) reported that on the farm overall, the machinery requirements had reduced since the incorporation of hemp in the rotation system.

Hemp seed for sowing Seeds are sown at a rate that will conduce to plants spaced to allow maximum seed head growth while still crowding out weeds. For dual purpose crops, such as are under consideration here, the sowing rate can be in the range 20-50 kg ha^{-1} (Bócsa and Karus, 1998) although other sources recommend 55 kg ha^{-1} (Hanfaes Research Centre, 2004). Hobson (2007) recommends a sowing rate of 37 kg ha^{-1} which is adopted on the case study farm (Squier, 2008). After drilling the seed, the seedbed is rolled to lightly compress the upper soil surface. Sowing into a moist seedbed is advised to ensure germination (Squier, 2008; Hanfaes Research Centre, 2004).

Pesticides and herbicides A broad-spectrum herbicide, Round-up, which has the chemical name glyphosate, is applied 2–3 weeks before sowing each crop to kill off weeds in the field. Hemp grows with a dense canopy of leaves and therefore weeds tend to be outcompeted (Hanfaes Research Centre, 2004). As a result, provided that the sowing density is adequate, hemp crops need no further herbicide applications. At the case study farm, glyphosate is applied in order to ensure that the straw crop is free from contamination by weeds so that no contamination is present further along the line at the straw processing facility. This is to maintain the quality of the fibre produced from the straw. However, were the straw to be used for bioenergy rather than fibre production, the application of glyphosate would not be required.

At the farm featured in the current case study, the occasional incidence of flea beetles in the crop has led to the additional application of cypermethrin, a pesticide, in some years at rates of 0.1 litres ha^{-1} (Beck, 2008).

In the UK, few diseases have been observed in hemp crops (Squier, 2008), however experience in Germany and Hungary shows that some pests and diseases can affect hemp. Rusts and moulds may afflict hemp crops, and this may become more prevalent with increased crop areas. Moulds such as *Botrytis cinera* (grey mould) and *Sclerotinina sclerotionim* (white mould) inhibit fibre growth in patches on the stems. These moulds also grow on oilseed rape, therefore to avoid the disease carrying over between subsequent crops, hemp should not be followed immediately by an oilseed rape crop (Squier, 2008). Fungicides can be used on these moulds but, as noted by Bócsa and Karus (1998), the increased revenues from growing the crop without chemical applications, and thereby earning the designation ‘organic’, outweigh the revenue lost through crop damage. However, the case study farm is not organic.

Lime Lime (calcium carbonate) is applied to the soil where necessary to maintain a pH level of 6 or higher (Hanfaes Research Centre, 2004). Typical application rates are 2000 kg ha^{-1} every three years (Turunen and van der Werf, 2006). Specific data was not available from the case study farm since the lime application is varied each time according to the results of soil pH tests. The average data provided by Turunen and van der Werf (2006) is therefore used in the life cycle assessment in this thesis (Chapter 6).

Fertilisers The standard fertiliser trio of nitrogen (N), phosphorous (P) and potassium (K) are applied in quantities that depend on the soil conditions. Bócsa and Karus (1998) recommend applying fertilisers at the following rates per hectare: 100–125 kg N, 70–90 kg P_2O_5 and 120-160 kg K_2O, with adjustments according to the soil type and nutrient levels. Squier (2008) applies 100 kg N, 45 kg P, 8.33 kg K (averaged over three years), and 21 kg MgO per hectare of hemp on the case study farm. Fertilisers have become more expensive in recent years, leading to farmers applying less PNK to the fields than is necessary (Defra, 2009; Squier, 2008). As a result, overall soil fertility is decreasing.

One significant advantage of hemp as a rotation crop is its short growing cycle which, beginning as it does in late April or early May, permits overwintering of biosolids on the fields allowing more time for the biosolids to break down in the soil than is possible in other crop rotations. Subject to availability, biosolids can be spread on the land every four years in the four-year rotation and immediately incorporated into the soil using a cultivator. Biosolids provide sufficient phosphorus and potassium for the full four years of the rotation (Squier, 2008). On average, and depending on the wastewater treatment process, biosolids contain 35 kg nitrogen and 20 kg phosphorous per tonne of dry matter (Marmo, 1999). Biosolids for agricultural applications is the solid fraction of sewage wastes that have been treated by anaerobic digestion, aerobic digestion, composting, pasteurisation or simple storage. These processes reduce the fermentability of the biosolids and prevent the spread of health hazards such as salmonellae, beef tapeworm eggs or viruses that may be present (Defra, 2006). In 2004, 64 % (878 thousand tonnes) of the total quantity of biosolids that were produced in the UK was used agriculturally while 19 % (265 thousand tonnes) was incinerated and 11 % was used for land reclamation or restoration (Defra, 2006). This quantity of biosolids can be used to treat approximately 16 thousand hectares of land each year, or 1.2 % of the total land used for growing crops over the course of four years (Defra, 2006).

Seed yield One hectare of dual-purpose hemp plants, grown for both seed and straw production, yields 1000–1200 kg ha^{-1} of seeds (Squier, 2010a). Not all hemp seeds on the plants will be harvested since the seeds ripen at different times and even on the same plant the seeds near to the stem will be mature before those at the tips of the plant (Bócsa and Karus, 1998). The hemp seed harvest is therefore timed to minimise seed loss. Lutman et al. (2005) reported on the inefficiencies of rapeseed harvesting in which average seed losses were 3575 seeds m^{-2}, or 15–18 kg ha^{-1} using rape seed weights reported by Diepenbrock (2000). This represents a harvesting loss of around 0.3 % from a total rape seed yield of 5000–6000 kg ha^{-1} in their work. Similar seed losses may occur in hemp seed harvesting.

Straw yield The straw yield of dual-purpose hemp is typically 5000 kg ha^{-1}, with yields in good years being up to 6000 kg ha^{-1} (Squier, 2008). These are lower than the typical yields of single-purpose (straw-only) crops, which are of the order of 6200 kg ha^{-1}, up to 7500 kg ha^{-1} in good years in the UK (Hobson, 2007). Straw yields of up to 11 600 kg ha^{-1} have been reported for single-purpose crops (Bócsa and Karus, 1998). The straw is baled into Hesstons which weigh 550 kg–800 kg, have dimensions $2.7 \times 1.2 \times 1.2$ m. The bales are bound with six loops of plastic twine which have a total length of 46.8 m and, at 6800 m kg^{-1}, weigh approximately 7 g (Squier, 2010a).

Grain and straw drying Hemp grain is harvested with a moisture content of 16–20 % (Bócsa and Karus, 1998) and is dried to a moisture content of 12 % which renders the seeds suitable for storage. Nix (2008) proposes a rule of thumb for the quantity of DERV fuel required to dry grain as 1 litre fuel per percentage point of drying per tonne of grain. Electricity is used to run the handling equipment at a rate of around 1.67 kWh $tonne^{-1}$ (Nix, 2008).

Straw is harvested with moisture contents in the range 12–16 % w/w, and damper harvests are dried indoors to 16 % w/w by passing air over the bales (Squier, 2010b).

Grain and straw storage Seed is stored in a grain silo until required at the pressing facility. At present, seed is grown for the production of premium edible oil and is transported off the farm in two batches in December and April or May (Squier, 2010a). Baled straw is stored in large, dry, concrete-floored barns prior to transport to the factory where the straw is used as a raw material in production processes.

Additional benefits of hemp cultivation Hemp's calendar of operations, being different from that of oilseed rape and wheat, led to a reduction in machinery requirements on the farm overall, with a reduced number of tractor units in use on the farm (Squier, 2008). Furthermore, the deep tap roots of the hemp plant reduced the number of ploughing operations required on the farm over the course of the four-year rotation.

Hemp can provide a barrier for pests and diseases between crops. Anecdotal evidence (Hobson, 2007) suggests that hemp is particularly useful to combat persistent grass weeds and low incidence of blackgrass has been observed in crops following the late seed drilling of hemp (Squier, 2008). Hemp has been grown year-on-year in the same fields without any apparent difficulties. The long taproot of the hemp plant is beneficial to the soil as it can loosen the soil as well as access nutrients that have sunk deeper into the soil than can be accessed by other rotation crops (Bócsa and Karus, 1998). Hemp stands are also used as cover crops for game birds which suggests that hemp may have a higher avian biodiversity than other annual crops. However, this is yet to be investigated.

Summary of cultivation and harvesting inputs The inputs to the cultivation and harvesting of hemp are summarised in Table 5.3, with data on rape seed cultivation from both the case study farm and from the literature for comparison. Field operations such as ploughing, tilling, sowing and rolling are the same for both crops and therefore omitted from Table 5.3. Lower quantities of fertilisers are used on the hemp crop than on the rape seed crops. The potassium application on the case study farm is lower than the UK averages presented in Stephenson et al. (2008) since the farm's soil is naturally high in potassium. Fewer spraying applications are required for hemp cultivation than rape seed cultivation, and on the case study farm (Squier, 2008) fewer applications of pesticides are made than the UK averages presented by Stephenson et al. (2008). Additional harvesting operations are required for hemp to collect both seed and straw products, whereas rape straw is returned to the field for inclusion in the soil in the ploughing which precedes the next crop. On a per hectare basis, the hemp crop requires fewer inputs and field operations than typical UK cultivation and harvesting of rapeseed. However, to compare these data a meaningful reference flow such as the quantity of seed or oil produced is needed and this is addressed in the life cycle assessment in Chapter 6.

Input	Hemp[1]	Rape seed[1]	Rape seed[2]	Rape seed[3]
Nitrogen, kg ha^{-1}	100	150	211	160
Phosphate, kg ha^{-1}	45	45	61	61
Potassium, kg ha^{-1}	8.3	8.3	72	72
Magnesium oxide, kg ha^{-1}	21	-	-	-
Sulphates, kg ha^{-1}	-	10	48	48
Lime, kg ha^{-1}	666[4]	-	1028	1028
Pesticide spraying operations	2	3	6	6
Fertiliser spraying operations	1	2	2	2
Harvesting operations	4	1	1	1

Table 5.3: Inputs to hemp and rape seed cultivation. Sources: [1] Squier (2008); [2] Stephenson et al. (2008), large scale; [3] Stephenson et al. (2008), small-scale; [4] Turunen and van der Werf (2006).

5.4 Laboratory analysis

In order to consider hemp as a bioenergy or biodiesel feedstock, data on the energy properties of the plant are required. More specifically, the gross heats of combustion of the straw, the seed oil and the biodiesel made from the seed oil are required. Furthermore, to assess the carbon storage potential of the straw, its carbon content, and thereby its CO_2 absorption, must be quantified.

The life cycle assessment of hemp biodiesel (Chapter 6) draws on the results of this analysis to determine the allocation ratios according to the energy contents and carbon contents of the various plant parts. Precise values for the energy contents are not required from the analysis since indicative values will suffice and deviations from these values are tested for their significance in the sensitivity analysis (Section 6.4).

In order to ascertain a reliable energy content for each plant part (straw, shiv, fibre, seed, oil and presscake), the moisture contents of the seeds and stem were tested. Next, the oil content of the seeds was determined using NMR analysis. The energy contents were measured using the bomb calorimeter, as described previously (Section 3.2.5). The moisture contents were used to determine the oven-dry (0 % moisture content) energy content of the samples. From the oven-dry energy contents, the energy contents of samples with typical moisture contents of 8 % for seeds and 16 % for straw (Squier, 2010b) were calculated. The energy content of the hemp biodiesel sample was measured without moisture compensation. Finally, the energy content of the presscake was calculated from the energy contents of dried seeds and hemp oil and the oil content of the seeds.

5.4.1 Literature

Hemp seeds Hemp seeds contain 26.25–37.50 % w/w oil (Kriese et al., 2004), which is lower than the oil content of rapeseeds which is typically 42 %. The rest of the seed forms the presscake once the oil has been extracted, and contains 25–30 % w/w protein, making it suitable for use as animal feed (Fortenbery and Bennett, 2004). The oil content of the seeds varies depending on the cultivar (Kriese et al., 2004; Höppner and Menge-Hartmann, 2007).

Höppner and Menge-Hartmann (2007) also assessed the yield and oil content of various hemp cultivars, however their results were lower than those of Kriese et al. (2004). Höppner and Menge-Hartmann (2007) recorded the yield and oil content at the point of initial maturity rather than overall seed maturity, which was the point used by Kriese et al. (2004), at which both parameters are higher, later on in the growing cycle of the plant.

No data were found in the literature for the energy content of hemp seeds or hemp presscake.

Hemp oil The main fatty acid present in hemp oil is linoleic acid, at 14.20–21.56 g / 100 g seed, or 49.06–58.01 % w/w in the oil. Stearidonic acid (0.39–1.60 % w/w) and γ-linolenic acid (0.67–4.08 % w/w) (Kriese et al., 2004) are present in hemp seed oil at relatively high proportions compared with other seed oils and these are the main components of nutritional interest which has led to interest in hemp oil as a niche food product (Matthäus and Brühl, 2008).

The high content of unsaturated fatty acids in virgin hemp oil leads to low oxidative stability of the oil (Matthäus and Brühl, 2008). However, the unhulled seeds are not susceptible to oxidation during storage because the seed hull protects the oil. Therefore oil can be stored in seed form for long periods of time. Once the oil has been extracted, oxidation can be slowed down by storing the oil in opaque containers which counter the catalysing effect of light (Abuzaytoun and Shahidi, 2006).

Extracted vegetable oils also contain substances other than the triglycerides from which biodiesels are made, namely tocopherols and lignins. These substances account for around 0.8 % of the oil content and can be removed from the oil via a refining process (Christie, 1973).

No data were found in the literature on the energy content of hemp oil.

Hemp biodiesel The properties of hemp biodiesel are influenced by the fatty acid profile of the hemp oil feedstock, which affects the density, viscosity and degree of saturation of both the oil and the biodiesel. The unsaturated fatty acids in the oil result in unsaturated fatty acid methyl esters in the biodiesel. The extent of this unsaturation is measured by the iodine value; the iodine value of hemp biodiesel produced via alkaline catalysis with sodium hydroxide (NaOH) is 164 g I_2 / 100 g. In its pure form, hemp biodiesel does not meet the EN 14214 (2004a) criteria for the iodine value, which has a maximum of 120 g I_2 / 100 g.

Hemp biodiesel, and hydrogenated hemp biodiesel have been produced and tested for their compliance with the EN 14214 standard (Yang et al., 2010). The results of their work are summarised in Table 5.4.

No data were found in the literature on the energy content of hemp biodiesel. However, the density and viscosity data in Yang et al. (2010) are combined with methods presented by (Demirbas, 2008) in Section 5.4.2 to obtain an energy content value for comparison with the experimental results in this thesis.

Hemp straw As mentioned above, hemp straw has been the subject of more research than hemp seeds or oil. However, that research has focused on its properties for fibre production rather than its bioenergy or carbon storage potential (Bócsa and Karus, 1998; Turunen and van der Werf, 2006; van der Werf and Turunen, 2008). In general, dry biomass has an energy content of approx-

Property	Hemp biodiesel	Hydrogenated biodiesel	EN 14214
Density (g cm^{-3})	0.872 (±0.011)	0.876 (± 0.012)	0.860–0.900
Kinematic viscosity (mm^2 s^{-1})	4.23 (± 0.05)	4.31 (± 0.04)	3.5–5.0
Flash point (°C)	131 (± 0.9)	137 (± 1.2)	$\geq$ 120
Cetane number	44.0 (± 2.3)	55.8 (± 2.1)	$\geq$ 51
Iodine value (g I_2/100 g)	164 (± 1.0)	113 (± 1.3)	$\leq$ 120
Acid number (mg NaOH/g)	0.01 (± 0.01)	0.01 (± 0.01)	$\leq$ 0.50

Table 5.4: Key fuel properties of hemp biodiesels (Yang et al., 2010). Kinematic viscosity is measured at 40 °C. All measurements were triplicated and the standard deviations are indicated in parentheses.

imately 18–20 MJ kg^{-1} (Sims, 2002), and this value is used in this thesis as a comparison for the experimental results in Section 5.4.2.

5.4.2 Laboratory methods

Sample collection A sample of hemp stem (Fig 5.2) was supplied by the case study farm. For energy content analysis, the hemp stem was separated into fibre (Fig. 5.3) and shiv (Fig. 5.4). Oilseeds (Fig 5.5) were purchased from a local wholefoods retailer. Hemp oil (Fig. 5.6), produced by Braham & Murray Ltd, was obtained from Waitrose. Hemp biodiesel, which used the hemp oil from Waitrose as feedstock was obtained from the Chemical Engineering and Biotechnology department at the University of Cambridge. This biodiesel was produced through transesterification with methanol in the presence of a sodium methoxide catalyst and subsequently purified using an ion exchange catalyst (Berrios and Skelton, 2008).

Not all of the samples collected were directly produced by the case study farm. In the case of the hemp oil, it is very likely to have been produced from seeds grown on the case study farm, or from other UK farms growing the same variety. Therefore the hemp oil sample is likely to be sufficiently representative of the oil produced from the farm for the purposes of this study. Data on the composition of hemp seeds are available in the literature (Bócsa and Karus, 1998; Kriese et al., 2004) for comparison with the results of the analysis in this chapter.

Figure 5.2: Hemp stem. The two stem components, fibre and shiv, can be seen at the frayed end of the stem.

Figure 5.3: Hemp fibre, broken into short lengths for CHNS analysis.

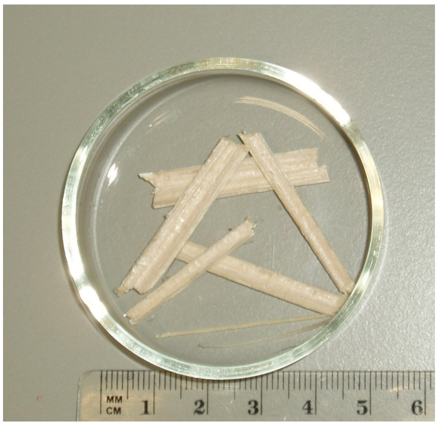


Figure 5.4: Hemp shiv

Figure 5.5: Hemp seeds

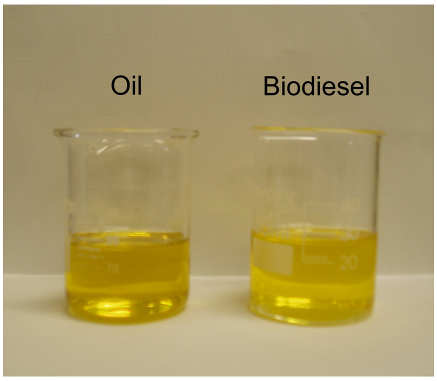


Figure 5.6: Hemp oil and biodiesel

Moisture content A 5 cm length of hemp straw was dried in an oven at 50 °C for 24 hours. The loss in mass during the time in the oven is assumed to be entirely due to loss of moisture from the sample. A 40 g sample of seeds was dried in the same way with the before and after weights recorded.

Oil content The oil content of the hemp seeds was measured at the John Innes Centre using NMR spectroscopy (Oxford Instruments model MQC). Five samples of oil seeds, with each sample weighing approximately 200 mg, were tested three times each.

Energy contents Gross energy contents of hemp plant parts were measured using a Parr plain jacket bomb calorimeter (model 1341) following the procedure described in Section 3.2.5. In some experiments a carbon residue remained in the sample capsule. This residue was weighed and an adjustment for the gross heat of the combustion of carbon was added to the result from the calorimeter operation. A correction for the presence of sulphur in the samples can be calculating using data from the sulphur content of the samples, detected using X-Ray Fluorescence (XRF) analysis.

Energy contents were determined for dried and undried seeds, and undried shiv and fibre samples. After recording the mass of the dried seeds, a few drops of water were added to the samples to slow down the combustion, since tinder-dry samples can burn too quickly with detrimental effects on the calorimeter bomb (Parr Instrument Company, 2006). The shiv and fibre samples were tested at their undried moisture content, 5.1 %. Both types of straw sample were cut into 1 cm lengths to fit into the calorimeter sample capsule.

For comparison, the gross heat of combustion of hemp biodiesel was calculated from data on the viscosity and density values provided by Yang et al. (2010) and two experimentally-derived relations which link the gross heat of combustion, E_{GHC}, of biodiesels and their viscosity, ν, and density, ρ, (Demirbas, 2008). These relations are as follow:

$$E_{GHC} = 0.4625\nu + 39.450 \tag{5.1}$$

$$E_{GHC} = 0.0259\rho + 63.776 \tag{5.2}$$

where the kinematic viscosity is in units of centiStokes (cSt, equivalent to $\mathrm{mm}^2\ \mathrm{s}^{-1}$) and the density in units of $\mathrm{kg\ m}^{-3}$.

The energy content of presscake was calculated from the energy contents of the dried seed and oil, and the seed moisture content. The energy content of the whole straw was calculated using estimates of 20 % fibre and 80 % shiv (Bócsa and Karus, 1998). The oven-dry energy content for each plant part was calculated by correcting for the moisture content as determined above.

Carbon content of hemp plant parts The elemental composition of hemp plant parts was determined in part using XRF, CHNS (Carbon, Hydrogen, Nitrogen, Sulphur) and CNO (Carbon, Nitrogen, Oxygen) detection equipment to provide indicative information for the life cycle assessment and correction data for the calorimetry tests.

Elemental analysis using X-Ray Fluorescence (XRF) relies on the physical mechanism of secondary emissions of electromagnetic radiation of characteristic wavelengths from a material when it is bombarded with x- or gamma-radiation. The seed sample was prepared by finely chopping it in a kitchen blender and pressing it into a pellet. During the pressing process, most of the oil in the seeds was expelled from the sample. The presscake was placed on absorbent paper for two days during which the remaining oil was drawn out of the presscake into the paper.

The CHNS analyzer for quantifying the carbon and nitrogen contents of solid samples uses quantitative flash combustion and gas chromatography to detect the proportions of carbon and nitrogen that are present in the sample, calibrated against a standard such as acetanilide (C_8H_9NO). Solid samples were finely ground, weighed and placed into tin containers which were sealed and crumpled into small, round pellets prior to insertion in the analyser.

Liquid samples can be analyzed using a similar instrument to the CHNS analyzer, however the process did not successfully combust the hemp oil samples. A calculation was therefore used to estimate the carbon content of the oil from the typical molecular formula for hemp oil. The ratio of the mass of carbon atoms per mole and the total molar mass of hemp oil gives the carbon content as a proportion of the overall oil mass.

A direct measurement of the carbon content of hemp seeds was difficult to achieve experimentally. The preparation of the sample involved milling and grinding which can result in oil losses from oilseeds. This loss of oil would skew the results and so a calculation method was selected to ascertain the seed carbon content, C_{seed}. The laboratory measurements of the oil content of the seeds, x_{oil}, and the carbon content of the presscake, $C_{presscake}$, and the calculated carbon content of the oil, C_{oil}, were used in Eqn. 5.3 to calculate the overall carbon content of the whole hemp seeds.

$$C_{seed} = x_{oil}C_{oil} + (1 - x_{oil})C_{presscake} \tag{5.3}$$

However, the result of Eqn. 5.3 is likely to be an overestimate of the seed carbon content since not all oil was removed from the presscake prior to analysis, and oil has a higher carbon content than the presscake.

Carbon dioxide storage in hemp The carbon contents of the hemp seeds and straw (Table 5.8) were used to calculate the carbon stored in the plant matter. All carbon in the plant matter is assumed to come from absorbed CO_2. The quantity of CO_2 that the plant absorbed during its growth was calculated from the carbon contents of the plant matter, the typical yields and the ratio of the molar masses of carbon dioxide and carbon.

Fatty acid profile Samples were taken to the nearby John Innes Centre for fatty acid profiling using gas chromatography. Each carbon chain has a distinctive elution time in the gas chromatogram. The carbon chains can be identified by reference to an internal standard which is most usually heptadodecanoic acid with a carbon chain of 17 atoms which does not occur naturally.

5.4.3 Results

Moisture content The moisture contents of seeds and straw were found to be 6.9 % w/w and 5.1 % w/w respectively. The shiv and fibre moisture contents were not measured separately and are assumed to be the same as the whole straw, 5.1 % w/w.

Oil content The NMR analysis of hemp seed samples shows that the average oil content is 31.5 % w/w, with a standard deviation of 0.97 % w/w (Table 5.5). The large size of hemp seeds, relative to rape seeds for which the machine is designed, resulted in variation in the measured oil contents since the gaps between the seeds reduced the proportion of seed in each transect.

Sample	Mass (mg)	Run 1	Run 2	Run 3
A	198.6	31.2	31.17	31.09
B	212.7	31.46	31.44	31.43
C	204.5	30.12	30.12	29.95
D	211.9	31.65	31.6	31.79
E	212.2	33.14	32.91	32.8

Table 5.5: NMR analysis of hemp seed oil contents

Fatty acid profile The gas chromatography results (Table 5.6) showed that the dominant fatty acid in hemp oil is linoleic acid, at 52.6 %, with significant proportions of oleic acid and α-linolenic acid.

Fatty acid	Fatty acid content (g / 100 g oil)	
	Experimental	Literature
Myristic (14:0)	.	0.03–0.06
Palmitic (16:0)	6.6	5.32–6.50
(16:1 D7)	.	0.09–0.20
Palmitoleic (16:1 D9)	.	0.00–0.03
Margaric (17:0)	.	0.03–0.09
Stearic (18:0)	3.6	2.08–2.80
Vaccenic (18:1 D11)	.	0.65–0.90
Oleic (18:1)	14.5	7.88–14.46
Linoleic (18:2)	52.6	50.62–60.00
α-linolenic (18:3)	17.0	16.70–24.46
γ-linolenic (18:3)	2.8[1]	0.95–3.43
Stearidonic (18:4)	1.0[1]	0.59–1.54
Arachidic (20:0)	1.0	0.61–0.98
(20:1 D11)	.	0.21–0.45
(20:2 D11,13)	.	0.06–0.10
Docosanoic (22:0)	0.4	0.16–0.38
Erucic (22:1 D13)	.	0.00–0.42
Lignoceric (24:0)	.	0.03–0.20
Selacholeic 24:1 D15	.	0.09–0.24

Table 5.6: Fatty acid contents of hemp oil. Exact values are given for the sample obtained and tested experimentally for this thesis; the ranges of the values are given for the data collected from the literature (Moes et al., 1999; Kriese et al., 2004; Matthäus and Brühl, 2008). [1]These values were not linked to these fatty acids by the contractor; their position here indicates the most likely correspondence between fatty acid and content values.

