

## Advances in biodiesel fuel research

Jüri Kann\*, Heino Rang, and Jüri Kriis

Institute of Chemistry, Tallinn Technical University, Akadeemia tee 15, 12618 Tallinn, Estonia

Received 7 November 2001, in revised form 11 March 2002

**Abstract.** The paper gives a thorough review of research on biodiesel fuel sources, properties, preparation methods, production, exhaust gases emitted by using biodiesel fuel, analytical methods, and economic aspects. The main advantage of biodiesel fuel is lower concentration of greenhouse gases (especially CO<sub>2</