Energy contents The energy contents of hemp plant parts are shown in Table 5.7. The oven-dry energy contents of all non-oil plant parts are around 16–18 MJ kg^{-1}. The energy content of hemp oil is just over double this, at 39.15 MJ kg^{-1} which is similar to the biodiesel energy content of 39.55 MJ kg^{-1}. Corrections for sulphur content and carbon residues were found to be much less than the accuracy of the calorimeter (± 0.3 MJ kg^{-1}) and are therefore negligible. The results for the gross heat of combustion calculated from the viscosity and density using Eqn 5.1 and Eqn 5.2 are also shown in Table 5.7.

The energy content of the presscake was calculated in two ways. Firstly, the energy content was calculated from the measured seed and oil energy contents under the assumption that the all oil (31.5 % w/w of the seed mass) is separated from the presscake. Secondly, the presscake energy content was calculated using the assumption that not all oil would be extracted from the presscake, as is the case in practical operations (Section 6.3.2). For seeds containing 31.5 % according to NMR analysis, only 30.5 g of oil is assumed to be extracted from 100 g seeds, with the remainder staying in the presscake. This assumption is based on the efficiency of oil extraction which is presented in Chapter 6. The results of the two calculations were found to differ by 0.33 MJ kg^{-1}, which represents 2 % of the energy contents calculated for the presscake.

The total energy content of hemp plant matter harvested from one hectare of land, at typical yields rates of 1100 kg ha^{-1} seed and 5500 kg ha^{-1} straw, was calculated to be 119 GJ overall in the four main plant parts: oil and presscake in the seed, and shiv and fibre in the straw (Fig.5.7). The oil content used in the calculation was 30.5 % and the $shiv : fibre$ ratio in the straw was 4:1 (Bócsa and Karus, 1998). The largest store of energy is the shiv part of the straw, containing 65 % of the total energy. The seed contains 21 % of the energy, with 11 % in the oil and 10% in the presscake.

Plant part	Average	Moisture, % w/w	GHC (oven-dry)
Seed	23.316	8.0	25.34
Dried seed	25.437	0.0	25.44
Oil	39.146	0 (assumed)	39.15
Presscake - zero oil content	16.04 (calc)		18.2
Presscake - inc. oil residue	16.37 (calc)		18.4
Shiv	17.416	5.1	18.36
Fibre	15.422	5.1	16.25
Whole straw	17.0		18.0
Biodiesel	39.55	0 (assumed)	39.55
Biodiesel, calculated from viscosity	41.41		41.41
Biodiesel, calculated from density	41.19		41.19

Table 5.7: Energy contents (gross heats of combustion) of hemp plant parts, MJ kg^{-1}.

Carbon contents of hemp plant parts The carbon contents of the various parts of the hemp plant varied from 40.4–77.0 % w/w (Table 5.8). The oil, with molecular formula $C_{18}H_{36}O_2$ contains a greater proportion of carbon than the other plant parts which also include elements such as nitrogen in the plant proteins.

Carbon dioxide storage in hemp The molar masses of carbon and carbon dioxide are 12.0108 and 44.0096 kg mol^{-1} respectively. Therefore, assuming that all carbon in the plant comes from atmospheric CO_2, 3.664 kg of CO_2 is sequestered for each 1 kg of carbon present in the plant. Combining data on seed and straw yields (Section 5.3) with the measured and calculated carbon contents of hemp plant matter (Table 5.8), the total temporary storage of CO_2 in hemp crop is calculated to be 11 434 kg CO_2 ha^{-1}.

The straw, which comprises the larger part of the harvest, can store around 9395 kg of CO_2 per hectare of hemp grown, and the seed around 2079 kg ha^{-1}. Variation in the straw yield to the minimum or maximum yields of 5000 or 6000 kg ha^{-1}, changes the CO_2 stored by ±854 kg ha^{-1}

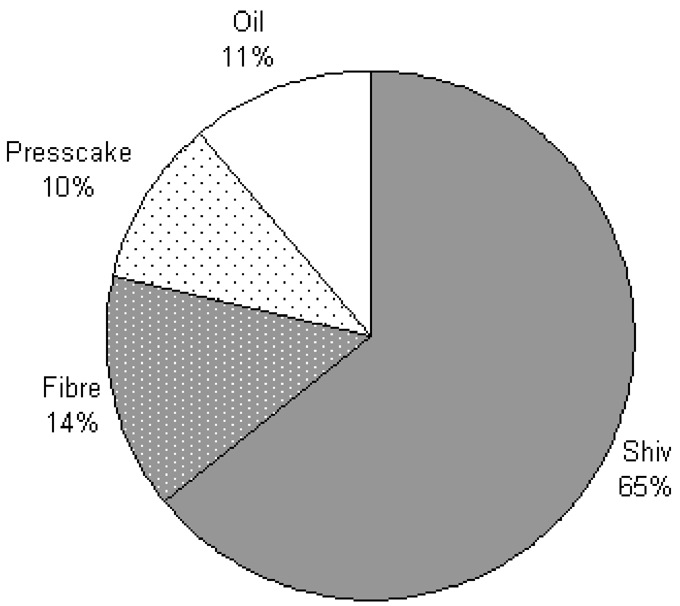


Figure 5.7: Energy content in hemp plant parts. The total energy per hectare of hemp harvested is 119 GJ.

while variation in the seed yield (1000–1200 kg ha^{-1}) changes the CO_2 stored by ± 190 kg ha^{-1}.

The most significant plant part for CO_2 storage is the shiv, at 65 % of the total CO_2 storage per hectare in the plant (Fig. 5.8), while the seed oil, which is the hemp product required for the production of biodiesel, stores only 8 % of the total CO_2 absorbed by the plant.

Plant part	Carbon content, % w/w	Method
Shiv	46.0	CHNS analyzer
Fibre	49.1	CHNS analyzer
Whole straw	46.6	calculated
Presscake	40.4	CHNS analyzer
Oil	77.0	calculated
Whole seed	51.9	calculated

Table 5.8: Carbon contents of hemp plant parts.

5.5 Discussions

5.5.1 Hemp agriculture

The data obtained through interviews and email exchanges show plainly that, contrary to reports in the popular press (Bowers, 2003), the cultivation of hemp does require inputs of fertilisers and pesticides, albeit in smaller quantities per hectare than are typically applied to oilseed rape. However, hemp does have certain advantages over rapeseed in its requirements and outputs, which are now outlined.

The inclusion of hemp in a rotation system on the case study farm changed the rotation system from six years to four years, eliminating the year of peas or beans, and reducing the years of wheat cultivation from four to three, averaged over six years. Wider adoption of hemp into arable rotations could lead to changes in the overall UK harvests of wheat, peas and beans, depending on the choices that the farmers make. In operating a four-year rotation system with hemp in, the number of tractor units required on the farm was reduced, leading to lower capital costs both financially and environmentally.

The longer growing season of the dual-purpose hemp crop allows the development and maturing of hemp seeds, which are not required in a single-purpose crop. The weather conditions in autumn are therefore more significant for dual-purpose crops. Sustained wet weather in the weeks

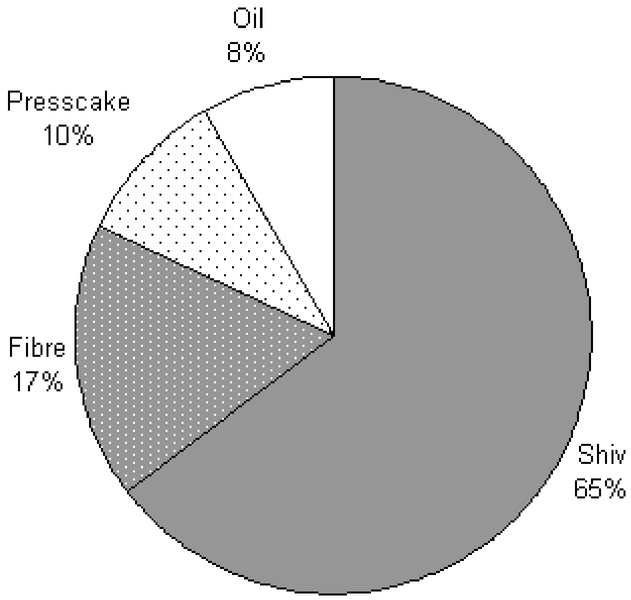


Figure 5.8: CO_2 stored in hemp plant parts

before and around the harvesting operations affects the drying rate of the straw in the field as well as the seed moisture content. The requirements for drying in the storage facilities for seed and straw are directly influenced by the weather around harvest time.

The quantity of seed used for sowing on the case study farm, 37 kg ha^{-1} concurs with the values presented in the literature for dual-purpose crops, 20–50 kg ha^{-1} (Bócsa and Karus, 1998). This rate of seed sowing allows for good crop cover, and hence weed suppression, whilst not overcrowding the hemp crop itself.

The inputs of fertilisers and pesticides to the hemp crop are lower than those required by oilseed rape crops on a per hectare basis. In particular, the application rate of nitrogen to hemp is 47–67 % of the application rate to oilseed rape, while the phosphate and potassium applications are approximately equivalent and, in any case, depend on the nutrient balance of the soils, tested annually. The soils of the case study farm are naturally rich in potassium, therefore the application rate is much lower, at 8.33 kg ha^{-1}, than the rates presented in the literature of 120-160 kg ha^{-1} (Bócsa and Karus, 1998).

The seed yield of the hemp crop, 1000–1200 kg ha^{-1}, is 30–34 % of the seed yield from oilseed rape. However, the straw yield of hemp, 5000-6000 kg ha^{-1}, is much greater than that of oilseed rape which is in any case usually reincorporated into the soil (Stephenson et al., 2008). Hemp straw is therefore a significant co-product of the hemp plant. Therefore, although the seed yield is considerably less for hemp than for oilseed rape, the straw crop compensates by providing a valuable co-product from the same stand of hemp as the seeds are harvested from.

The range of straw moisture contents reported by Squier (2010b), 12-20 % w/w, is greater than that indicated in the literature, 15–20 % (Bócsa and Karus, 1998). The occurence of drier harvests in the case study farm may reflect on the differences in the weather conditions experienced in the typically windy and dry East Anglia for the farm studied in this thesis, compared with the eastern European countries that form the majority of the research sites for Bócsa and Karus (1998).

The findings in Section 5.3 are used in the life cycle assessment of hemp biodiesel in this thesis (Chapter 6) to make a comparison between hemp and rape seed based on a reference product flow, a quantity of biodiesel, rather than on a reference of land occupation, the hectare. Further, these findings add to the international literature on single-and dual-purpose hemp crops in different climatic and geographical conditions. The current work could be extended to include an analysis of all hemp cultivation data for recent years (circa. 2003 onwards) in the UK, since such data are held by the licensing company, Hemp Technology Ltd. An analysis of all available data would provide more rigorous average values for UK hemp cultivation than are provided by the case study in this chapter of a single UK farm. This type of analysis would eliminate any anomalies from the case study farm data, such as the very low application rate of potassium, and provide better UK averages. In addition, an analysis of the overall changes in farm practice caused by the inclusion of hemp in the rotation, in particular in the use of machinery and consumption of fertilisers and pesticides, would provide useful data to farmers and researchers seeking to lessen the environmental impact of arable farming. Further investigation of the relative environmental impacts of the use of sewage biosolids in place of mineral fertilisers would also be of interest.

5.5.2 Analysis of hemp plant products

The laboratory analyses of hemp plant parts provide data not published elsewhere in the research literature, including the energy contents of hemp oil and straw, and the carbon contents of hemp plant parts. In the main, the energy content data obtained through the tests in this chapter concur with data in the literature for other cereal and oilseed crops. The results are discussed in more detail in the following paragraphs.

The moisture content of the oilseeds tested experimentally, 6.9 %, concurs with the standard moisture content of 8 % w/w for farm-stored hemp seeds which prevents the seed oil from going rancid (Squier, 2010b). The difference may have arisen from the approximate nature of the experimental method used, in which case a higher moisture content would be expected to be recored if, for example, a vacuum oven were used to conduct the test. Furthermore, the seeds were exposed to ambient temperature and humidity air in the laboratory between removal from the oven and weighing on the balance. During that period of exposure, some moisture may have been absorbed by the plant matter. Alternatively, the shop-bought hemp seeds, which are intended for human consumption, may be more thoroughly dried to avoid the onset of rancidity were moisture to be absorbed by the seeds during their shelf life. In further calculations, the expected level of 8 % w/w moisture, as reported by Squier (2010b), is adopted.

The moisture content of the straw, at 5.12 %, is lower than the Hungarian hemp straw industry's upper limit of 16 % (Bócsa and Karus, 1998). The UK hemp straw processing industry can tolerate up to 20 % moisture, with financial deductions for straw which exceeds 16 % (Hobson, 2007). The sample tested in this study was stored indoors at temperatures which exceed those typically found in straw storage barns, and at reduced humidity levels due to the air-conditioning units, hence the sample was drier than straw located in storage facilities.

The seed composition was found to be 31.5 % oil and 68.5 % presscake by weight. These results are in the middle of the range presented by Kriese et al. (2004) of 26.25–37.50 % w/w. Furthermore, the NMR results of the hemp seed oil content agree with the oil contents reported by Squier (2010b) for hemp seeds grown on the case study farm in Essex which typically have an oil content of 32 % at 8 % moisture.

The fatty acid profile obtained for the hemp oil sample is similar to data presented in the literature (Section 5.4.1), with the dominant fatty acids being linoleic, α-linolenic and oleic, all with 18 carbon atoms in the main carbon chain. The close match between fatty acid profile in this thesis with the literature results means that the results in this thesis for the other properties quantified for hemp oil, such as the energy content, is extensible to other hemp oils. Some minor discrepancies between the profile obtained for this thesis with ranges given in the literature include the slightly higher values in this thesis for palmitic acid at 6.6 %, compared with a standard range of 5.32–6.50 % w/w, stearic acid, which falls outside the literature range of 2.08-2.80 % w/w at 3.60 % w/w, and oleic acid which is just above the upper value reported in the literature of 14.46 % w/w, at 14.5 % w/w. However, these differences are at most 0.8 % w/w in the case of stearic acid, which is not significant given the general variation in results from the literature base as indicated in Table 5.6.

The experimentally measured energy content for the hemp oil, 39.15 ± 0.4 MJ kg^{-1}, is comparable with results in the literature for vegetable oils, 39.30–40.38. (Demirbas, 2008). The energy contents measured for the shiv and fibre, 17.42 and 15.42 MJ kg^{-1} are lower than the typical average energy content of general biomass, 18 MJ kg^{-1}. The seed energy content, 23.32 MJ kg^{-1} is higher than the general biomass energy content as a result of the 31.5 % oil content. The gross heats of combustion are towards the lower end of the range of results in the literature.

The overall energy yield of hemp cultivated is 119 GJ ha^{-1}, of which the oil represents only 11 % (Fig. 5.7). This low proportion of the total energy in the oil will have consequences in the allocation of life cycle impacts according to the energy contents of the product and co-product flows, which is explored further in Section 6.4.2.

The carbon contents of the various hemp plant parts range from 40.4–70.0 % w/w, with the lowest carbon content in the presscake and the highest in the seed oil. The presscake contains significant quantities of proteins (25-30 %, Fortenbery and Bennett (2004)) and moisture which reduce the overall carbon content of the presscake. Similiarly the shiv and fibre from the straw also contain proteins and their carbon contents are 46.0 and 49.1 % w/w respectively. The oil, being free of proteins has the highest carbon content, calculated at 77.0 %, although this could not be verified experimentally. Future experimental confirmation of the oil's carbon content would be a useful addition to the data presented in this thesis.

The total carbon stored per hectare of hemp, at typical yields rates for both straw and seed, is 11 473 kg ha^{-1}. If the seed oil is subsequently converted to biodiesel and combusted, while the straw is neither combusted nor allowed to decay biologically, 9395 kg ha^{-1} CO_2 can be stored, at least for the lifetime of the straw. Straw from oilseed rape has much lower yields and utility than hemp straw, which may provide hemp with overall benefits when compared with oilseed rape. The CO_2 storage potential of the hemp seed's co-product, hemp straw, is significant in considering the climate change impact potential of hemp biodiesel, and this is taken into account in the life cycle assessment of hemp biodiesel (Chapter 6).

The proportions of the total energy content and carbon content per hectare of hemp grown for each plant component (oil, presscake, shiv and fibre) are similar (Figs. 5.7 and 5.8). The plant parts are mainly carbon-based, with some hydrogen, nitrogen and other elements. The gross heat of combustion is determined by the number of molecular bonds that can be broken and the resultant ions oxidised. In carbon-based plant parts such as those of the hemp plant, the carbon content and energy content proportions are similar since the two properties of energy and carbon content are related to one another.

5.6 Conclusions

In this chapter, data on hemp agriculture collected from a case study farm in East Anglia were presented and compared with data for hemp cultivation in other countries and with oilseed rape agriculture in the UK.

Selected properties of hemp oil, presscake, shiv and fibre were analysed experimentally and others deduced through calculations. The gross heats of combustion of hemp products were analysed and the carbon dioxide storage potential of a hemp crop was estimated.

Chapter 6

Life cycle assessment of hemp biodiesel: methodology and results

6.1 Introduction

The principal objective of the life cycle assessment reported on in this thesis was to ascertain the environmental impacts of producing biodiesel from hemp seed oil in UK conditions, in order to meet Aim 6 of the thesis: *to evaluate the net climate change impact potential of substituting hemp biodiesel grown in the UK for petroleum diesel at the rate advised in the Renewable Transport Fuels Obligation* (Section 1.2). To this end, data were collected from the literature and from interviews with hemp growers in order to build a life cycle inventory. The inventory data were analysed using standard methods to obtain the overall greenhouse gas emissions across the biodiesel production life cycle, from preparing the land prior to drilling the seed, to final combustion of the fuel in a road vehicle.

The following questions were established as the focus of the life cycle assessment:

1. What is the potential climate change impact of the production of biodiesel from hemp oil?
2. How does the potential climate change impact of biodiesel from hemp oil compare with the impacts of biodiesel from rapeseed oil and fossil diesel, as reported in the literature

(Section 4)?

3. What are the implications for UK greenhouse gas emissions of growing hemp for biodiesel in the UK?

The process and results of this life cycle assessment are presented in the four sections of the ISO standard (ISO, 2006a) for LCA (Goal and Scope, Inventory, Impact Assessment, and Interpretation) in Sections 6.2 to 6.5.

6.2 Goal and scope definitions

6.2.1 LCA goal

The goal of the LCA is set out as required by the ISO (2006a) standard for life cycle assessment.

Intended applications

This study is intended to:

- evaluate the climate change impacts of producing biodiesel from hemp oil in the UK
- compare the climate change impacts of hemp biodiesel with rapeseed biodiesel and fossil diesel
- estimate the climate change impacts of substituting hemp biodiesel for petroleum diesel.

An attributional approach is taken in this LCA to quantify the environmental impacts associated with an existing production system.

Furthermore, the results of this study may be subsequently applied to:

- inform the debate on biodiesel feedstock selection and cultivation in the UK, Europe, and other regions of the world where the climate is favourable for growing hemp
- contribute to the evaluation of the life cycle impacts of dual-purpose crops and of hemp fibre grown in the UK

- inform the calculation of Renewable Transport Fuel Certificate weightings if these certificates are later weighted according to the relative reductions in carbon dioxide emissions achieved by substituting petroleum diesel with biodiesels from different feedstocks.

Reasons for conducting the study

As discussed earlier in the thesis, the reasons for this LCA are:

- the over-arching concerns regarding climate change (Sections 2.1)
- the reporting requirements of the EU renewable energy directive (European Parliament and the Council of the European Union, 2009) and RTFO (Bauen et al., 2008)
- to quantify the environmental impacts of hemp biodiesel in order to inform policy debate.

There is some overlap between the intended applications and the reasons for conducting the study as these are difficult to disentangle into two sections.

Intended audience for results

The results of this study are intended for several audiences who each have different interests in the study. These include:

- the peer community of LCA practitioners
- hemp growers
- hemp processors
- farmers who may or may not consider growing hemp in future years
- the Renewable Fuels Agency, particularly if hemp biodiesel is made available in the UK road transport fuel market
- hemp oil extractors, who may consider biodiesel production as an alternative outlet for their product.

Public disclosure intentions

The results will be publicly disclosed via peer-reviewed journals and the publication of this thesis. The results will be privately disclosed to the hemp growers who contributed data to this study, and there exists the possibility of disseminating the results to the general farming community via magazine publications such as Farmers' Weekly, if the growers who supplied data for this thesis are in agreement.

6.2.2 Scope

The decisions of key elements of the scope for the LCA are presented and justified below, using the framework for the standard LCA procedure (ISO, 2006a).

Product system

The hemp biodiesel product system (Fig. 6.1) includes four co-products (straw, presscake, glycerol and potassium phosphate) and two intermediate products (hemp seeds and hemp oil) in addition to the hemp biodiesel. The production processes are hemp cultivation, harvesting, extraction of oil from the seeds, transesterification of the oil to biodiesel, and finally combustion in a road vehicle diesel engine. Sub-processes are not illustrated in Fig. 6.1.

Product functions

The primary function of the hemp biodiesel product is the supply of energy to a road-vehicle (Section 4.2.6). However, the hemp straw co-product has multiple functions (Section 5.2), including insulation and strengthening as well as bioenergy supply. The presscake co-product from oil extraction is used for animal feed. The biodiesel-conversion co-product, glycerol, can be used as a chemical feedstock, pharmaceutical compound or as a fuel. The second transesterification co-product, potassium salts, can be used in fertiliser production.

A consequential life cycle assessment of producing biodiesel from hemp seed oil in the UK

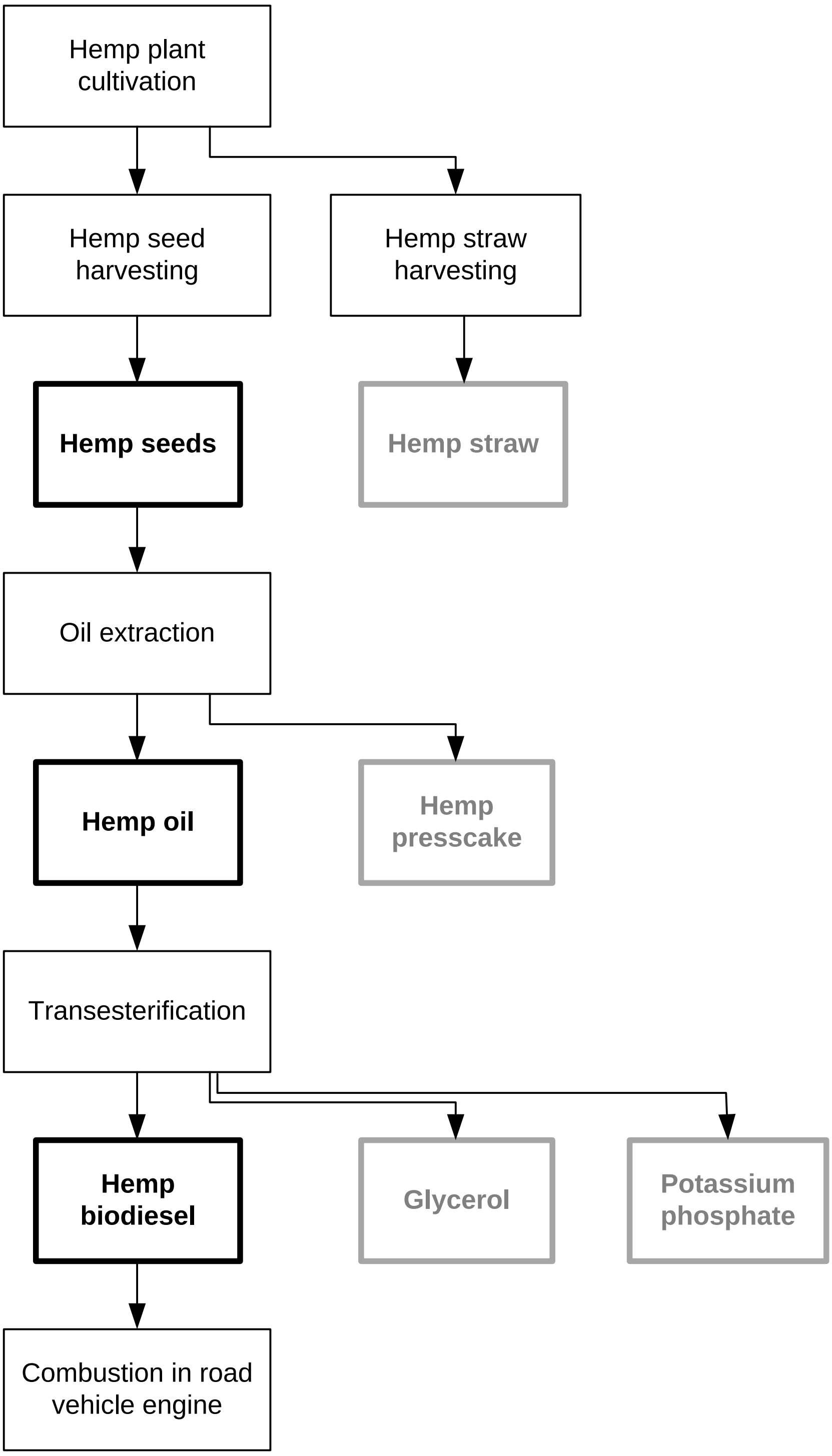


Figure 6.1: Hemp biodiesel product system including co-products (in grey).

would require a great deal of data for which only estimates are available, such as the extent and nature of the displacement of other crops or of land use changes. Further, the four co-products can each be used for more than one function, therefore identifying the marginal change in other production routes for avoided products would be a complex endeavour and, again, only estimated data is available. A study that relies on so many estimates would not be reliable for the calculation of environmental impacts. Therefore the present study is attributional in its scope, assessing the environmental impacts of existing agricultural processes, without crop displacement or land use change impacts. Allocation of climate change impact potentials between the product and co-products is used instead of system expansion.

The scope of the present LCA defines the most important or representative function for the co-products in order to allocate environmental impacts between the product and co-products. In this instance, the function of the main product is the provision of energy and therefore the co-products are also assessed on the basis of their energy contents. However, such a product function is not applicable to the potassium salts which have the function of being raw materials for fertiliser production. The masses of product and co-product are therefore also used for allocation and the implications of these decisions are discussed in Section 6.5.

Functional unit

The key function of the hemp biodiesel product is the delivery of energy to an engine. Therefore, the functional unit selected for this LCA is 1 MJ of delivered energy in the fuel. The delivered energy is measured by the gross heat of combustion of the fuel which is in keeping with the UK government's reporting of delivered energy in the annual Digest of UK Energy Statistics (Department of Energy and Climate Change, 2009). A functional unit of 1 MJ energy also enables direct comparison of the results of this life cycle assessment with the carbon reporting data for the Renewable Transport Fuels Obligation (Renewable Fuels Agency, 2009b).

System boundaries

In this section, the boundaries that define the system with regard to the environment and other technical systems are described. No cut-off criteria to distinguish between significant and insignificant processes are defined. Temporal and geographical boundaries are defined by the boundaries between the system, the environment and other technical systems.

Boundary between the system and the environment The boundary with the environment is set at the point at which raw materials are taken into the processes and subprocesses in the hemp biodiesel life cycle system.

Boundary between the system and other technical systems In accordance with standard practice in agricultural LCAs (Nemecek and Kägi, 2007), the start of the hemp cultivation process is defined as immediately after the harvest of the previous crop, and ends with the hemp harvest. The final end point for the LCA of the hemp biodiesel system is combustion in a road vehicle engine.

The current study was undertaken in the context of the EU Directive and the RTFO which have temporal limits respectively of 2020 and 2011 in the first phase. Therefore one possible temporal limit to the study could be the policy life time. However, the effects of the emissions endure for much longer than the policy lifetimes, therefore a longer timeframe is used in this study.

The hemp cultivation system under consideration is in Essex, England. The soil at the case study farm mostly consists of brick earth and clay soils, varying from London clay towards marshy, heavy clay (Squier, 2008). Where necessary, additional data from the literature on hemp cultivation in central European locations, namely Germany and Hungary, have been used. The present LCA focuses on the production of biodiesel from crops grown and processed in the UK, therefore the LCA results are applicable to regions that are similar in climate, soil types, day lengths and so forth. The effects of changes in climate, soil type and so on can be estimated, or in some cases quantified, where sufficient data is available to conduct such an investigation. However, such an assessment of the influence of changes in geographical conditions is beyond the scope of this thesis.

The boundary between the hemp biodiesel system and the co-products of hemp biodiesel production is set just after the production of the co-products. The final use of the co-products is not considered, nor is the disposal of the co-products included in this life cycle assessment. The co-products are assumed to go into another product system.

System expansion, recommended by Bauen et al. (2008) in the Renewable Fuel Agency guidelines for carbon reporting for the Renewable Transport Fuel Obligation, is not used in this LCA for three reasons pertaining to the product system, and one reason pertaining to the goal. Hemp straw, the co-product of hemp seed, can be sold into a number of different markets, therefore the identification of marginal technologies or products is not a straightforward task. The wide variety of applications of hemp straw also render difficult the identification of marginally displaced products. Finally, the variable value of hemp straw products according to the product use and the variability of the markets, particularly during the volatile period of 2008-2009 in which the data for this thesis were collected, compounds the difficulties listed above.

System expansion is inappropriate for the current LCA with regard to the goal specified above (Section 6.2.1) which is attributional, rather than consequential in nature. A system expansion approach assumes that the LCA is consequential, which would address a question of a consequential nature such as “What is the net climate change impact potential of supplying biodiesel in to the road transport fuel supply *in place of* fossil diesel?”. In this life cycle assessment, co-products are therefore handled using allocation, described below.

Allocation

The environmental impacts of the production of hemp biodiesel and its co-products are allocated in this life cycle assessment according to mass, energy content and carbon content. Allocation according to market value, as recommended by Bauen et al. (2008) as the their preferred alternative to system expansion, is not appropriate for hemp biodiesel since at present hemp seeds and their oil are sold as prestige health foods at premium prices which are not representative of the market value that hemp seeds and oils would obtain were they produced in quantities suitable for bulk production of biodiesel. Furthermore, the variability of market values over time would render this LCA obsolete, whereas allocation based on mass, energy content and carbon content, which are all intrinsic physical and chemical properties of the system product and co-products, is more likely to be valid for a longer time period.

The three allocation methods selected, mass, energy content and carbon content, are applied to the product system at each point where the product streams separate: to hemp seed and hemp straw at the farm gate, to hemp oil and presscake at the oil mill gate, and to hemp biodiesel, glycerol and potassium salts at the esterification plant gate. The three methods are compared with one another and with the default case of allocating all climate change impacts to the hemp biodiesel.

Impact categories, methods and interpretation

For the purposes of the present thesis, the principal impact category of interest is that of the system's potential to induce climate change, known as the climate change impact potential. The required output of the estimated climate change potential from the life cycle of hemp biodiesel can be characterised using the IPCC method for global warming potential calculations in the SimaPro LCA software. The method includes characterisation factors for the direct global warming potential of air emissions, with the exception of methane, CH_4, for which only the indirect effects are quantified. Biogenic CO_2 uptake is considered as a negative impact. The method does not include the following: the indirect formation of dinitrogen monoxide from nitrogen emissions; the radiative forcing due to emissions of, for example, NOx, water or sulphate in the lower stratosphere or upper troposphere; or, the range of indirect effects given by the IPCC; CO_2 formation from CO emissions. The IPCC method does not include normalisation or weighting and is based on the science basis presented in IPCC (2007).

The IPCC method (Solomon et al., 2007) uses weighted characterisation factors for climate change potential over three time horizons: 20 years, 100 years and 500 years. These weightings correspond to the three cultural perspectives: individualist, hierarchical and egalitarian (Section 4.4.6). The selection of a time horizon requires a value judgement between the three perspectives and it is difficult to assess the implications of this selection objectively (Solomon et al., 2007). On this basis, the results of the LCA in this thesis are reported using the hierarchical perspective with the 100 year time horizon, since it produces results that are in between those for the individualist (20 year) and egalitarian (500 year) perspectives.

The inventory data (Section 6.3) were analysed using the ReCiPe midpoint indicator method in SimaPro 7.1 to calculate the global warming potential indicator for the complete hemp oil biodiesel life cycle (Section 6.4).

Data requirements

Detailed data are required for the hemp cultivation and harvesting processes. Average data is used for oil extraction, transesterification, distribution and storage, and combustion in a road vehicle. Data that are specific to the properties of hemp are used where appropriate to adjust average data on the industrial process of oil extraction.

Assumptions

The processes for producing biodiesel from vegetable seed oil, as outlined in Section 2.7, are assumed to be uniform for all oilseed crops. This assumption permits the scope of these LCAs to be focused on the agricultural component of the process. The oil-pressing stage is modified to account for the lower oil contents of hemp seeds when compared with rape seeds. Transport between the stages in the product life cycle and the chemical conversion of the vegetable oils to biodiesel via transesterification are also assumed to be equivalent for hemp and rape seed oils. The final distribution phase of the diesel fuels is assumed to be the same for all fuel types, regardless of the scale of production. This follows the procedure used by Stephenson et al. (2008) on the basis that the environmental impacts of the transportation phase are equivalent for transporting both biodiesel and petroleum diesel.

Limitations

This LCA is limited to one farm site in south-east England.

Initial data quality requirements

The data are required to be current, to within 10 years of 2010, so that they represent typical and current farming and production practices. The data must lie within, or be relevant to, the geographical scope of the LCA. In this instance, the data must be European, adjusted where appropriate to reflect better the UK situation, for example the electricity mix can be updated to the proportions in the current UK electricity supply.

Critical review

A critical review of an LCA study is required particularly when the results of LCAs are to be published in the public domain. In the current study, the review is undertaken by thesis examiners and, when the results are prepared for publication in the peer-reviewed academic journals, the LCA will undergo peer review at that stage. No further critical review has been sought.

Study report type and format

The critical review is more relevant to commercial studies than to academic ones. However, in the academic context the study report is the present thesis, and subsequently the results will be reported in papers in academic journals. The study report therefore takes these formats: of a PhD thesis and of academic papers.

6.3 Inventory analysis

The inventory analysis is separated into five sections which correspond to the phases in Fig. 6.1 and comprise oilseed cultivation and harvesting (Section 6.3.1), production of vegetable oil (Section 6.3.2), conversion to biodiesel (Section 6.3.3), transport for distribution and storage (Section 6.3.4), and combustion of biodiesel in road vehicles (Section 6.3.5). Finally, the phases are linked together across the full hemp biodiesel life cycle with conversion factors (Section 6.3.6).

Data for this LCA have been obtained from both primary and secondary sources. Experimental data on the properties of hemp plant parts were obtained through laboratory analysis methods (Chapter 5.4.3). Primary data from a farm in Essex, south-east England, were gathered through informal interviews with the farmer and his agronomist (Section 5.3.2). The data on inputs to the process are exact in some cases, for example the rates of chemicals applied to the land and to the crops. In other cases, data have been estimated from the ecoinvent database and modifications have been applied to the data to reflect process- or crop-specific circumstances. For example the fuel consumption of the combine harvester is lower when it harvests just the tops of hemp crop to collect the seed heads, rather than when the whole crop, including the stems, goes through the machinery.

Secondary data have been collated from the literature in order to obtain comparison for the primary data, and to assess how extensible the results from this LCA may be to hemp grown in other conditions and situations. These secondary data have been taken from Bócsa and Karus (1998) and Höppner and Menge-Hartmann (2007) which both contain data specific to dual-purpose hemp crops.

The processes referred to in this section all have their own inputs and outputs of subprocesses and raw substances, and corresponding exchanges with the environment. The SimaPro software compiles the data on these subprocesses, substances and exchanges, and collates the results in a detailed inventory table. The ReCiPe method is applied to the collated data in the detailed inventory table to calculate the category indicators selected for the LCA, whether midpoint or endpoint.

The electricity mix used as an input in several processes in the LCA represents the average electricity supply for Great Britain in 2008 which is the latest year for which data are available at the time of writing (Table 6.1).

Generation type	Percentage
Hard coal	32.161
Oil	1.5658
Natural gas	45.361
Hydropower	1.3263
Hydropower, pumped storage	1.0494
Nuclear	13.47
Wind	2.6523
Imported electricity from France	2.5313
Imported electricity from Ireland	0.0022

Table 6.1: Electricity supply mix for Great Britain, 2008 (Department of Energy and Climate Change, 2009).

6.3.1 Hemp cultivation and harvesting

The hemp cultivation process is summarised in Fig. 6.2 while the input and output quantities are detailed in Table 6.2. The input processes and quantities are taken from the case study farm data (Section 5.3.2). The output data come from varied sources: the hemp plant data from the information provided by the farm while the emissions to air come from calculations and from data on rape seed cultivation and harvesting (ecoinvent Centre, 2009).

Nitrogen, phosphorus and potassium fertilisers are applied with magnesium oxide in a single operation to the hemp crop during its growth period (Squier, 2008). One application of lime is made to the land every third year (Turunen and van der Werf, 2006), giving an annual total of 1.33 ha fertiliser applications.

Glyphosate, a herbicide, is applied in a single operation prior to sowing the hemp seed. The land is tilled with a spring tine harrow to prepare the seed bed. The seed is sown and subsequently the seed bed is rolled to encourage good crop establishment.

Process	Units	Quantity
Inputs		
Ploughing	ha	1.0
Fertiliser application	ha	1.33
Lime	kg	666.0
Glyphosate	kg	0.413
Pesticide application	ha	1.0
Tillage by spring tine harrow	ha	1.0
Hemp seed	kg	37.0
Sowing	ha	1.0
Tillage, rolling	ha	1.0
Ammonium nitrate	kg	100.0
Triple superphosphate	kg	45.0
Potassium chloride	kg	8.33
Magnesium oxide	kg	21.0
Outputs		
Hemp plants, in field	ha	1.0
Emissions to air		
Ammonia	kg	0.00394
Nitrous oxide	kg	0.68746
Nitrogen oxides	kg	2.51×10^{-4}

Table 6.2: Inputs and outputs from the cultivation of 1 hectare hemp.

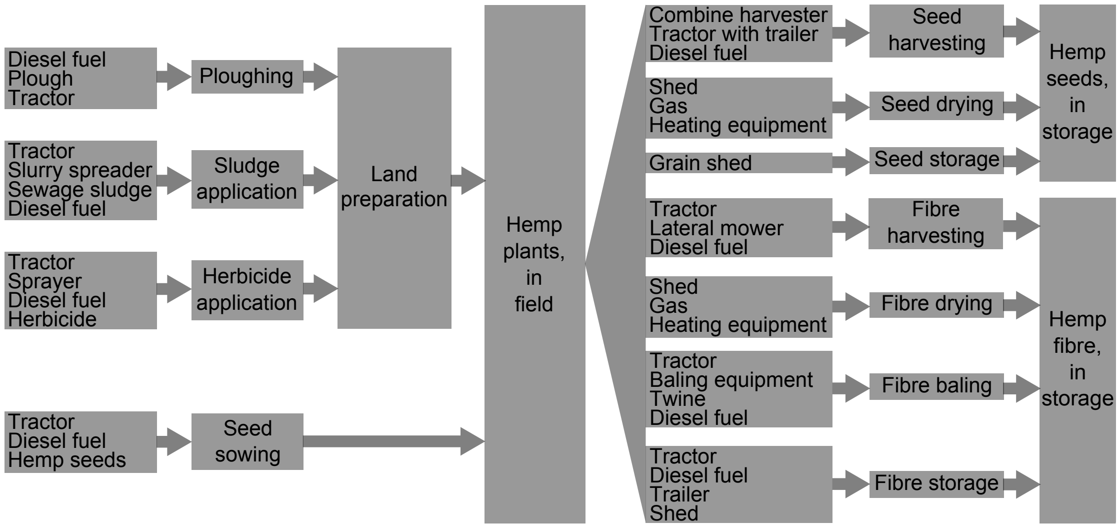


Figure 6.2: Technological input processes to the cultivation and harvesting of hemp products

The output of the hemp cultivation process is one hectare of hemp plants.

Nitrous oxide (N_2O) is produced as an intermediary in the conversion of nitrates (NO_3^-)from nitrogen fertiliser to nitrogen gas (N_2) by soil micro-organisms (Nemecek and Kägi, 2007). Exact figures on the quantity of N_2O released from fertilised soils can be determined experimentally. However, for the purposes of this LCA estimates are taken from data on N_2O emissions from rape seed cultivation (ecoinvent Centre, 2009). These data may not be strictly accurate owing to the different effects that rape and hemp plants, and their crop rotations, have on the soil. Estimates of ammonia and nitrogen oxides other than N_2O were taken from data for rape seed to complete the inventory of emissions to air. However, ammonia and nitrogen oxides are not significant for the climate change potential.

Emissions of heavy metals, nitrates and phosphates to waterways and soil are excluded from the inventory. Although data were available for rape seed cultivation which can be adopted as estimates for hemp seed cultivation, these emissions were found to have no effect on the impact assessment calculations for climate change impact potential, and are therefore omitted from the inventory.

The inputs and outputs of harvesting hemp seeds from one hectare of hemp plants are detailed in Table 6.3.

Process	Units	Quantity
Inputs		
Hemp plants	ha	1.0
Combine harvesting	ha	0.0003
Grain drying	kg	0.122
Transport to store	tkm	0.003
Outputs		
Hemp seed	kg	1100.0

Table 6.3: Inputs and outputs from the harvesting of seeds from 1 hectare hemp.

The combine harvesting input data (ecoinvent Centre, 2009) assumes that the machine processes both the grain and the straw of the crop, whereas in the combine harvesting of hemp seeds only the tops of the crop are processed through the machine. A factor of 0.33 was applied to the data to take into account the lower load reported by Squier (2008) when harvesting the seeds only and not processing the straw through the machine.

The grain drying process (ecoinvent Centre, 2009) has a functional unit of 1 kg water dried out from the grain. The grain drying load, L, in terms of the mass of water in kg that is dried out of the grain, was calculated from the moisture contents of the fresh seed from the field, M_{fresh} (18 % w/w), and the dried seed, M_{dry} (8 % w/w) using Eqn. 6.1.

$$L = \left(\frac{1 - M_{dry}}{1 - M_{fresh}}\right) M_{fresh} - M_{dry} \tag{6.1}$$

The average distance that the seed is transported from the field to the store is assumed to be 3 km, therefore the transport for each kilogram of seed is 0.003 tkm.

The seed yield is typically 1000–1200 kg ha^{-1}, therefore a mid-range value of 1100 kg ha^{-1} is used as the default. The seeds contain 51.9 % carbon (Section 5.4.3), therefore in 1100 kg seeds, 570.9 kg of carbon is stored. Assuming that all stored carbon in the plant matter comes from CO$_2$

that has been absorbed from the atmosphere, 2092 kg ha^{-1} of CO_2 was absorbed by the plants and stored in the seeds. The uptake and storage of carbon in the crop residues (the root matter and stubble left in the field) is not included in this assessment.

The inputs and outputs of harvesting hemp straw from one hectare of hemp plants are detailed in Table 6.4.

Process	Units	Quantity
Inputs		
Hemp plants	ha	1.0
Mowing	ha	0.000182
Tedding	tkm	0.00204
Baling with twine	units	0.00426
Transport to store	tkm	0.003
Outputs		
Hemp straw	kg	5500.0

Table 6.4: Inputs and outputs from the harvesting of straw from 1 hectare hemp.

Data for mowing using a rotary mower (ecoinvent Centre, 2009) is used as an approximation to the five-bar sickle mower used to chop the hemp stems into regular lengths in the field.

The process of tedding involves the turning over of the hemp straw in the field by a tractor with a fixed device attached. Standard tedder widths are 4.8–8 m and a tractor with a tedder attached sweeps out an area of 4800-8000 m^2 in each 1 km. One hectare of land can be tedded by a tractor traveling 1.25–2.08 km and in this LCA a mid-range value of 1.75 km is used as the default. From these data, the total tedding distance that is required for 1 kg straw is 0.00204 km. The process is approximated by using the LCA data for a tractor and trailer traveling 0.00204 km.

The hemp straw is baled into bales measuring 2.7 × 1.2 × 1.2 m (Squier, 2010a). Each bale weighs 550–800 kg and is bound with approximately 13.6 m plastic twine weighing 0.002 kg. Data for a baling process for round bales (ecoinvent Centre, 2009) were adapted to model baling hemp straw bales. Data on the film extrusion of polyethylene (ecoinvent Centre, 2009) were adapted to estimate the production of plastic twine. Combining these approximations, a final value of 0.00426 bales to each 1 kg hemp straw was adopted.

The average distance that the straw is transported from the field to the store is assumed to be 3 km, therefore the transport for each kilogram of straw is 0.003 tkm.

The straw yield is typically 5000–6000 kg ha^{-1}, therefore a mid-range value of 5500 kg ha^{-1} is used as the default. The straw contains 46.6 % carbon (Section 5.4.3), therefore in 5500 kg straw, 2563 kg of carbon is stored. Assuming that all stored carbon in the plant matter comes from CO_2 that has been absorbed from the atmosphere, 9391 kg of CO_2 was absorbed by the plants and stored in the straw. The uptake and storage of carbon in the crop residues (the root matter and stubble left in the field) is not included in this assessment.

6.3.2 Oil extraction

Input and output data for the oil mill process (Table 6.5) were taken from the ecoinvent data on oil extraction from rape seed and supplemented with experimental data on the oil content of hemp seeds (Section 5.4.3) and data on oil extraction efficiencies calculated from the literature (Stephenson et al., 2008). The oil extraction process includes the transport of hemp seeds to the mill, and the processing of the seeds to hemp oil and hemp meal.

The proportion of oil that can be extracted from the seeds using a screw press is 60–80 % of the total seed oil content (Matthäus and Brühl, 2008). Commercial solvent extraction of oil from rape seeds has an efficiency rate of 97.40 % from seeds with an oil content of 42.08 % w/w and an overall seed moisture content of 9 % w/w. Future extraction rates of hemp oil from seeds may reach the same efficiency levels as current methods for oil extraction from rape seeds and in the sensitivity analysis of the inventory data, 60–80 % is used as the typical extraction efficiency, and 97 % as the maximum extraction efficiency. In this LCA, the typical oil content of hemp seeds is 31.5 % (Section 5.4.3) and with a maximum extraction rate using solvent extraction of 97 %, the

Process	Units	Quantity
Inputs		
Hemp seed	kg	1.0
Heat, natural gas, at industrial furnace	MJ	1.349
Transport, freight, rail	tkm	0.0043404
Transport, lorry >16t, fleet average	tkm	0.00072339
Transport, lorry 3.5-16t, fleet average	tkm	0.19061
Oil mill	1 unit	6.3537×10^{-10}
Bentonite	kg	0.0044658
Hexane	kg	0.002092
Phosphoric acid, industrial grade, 85 % in H_2O	kg	0.00067618
Electricity, medium voltage, GB 2008 mix	kWh	0.081412
Outputs		
Hemp oil	kg	0.305
Hemp presscake	kg	0.695
Disposal to wastewater treatment	m^3	1.2×10^{-6}

Table 6.5: Input and outputs for the extraction of oil from 1 kg hemp seeds.

total oil yield is 30.5 % of the seed mass, assuming a seed moisture content of 8 % w/w.

The remainder of the hemp seeds after the oil has been extracted is the presscake. The process is assumed to be lossless, although in practice some of the initial quantity of seeds enters the waste stream. The waste stream from the production of 1 kg oil from rape seed is 5.142×10^{-6} m^3. Multiplying this figure by 0.305, the yield of hemp oil from 1 kg, gives 1.568×10^{-6} m^3.

6.3.3 Conversion to biodiesel

The input and output data for the conversion of 1.0 kg of hemp oil to hemp methyl ester are detailed in Table 6.6. Data for the conversion of rape oil to rape methyl ester (ecoinvent Centre,

2009) were used for this phase of the hemp biodiesel life cycle.

The inputs to the transesterification process include the chemical and heat inputs for the conversion of oil to biodiesel (Section 2.7), storage and transport of the oil. Treatment of specific wastewater effluents was also included. No adjustments, other than the selection of hemp oil as the feedstock and the use of electricity data specific to Great Britain, were made to the LCA data of this process.

The transesterification of one tonne of rape oil results in 972.7 kg rape methyl ester, 106.1 kg glycerine and 16.4 kg potassium phosphate (Jungbluth et al., 2007). These figures are assumed to apply equally to the products of transesterification of hemp oil (hemp methyl ester, glycerol and potassium phosphate) since hemp oil and rape oil are not significantly different in their overall composition.

Process	Units	Quantity
Inputs		
Hemp oil	kg	1.0
Methanol	kg	0.110499
Electricity, GB mix	kWh	0.0411409
Heat from natural gas	MJ	0.898557
Transport, freight, rail	tkm	0.075647
Transport, lorry >16t, fleet average	tkm	0.0126016
Vegetable oil esterification plant	unit	9.09091×10^{-10}
Tap water	kg	0.0265779
Phosphoric acid, industrial grade, 85 % in H_2O	kg	0.00447675
Potassium hydroxide	kg	0.0110459
Outputs		
Hemp biodiesel	kg	0.9727
Glycerol	kg	0.1061
Potassium phosphate	kg	0.0164
Heat, waste	MJ	1.463812588
Treatment, sewage, to wastewater treatment	m^3	0.006324178

Table 6.6: Inputs and outputs for the conversion of 1 kg hemp oil to biodiesel and co-products.

6.3.4 Transport and storage in distribution centres

The inputs and outputs in the distribution of biodiesel to petrol stations are shown in Table 6.7. These processes assume distribution to regional storage and to commercial fuel retail outlets. The transport and storage processes are assumed to include a loss of 0.5 % w/w biodiesel through spillages and through traces of biodiesel that remain in vehicles or tanks after emptying. These fuel traces are washed out and the wastewater processed in sewage treatment facilities. Rainwater contamined by fuel is held in storage and treated in specialist wastewater treatment. The data are adapted from data for the distribution and storage of rape seed methyl ester (ecoinvent Centre, 2009). The adaptation consists in the specification of hemp methyl ester and in the use of the electricity mix for Great Britain.

Process	Units	Quantity
Inputs		
Hemp methyl ester	kg	1.005
Electricity, low voltage, GB	kWh	0.0067
Light fuel oil, burned in boiler	MJ	0.000621
Rail freight transport	tkm	0.1005
Transport by lorry, 16-32 t	tkm	0.15007
Regional distribution of oil products	unit	2.6205×10^{-10}
Tap water	kg	0.000689
Outputs		
Hemp biodiesel, distributed	kg	1.0000
Disposal to hazardous waste incineration	kg	0.00016
Disposal to sanitary landfill	kg	0.00000627
Rainwater to wastewater treatment	m^3	0.000075
Wastewater sewage treatment	m^3	0.000000689

Table 6.7: Inputs and outputs for the transport and storage of 1 kg hemp biodiesel.

6.3.5 Final use - biodiesel combustion in a road vehicle

The inputs and outputs from the combustion of 1 kg of hemp methyl ester are detailed in Table 6.8. This phase of the biodiesel life cycle assumes, for simplicity and for the purposes of generalisation, that all biodiesel undergoes complete combustion to CO_2 and H_2O, with no hydrocarbon emissions.

Process	Units	Quantity
Inputs		
Hemp biodiesel	kg	1.0
Outputs		
Carbon dioxide	kg	2.98
Carbon monoxide	kg	6.67×10^{-3}
Nitrogen oxides	kg	9.76×10^{-3}
Dinitrogen monoxide	kg	1.67×10^{-4}

Table 6.8: Inputs and outputs for the combustion of 1 kg hemp biodiesel in a road vehicle engine (Delft University of Technology, 2001).

The carbon content of hemp biodiesel is calculated from molar masses and the typical molecular formula for hemp biodiesel, $C_{18}H_{34}O_2$. Assuming no contaminants, the carbon content of hemp biodiesel is 77.0 % w/w. Assuming that all carbon in the biodiesel is fully combusted to CO_2, 2.82 kg CO_2 is emitted from the combustion of 1 kg hemp biodiesel.

Combustion of diesel fuels in vehicle engines also produces nitrogen oxides which form from the nitrogen in the intake air when it is oxidised in the combustion chamber. The inclusion of biodiesel in a diesel fuel blend increases the nitrogen oxide output in the exhaust (Szybist et al., 2005). At 100 % biodiesel, the nitrogen oxide emissions are 6–9 % higher than the emissions from petroleum diesel in the same engine. At 40 %, the emissions are only 4–6 % higher, and at 20 % the emissions are 3–4 % higher with biodiesel in the fuel than when using the pure petroleum diesel. From these data, an estimate was made of a 1 % increase in nitrogen oxide emissions for vehicles running on fuel which include 5 % biodiesel.

Life cycle inventory data for traveling 1 km in an average diesel-fueled car (Delft University of Technology, 2001) were used to calculate the emissions from 1 kg diesel fuel by normalising the emissions with the quantity of diesel used in driving 1 km. The nitrogen oxides emissions were increased by 1 % to account for the estimated effects of blending 5 % biodiesel with petroleum diesel.

6.3.6 Connecting the life cycle phases

The connections between the process stages in the hemp biodiesel life cycle are shown in Table 6.9. The typical values for the conversion factors and the required inputs to each stage from each preceding stage are detailed. The processes are presented in reverse order since the quantity required in each of the upstream processes is governed by the quantities of product flow in subsequent stages and ultimately by the functional unit of energy in biodiesel which is the reference flow of the LCA. Minimum and maximum values for the conversion factors are also shown Table 6.9. During the impact assessment phase of this LCA (Section 6.4), the sensitivity of the overall results to changes in the conversion factors is assessed.

The functional unit is 1 MJ energy supplied in the form of biodiesel to a diesel engine. With a gross heat of combustion of 39.6 MJ kg^{-1} (Section 5.4.3), 0.0253 kg of hemp biodiesel is required to supply 1 MJ energy. The measured energy content with the calculated deviation of the calorimeter, ± 0.3 MJ kg^{-1}, is taken to be the minimum value for this conversion factor, i.e. 39.3 MJ kg^{-1}. The gross heat of combustion of hemp biodiesel calculated from data in the research literature is 41.3 MJ kg^{-1} (Section 5.4.3) which provides a maximum value for the energy content.

Allowing for losses in distribution and storage (Table 6.7), 0.0254 kg hemp biodiesel is required at the esterification plant to ensure that 0.0253 kg biodiesel is supplied to the vehicle. Minimum losses of 0 % are assumed, and an estimate of 2 % loss is used for the maximum. The 2 % value was selected to establish the sensitivity of the life cycle assessment results to the distribution

Product flow *Conversion factor*	Quantity	*Typical*	*Minimum*	*Maximum*
Biodiesel energy, MJ	1			
Biodiesel energy content, MJ kg^{-1}		*39.6*	*39.3*	*41.3*
Biodiesel, distributed, kg	0.0253			
Biodiesel after distribution losses, %		*99.5*	*98.0*	*100.0*
Biodiesel available for distribution, kg	0.0254			
Biodiesel after losses, %		*99.5*	*98.0*	*100.0*
Biodiesel produced, kg	0.0255			
Transesterification conversion, %		*97.27*	*90.0*	*97.27*
Hemp oil (extracted), kg	0.0262			
Oil extraction efficiency, %		*97.0*	*90.0*	*97.0*
Oil in seeds, kg	0.0270			
Seed oil content, % w/w		*31.5*	*26.25*	*37.50*
Hemp seeds, kg	0.0858			
Hemp seed yield, kg ha^{-1}		*1100*	*1000*	*1200*
Cultivated area of hemp plants, ha	7.80×10^{-4}			

Table 6.9: Conversion factors between life cycle stages. Quantities shown are calculated for the typical conversion factors.

and storage losses.

The transesterification process produces 0.9727 kg biodiesel for each 1 kg of hemp oil transesterified (Table 6.6). Losses in the transesterification plant may be up to 0.5 % of the total biodiesel produced. From these rates of conversion and loss, the quantity of hemp oil required to produce 0.0255 kg biodiesel available for distribution is 0.0262 kg. The conversion rate was taken from data on the commercial transesterification of rape seed oil to biodiesel and is therefore assumed to be the operational maximum for the process. A minimum conversion rate of 90 % is assumed for a less efficient plant. The maximum loss is estimated at 2 % and the minimum loss is the theoretical 0.0 %, or complete transfer of all biodiesel produced to distribution.

The oil extraction process recovers 97 % of the oil in the seeds (Section 6.3.2). A total of 0.0269 kg oil in the hemp seeds is required to the 0.0262 kg hemp oil. The 97 % extraction efficiency is for a solvent extraction facility and is assumed to be the best possible rate for this technology. Mechanical oil extraction can extract 60–80 % of the oil in the seeds (Matthäus and Brühl, 2008). In this LCA, a solvent extraction process is assumed in order to compare the likely impact of commerical hemp biodiesel production with commercial rapeseed biodiesel production. Therefore minimum and maximum extraction efficiency rates of 90 % and 97 % are assumed.

Seeds at 8 % w/w moisture content contain 31.5 % w/w oil (Section 5.4.3). Therefore to produce 0.0270 kg oil, 0.0858 kg hemp seeds are required. Seeds are assumed to have a standard, invariable moisture content of 8 % since they are harvested with higher moisture contents and then dried to and kept at 8 % moisture to ensure that they do not spoil in storage (Squier, 2010a). The oil content can vary according to cultivar from 26.25–37.50 % (Section 5.4.1) and these values are adopted as the minimum and maximum for the oil content conversion factor.

At a typical yield rate of 1100 kg ha^{-1}, an area of 7.81 $\times 10^{-4}$ ha of cultivated hemp plants are required to produce 0.0858 kg hemp seeds. The yield rates of seed from dual purpose hemp crops range from 1000–1200 kg ha^{-1} (Section 5.3.2) and these values are used as the minimum and maximum conversion factors from the area of cultivated hemp plants to the seed yield.

6.4 Impact assessment results

The results of the impact assessment for the climate change impact potential, calculated using the ReCiPe midpoint indicator method in SimaPro 7.1, are presented in this section. First, an overview of the hemp biodiesel life cycle climate change impact potential is presented (Section 6.4.1), using the default (typical) values for the processes described above (Section 6.3). Sensitivity analysis of the most significant subprocesses in the hemp biodiesel life cycle was carried out (Section 6.4.4). The effects of including and excluding carbon dioxide absorption during plant growth and final emissions from the combustion of hemp biodiesel were calculated (Section 6.4.3). Sensitivity of the results to changes in the conversion factors (Table 6.9) was investigated (Section 6.4.5). Mass, energy and financial allocation methods were applied to the environmental impacts (Section 6.4.2).

6.4.1 Overview of climate change impact potential

The total global warming potential of 1 MJ hemp biodiesel calculated for all processes in the hemp biodiesel life cycle except for CO_2 absorption during crop growth and direct CO_2 emission during fuel combustion, using typical values for inputs, outputs and conversion (Section 6.3), is 0.137 kg CO_2-e. This calculation is the default scenario. In accordance with standard practice in biodiesel life cycle assessments (Chapter 4), the direct absorption and emissions of CO_2 are omitted from the calculation at this stage and are considered later (Section 6.4.3). All impacts are allocated to the hemp biodiesel product chain, with no allocation to hemp straw, hemp presscake, glycerol or potassium phosphate. Allocation to co-products is addressed in Section 6.4.2.

The cultivation and harvesting processes together contribute 91.9 % of the total climate change impact potential of hemp biodiesel production (Fig. 6.3), while the oil extraction and esterification stages contribute 4.1 % and 3.4 % respectively. Distribution of the final product to regional storage accounts for just 0.6 % of the total climate change impact potential.

Forty-five separate sub-processes contribute to the overall climate change impact potential in the hemp biodiesel life cycle, of which seventeen processes contribute more than 1 % each (Fig. 6.4). The most significant contributions come from the production of ammonium nitrate fertiliser (0.0678 kg CO_2-e, 49.37 % of the total climate change impact potential of producing

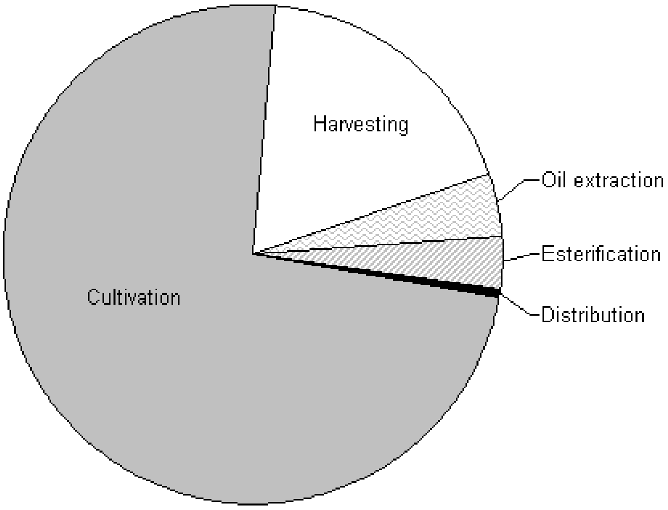


Figure 6.3: Life cycle climate change impact potential of hemp biodiesel production by production process stage.

1 MJ hemp biodiesel), grain drying (0.0134 kg CO_2-e, 9.79 %) and ploughing (0.0092, 6.72 %). The production of seed for sowing accounts for 0.0048 kg CO_2-e (3.47 %). The impact from the ammonium nitrate fertiliser is almost five times larger than the next highest contributing process, which is the grain drying process. Any variation in impacts from processes other than nitrogen fertiliser is therefore unlikely to make a significant difference to the overall results. However, these results are allocated entirely to the hemp biodiesel and allocation between product and co-products can affect the significance of individual subprocesses. This is investigated in the next subsection.

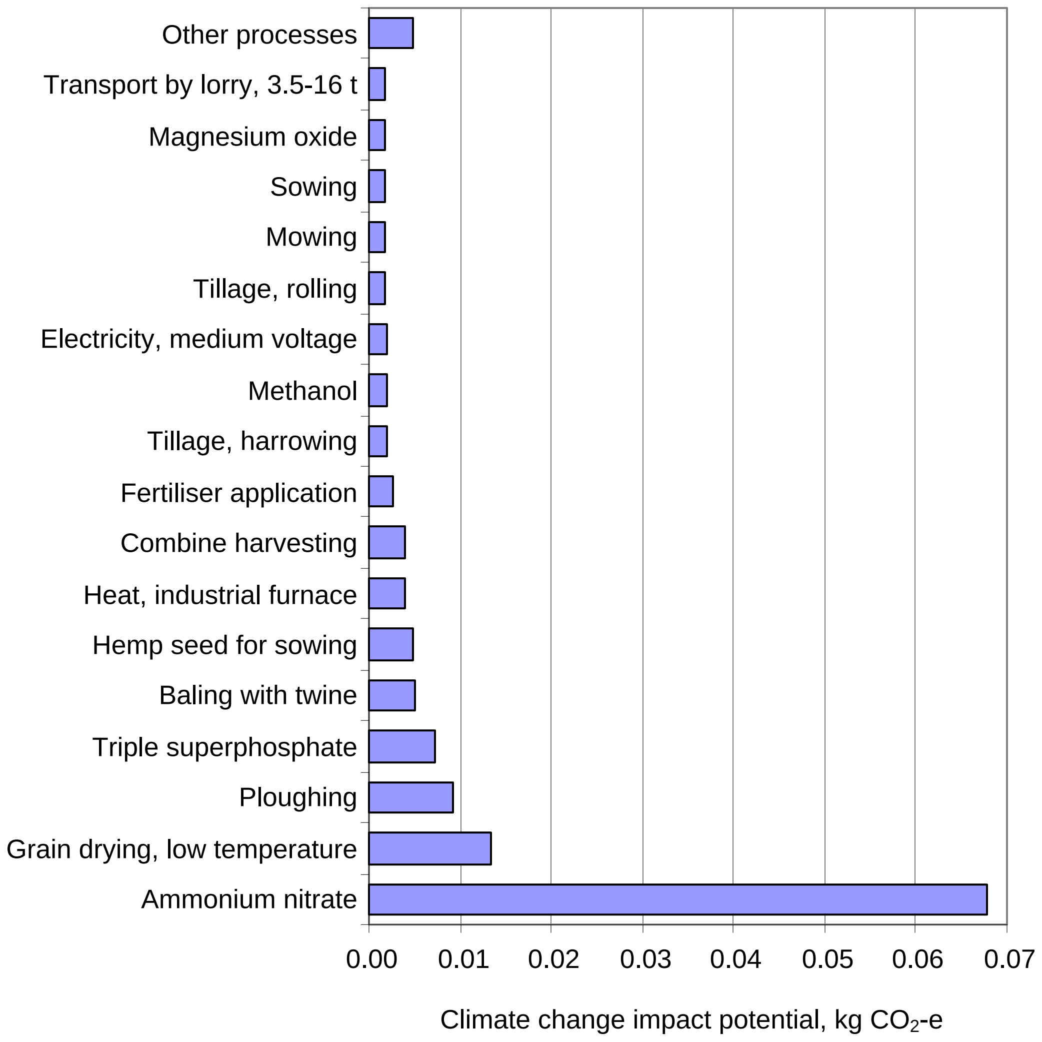


Figure 6.4: Contributions of subprocesses to the climate change impact potential of 1 MJ hemp biodiesel. “Other processes” is the sum of all subprocesses which each contribute less than 1 % of the total climate change impact potential, a total of 0.0048 kg CO_2-e (3.46 %).

6.4.2 Allocation

The contributions to the climate change impact potential are allocated to the product and co-products using mass, energy content and carbon content ratios at the point where the product and co-product streams separate (Fig. 6.5). Allocation point 1 corresponds to the farm gate, allocation point 2 to the oil mill gate and allocation point 3 to the transesterification plant gate. The allocation ratios for mass, energy content and carbon content are compared and the sensitivity of the results to changes in the allocation ratios is also investigated.

At each allocation point, the upstream contributions to the climate change impact potential are split in proportion with the allocation ratio at that point. For example, at allocation 2 in Fig. 6.5, the climate change impact potential contributions from the cultivation and harvesting of hemp seed and from the process of oil extraction are divided between the hemp oil and the hemp presscake. However, at allocation 2, the downstream processes of transesterification, storage and distribution are not allocated to the presscake since these processes occur afterwards and cannot be allocated to this earlier co-product.

The allocation ratios (Table 6.10) are calculated from the inventory data (Section 6.3). In the case of potassium salts at allocation point 3, energy content and carbon content allocation is zero since the product is not an energy product but used for fertiliser, therefore its energy content is not meaningful in this context. The three parameter sets of mass, energy and carbon contents on which the allocation ratios are based lead to some variation in the allocation ratios, with the mass allocation ratio being the lowest at all three allocation points. The energy and carbon content allocation ratios are similar and only in the case of the third allocation point at the transesterification plant gate is the carbon content allocation ratio marginally higher than the energy content allocation ratio. As noted previously (Section 5.5.2), energy content is determined by chemical composition and this gives rise to the correlation between energy content and carbon content allocation ratios.

The climate change impact potential of producing 1 MJ hemp biodiesel was calculated using the allocation ratios (Table 6.10) with the following combinations of allocation points in the calculations:

- allocation point 1

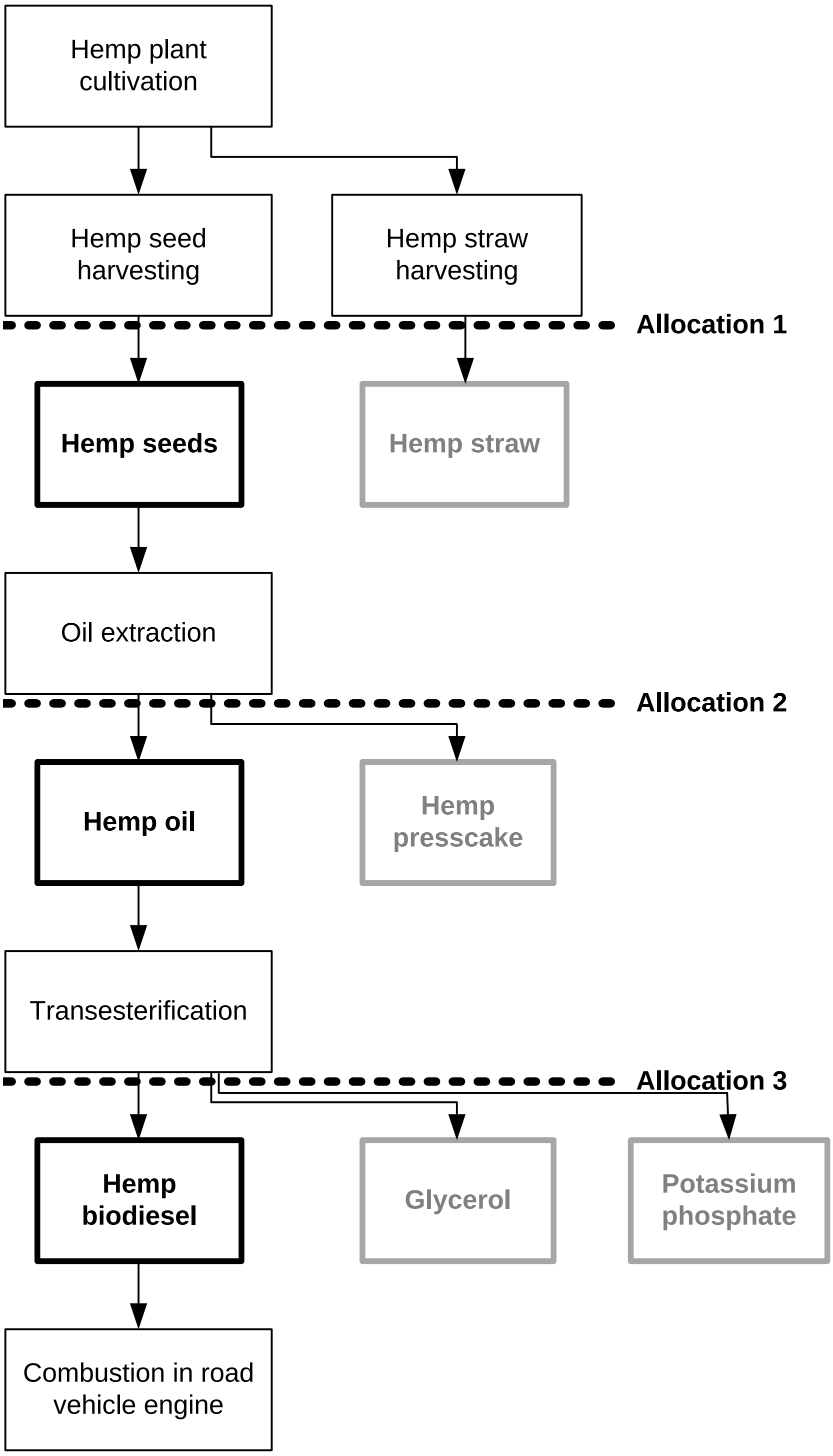


Figure 6.5: Allocation points in the hemp biodiesel life cycle

- allocation point 2
- allocation points 1 and 2
- allocations point 3
- allocation points 1, 2 and 3.

The results of changing the allocation method and the allocation points included in the calculation (Fig. 6.6) show that both the allocation method and the selection of allocation points to include affect the overall climate change impact potential of producing hemp biodiesel. The application of all three allocation methods, mass, energy and carbon content, reduces the overall climate change impact potential attributed to hemp biodiesel. The inclusion of more allocation points in the calculation also reduces the overall climate change impact potential attributed to hemp biodiesel.

The three allocation methods give similar results for each combination of allocation points. The largest difference is when allocation is only applied at point 2, with the energy content allocation result at 0.0737 kg CO_2-e and the mass content results at 0.0456 kg CO_2-e for each 1 MJ of hemp biodiesel. In all other allocation combinations, the results differ by no more than 0.0088 kg CO_2-e.

Allocation at allocation point 1, which corresponds to the farm gate, has the largest impact on the overall climate change impact potential of the three allocation points when considered separately, reducing the climate change impact potential of hemp biodiesel production from 0.137 kg CO_2-e MJ^{-1} to around 0.033 kg CO_2-e MJ^{-1}, depending on the allocation method used. At allocation points 2 and 3 the climate change impact potential is reduced by 0.0756 kg CO_2-e MJ^{-1} and 0.0105 kg CO_2-e MJ^{-1} respectively for allocation only at those points, or 0.119 kg CO_2-e MJ^{-1} and 0.120 kg CO_2-e MJ^{-1} when all cumulative allocations are taken into account.

When all three allocation points are included, the climate change impact potential is reduced to 0.0210 kg CO_2-e MJ^{-1} (15.3 % of the default case result) by energy allocation, 0.0176 kg CO_2-e MJ^{-1} (12.8 %) by allocation according to carbon content, and 0.0122 kg CO_2-e MJ^{-1} (8.9 %) by mass allocation (Fig. 6.6).

The contributions from the individual subprocesses are affected according to the number of

Allocation method	Product 1	Product 2	Product 3
Allocation point 1	*Seed*	*Straw*	
Mass	0.1667	0.8333	
Energy	0.2151	0.7849	
Carbon content	0.1822	0.8178	
Allocation point 2	*Oil*	*Presscake*	
Mass	0.305	0.695	
Energy	0.5175	0.4825	
Carbon content	0.4555	0.5445	
Allocation point 3	*Biodiesel*	*Glycerol*	*Potassium salts*
Mass	0.8881	0.0969	0.0150
Energy	0.9328	0.0672	–
Carbon content	0.9475	0.0525	–

Table 6.10: Allocation ratios in the hemp biodiesel life cycle.

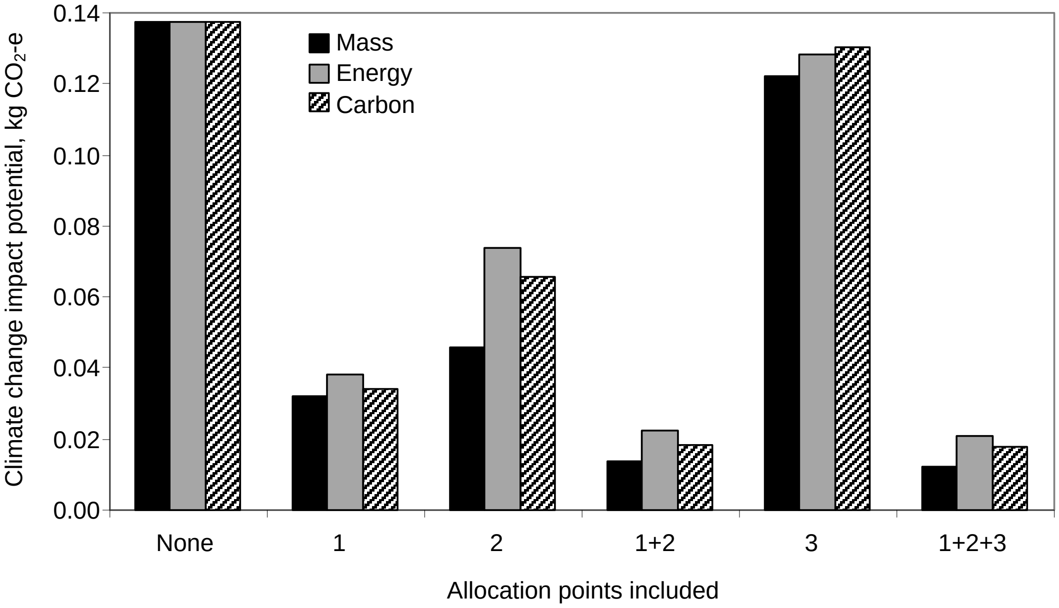


Figure 6.6: Comparison of climate change impact potential for the production of 1 MJ hemp biodiesel, with allocation by mass, energy and carbon content of the product and co-products, with allocation at selected allocation points

allocation points that they are allocated at (Fig. 6.7). The data are arranged in ascending order of magnitude in the default case in Fig. 6.7. The contributions from the agricultural subprocesses are affected the most, with reductions of 90–95 % from their contributions in the default case in which all contributions are allocated to hemp biodiesel. By comparison, the subprocesses in the tranesterification stage are reduced by 5–11 %, depending on the allocation method.

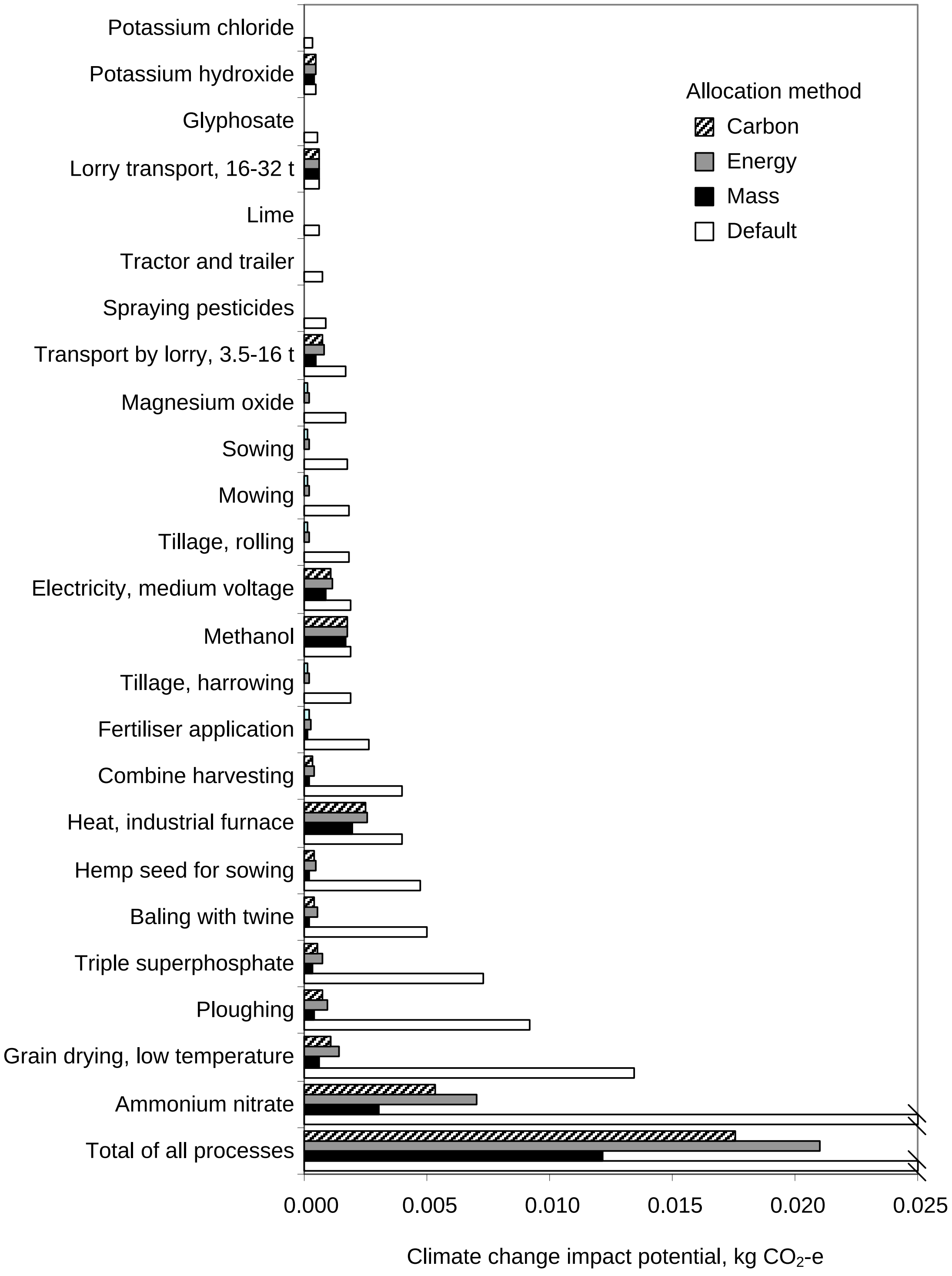


Figure 6.7: Effect of allocation by three different methods on the climate change impact potential contributions from subprocesses in the life cycle of 1 MJ hemp biodiesel. The default allocation method attributes all contributions to the hemp biodiesel. The two truncated processes can be seen in full in Fig. 6.4

6.4.3 CO_2 absorption and emission

Up to this point in the impact assessment, the CO_2 absorption during plant growth and emission during fuel combustion have been excluded from the impact assessment calculations on the grounds that these processes are generally excluded in biodiesel LCAs (Section 4.2.8). However, as discussed in Chapter 5, the straw co-product of hemp seed is produced in significant quantities per hectare and can be put to many uses. Thus hemp straw can act as a carbon store, at least for a number of years or a small number of decades, and the inclusion of CO_2 absorption during plant growth is therefore included in the present LCA. For balance, the emission of CO_2 from combustion of the fuel in a vehicle engine is also included.

The absorption of CO_2 during the growth of hemp plants was calculated as 1.90 kg CO_2 per 1 kg of seed and 1.71 kg CO_2 per 1 kg straw. In the production of 1 MJ hemp biodiesel, the hemp plant absorbs 0.163 kg CO_2 into the seeds and 0.733 CO_2 into the straw, assuming the default yield values of 1100 and 5500 kg ha^{-1} for seed and straw respectively. For every 1 MJ hemp biodiesel produced, the total plant storage of carbon dioxide is 0.896 kg (Fig. 6.8). The uptake of CO_2 is almost seven times greater in the case of both seed and straw uptakes than the release of greenhouse gas emissions from the production processes (0.137 kg CO_2-e MJ^{-1}).

Combustion of hemp biodiesel releases CO_2 as well as nitrogen oxides into the atmosphere (Section 6.3.5), with a total greenhouse gas emission of 0.0745 kg CO_2-e per 1 MJ of hemp biodiesel at this stage of the life cycle.

The absorption and emissions of CO_2 during the growth of the hemp plant and the combustion of the hemp biodiesel can be included in the life cycle assessment in different combinations (Fig.6.8). Option 1 in Fig.6.8 shows the default values, which include neither plant growth CO_2 absorption nor CO_2 emissions from fuel combustion. When the life cycle is extended to include both CO_2 absorption during plant growth and CO_2 emissions during biodiesel combustion, the overall climate change impact potential of 1 MJ hemp biodiesel is -0.684 kg CO_2-e which is a net reduction overall in the atmospheric greenhouse gas levels (4 in Fig.6.8). Other combinations of included or excluded emissions and absorptions lead to climate change impact potentials in the range -0.759 to 0.212 kg CO_2-e MJ^{-1} for hemp biodiesel.

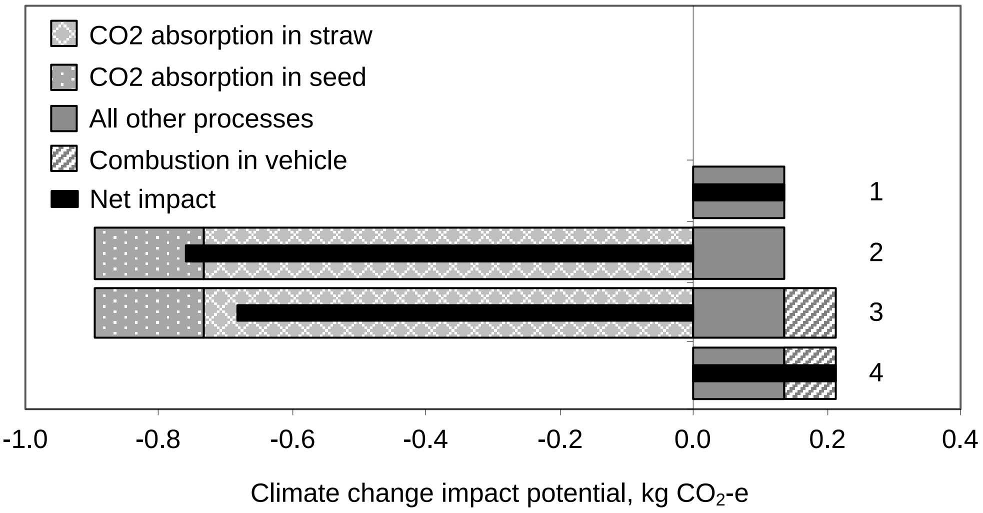


Figure 6.8: Effect of including carbon dioxide absorption during hemp plant growth and combustion of biodiesel in a vehicle engine on the overall climate change impact potential of 1 MJ hemp biodiesel, with all impacts allocated to hemp biodiesel. The four CO_2-handling scenarios are: 1 - plant absorption of CO_2 and vehicle combustion of fuel excluded; 2 - plant absorption of CO_2 included, vehicle combustion of fuel excluded; 3 - plant absorption of CO_2 and vehicle combustion of fuel included; 4 - plant absorption of CO_2 excluded, vehicle combustion of fuel included.

The hemp plant absorbs more CO_2 during its growth than is emitted from the combustion of hemp biodiesel in a vehicle (Fig. 6.8, scenario 3). The hemp oil from which the biodiesel is produced represents 5 % of the total biomass grown in the field. Therefore, if the other parts of the hemp plant are not combusted or allowed to decay, the CO_2 stored in the rest of the hemp plant far outweighs the emissions from combustion of the hemp biodiesel and emissions during the production of hemp biodiesel combined.

The CO_2 absorption and emission scenarios (Fig. 6.8) were combined with the mass, energy and carbon content allocation methods was applied in the calculation of climate change impact potential results, for four scenarios which included or excluded CO_2 absorption by plants and/or emissions from biodiesel combustion in a vehicle (Fig. 6.9). The allocation methods affect the results which include CO_2 absorption by plants or emissions from vehicles more strongly than the results without these subprocesses included. In scenario 3, which includes both CO_2 absorption by plants and CO_2 emissions during combustion in a vehicle, the choice of allocation method affects the results by a factor of 19, with the energy allocation result at 0.00244 kg CO_2-e while the mass allocation result is 0.0462 kg CO_2-e (Fig. 6.9)

Scenarios 1 and 3 handle the CO_2 absorption by plants and emissions during combustion in a vehicle in the same way, with both subprocesses excluded in scenario 1 and both included in scenario 3. These two scenarios are selected for further investigation on the basis of their equivalent treatments of CO_2 absorption and emissions processes.

The climate change impact potential contributions from agricultural and industrial subprocesses in the production of 1 MJ hemp biodiesel are dwarfed by the CO_2 absorption during plant growth and CO_2 emissions in combustion of the fuel in a vehicle (Fig. 6.10).

Since the usual practice in biodiesel LCAs is to omit CO_2 absorption in plant growth and CO_2 emissions from fuel combustion, the following sections exclude these processes in order to obtain results which are comparable with results from other biodiesel LCAs.

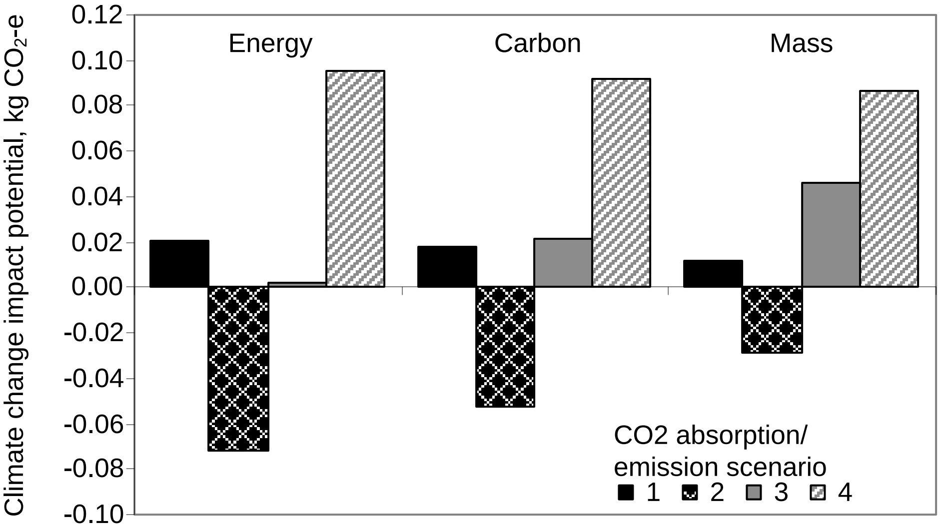


Figure 6.9: Net impact assessment results for 1 MJ hemp biodiesel under three allocation methods and with four CO_2 handling scenarios: 1 - plant absorption of CO_2 and vehicle combustion of fuel excluded; 2 - plant absorption of CO_2 included, vehicle combustion of fuel excluded; 3 - plant absorption of CO_2 and vehicle combustion of fuel included; 4 - plant absorption of CO_2 excluded, vehicle combustion of fuel included.

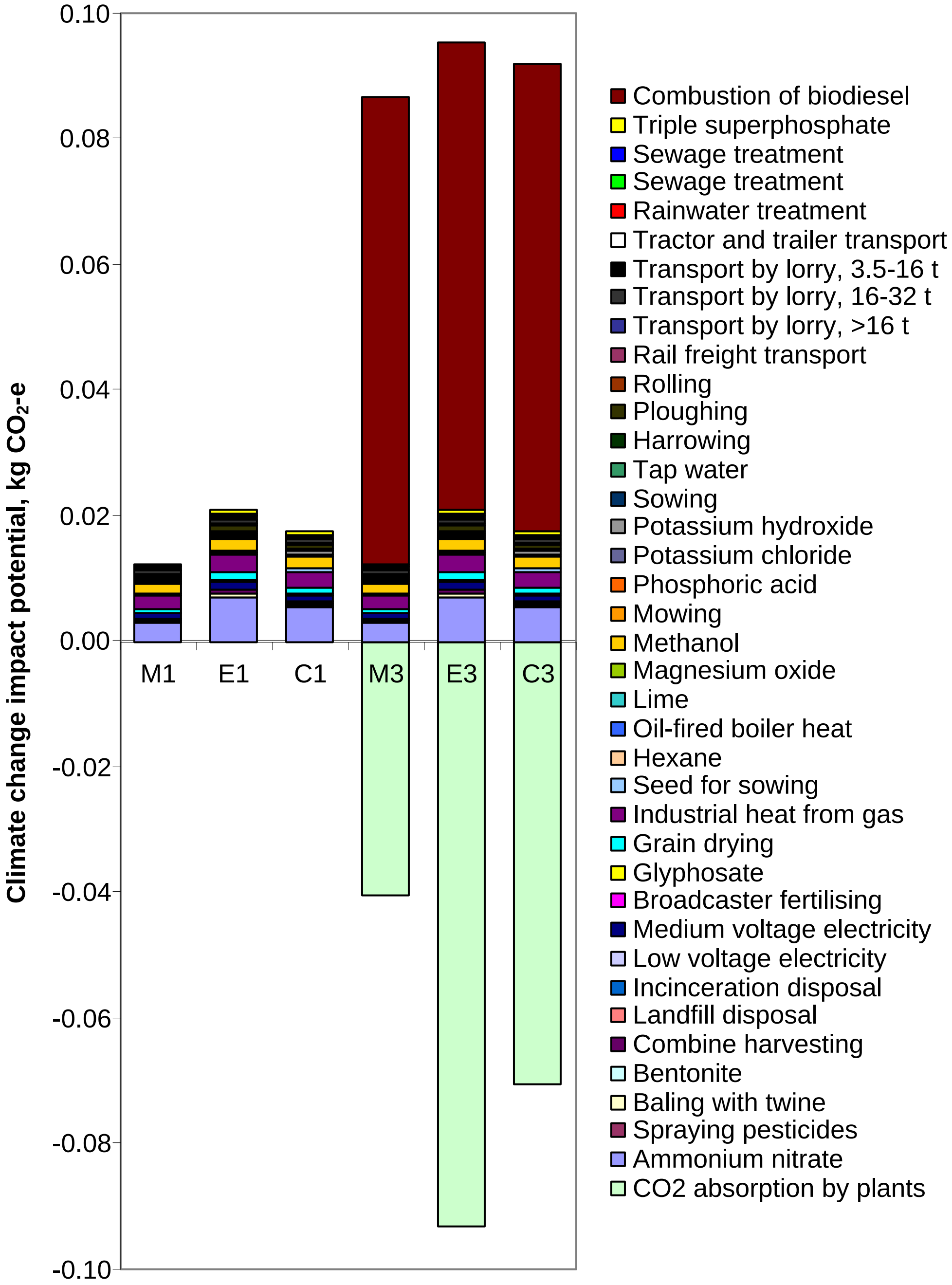


Figure 6.10: Climate change impact potential contributions from subprocesses in production and use of 1 MJ hemp biodiesel. Each scenario is labeled with a two-part code. The letters E, M and C represent energy content, mass and carbon content allocation methods. The numbers 1 and 3 represent the CO_2-handling scenario: 1 - plant absorption of CO_2 and vehicle combustion of fuel excluded; 3 - plant absorption of CO_2 and vehicle combustion of fuel included.

6.4.4 Sensitivity analysis of fertiliser application

The effects on the climate change impact potential of hemp biodiesel of changes in the type and quantity of fertiliser was analysed. The climate change impact potential was calculated for each of five levels of nitrogen fertiliser application, assuming no change in the number of field operations to apply the fertiliser. Changes in seed yield as a result of changes in the nitrogen fertiliser application rate were estimated using data from Amaducci et al. (2002). In their work, Amaducci et al. (2002) reported that the dry matter yield from hemp increased by 20 kg ha^{-1} for each additional 1 kg ha^{-1} nitrogen fertiliser over the base application rate of 100 kg ha^{-1}. This is equivalent to a proportional change in the yield of 0.2 % for each extra 1 kg ha^{-1} nitrogen fertiliser. No data that were specific to hemp seed yields were found in the literature, therefore the proportional change is assumed to hold true for seed as well as straw in this instance.

The results of the sensitivity analysis on the nitrogen fertiliser application rate (Fig.6.11) show that the climate change impact potential of the ammonium nitrate fertiliser varies linearly with the application rate when the seed yield is unchanging (1100 kg ha^{-1}). However, when the seed yield increases with nitrogen application rate, the global warming potential increases more slowly with nitrogen fertiliser application rate as the effects of increasing in fertiliser application rate are countered by the increase in seed yield. At an application rate of 150 kg ha^{-1}, the seed yield is increased to 1210 kg ha^{-1} and therefore the fertiliser per 1 kg of seed yield is 0.124 kg, whereas with a seed yield of 1100 kg ha^{-1}, the fertiliser application rate per 1 kg of seed yield is 0.136 kg.

Although Squier (2010a) reported a typical fertiliser application of 100 kg ha^{-1}, Bócsa and Karus (1998) reported a range of 100-125 kg ha^{-1}. Increasing the fertiliser application rate to 125 kg ha^{-1}, and compensating with the estimated seed yield increase calculated from Amaducci et al. (2002), the increase in the climate change impact potential associated with fertiliser use is of the order of 19 %. This increase in the impacts from the nitrogen fertiliser results in an overall increase of 0.0112 kg CO_2-e or 8.2 % from the default scenario of the production and supply of 1 MJ hemp biodiesel (Section 6.4.1).

The case study farm uses ammonium nitrate to provide nitrogen to the hemp crop. However, other nitrogen fertilisers are available and the climate change impacts of the production of the

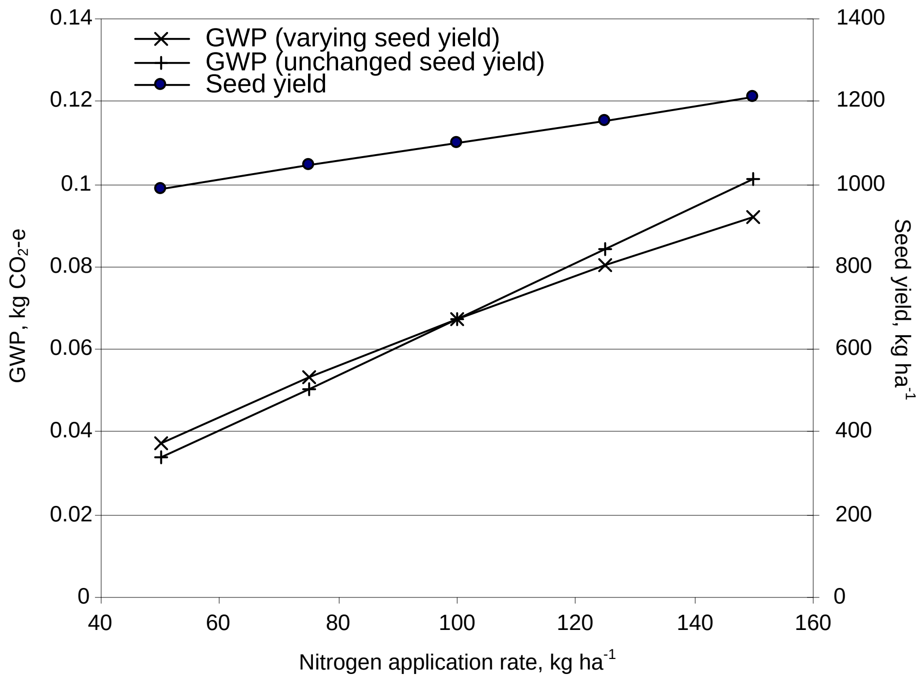


Figure 6.11: Global warming potential from the application of ammonium nitrate fertiliser in the production of 1 MJ hemp biodiesel

quantity required to produce 1 MJ hemp biodiesel in the default scenario, 0.00780 kg, of different fertilisers were calculated from database values (ecoinvent Centre, 2009) and compared (Figure 6.12).

Ammonium sulphate has the lowest impacts (0.0218 kg CO_2-e) of all the fertilisers compared in Fig. 6.12, which have an average climate change impact potential of 0.0387 kg CO_2-e per 0.00780 kg. Urea is one of the lower impact fertilisers (0.0264 kg CO_2-e) while ammonium nitrate, which is used on the case study farm, is one of the higher impact fertilisers (0.0679 kg CO_2-e), only surpassed by calcium ammonium nitrate (0.0688 kg CO_2-e). Both ammonium nitrate and calcium nitrate fertilisers make a greater contribution to the overall climate change impact potential associated with cultivating and harvesting hemp than all other contributing processes combined (0.0584 kg CO_2-e).

As noted in Chapter 5, the natural potassium level in the soil on the case study farm is high, leading to a much lower potassium fertiliser application rate than on average UK farms. The UK farm average potassium application rate is approximately ten times higher than that used on

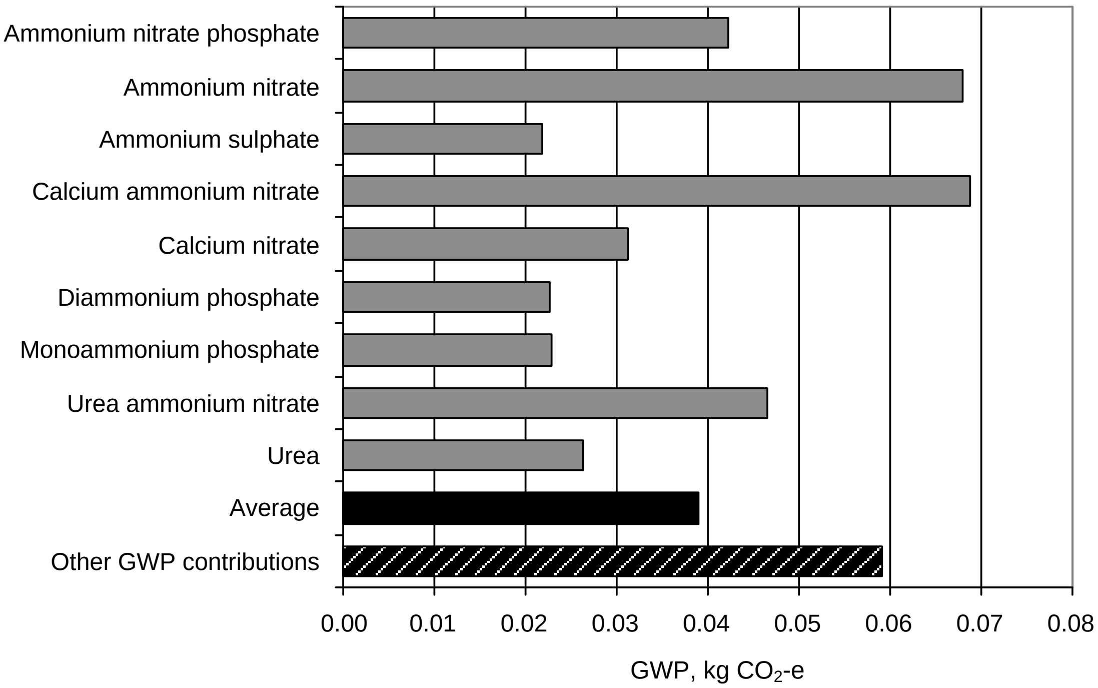


Figure 6.12: Comparison of climate change impact potentials of 0.00780 kg nitrogen fertilisers. The total climate change impact potential contributions from other operations and applications to hemp cultivation and harvesting are shown for comparison.

the case study farm, whereas the application rate recommended by Bócsa and Karus (1998) is approximately twenty times the default application rate. A sensitivity analysis of the unallocated climate change impact potential to ten- and twenty-fold increases in the potassium application rate was carried out. The climate change impact potential increased linearly with application rate from 0.000347 kg CO_2-e for the default case to 0.00347 kg CO_2-e and 0.00693 kg CO_2-e for ten- and twenty-fold increases respectively. These three results represent 0.2 %, 2.5 % and 4.9 % of the total contributions of all processes. With allocation, these results are reduced by up to 95 % (Section 6.4.2) and after such reductions the changes in climate change impact potential according to the application rate of potassium fertiliser is negligible.

6.4.5 Sensitivity to changes in conversion factors

The conversion factors (Table 6.9) were subjected to a sensitivity test. The maximum and minimum values for each conversion factor were used in the calculation of the overall life cycle climate change impact potential for 1 MJ hemp biodiesel (Fig. 6.13). Next, calculations were made of the climate change impact potential when all of the conversion factors were at their minimum or at their maximum values.

In all cases, the minimum conversion factor values were found to result in increased climate change impact potential, and the maximum conversion factor values in decreased climate change impact potential. The conversion factors are therefore measures of the efficiencies between the processes.

The most significant decreases in the climate change impact potential were the result of increased seed yield and increased oil content of hemp seeds. Increasing the seed yield to 1200 kg ha^{-1} results in a 6.9 % decrease in the climate change impact potential to 0.128 kg CO_2-e per 1 MJ of hemp biodiesel. Increasing the oil content of hemp seeds to 37.5 % results in a decrease in the climate change impact potential of 14.7 % to 0.117 kg CO_2-e per 1 MJ of hemp biodiesel. These two improvements in the seed quantity and quality combine to make a total of a 20.5 % decrease in the climate change impact potential, to 0.109 kg CO_2-e per 1 MJ of hemp biodiesel. Conversely, decreases in the two conversion factors of seed yield and seed oil content are significant causes of increases in the climate change impact potential, as are the transesterification conversion rate and the efficiency of extracting oil from the seeds.

Reductions in the climate change impact potential range from 0.0–14.7 % with an average of 3.8 %, while increases in the climate change impact potential are in the range 0.8–19.5 % with an average of 8.2 % (Fig. 6.13). This reflects the nature of the changes in the conversion factors: most of the conversion factors are already very high, therefore there is slight room for improvement through a reduction in the climate change impact potential, whereas there is much more scope for inefficiencies to arise in the system and hence increase the impact.

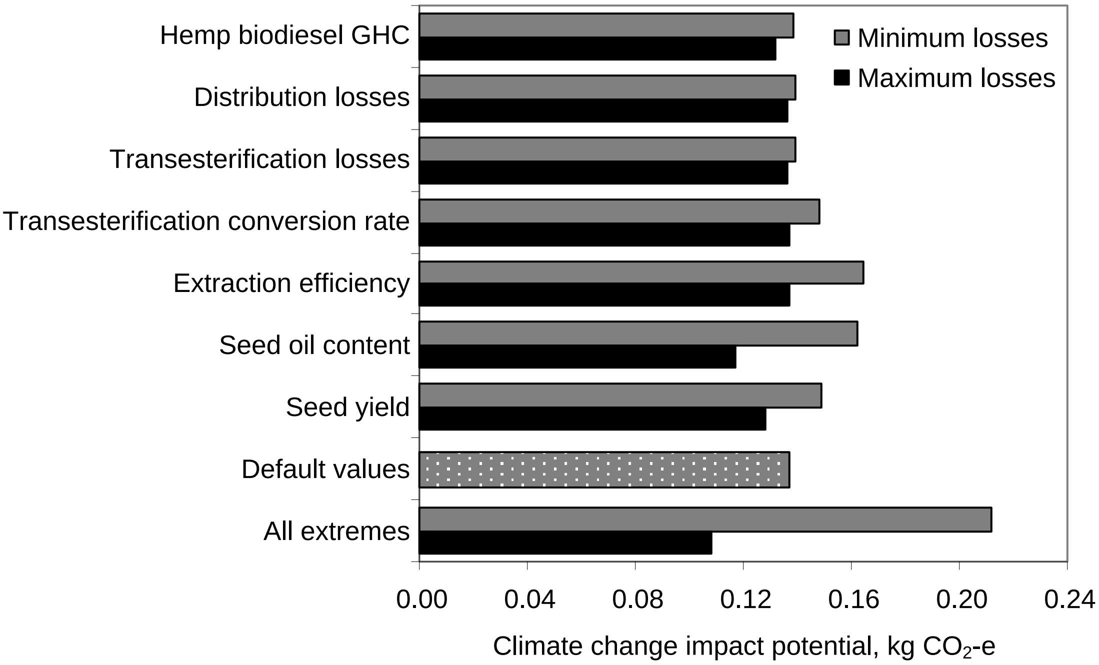


Figure 6.13: Sensitivity of climate change impact potential result to changes in conversion factors in the hemp biodiesel life cycle. Minimum and maximum losses correspond to minimum and maximum conversion factors (Table 6.9).

6.5 Interpretation of LCA results

In order to address Aim 6 of this thesis (to evaluate the net climate change impact potential of producing biodiesel from hemp biodiesel grown in the UK), the following questions were posed in the goal and scope of this life cycle assessment (Section 6.1):

1. What is the potential climate change impact of the production of biodiesel from hemp oil?
2. How does the potential climate change impact of biodiesel from hemp oil compare with the impacts of biodiesel from rapeseed oil and fossil diesel?
3. What are the implications for UK greenhouse gas emissions of growing hemp for biodiesel in the UK?

These questions are now addressed, drawing on the LCA inventory and impact assessment results (Sections 6.3 and 6.4).

6.5.1 Climate change impact potential of producing hemp biodiesel

This research found the net climate change impact potential of producing hemp biodiesel to be 0.137 kg CO_2-e MJ^{-1} in the default scenario (Fig. 6.14). However, this result is significantly affected by the allocation methodology adopted in the life cycle assessment (Section 6.4.2), the boundaries used to define the system (Section 6.4.3), and by the values used (Sections 6.4.4 and 6.4.5).

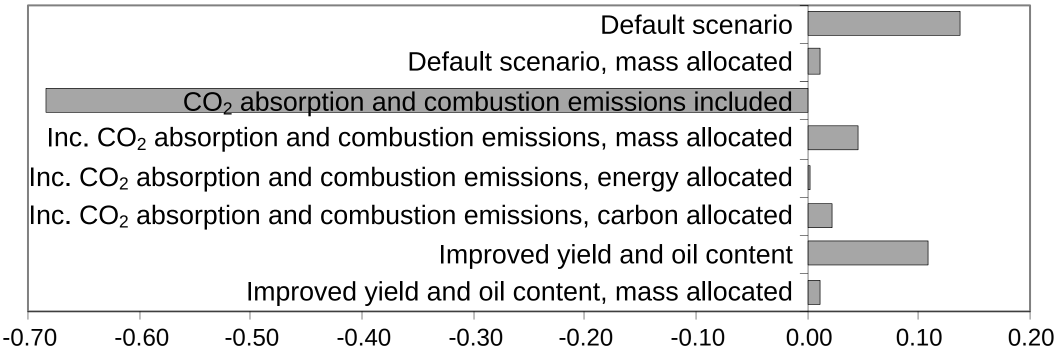


Figure 6.14: Summary of LCA results for hemp biodiesel

When all the impacts are allocated to hemp biodiesel, the environmental impacts of cultivating and harvesting hemp accounted for 91.9 % of the overall life cycle climate change impact potential (Fig. 6.3). These findings concur with those of Bernesson et al. (2004), who reported that the environmental impacts of the cultivation phase were most significant in the production of biodiesel from oilseed rape and in particular the contributions from the production of fertilisers, soil emissions and tractive power.

The most significant contribution from a single subprocess in the life cycle to the climate change impact potential came from the ammonium nitrate fertiliser application, regardless of the allocation method applied. A sensitivity analysis revealed that a 25 % increase in the application rate of ammonium nitrate produced a 19 % increase in the overall climate change impact potential of producing hemp biodiesel, when all impacts are allocated to hemp biodiesel. The sensitivity of the life cycle impact to the fertiliser application rate is reduced by allocating the impacts between the product and co-products.

The subprocesses in the production of nitrogen fertilisers which contribute the most to the overall climate change impact potential are the production of ammonia through steam reforming, and the production of nitric acid. These processes are energy intensive and also release nitrogen oxide emissions. Biosolids are a viable alternative to inorganic mineral fertilisers for use on hemp (Section 5.3.2) with the advantage over mineral fertilisers of not requiring the reformation of nitrogen products. Further, biosolids are also rich in phosphates and their application therefore removes the requirement for mineral phosphate fertilisers as well. However, life cycle inventory data are not available for biosolids at the time of writing, so a comparison between the application of biosolids and fertilisers cannot be made in this thesis.

The unusually low requirement on the case study farm for potassium applications was also tested using sensitivity analysis and compared with average data for the UK and literature data for hemp cultivation in general. The contribution to the climate change impact potential of potassium fertiliser was found to be low (0.2 %) in the case study and more significant at higher application rates. However, the allocation of the impacts between the hemp biodiesel product and all co-products of the system acted on these contributions such that they became negligible, unlike the impacts from nitrogen fertilisers which are much higher.

In this thesis, the production of hemp seed for sowing was found to contribute 0.0048 kg CO_2-e to the climate change impact potential of the production of 1 MJ hemp biodiesel, with all contributions allocated to the hemp biodiesel. This represents 3.5 % of the total climate change impact potential for hemp biodiesel. However, under allocation the production of seed for sowing contributes less than 1 % of the total climate change impact potential and can therefore be regarded as insignificant in the allocated LCA results, thus confirming the recommendation made by Bauen et al. (2008) for the Renewable Transport Fuels Obligation carbon reporting methodology in which the contribution of seed production for sowing for biodiesel crop cultivation is systematically excluded from the life cycle system.

This research found that choices in the methodology concerning allocation and the setting of boundaries to include or exclude CO_2 absorption by plants and emission during biodiesel combustion in vehicles significantly affected the results of the life cycle assessment (Fig. 6.14).

The application of different methods of allocation between the product and co-products reduced the climate change impact potential by up to 91.1 % (Section 6.4.2). The three allocation methods tested in this thesis produced similar overall effects on the impact potential results, varying by 0.0083 kg CO_2-e (6 % of the default case) when all three allocation points (farm gate, oil mill gate and esterification plant gate) are included. Allocation is identified in the literature as a significant influence on the results of biodiesel life cycle assessments (Section 4.2.9) and the current LCA is no exception.

The boundaries of the life cycle assessment were drawn in two ways with regard to the direct CO_2 absorption during plant growth and the emission during fuel combustion. The net balance of CO_2-e in the hemp biodiesel life cycle depends on both the uptake and release of CO_2 by the plant, as well as the emissions of greenhouse gases during the agricultural and industrial stages of the life cycle. If the analysis assumes that all CO_2 stored in the hemp straw is kept in the straw and not combusted or allowed to decay, the climate change impact potential is reduced significantly, and actually becomes a net absorption of CO_2 from the atmosphere of -0.684 kg CO_2-e MJ^{-1}. This net decrease in atmospheric greenhouse gas concentrations indicates a potential climate change mitigation strategy through the use of hemp biodiesel in place of petroleum diesel and CO_2 storage in hemp straw.

The fate of carbon stored in the co-products, straw, presscake and glycerol, would influence the net results if they were included in the system. However, in the system defined for this life cycle assessment the boundaries are set at the point at which co-products are released into the technosphere for storage or use. At that point, the CO_2 absorbed during the hemp's growth stage is still present in the presscake, glycerol and straw at the system boundary and hence the fates of the co-products are not included in this life cycle assessment. However, if all carbon that is stored in the hemp plant during its growth is emitted as carbon dioxide through the combustion or decay of hemp biodiesel and its co-products, the net climate change impact potential of the production of hemp biodiesel is the sum of the agricultural and industrial processes that occur during the biodiesel life cycle, 0.137 kg CO_2-e per 1 MJ of hemp biodiesel. If hemp straw were to replace fossil fuels in electricity or heat generation, the release of additional fossil CO_2 to the atmosphere would be avoided. Further research and quantification of the environmental impacts of hemp straw products would be a useful complement to the work of this thesis.

The choices of whether or not to allocate the impacts to the co-products, and the inclusion or otherwise of the direct CO_2 absorption during plant growth and emissions during combustion are the most significant in this life cycle assessment. This finding indicates that transparency in reporting the methods selected in a life cycle assessment of biodiesel is important in order to provide sufficient information to make fair comparisons between results from different studies. Further changes to the overall result arise from changes in the quantities assumed during the life cycle, particularly the fertiliser applications, as discussed above, and the conversion factors selected to connect the life cycle stages.

The results of the sensitivity analysis of the conversion factors that connect the life cycle stages revealed that when seed oil content is increased to 37.5 % from 31.5 % and seed yield increased to 1200 kg ha^{-1} from 1100 kg ha^{-1}, a 20 % reduction in the climate change impact potential from hemp biodiesel production. It has been suggested that seed yield up to 2000 kg ha^{-1} may be possible (Casas and Rieradevall i Pons, 2005), which would reduce the climate change impact potential of hemp biodiesel even further than indicated by the sensitivity analysis.

Accuracy of study

The data collected through interviews and email exchanges on the cultivation and harvesting of dual-purpose hemp (Squier, 2008, 2010a) are assumed to be complete for the purposes of this LCA. However, some inputs or outputs may have been overlooked. For the most part, the data obtained from the case study farm corresponds well with published data (Bócsa and Karus, 1998; Turunen and van der Werf, 2006), thereby supporting the assumption that the collected data are complete.

The accuracy of the quantities of chemicals reported by Squier (2008) is unknown. The actual application rates of fertilisers, pesticides and seed for sowing may vary by a small number of kilograms per hectare, depending on the accuracy of the handling equipment used. As identified earlier, changes in the rate of nitrogen fertiliser application to the crop affect the overall climate change impact potential. However, to effect a significant change in the impact potential of, say, more than 10 %, an inaccuracy of around 15 % in the fertiliser application would be required, and such a large inaccuracy is unlikely given the stringent regulations on fertiliser applications that demand good measuring equipment on farms.

Experimental data on the oil content of hemp seeds (Section 5.4.3) were used to adapt published data on oil extraction rates and oil mill processes (ecoinvent Centre, 2009). Data on the efficiency of the oil extraction process were derived from results published by Stephenson et al. (2008). Overall, the inaccuracies in the data for the oil extraction processes are likely to be within the range of conversion factor values tested (Section 6.4.5), and close to the default values used with little consequence for the climate change impact potential of the whole life cycle. The inaccuracies in this stage of the life cycle are much less significant than the effects of methodological choices for allocation or CO_2 boundaries.

The industrial process to convert hemp oil into biodiesel was assumed to have the same inputs and outputs as the process to produce rape seed oil biodiesel (ecoinvent Centre, 2009). This assumption was based on the very small, or zero, variation in the biodiesel production process after the delivery of vegetable oil to the esterification plant. However, this assumption does not account for the higher degree of unsaturation in the hemp oil which may need additional treatment in order to produce biodiesel with the required oxidative stability and iodine number properties (Yang et al., 2010).

Data on transport and distribution of biodiesels were calculated for typical freight modes and distances in Switzerland (ecoinvent Centre, 2009). The distribution centre data, on emissions to sewage works and water treatment are also from Swiss data. The combined contribution of these processes in the default case is 7.09×10^{-4} kg CO_2-e per 1 MJ hemp biodiesel, representing 0.5 % of the total climate change impact potential. However, when the life cycle impacts are allocated, these processes are more significant since there are no co-products at this stage of the life cycle. When allocated by mass these processes contribute 5.8 %, or 3.4 % allocated by energy content, or 4.0 % allocated by carbon content. At these low proportions, changes in the transport and distribution data are unlikely to have a significant effect on the overall results of the life cycle impact assessment calculation, with any of the three allocation methods applied.

In summary, the accuracy of the data collected is sufficient for the purposes of the present LCA, which has the objective of quantifying the likely climate change impact potential of producing hemp biodiesel from hemp seed grown in the UK. Life cycle assessment results, as discussed in Chapter 4, are not generally extensible to other product systems because of variations in geography, time and exact details of the processes involved. Therefore the results of this LCA should be treated as reliable for biodiesel produced from hemp seed grown on the case study farm from which data were obtained, and indicative for hemp biodiesel from other sources.

6.5.2 Comparison of hemp biodiesel with other diesel fuels

In this analysis of the climate change impacts from hemp biodiesel, a comparison with rapeseed and used vegetable oil biodiesels found that hemp oil, with no allocation to co-products, results in the highest climate change impact potential (Fig. 6.15). Rapeseed methyl ester (ecoinvent Centre, 2009) has less than half the impact associated with hemp biodiesel, and used vegetable oil biodiesel, having no agricultural production or oil extraction processes, has even less impact at 5 % of the impact of hemp biodiesel. However, the impacts associated with hemp biodiesel are significantly reduced through allocation by mass ratios (Section 6.4.2) to less than the impacts for rapeseed biodiesel, even when the rapeseed biodiesel impacts are allocated by mass in the same manner as the hemp biodiesel impacts were.

The results obtained through the life cycle assessment in this chapter (Fig. 6.15) show a wide variation depending on the methodology selected. The default scenario in this LCA has a higher results than all other biodiesels, with the exception of unallocated sunflower oil biodiesel (Chiaramonti and Recchia, 2010). The effect of allocation observed in this thesis is similar to the wide range of results in Chiaramonti and Recchia (2010) who also addressed the issue of variable allocation procedures. The allocation of impacts using mass, energy or carbon content methods reduces the impacts from hemp biodiesel to a level which is comparable with the impacts associated with biodiesels from tallow and used oils, feedstocks which have no associated production chain impacts since the feedstock is classified as a waste stream from another production process. Furthermore, when the processes of CO_2 absorption and emission are included, without allocating the impacts, the advantage of hemp biodiesel is clear in its much larger and negative overall climate change impact potential.

Selecting comparable results, obtained through similar methods which include mass allocation and inclusion of fossil diesel combustion emissions, show that hemp biodiesel is not only comparable with other vegetable-oil biodiesels, but also meets the EU Renewable Energy Directive (European Parliament and the Council of the European Union, 2009) criterion for sustainability: a reduction of at least 35 % when compared with petroleum diesel emissions (Fig. 6.16).

When the impacts of hemp biodiesel, including CO_2 absorption and emission, are allocated by mass, energy or carbon content, the results vary from 0.0024–0.0462 kg CO_2-e MJ^{-1} and are less than most of the rapeseed biodiesel results. The data collected in Chapter 5 on the cultivation of hemp and rape seed showed that rape seed requires a higher input of chemicals than hemp, and the consequence is revealed here in the higher climate change impact potential for the life cycle of the rape seed biodiesel compared with the hemp biodiesel.

The mass-allocated hemp biodiesel life cycle climate change impact potential is slightly higher than all of the values for petroleum diesel (Fig. 6.15), except for those of Edwards et al. (2007) and Niederl and Narodoslawsky (2004) which were previously identified as including the combustion emissions as well as production emissions. Therefore, the production of hemp biodiesel has a greater emissions of greenhouse gases than the production of petroleum diesel, when CO_2

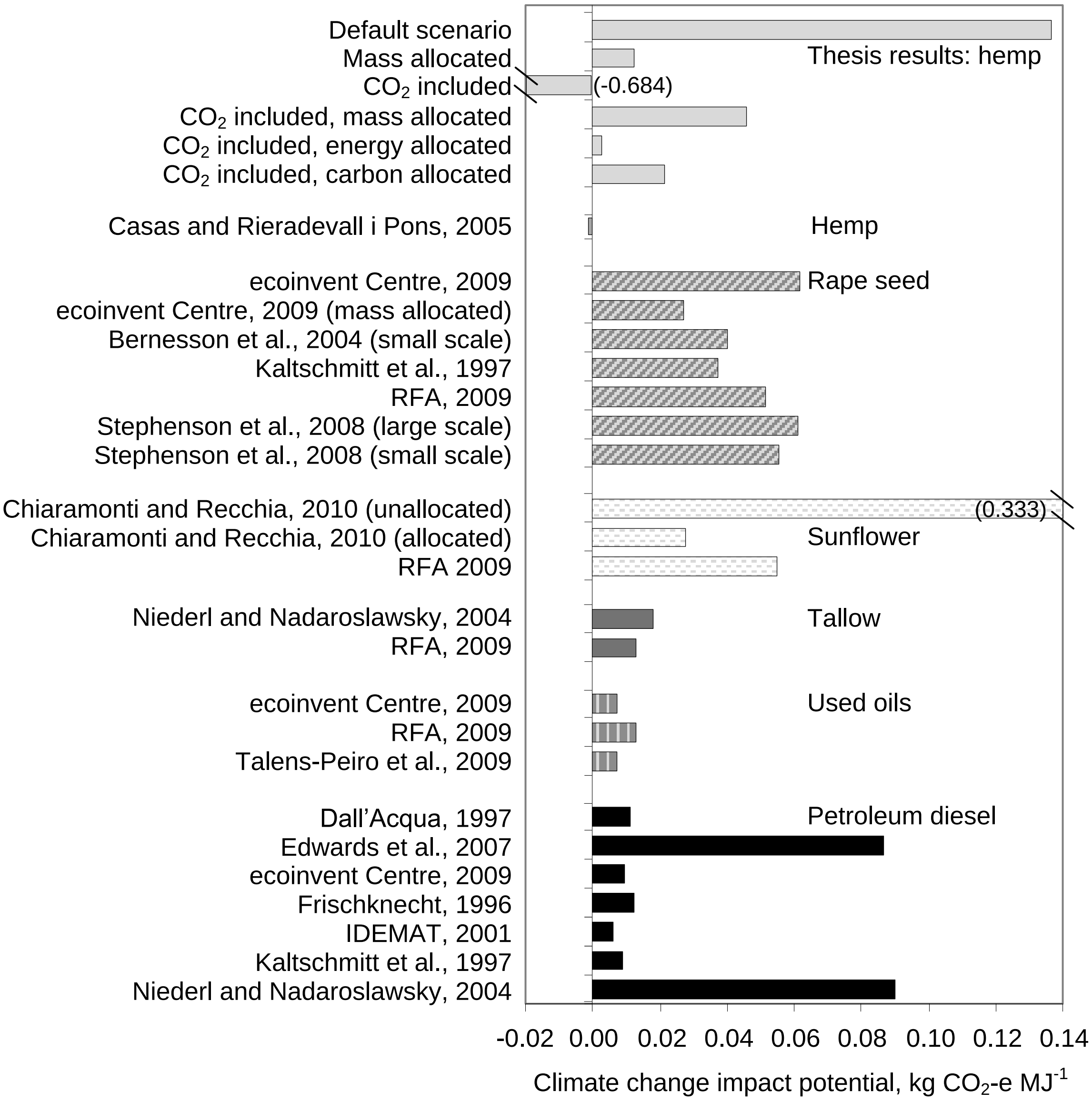


Figure 6.15: Comparison of climate change impact potential of 1 MJ biodiesel from different feedstocks. Selected results from this thesis are shown to illustrate the range of results that arises from different methodology choices.

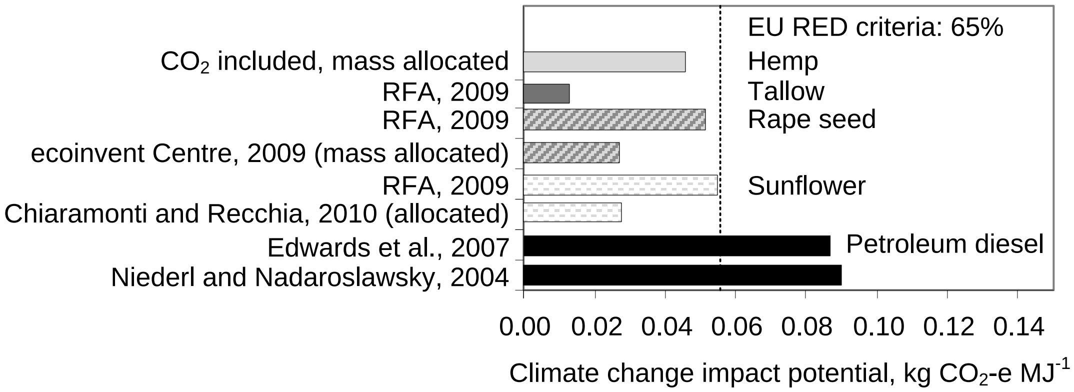


Figure 6.16: Comparison of selected and comparable climate change impact potential result for 1 MJ biodiesel from different feedstocks. The dashed line indicates a reduction of 35 % from the petroleum diesel emissions, the EU Renewable Energy Directive criterion for sustainability.

absorption and combustion emissions are excluded from the life cycle assessment.

When CO_2 absorption is included in the calculations of the hemp biodiesel life cycle assessment, and combustion emissions are included for both hemp biodiesel and petroleum diesel, the hemp biodiesel has lower associated climate change impact potential than the petroleum diesels, even when any of the four allocation methods is applied. This result highlights the importance of including all input and output data for CO_2 to the atmosphere, since in the standard procedure of producing petroleum diesel no CO_2 is absorbed, whereas in cultivating oilseed crops, significant quantities of CO_2 can be absorbed for later release or, in some cases, storage.

6.5.3 Implications for UK greenhouse gas emissions of growing hemp for biodiesel in the UK

The results from the life cycle assessment of hemp biodiesel in this thesis showed that, in the unallocated scenario, the main greenhouse gas emissions arise in the agricultural operations and the application of mineral fertiliser in particular. In the UK emissions inventory (National Atmospheric Emissions Inventory, 2009), these emissions are accounted for in the industry and agriculture categories. However, when fertilisers are produced outside of the UK, the emissions associated with their production are not included in the UK's emissions inventory. The life cycle assessment approach takes a more holistic, system-based view of production processes, with their associated causal connections, than the emissions inventory does.

When hemp is integrated into an arable farm's rotation system, the overall demand for fertiliser and for field operations is reduced for the whole system. Furthermore, as noted in Chapter 5, the machinery requirements of a farm can be reduced since field operations are fewer in number and spread more evenly through the year than in a standard six-year cereal rotation. If many arable farms in the UK were to adopt hemp as a standard crop in their cereal rotations, the throughput of tractors and so forth in the agricultural sector in the UK may be marginally reduced, and hence the industrial emissions associated with the reduced production levels of those tractors would also decrease, assuming that the demand for tractors did not increase elsewhere.

If the production of hemp biodiesel in the UK results in additional capacity alongside existing biodiesel production facilities, the greenhouse gas emissions from the industrial sector will increase. However, since at present much of the UK's biodiesel supply is imported (Renewable Fuels Agency, 2009b), the domestic production of biodiesel is unlikely to increase within the timeframe set by the Renewable Transport Fuels Obligation, and therefore industrial emissions from biodiesel production are likely to remain at their current levels even if hemp is introduced as a feedstock.

It is interesting to note that in the transport sector, the tailpipe emissions from the combustion of biodiesel and petroleum diesel are very similar and therefore emissions from road transport will remain constant provided that the overall rate of consumption of petroleum-based transport fuels remains constant. Only if the quantities of fuel consumed are reduced, perhaps through the application of alternative options for road transport policy (Section 2.3), will the tailpipe emissions be reduced.

From the perspective of the atmosphere itself, the use of hemp biodiesel in place of petroleum diesel will have a net effect of reducing atmospheric CO_2 concentrations, however slightly, since the amount of CO_2 absorbed by the whole plant during its growth far exceeds the CO_2 used during the production and combustion of hemp biodiesel. This is true provided that the straw co-product is not burned or allowed to decay, thereby emitting either CO_2 or CH_4, but stored in solid materials such as building blocks or insulation panels, as mentioned in Chapter 5. However, as noted previously, if hemp straw is used for bioenergy purposes and thereby displaces fossil fuels, less CO_2 of fossil origin will be released into the atmosphere.

6.6 Conclusions

In this chapter, an attributional life cycle assessment of 1 MJ hemp biodiesel, delivered to the vehicle and subsequently combusted, was presented. Inventory data from literature, commercial and primary data sources (Chapter 5) were collated. The climate change impact potential was calculated using the ReCiPe midpoint indicator “climate change”, which is based on the methodology set out by IPCC (2007), in SimaPro software, version 7.2 (Pre Consultants, 2007).

Hemp oil biodiesel was found to result in the greatest climate change impact when compared with other biodiesels, except for sunflower biodiesel, and fossil diesels. However, when the impacts of producing hemp biodiesel were allocated to the hemp biodiesel and its co-products, the climate change impact was reduced to the same magnitude as the other biodiesels. The inclusion of complete accounting for CO_2 in the life cycle, including absorption from the atmosphere during plant growth and emission during combustion in a vehicle, changed the result heavily in favour of hemp biodiesel when impacts were not allocated to co-products. Furthermore, hemp compares favorably to fossil diesel where full CO_2 accounting is applied. When the impacts were allocated, the hemp biodiesel climate change impact was of the same order as those of other biodiesels.

Key sensitivities were identified:

- inclusion or exclusion of CO_2 absorption during plant growth and emissions during fuel combustion in a vehicle
- choice of allocation to either hemp biodiesel alone or to all products and co-products of the life cycle system
- changes to the conversion factors used to link together the stages of the life cycle
- the quantities of mineral fertilisers applied to the crop.

The selection of allocation method, using either mass, energy or carbon content values for the product and co-products, was found to be less significant than the choice of which allocation points to include or exclude from the calculation of the climate change impact potential.

The implications for the overall level of emissions in the UK of greenhouse gases were mixed:

- industrial emissions may increase if overall levels of biodiesel production in the UK increase, or stay constant if biodiesel production occurs overseas
- agricultural emissions may decrease through the reduced use of fertiliser
- transport emissions are unaffected since the accounting is of tailpipe emissions, not of production emissions.

The Renewable Transport Fuels Obligation method for carbon reporting (Bauen et al., 2008) was identified to be at odds with the methodology in compiling the national emissions inventory (National Atmospheric Emissions Inventory, 2009) since the former uses consumption-based accounting whereas the latter uses production-based accounting.

Through the course of executing this LCA, a number of areas for further investigation have been identified. The effects of introducing hemp into cereal crop rotations on the environmental impacts of the rotation system as a whole have not been quantified. Discussions with the farmer and agronomist who provided the data in this case study indicated that fewer field operations were required for the rotation as a whole when hemp was introduced into the crop cycle. Investigation of the overall effect of changing a cereal rotation system through the introduction of hemp would be a useful extension to the work carried out in the present LCA.

Chapter 7

Conclusions

In this chapter, the main findings of the research are summarised with reference to the aims of this thesis which were set out in Chapter 1 and are repeated here for reference:

1. to determine how the densities and energy contents of blends of European-specification biodiesel and petroleum diesel change according to the blend proportions
2. to determine how closely the mass, volume and energy proportions of biodiesel in a biodiesel-petroleum diesel fuel blend compare
3. to document the cultivation and harvesting of a hemp crop grown for both straw and seed
4. to document the gross heat of combustion of the parts of the hemp plant
5. to estimate the potential of the hemp crop for carbon storage
6. to evaluate the net climate change impact potential of producing biodiesel from hemp biodiesel grown in the UK, in the context of the Renewable Transport Fuels Obligation.

Suggestions for continuation of this research are also presented.

7.1 Key findings

The density and energy properties of biodiesel and petroleum diesel blends using European standard fuels were experimentally investigated to address Aim 1 of the thesis, and found to be the sum of the properties of their component parts, in agreement with prior research on American standard fuels. The mass and volume proportions of blended biodiesel and petroleum diesel fuels agree to ± 2.3 % while the volume and energy proportions for describing biodiesel-petroleum diesel blends agree to ± 3.6 %, and these results fulfil Aim 2 of the thesis.

In addition to fulfilling Aims 1 and 2, the experimental work in this thesis also found that the densities of the blended diesel fuels varied linearly with temperature. The energy density of a blend can be predicted from the energy densities of the blend components. The energy densities of the biodiesels and petroleum diesel measured experimentally in this thesis differ by 3 MJ litre^{-1} which is less than the difference reported by Sims (2002). The low degree of difference between the energy densities of the fuels from biogenic or fossil origin means that when used in a diesel engine, little difference will be observed in the operational performance of the engine when run on different blends of the fuels.

Prior to conducting the life cycle assessment of hemp biodiesel, data on hemp agriculture collected from a case study farm in East Anglia and compared with data for hemp cultivation in other countries and with oilseed rape agriculture in the UK (Section 5.3), thereby addressing Aim 3 of the thesis. Hemp was found to have lower inputs than rapeseed and lower seed outputs while having a much higher output of a usable straw co-product which stores CO_2 in its biomass and is therefore much more useful for practical purposes, including climate change mitigation, than rapeseed straw.

Analysis of the energy and carbon contents of hemp plant parts was conducted, as well as oil and moisture contents tests (Section 5.4) to fulfil Aim 4 of the thesis. The hemp seed oil was found to have a comparable energy content to those of other seed oils, while the hemp straw energy content was similar to other straw and woody biomass substances. The carbon content of the hemp straw and seeds was used to estimate a value of 11 400 kg CO_2 ha^{-1} for the carbon storage potential of the hemp plant, some of which could be preserved for timescales of years, or perhaps decades, in straw buildings. Through these calculations, Aim 5 of the thesis was fulfilled.

An attributional life cycle assessment of 1 MJ hemp biodiesel, delivered to the vehicle and subsequently combusted, was presented (Chapter 6), set out in accordance with the ISO standard for life cycle assessment (ISO, 2006a). The climate change impact potential was calculated from primary data (Chapter 5), supplemented by data from the literature and commercial sources, using the ReCiPe midpoint indicator "climate change", which is based on the methodology set out by IPCC (2007), in SimaPro software, version 7.2 (Pre Consultants, 2007).

Hemp oil biodiesel was found to result in the greatest climate change impact when compared with other biodiesels and fossil diesels, of 0.137 kg CO_2-e MJ^{-1}. The life cycle assessment of hemp biodiesel, and comparison of its results with results from other studies, as well as consideration of the impacts for national emissions of greenhouse gases, fulfilled Aim 6 of the thesis

Key sensitivities of the life cycle assessment result for the climate change impact potential to changes in the method and parameter values used in the calculations were identified as follows:

- inclusion of CO_2 absorption during plant growth and emissions during fuel combustion in a vehicle changed the result by a factor of -500 % to -0.684 kg CO_2-e MJ^{-1}
- choice of allocation to either hemp biodiesel alone or to all products and co-products of the life cycle system reduced the climate change impact potential to 0.012–0.021 kg CO_2-e MJ^{-1}
- changes to the conversion factors between the stages of the life cycle increased the climate change impact potential to 0.117–0.164 kg CO_2-e MJ^{-1}, and in particular, increasing the seed yield to 1200 kg ha^{-1} and the seed oil content to 37.5 % w/w reduces the climate change impact potential to 0.117 kg CO_2-e MJ^{-1}
- a 25 % increase in the quantity of mineral nitrogen fertilisers applied to the crop increases the overall life cycle climate change impact potential by 8.2 %.

Hemp biodiesel has approximately the same climate change impact, when impacts are also allocated to co-products, when compared with biodiesels from other European feedstocks. Hemp biodiesel compares favorably to fossil diesel where full CO_2 accounting is applied since the CO_2 absorbed by the plant during its growth phase compensates for some of the emissions during fuel production and combustion.

The implications for the overall level of emissions in the UK of greenhouse gases were mixed:

- industrial emissions may increase or stay constant, depending on whether domestic production of biodiesel increases or remains constant
- agricultural emissions may decrease through the reduced use of fertiliser
- transport emissions are unaffected since the accounting is of tailpipe emissions, not of production emissions.

This research found that hemp biodiesel has a similar impact potential for greenhouse gas emissions to the impact potential of biodiesel from rapeseed, provided that impacts are allocated between the co-products. However, the main distinction between hemp and rape is the production of a useful and valuable straw product from the hemp plant, which can be used as a temporary CO_2 store.

7.2 Implications of using hemp biodiesel

The research in this thesis has determined that hemp biodiesel is a qualifying biofuel for the purposes of the Renewable Transport Fuel Obligation (Department for Transport, 2007b) and the Renewable Energy Directive (European Parliament and the Council of the European Union, 2009). The results presented in Chapter 6 show that the emissions of climate change gases from the production and use of hemp biodiesel are better by more than 35 % of the emissions from fossil diesel, thereby satisfying the requirements of the Renewable Energy Directive. Hemp can therefore be cultivated by farmers for the production of biodiesel, with the knowledge that the fuel will satisfy the legal requirements for renewable transport fuel, provided that the crop agronomy is not too dissimilar from that used in the case study in this thesis. In addition, the potential of the straw co-product for further climate change mitigation could be significant and is worthy of further investigation.

7.3 Recommendations for future research

The research reported in Chapter 3of this thesis indicates that some government data do not concur with the research basis or with EN specifications. Verification and correction of government figures for the following data points is recommended:

- standard density of biodiesel (Department for Transport, 2006)
- gross heat of combustion of biodiesel (Department for Transport, 2006)
- rate of density change with temperature of diesel fuels (National Measurement Office, 2009)

Further, the inclusion of data on the energy content and density of biodiesel in the annual publication of the Digest of UK Energy Statistics (see, for example, Department of Energy and Climate Change (2009)) would create a more complete dataset on typical properties of fuels sold and used in the UK.

Continuation of the experimental research on biodiesel-petroleum diesel blends in this thesis could measure the energy and density properties of a wider sample of UK diesel fuels which would take into account both geographical and seasonal variability. As mentioned above, further research into the variation of density with temperature would be of use to clarify the accuracy of the data used by Trading Standards to compensate for temperature when measuring the accuracy of diesel dispensing equipment. Finally, further investigation of the properties of hemp biodiesel and its blends with petroleum diesel would be of benefit to confirm the suitability of hemp biodiesel for use in vehicles currently on the road in the UK.

This thesis has concentrated on the production of hemp biodiesel and treated the straw as a co-product. However, the main body of the plant, its stem, has considerable potential for use in the energy system in at least two distinct modes. Firstly, as a source of biomass for combustion to generate either heat or electricity, or both. Secondly, hemp stem is used as a raw material for construction materials which have good insulating properties. In this mode, hemp is used in energy conservation technologies. The assessment of hemp as an insulator, and the environmental impacts of producing hemp construction materials, has not been directly assessed nor compared with insulation materials that are more widely in use, for instance glass fibre insulation and foam boards. Hemp straw, when used as a substitute for breeze blocks or bricks in the walls of domestic or commercial buildings may reduce the climate change impact potential of the buildings through two mechanisms: the storage of CO_2 in the straw itself and the displacement of energy-intensive methods of producing conventional building materials. The environmental impacts and insulative properties of hemp construction products could prove to be an interesting and important avenue for future research.

A consequential LCA of hemp for biodiesel and bioenergy is recommended to complement the present study and to indicate the potential wider impacts of increasing the area of arable land for growing hemp, and the consequences of displacing other crops. The results of the consequential LCA could be used in conjunction with those in this thesis, in accordance with the recommendation by Schmidt (2008) that both attributional and consequential LCAs be performed for the purpose of informing decision- and policy-making. Furthermore, the consequential elements of the Renewable Transport Fuels Obligation carbon-reporting guidelines could be appropriately addressed by a consequential LCA.

During this research project, several gaps were found in the research basis concerning the hemp plant. However, published research on hemp already exists in other European languages, for example in German and in Hungarian, amongst others. In the first instance, translation of research from other languages into English and dissemination of that research would be a great advantage to English-speaking researchers.

Anecdotal evidence (Chapter 5) suggests that hemps stands contribute positively to biodiversity, for instance their use for game cover is well established. Overall farm requirements for heavy tillage, which requires significant fuel inputs, are reduced through the introduction into a cereal rotation of hemp which has deep tap roots which contribute to good soil structure. Further investigation of the the organisms that inhabit and make use of hemp stands would be of interest, as would quantification of the impacts of different cereal crops on soil structure and the consequences for environmental impacts. Data on the effects of plants on soil structure would contribute towards the field of agricultural land use assessment as outlined by Mattsson et al. (2000).

Research into the crop uptake of elements from the soil and quantification of emissions to the soil and from there to water and air, particularly in the case of fertiliser emissions, would enable assessment of the impact categories not considered in this thesis, including freshwater eutrophication, acidification and so forth. Knowledge of these environmental impacts could contribute to better farming practices and readjustment of the results of this thesis, particularly with regard to the emissions of nitrous oxides from reactions that involve ammonia which is applied to the fields.

The life cycle assessment of hemp biodiesel in this thesis concentrated on the impacts for climate change alone. A full assessment of hemp biodiesel across all currently-identified life cycle impact assessment categories would provide a more thorough indication of the overall sustainability of hemp as a feedstock for biodiesel. However, the results for the climate change impact potential of hemp biodiesel obtained in this thesis indicate that hemp biodiesel has similar impacts to those of rapeseed oil biodiesel and has highlighted potential for climate change mitigation in the use of the straw co-product to store CO_2, thereby contributing further towards a sustainable future for the UK.

References

Abuzaytoun, R. and F. Shahidi (2006). Oxidative stability of flax and hemp oils. *Journal of the American Oil Chemists' Society 83*(10), 855–861.

AEA Energy and Environment (2008, April). UK Greenhouse Gas Inventory, 1990 to 2006: Annual Report for submission under the Framework Convention on Climate Change. `http://www.naei.org.uk/report_link.php?report_id=507` Accessed 03/11/2008.

Agarwal, D., L. Kumar, and A. K. Agarwal (2008). Performance evaluation of a vegetable oil fuelled compression ignition engine. *Renewable Energy 33*(6), 1147–1156.

Albuquerque, M., Y. Machado, A. Torres, D. Azevedo, J. C.L. Cavalcante, L. Firmiano, and J. E.J.S. Parente (2009). Properties of biodiesel oils formulated using different biomass sources and their blends. *Renewable Energy 34*(3), 857–859.

Alptekin, E. and M. Canakci (2008). Determination of the density and the viscosities of biodiesel-diesel fuel blends. *Renewable Energy 33*(12), 2623–2630.

Alptekin, E. and M. Canakci (2009, JAN). Characterization of the key fuel properties of methyl ester-diesel fuel blends. *Fuel 88*(1), 75–80.

Amaducci, S., M. Errani, and G. Venturi (2002). Response of hemp to plant population and nitrogen fertilisation. *Italian Journal of Agronomy 6*(2), 103–111.

Anderson, K., A. Bows, and S. Mander (2008). From long-term targets to cumulative emission pathways: Reframing UK climate policy. *Energy Policy 36*(10), 3714–3722.

Antolín, G., F. V. Tinaut, Y. B. no V. Castaño, C. Pérez, and A. I. Ramírez (2002). Optimisation of biodiesel production by sunflower oil transesterification. *Bioresource Technology 83*(2), 111–114.

ASTM D975 (2010). *ASTM D975 - 08a Standard Specification for Diesel Fuel Oils*.

Bagwell, P. and P. Lyth (2002). *Transport in Britain: From Canal Lock to Gridlock*. Hambledon and London, London and New York.

Barkenbus, J. N. (2010). Eco-driving: An overlooked climate change initiative. *Energy Policy 38*(2), 762 – 769.

Baroutian, S., M. K. Aroua, A. A. A. Raman, and N. M. N. Sulaiman (2008). Density of palm oil-based methyl ester. *J Chem Eng Data 53*, 877–880.

Bauen, A., P. Watson, and J. Howes (2008). *Carbon Reporting within the Renewable Transport Fuel Obligation—Methodology*. `http://www.globalbioenergy.org/uploads/media/0802_E4tech_-_Carbon_Reporting_within_the_Renewable_Transport_Fuel_Obligation_-_Methodology.pdf` accessed 15/03/2011.

Baumann, H. and A.-M. Tillman (2004). *The Hitch Hiker's Guide to LCA - An Orientation in Life Cycle Assessment Methodology and Application*. Studentlitteratur, Lund, Sweden.

Beck, R. (2008). *Private communication*.

Bell, S. and S. Morse (1999). *Sustainability Indicators: Measuring the Immeasurable*. London: Earthscan.

Benjumea, P., J. Agudelo, and A. Agudelo (2008). Basic properties of palm oil biodiesel-diesel blends. *Fuel 87*(10-11), 2069–2075.

Bernesson, S., D. Nilsson, and P.-A. Hansson (2004). A limited LCA comparing large- and small-scale production of rape methyl ester (RME) under Swedish conditions. *Biomass and Bioenergy 26*(6), 545–559.

BERR (2007a). Energy Flow Chart. `http://www.berr.gov.uk/files/file46984.pdf` Accessed 03/11/2008.

BERR (2007b). *UK Biomass Strategy 2007: Working Paper 1 - Economic analysis of biomass energy*. HMSO, London.

BERR (2008). *Digest of UK Energy Statistics 2008*. The Stationery Office.

Berrios, M. and R. Skelton (2008). Comparison of purification methods for biodiesel. *Chemical Engineering Journal 144*(3), 459 – 465.

Bócsa, I. and M. Karus (1998). *The Cultivation of Hemp. Botany, Varieties, Cultivation and Harvesting*. Hemptech, Sebastopol, California.

Bona, S., G. Mosca, and T. Vamerali (1999). Oil crops for biodiesel production in Italy. *Renewable Energy 16*(1-4), 1053–1056.

Boswell, A. (2007). Biofuels for transport - a dangerous distraction? *Scientists for Global Responsibilty Newsletter Winter*(33), 10–13.

Bournay, L., D. Casanave, B. Delfort, G. Hillion, and J. Chodorge (2005). New heterogeneous process for biodiesel production: A way to improve the quality and the value of the crude glycerin produced by biodiesel plants. *Catalysis Today International Conference on Gas-Fuel 05 - International Conference on Gas-Fuel 05 106*(1-4), 190–192.

Bowers, J. (2003). Seeds of Hope. *The Ecologist 33*, 46–49.

Bradshaw, R. H. W., P. Coxon, J. R. A. Greig, and A. R. Hall (1981). New fossil evidence for the past cultivation and processing of Hemp (*Cannabis Sativa L.*) in Eastern England. *New Phytologist 89*(3), 503–510.

Braham, H. and I. Low (2008). *Private communication*.

Brander, M., R. Tipper, C. Hutchison, and G. Davis (2008). *Technical Paper: Consequential and Attributional Approaches to LCA: a Guide to Policy Makers with Specific Reference to Greenhouse Gas LCA of Biofuels*. `http://www.ecometrica.co.uk/wp-content/uploads/Consequential_and_attributional_approaches_to_LCA.pdf` accessed 15/03/2011.

British Standards Institution (2004a). *EN 14214 Automotive fuels Fatty acid methyl esters (FAME) for diesel engines: Requirements and test methods*.

British Standards Institution (2004b). *EN 590:2004 Automotive fuels - Diesel - Requirements and test methods*.

Brundtland, G. H. (1987). *Our Common Future*. Oxford: Oxford University Press.

Canakci, M. (2007). The potential of restaurant waste lipids as biodiesel feedstocks. *Bioresource Technology 98*(1), 183–190.

Canakci, M. and J. Van Gerpen (2001). Biodiesel production from oils and fats with high free fatty acids. *Transactions of the American Society of Agricultural Engineers 44*(6), 1429–1436.

Carolan, M. S. (2009). Environmental Review: The Cost and Benefits of Biofuels: A Review of Recent Peer-Reviewed Research and a Sociological Look Ahead. *Environmental Practice 11*, 17–24.

Carus, M., T. Breuer, and F. Gerlach (2007). *Examination of hemp oil with regard to its suitability as fuel for engines adapted to pure plant oil use: Motivation, Summary and Outlook.* nova-Institut GmbH, Huerth, Germany and Technologie- und Foerderzentrum (TFZ), Straubing, Germany.

Casas, X. A. and J. Rieradevall i Pons (2005). Environmental analysis of the energy use of hemp analysis of the comparative life cycle: diesel oil vs. hemp diesel. *International Journal of Agricultural Resources, Governance and Ecology 4*(7), 133–139.

Cherubini, F., N. D. Bird, A. Cowie, G. Jungmeier, B. Schlamadinger, and S. Woess-Gallasch (2009). Energy- and greenhouse gas-based LCA of biofuel and bioenergy systems: Key issues, ranges and recommendations. *Resources, Conservation and Recycling 53*(8), 434 – 447.

Chiaramonti, D. and L. Recchia (2010). Is life cycle assessment (LCA) a suitable method for quantitative CO2 saving estimations? the impact of field input on the LCA results for a pure vegetable oil chain. *Biomass and Bioenergy 34*(5), 787–797.

Chisti, Y. (2007). Biodiesel from microalgae. *Biotechnology Advances 25*(3), 294 – 306.

Christie, W. W. (1973). *Lipid Analysis - Isolation, separation, identification and structural analysis of lipds*. Oxford: Pergamon Press.

Clements, L. D. (1996, September). Blending rules for formulating biodiesel fuel. In *Liquid Fuels and Industrial Products from Renewable Resources, Proceedings of the Third Liquid Fuel Conference, Nashville, TN, September 15-17, 1996*, pp. 44–53.

Conceicao, M. M., R. A. Candeia, F. C. Silva, A. F. Bezerra, V. J. Fernandes Jr., and A. G. Souza

(2007). Thermoanalytical characterization of castor oil biodiesel. *Renewable and Sustainable Energy Reviews 11*(5), 964–975.

Consoli, F., D. Allen, I. Boustead, J. Fava, W. Franklin, A. Jensen, N. de Oude, R. Parrish, D. Postlethwaite, B. Quay, J. Seguin, and B. Vigon. (Eds.) (1993). *Guidelines for Life-Cycle Assessment: A "Code of Practice"*. Society of Environmental Toxicology and Chemistry, Brussels, Belgium & Pensacola, FL, USA.

Council of the European Communities (1992). Council Directive 92/75/EEC of 22 September 1992 on the indication by labelling and standard product information of the consumption of energy and other resources by household appliances. *Official Journal of the European L 297, 13.10.1992 L*, 16–19.

Crutzen, P. J., A. R. Mosier, K. A. Smith, and W. Winiwarter (2007). N_2O release from agro-biofuel production negates global warming reduction by replacing fossil fuels. *Atmospheric Chemistry and Physics Discussions 7*(4), 11191–11205.

Deeley, M. R. (2000). *Cannabis: an environmentally and economically viable method for climate change mitigation.* Ph. D. thesis, University of Strathclyde, Graduate School of Environmental Studies.

Defra (2006). Agricultural Land By Type Of Use: United Kingdom (a) 1983 - 2005 (At June Survey). `http://www.defra.gov.uk/esg/work_htm/publications/cs/farmstats_web/2_SURVEY_DATA_SEARCH/HISTORICAL_DATASETS/HISTORICAL_DATASETS/LAND/LAND_83-2005_UK.XLS`.

Defra (2006). *Code of practice for agricultural use of sewage sludge.* Defra. `http://www.defra.gov.uk/environment/quality/water/waterquality/sewage/documents/sludge-cop.pdf` Accessed 19/01/2010.

Defra (2006). Sewage sludge arisings and management. `http://www.defra.gov.uk/evidence/statistics/environment/waste/download/xls/wrtb11-12.xls` accessed 15/03/2011.

Defra (2009). *The British Survey of Fertiliser Practice: Fertiliser Use on Farm Crops for Crop Year 2008*. Department for Environment, Food and Rural Affairs, UK.

Delft University of Technology (2001). *IDEMAT*.

Demirbas, A. (2007). Progress and recent trends in biofuels. *Progress in Energy and Combustion Science 33*(1), 1–18.

Demirbas, A. (2008). Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel 87*, 1743–1748.

Department for the Environment, Food and Rural Affairs (2008). *UK Greenhouse Gas Inventory 1990 to 2006: Annual Report for submission under the Framework Convention on Climate Change*.

Department for Transport (2006). *International resource costs of biodiesel and bioethanol*. HMSO, London, UK.

Department for Transport (2007a). Explanatory Memorandum to the Renewable Transport Fuel Obligation Order 2007. Technical report. `http://www.opsi.gov.uk/si/si2007/draft/em/ukdsiem_9780110788180_en.pdf` accessed 15/03/2011.

Department for Transport (2007b). The Renewable Transport Fuels Obligation Order 2007.

Department for Transport (2008). *Transport Statistics Bulletin, National Travel Survey: 2007 Interview Data*. Transport Statistics.

Department for Transport (2009, March). TSGB 2008: Energy and the Environment - data tables. `http://www.dft.gov.uk/pgr/statistics/datatablespublications/energyenvironment/tsgbchapter3energyenvi1862.xls` accessed 15/10/2009.

Department of Energy and Climate Change (2009). *Digest of UK Energy Statistics 2009*. TSO, London.

DETR (2000). *Climate Change The UK Programme*. TSO, London.

Diepenbrock, W. (2000). Yield analysis of winter oilseed rape (Brassica napus L.): a review. *Field Crops Research 67*(1), 35 – 49.

Dorado, M., F. Cruz, J. Palomar, and F. Lopez (2006). An approach to the economics of two vegetable oil-based biofuels in Spain. *Renewable Energy 31*(8), 1231–1237.

Dornburg, V., G. Termeer, and A. Faaij (2005). Economic and greenhouse gas emission analysis of bioenergy production using multi-product crops–case studies for the netherlands and poland. *Biomass and Bioenergy 28*(5), 454 – 474.

Druckman, A., P. Bradley, E. Papathanasopoulou, and T. Jackson (2008). Measuring progress towards carbon reduction in the UK. *Ecological Economics 66*(4), 594–604.

DTI (2007a). *Digest of UK Energy Statistics 2006.* TSO, London.

DTI (2007b). *Energy White Paper 2007.* TSO, London.

Dufreche, S., R. Hernandez, T. French, D. Sparks, M. Zappi, and E. Alley (2007). Extraction of lipids from municipal wastewater plant microorganisms for production of biodiesel. *Journal of the American Oil Chemists' Society V84*(2), 181–187.

DVLA (2007a, March). Driving licence statistics. `http://www.dvla.gov.uk/media/doc/press_stats/driving_lic_age_full_prov.xls` Accessed 03/11/2008.

DVLA (2007b, February). Licensed vehicles. `http://www.dvla.gov.uk/media/doc/press_stats/vehicle_taxed_class_body.xls` Accessed 03/11/2008.

ecoinvent Centre (2009). *ecoinvent data v2.0. Final reports ecoinvent 2000 No. 1-15.* Swiss Centre for Life Cycle Inventories, Dubendorf, Switzerland. `http://www.ecoinvent.ch`, accessed 25/03/2010.

Edwards, R., J.-F. Larivé, V. Mahieu, and P. Rouveirolles (2007). *Well-to-Wheels analysis of future automotive fuels and powertrains in the European context. Report Version 2c.* `http://ies.jrc.ec.europa.eu/uploads/media/WTW_Report_010307.pdf` accessed 15/03/2011.

Ekvall, T. and B. P. Weidema (2004). System Boundaries and Input Data in Consequential Life Cycle Inventory Analysis. *International Journal of Life Cycle Assessment 9*(3), 161 – 171.

EPR (2010). *Overview - Ely - Assets - Energy Power Resources.* `http://www.eprl.co.uk/assets/ely/overview.html` Accessed 27 July 2010.

Erdoel Vereinigung Union Petroliere (2009). *Consommation par produits.* `http://www.erdoel-vereinigung.ch/UserContent/Documents/EV/FAQ/Tab13_2008%20F.pdf` accessed 15/03/2011.

European Commission (2003). *Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport.*

European Commission: Agriculture and Rural Development (2009). The 2008 Agricultural Year: Agricultural Markets: Oilseeds, Oils and Fats. `http://ec.europa.eu/agriculture/agrista/2008/table_en/en44.htm` accessed 15/03/2011.

European Parliament and the Council of the European Union (2009). Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. *Official Journal of the European Union 140*, 16–62.

Finnveden, G. (1997). Valuation methods within LCA - Where are the values? *International Journal of Life Cycle Assessment 2*(3), 163–169.

Finnveden, G., M. Z. Hauschild, T. Ekvall, J. Guinée, R. Heijungs, S. Hellweg, A. Koehler, D. Pennington, and S. Suh (2009). Recent developments in Life Cycle Assessment. *Journal of Environmental Management 9*, 1–21.

Fortenbery, T. R. and M. Bennett (2004). Opportunities for Commercial Hemp Production. *Review of Agricultural Economics 26*(1), 97–117.

Freedman, B., R. O. Butterfield, and E. H. Pryde (1986). Transesterification kinetics of soybean oil. *Journal of the American Oil Chemists' Society 63*, 1375–1380.

Frischknecht, R. and N. Jungbluth (Eds.) (2007). *Overview and Methodology Data v2.0*. ecoinvent Centre.

Furuholt, E. (1995). Life cycle assessment of gasoline and diesel. *Resources, Conservation and Recycling Life Cycle Management 14*(3-4), 251–263.

Garcez, C. A. G. and J. a. N. de Souza Vianna (2009). Brazilian Biodiesel Policy: Social and environmental considerations of sustainability. *Energy 34*(5), 645–654.

Giannelos, P., S. Sxizas, E. Lois, F. Zannikos, and G. Anastopoulos (2005). Physical, chemical and fuel related properties of tomato seed oil for evaluating its direct use in diesel engines. *Industrial Crops and Products 22*, 193–199.

Gnansounou, E., A. Dauriat, J. Villegas, and L. Panichelli (2009). Life cycle assessment of biofuels: Energy and greenhouse gas balances. *Bioresource Technology 100*, 4919–4930.

Goedkoop, M., R. Heijungs, M. Huijbregts, A. De Schryver, J. struijs, and R. van Zelm (2008). *ReCiPe 2008*. `http://www.lcia-recipe.net/` accessed 15/03/2011.

Goedkoop, M. and R. Spriensma (2001). *The Eco-indicator 99: A damage-oriented method for Life Cycle Impact Assessment. Methodology report*. Pre Consultants B.V, Netherlands.

Gouw, T. and J. Vlugter (1964). Physical properties of fatty acid methyl esters. I. density and molar volume. *Journal of the American Oil Chemists' Society 41*, 142–145.

Gui, M. M., K. T. Lee, and S. Bhatia (2009). Supercritical ethanol technology for the production of biodiesel: process optimization studies. *The Journal of Supercritical Fluids 49*, 286–292.

Guinee, J., M. Gorree, R. Heijungs, G. Huppes, R. Kleijn, A. de Koning, L. van Oers, A. Wegener Sleeswijk, S. Suh, H. Udo de Haes, J. de Bruijn, R. van Duin, and M. Huijbregts (2002). *Handbook on Life Cycle Assessment: Operational Guide to the ISO Standards. Series: Eco-efficiency in Industry and Science*. Kluwer Academic Publishers, Dordrecht.

Haas, M. J., K. M. Scott, W. N. Marmer, and T. A. Foglia (2004). In situ alkaline transesterification: An effective method for the production of fatty acid esters from vegetable oils. *Journal of the American Oil Chemists' Society 81*(1), 83–89.

Hall, D. O. and J. I. Scrase (1998). Will biomass be the environmentally friendly fuel of the future? *Biomass and Bioenergy 15*(4-5), 357 – 367.

Hanfaes Research Centre (2004). Guidelines for growing Hemp. Technical report, University of Bangor.

Harris, K. R. (2000). Temperature and density dependence of the viscosity of toluene. *Journal of Chemical & Engineering Data 45*(5), 893–897.

Harwood, H. (1984). Oleochemicals as a fuel: Mechanical and economic feasibility. *Journal of the American Oil Chemists' Society 61*, 315–324.

Hemp Technology Ltd. (2010). *Products - Hemcore Hemp Logs*. `http://www.hemcore.co.uk/logs.htm`.

Hersener, J.-L. and U. Meier (1999). *Energetisch nutzbares Biomassepotential in der Schweiz sowie Stand der Nutzung in ausgewählten EU-Staaten und den USA*. Bundesamt fur Energiewirtschaft. `http://www.meritec.ch/pdf/biomassen-potential-1999.pdf` accessed 15/03/2011.

Hilton, G. (2006). RTFO - Commercial Implications for the UK Biofuels Industry. In *Fuelling the Future: Making a Success of the Renewable Transport Fuels Obligation*, London.

HM Government (2004). *Energy Act 2004.* `http://www.opsi.gov.uk/Acts/acts2004/pdf/ukpga_20040020_en.pdf` Accessed 04/11/2008.

HM Government (2008). Improving the energy efficiency of our homes and buildings. `http://www.communities.gov.uk/documents/planningandbuilding/pdf/714826.pdf` accessed 15/03/2011.

HM Treasury (2006, 22 March 2006). Budget 2006: A strong and strengthening economy: Investing in Britain's future. Technical report, HM Treasury. `http://www.hm-treasury.gov.uk/budget/budget_06/budget_report/bud_bud06_repindex.cfm` Accessed 03/11/2008.

Hobson, J. (2007). *Hemcore - Guide to Hemp Growing 2007.*

Höppner, F. and U. Menge-Hartmann (2007). Yield and quality of fibre and oil of fourteen hemp cultivars in Northern Germany at two harvest dates. *Landbauforschung Völkenrode 3 57*, 219–232.

IPCC (2007). *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. IPCC, Geneva, Switzerland. [Core Writing Team, Pachauri, R.K and Reisinger, A. (eds.)].

Iriarte, A., J. Rieradevall, and X. Gabarrell (2010). Life cycle assessment of sunflower and rapeseed as energy crops under Chilean conditions. *Journal of Cleaner Production 18*(4), 336–345.

ISO (2006a). *BS EN ISO 14040:2006 Environmental management - Life cycle assessment - Principles and framework.* British Standards Institute.

ISO (2006b). *BS EN ISO 14044:2006 Environmental management - Life cycle assessment - Requirements and guidelines.* British Standards Institute.

Jolliet, O., R. Müller-Wenk, J. Bare, A. Brent, M. Goedkoop, R. Heijungs, N. Itsubo, C. Peña, D. Pennington, J. Potting, G. Rebitzer, M. Stewart, H. U. de Haes, and B. Weidema (2004). The

LCIA midpoint-damage framework of the UNEP/SETAC life cycle initiative. *International Journal of Life Cycle Assessment 9*(6), 394–404.

Jungbluth, N., M. F. Emmenegger, F. Dinkel, C. Stettle, G. Doka, M. Chudacoff, A. Dauriat, E. Gnansounou, M. Spielmann, J. Sutter, N. Kljun, M. Keller, and K. Schleiss (2007). *Life Cycle Inventories of Bioenergy Data v2.0 (2007).* ecoinvent Centre.

Kaltschmitt, M., G. A. Reinhardt, and T. Stelzer (1997). Life cycle analysis of biofuels under different environmental aspects. *Biomass and Bioenergy 12*(2), 121–134.

Karinen, R. and A. Krause (2006). New biocomponents from glycerol. *Applied Catalysis A: General 306*, 128–133.

Kendell, R. (2003). Cannabis condemned: the proscription of Indian hemp. *Addiction 98*(2), 143–151.

Kim, S. and B. E. Dale (2005). Life cycle assessment of various cropping systems utilized for producing biofuels: Bioethanol and biodiesel. *Biomass and Bioenergy 29*(6), 426–439.

King, J. (2007). *The King Review of low-carbon cars Part I: the potential for CO_2 reduction.* TSO, London.

Klopfenstein, W. E. and H. S. Walker (1983). Efficiencies of various esters of fatty acids as diesel fuels. *Journal of the American Oil Chemists' Society 60*(8), 1596–1598.

Knothe, G. (2006). Biodiesel and the issue of diesel fuel lubricity. *Lipid Technology 18*(5), 105–108.

Koh, L. P. and J. Ghazoul (2008). Biofuels, biodiversity, and people: Understanding the conflicts and finding opportunities. *Biological Conservation 141*(10), 2450 – 2460.

Kriese, U., E. Schumann, W. Weber, M. Beyer, L. Brühl, and B. Matthaüs (2004). Oil content, tocopherol composition and fatty acid patterns of the seeds of 51 *Cannabis sativa L.* genotypes. *Euphytica 137*(3), 339–351.

Lapinskienė, A., P. Martinkus, and V. Rėbždaitė (2006). Eco-toxicological studies of diesel and biodiesel fuels in aerated soil. *Environmental Pollution 142*(3), 432–437.

Lechón, Y., H. Cabal, C. de la Rúa, N. Caldés, M. Santamaría, and R. Sáez (2009). Energy and greenhouse gas emission savings of biofuels in Spain's transport fuel. The adoption of the EU policy on biofuels. *Biomass and Bioenergy 33*(6-7), 920–932.

Liang, X., S. Gao, J. Yang, and M. He (2009). Highly efficient procedure for the transesterification of vegetable oil. *Renewable Energy 34*(10), 2215–2217.

Lide, D. R. (Ed.) (2005). *CRC handbook of chemistry and physics*. Boc Raton, London.

Lin, C.-Y. and R.-J. Li (2009). Fuel properties of biodiesel produced from the crude fish oil from the soapstock of marine fish. *Fuel Processing Technology 90*(1), 130 – 136.

Luo, L., E. van der Voet, G. Huppes, and H. A. Udo de Haes (2009). Allocation issues in LCA methodology: a case study of corn stover-based fuel ethanol. *The International Journal of Life Cycle Assessment 14*(6), 529–539.

Lutman, P. J. W., K. Berry, R. W. Payne, E. Simpson, J. B. Sweet, G. T. Champion, M. J. May, P. Wightman, K. Walker, , and M. Lainsbury (2005). Persistence of seeds from crops of conventional and herbicide tolerant oilseed rape (*Brassica napus*). *Proceedings of the Royal Society B 272*, 1909–1915.

Ma, F. and M. A. Hanna (1999). Biodiesel production: a review. *Bioresource Technology 70*, 1–15.

Mahajan, S., S. K. Konar, and D. G. B. Boocock (2007). Variables affecting the production of standard biodiesel. *Journal of the American Oil Chemists' Society 84*(2), 189–195.

Mallik, M. K., U. K. Singh, and N. Ahmad (1990). Batch digester studies on biogas production from *Cannabis sativa*, water hyacinth and crop wastes mixed with dung and poultry litter. *Biological Wastes 31*(4), 315 – 319.

Marmo, L. (1999). Sewage sludge and the Community waste strategy. In *Workshop on problems around sludge*.

Matthäus, B. and L. Brühl (2008). Virgin hemp seed oil: An interesting niche product. *Eur. J. Lipid Sci. Technol. 110*, 655–661.

Mattsson, B., C. Cederberg, and L. Blix (2000). Agricultural land use in life cycle assessment (LCA): case studies of three vegetable oil crops. *Journal of Cleaner Production 8*(4), 283 – 292.

McDonough, W. and M. Braungart (2002). *Cradle to cradle: Remaking the way we make things*. North Point Press, New York.

Meher, L., D. Vidya Sagar, and S. Naik (2006). Technical aspects of biodiesel production by transesterification–a review. *Renewable and Sustainable Energy Reviews 10*(3), 248–268.

Miao, X. and Q. Wu (2006). Biodiesel production from heterotrophic microalgal oil. *Bioresource Technology 97*(6), 841–846.

Mittelbach, M. and H. Enzelsberger (1999). Transesterification of heated rapeseed oil for extending diesel fuel. *Journal of the American Oil Chemists' Society 76*(5), 545–550.

Mittelbach, M. and C. Remschmidt (2004). *Biodiesel - The Comprehensive Handbook*. Vienna: Boersedruck Ges.m.b.H.

Moes, J., A. Sturko, and R. Przybylski (1999). Agronomic Research on Hemp in Manitoba. In J. Janick (Ed.), *Perspectives on new crops and new uses*, pp. 300 – 305. ASHS Press.

Mohibbe Azam, M., A. Waris, and N. Nahar (2005). Prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel in India. *Biomass and Bioenergy 29*(4), 293–302.

Mortimer, N. D., P. Cormack, M. A. Elsayed, and R. E. Horne (2003, January 2003). Evaluation of the comparative energy, global warming and socio-economic costs and benefits of biodiesel. Technical report, Resources Research Unit, School of Environment and Development, Sheffield Hallam University.

National Atmospheric Emissions Inventory (2009). *UNECE Emission Estimates to 2007 Carbon Dioxide as Carbon*. `http://www.naei.org.uk/emissions/emissions_2007/summary_tables.php?action=unece&page_name=C07.html` accessed 15/10/2009.

National Measurement Office (2009, January). *NWML guidance note for retail fuel dispensers (petrol pumps) fitted with Standard Temperature Accounting (STA) displays - Advice for retailers, manufacturers, local authority trading standards, and approved verifiers*.

Nemecek, T. and T. Kägi (2007). Life cycle inventories of agricultural production systems. Technical report, Swiss Centre for Life Cycle Inventories.

Niederl, A. and M. Narodoslawsky (2004). Life cycle assessment - study of biodiesel from tallow and used vegetable oil. Technical report, Institute for Resource Efficient and Sustainable Systems. `http://www.argentenergy.com/articles/uploads/BiodieproLCAFinalReport210105.pdf` accessed 15/03/2011.

NISRA (2003). *Census 2001: Key Statistics, Table KS16: Dwellings, Household Spaces and Accommodation Type*. `http://www.nisranew.nisra.gov.uk/Census/Excel/KS16DC.xls`, accessed 08/10/2009.

Nix, J. (2008). *Farm Management Pocketbook 39th edition (2009)*. The Andersons Centre.

Noureddini, H., B. C. Teoh, and L. D. Clements (1992). Densities of vegetable oils and fatty acids. *Journal of the American Oil Chemists' Society 69*, 1184–1188.

Noureddini, H. and D. Zhu (1997). Kinetics of transesterification of soybean oil. *Journal of the American Oil Chemists' Society 74*(11), 1457–1463.

Office for National Statistics (2003). Census 2001 - people and their homes in england and wales. `http://www.statistics.gov.uk/census2001/profiles/commentaries/housing.asp`, accessed 08/10/2009.

Office for National Statistics (2005). *UK 2005 - The Official Yearbook of the United Kingdom of Great Britain and Northern Ireland*. TSO.

Office for National Statistics (2008, August). *Population: age and sex, 1981 onwards: Population Trends 132*. `http://www.statistics.gov.uk/statbase/Expodata/Spreadsheets/D9543.xls` Accessed 03/11/2008.

O'Riordan, T. and A. Jordan (2000). *Environmental Science for environmental Management*, Chapter Managing the global commons, pp. 485–511. Prentice Hall, Pearson Education, Harlow.

Panichelli, L., A. Dauriat, and E. Gnansounou (2009). Life cycle assessment of soybean-based biodiesel in Argentina for export. *International Journal of Life Cycle Assessment 14*(2), 144–159.

Parr Instrument Company (2006). *Operating Instructions for the 1341 Oxygen Bomb Calorimeter*.

Parr Instrument Company (2007). *Analytical Methods for Oxygen Bombs*.

PE International (2010). `http://www.gabi-software.com/` accessed 15/03/2011.

Pehnt, M. (2006). Dynamic life cycle assessment (LCA) of renewable energy technologies. *Renewable Energy 31*(1), 55–71.

Pennington, D. W., J. Potting, G. Finnveden, E. Lindeijer, O. Jolliet, T. Rydberg, and G. Rebitzer (2004). Life cycle assessment Part 2: Current impact assessment practice. *Environment International 30*(5), 721–739.

Police Standards Unit (2004). *Police Performance Monitoring 2003/04*. Home Office Communication Directorate.

Ponton, J. W. (2009). Biofuels: Thermodynamic sense and nonsense. *Journal of Cleaner Production 17*(10), 896 – 899. Early-Stage Energy Technologies for Sustainable Future: Assessment, Development, Application.

Powell, J. C., D. W. Pearce, and A. L. Craighill (1997). Approaches to valuation in LCA impact assessment. *The International Journal of Life Cycle Assessment 2*(1), 11–15.

Pre Consultants (2007). *SimaPro v7.2*. Pre Consultants B.V., Netherlands. `http://www.pre.nl` accessed 15/03/2011.

Rabl, A., A. Benoist, D. Dron, B. Peuportier, J. V. Spadaro, and A. Zoughaib (2007). How to Account for CO_2 Emissions from Biomass in an LCA. *International Journal of Life Cycle Assessment 12*(5), 281.

Ramachandran, S., S. K. Singh, C. Larroche, C. R. Soccol, and A. Pandey (2007, July). Oil cakes and their biotechnological applications - a review. *Bioresource Technology 98*, 2000–2009.

Ramadhas, A., C. Muraleedharan, and S. Jayaraj (2005). Performance and emission evaluation of a diesel engine fueled with methyl esters of rubber seed oil. *Renewable Energy 30*(12), 1789–1800.

Ranalli, P. (2004). Current status and future scenarios of hemp breeding. *Euphytica 140*, 121–131.

Reijnders, L. and M. Huijbregts (2008). Biogenic greenhouse gas emissions linked to the life cycles of biodiesel derived from European rapeseed and Brazilian soybeans. *Journal of Cleaner Production 16*, 1943–1948.

Reinhard, J. and R. Zah (2009). Global environmental consequences of increased biodiesel consumption in Switzerland: Consequential Life Cycle Assessment. *Journal of Cleaner Production 17*(Supplement 1), S46–S56.

Renewable Fuels Agency (2008). *The Gallagher Review of the indirect effects of biofuels production*. Renewable Fuels Agency.

Renewable Fuels Agency (2009a). *Carbon and Sustainability Reporting Within the Renewable Transport Fuel Obligation Technical Guidance Part 1 Version 2.0*. Renewable Fuels Agency `http://www.renewablefuelsagency.org/cands` accessed 15/03/2011.

Renewable Fuels Agency (2009b). RFA Monthly Report 7: 15 April - 14 November 2008. Technical report, Renewable Fuels Agency, Department for Transport.

Reyes, J. and M. Sepúlveda (2006). PM-10 emissions and power of a Diesel engine fueled with crude and refined biodiesel from salmon oil. *Fuel 85*(12-13), 1714 – 1719.

Romig, C. and A. Spataru (1996). Emissions and engine performance from blends of soya and canola methyl esters with ARB No. 2 diesel in a DDC 6V92TA MUI engine. *Bioresource Technology 56*(1), 25–34. A Collection of Papers Presented at An Alternative Energy Conference - Liquid Fuels, Lubricants and Additives from Biomass.

Ruan, C.-J., H. Li, Y.-Q. Guo, P. Qin, J. Gallagher, D. Seliskar, S. Lutts, and G. Mahy (2008). *Kosteletzkya virginica*, an agroecoengineering halophytic species for alternative agricultural production in China's east coast: Ecological adaptation and benefits, seed yield, oil content, fatty acid and biodiesel properties. *Ecological Engineering 32*(4), 320 – 328.

Saka, S. and D. Kusdiana (2001). Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel 80*(2), 225–231.

Sangha, M., P. Gupta, V. Thapar, and S. Verma (2004). Storage studies on plant oils and their methyl esters. *Agricultural Engineering Internationl: the CIGR Journal of Scientific Research and Development VI*(Manuscript EE 03 005).

Schmidt, J. H. (2008). System delimitation in agricultural consequential LCA: Outline of methodology and illustrative case study of wheat in Denmark. *International Journal of Life Cycle Assessment 13*, 350Ű364.

Scholz, V. and R. Ellerbrock (2002). The growth productivity, and environmental impact of the cultivation of energy crops on sandy soil in Germany. *Biomass and Bioenergy 23*(2), 81 – 92.

Searchinger, T., R. Heimlich, R. A. Houghton, F. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes, and T.-H. Yu (2008). Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change. *Science 319*(5867), 1238–1240.

Shu, Q., B. Yang, J. Yang, and S. Qing (2007). Predicting the viscosity of biodiesel fuels based on the mixture topological index method. *Fuel 86*(12-13), 1849–1854.

Sims, R., M. Taylor, J. Saddler, and W. Mabee (Eds.) (2008). *From 1st to 2nd Generation Biofuel Technologies*. IEA, Paris, France.

Sims, R. E. H. (2002). *The Brilliance of Bioenergy - In Business and in Practice*. London: James & James.

Sipos, B., E. Kreuger, S.-E. Svensson, K. Réczey, L. Björnsson, and G. Zacchi (2010). Steam pretreatment of dry and ensiled industrial hemp for ethanol production. *Biomass and Bioenergy In Press, Corrected Proof*, –.

Skelton, R., M. Mackley, and A. Harvey (2004). Biodiesel. `http://www.ceb.cam.ac.uk/pages/biofuels.html` accessed 15/03/2011.

Small, E. and D. Marcus (2002). Hemp: A New Crop with New Uses for North America. In J. Janick and A. Whipkey (Eds.), *Trends in new crops and new uses*, pp. 282 – 326. Alexandria, VA: ASHS Press.

Solomon, S., D. Qin, M. Manning, Z.Chen, M. Marquis, K. Averyt, M. Tignor, and H. Miller (Eds.) (2007). *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press, UK.

Spirinckx, C. and D. Ceuterick (1996). Biodiesel and fossil diesel fuel: Comparative life cycle assessment. *International Journal of Life Cycle Assessment 1*(3), 127–132.

Squier, D. (2008). *Private communication*. Interview.

Squier, D. (2010a). *Private communication*.

Squier, D. (2010b). *Private communication*.

Starkey, R. and K. Anderson (2005). *Domestic Tradable Quotas: A policy instrument for reducing greenhouse gas emissions from energy use*. Tyndall Centre.

Stephenson, A., J. Dennis, and S. Scott (2008). Improving the sustainability of the production of biodiesel from oilseed rape in the UK. *Process Safety and Environment Protection 86*(6), 427–440.

Stern, N. (2007). *The Economics of Climate Change: The Stern Review*. Cambridge University Press.

Sun, L., J. Ni, and A. G. Borthwick (2010). Rapid assessment of sustainability in mainland China. *Journal of Environmental Management 91*(4), 1021 – 1031.

Szybist, J. P., S. R. Kirby, and A. L. Boehman (2005). NOx Emissions of Alternative Diesel Fuels: A Comparative Analysis of Biodiesel and FT Diesel. *Energy & Fuels 19*, 1484–1492.

Talens-Peiró, L., L. Lombardi, G. V. Méndez, and X. G. i Durany (2010). Life cycle assessment (LCA) and exergetic life cycle assessment (ELCA) of the production of biodiesel from used cooking oil (UCO). *Energy 36*(2), 889–893.

Tat, M. E. and J. H. Van Gerpen (1999). The kinematic viscosity of biodiesel and its blends with diesel fuel. *Journal of the American Oil Chemists' Society 76*(12), 1511–1513.

Tat, M. E. and J. H. Van Gerpen (2000). The specific gravity of biodiesel and its blends with diesel fuel. *Journal of the American Oil Chemists' Society 77*(2), 115–119.

Ten Brink, B., S. Hosper, and F. Colijn (1991). A quantitative method for description & assessment of ecosystems: The AMOEBA-approach. *Marine Pollution Bulletin 23*, 265 – 270. Environmental Management and Appropriate Use of Enclosed Coastal Seas.

Tesco plc. (2010). *Carbon footprints and labelling*. `http://www.tesco.com/greenerliving/greener_tesco/faqs/qa_carbon_footprint_and_labelling.page?` accessed 15/03/2011.

The Royal Society (2008, 14 January 2008). Sustainable biofuels: prospects and challenges. Technical report, The Royal Society.

The Scottish Government (2005). Census 2001 adjusted tenure tables: Household composition table. `http://www.scotland.gov.uk/Resource/Doc/1035/0009706.csv` accessed 15/03/2011.

Thompson, M., R. Ellis, and A. Wildavsky (1990). *Cultural Theory (Political Cultures series)*. Westview Press, Boulder, USA.

Tovey, N. K. (2008). *Personal communication*.

Tuck, G., M. J. Glendining, P. Smith, J. I. House, and M. Wattenbach (2006). The potential distribution of bioenergy crops in Europe under present and future climate. *Biomass and Bioenergy 30*(3), 183 – 197.

Turunen, L. and H. M. G. van der Werf (2006, 31 May 2006). Life Cycle Analysis of Hemp Textile Yarn: Comparison of three hemp fibre processing scenarios and a flax scenario. Technical report, Institut National de la Recherche Agronomique.

UNFCCC (1997, December). Kyoto Protocol to the United Nations Framework Convention on Climate Change. `http://unfccc.int/resource/docs/convkp/kpeng.pdf` accessed 15/03/2011.

Upham, P., P. Thornley, J. Tomei, and P. Boucher (2009). Substitutable biodiesel feedstocks for the UK: a review of sustainability issues with reference to the UK RTFO. *Journal of Cleaner Production 17*(Supplement 1), S37–S45.

US Census Bureau (2009). *International Data Base (IDB) - World Population*. `http://www.census.gov/ipc/www/idb/worldpopinfo.html` accessed 13 January 2009.

van der Voet, E., R. J. Lifset, and L. Luo (2010). Life-cycle assessment of biofuels, convergence and divergence. *Biofuels 1*(3), 435–449.

van der Werf, H. M. G. and L. Turunen (2008). The environmental impacts of the production of hemp and flax textile yarn. *Industrial Crops and Products 27*, 1–10.

Van Gerpen, J. and G. Knothe (2005). The Biodiesel Handbook. In G. Knothe, J. Krahl, and J. Van Gerpen (Eds.), *The Biodiesel Handbook*, Chapter Biodiesel Production: Basics of the Transesterification Reaction, pp. 26–41. Champaign: AOCS Press.

Veljković, V., S. Lakićević, O. Stamenković, Z. Todorović, and M. Lazić (2006). Biodiesel production from tobacco (*Nicotiana tabacum L.*) seed oil with a high content of free fatty acids. *Fuel 85*(17-18), 2671–2675.

von Blottnitz, H. and M. A. Curran (2007). A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. *Journal of Cleaner Production 15*(7), 607–619.

Walton, J. (1938). The fuel possibilities of vegetable oils. *Gas Oil Power 33*, 167–168.

Weidema, B. P., N. Frees, and A.-M. Nielsen (1999). Marginal production technologies for life cycle inventories. *The International Journal of Life Cycle Assessment 4*(1), 48–56.

Wenzel, H. (1998). Basis of the EDIP method's allocation model. In M. Hauschild and H. Wenzel (Eds.), *Environmental Assessment of Products Volume 2: Scientific Background*. London: Chapman & Hall.

Xu, Y. and M. Hanna (2009). Synthesis and characterization of hazelnut oil-based biodiesel. *Industrial Crops and Products 29*(2-3), 473–479.

Yang, R., M. Su, M. Li, J. Zhang, X. Hao, and H. Zhang (2010). One-pot process combining transesterification and selective hydrogenation for biodiesel production from starting material of high degree of unsaturation. *Bioresource Technology 101*(15), 5903–5909.

Yoon, S. H., S. H. Park, and C. S. Lee (2008). Experimental investigation on the fuel properties of biodiesel and its blends at various temperatures. *Energy & Fuels 22*(1), 652–656.

Yuan, W., A. C. Hansen, and Q. Zhang (2004). The specific gravity of biodiesel fuels and their blends with diesel fuel. *Agricultural Engineering International: the CIGR Journal of Scientific Research and Development VI*, Manuscript EE 04 004.

Zhang, X., C. L. Peterson, D. Reece, G. Moller, and R. Haws (1998). Biodegradability of biodiesel in the aquatic environment. *Transactions of the American Society of Agricultural Engineers 41*(5), 1423–1430.

Zhong, C., C. Peters, and J. de Swaan Arons (2002). Thermodynamic modeling of biomass conversion processes. *Fluid Phase Equilibria 194-197*, 805–815.

Zhou, Z., H. Jiang, and L. Qin (2007). Life cycle sustainability assessment of fuels. *Fuel 86*(1-2), 256–263.

Zullaikah, S., C.-C. Lai, S. R. Vali, and Y.-H. Ju (2005). A two-step acid-catalyzed process for the production of biodiesel from rice bran oil. *Bioresource Technology 96*, 1889–1896.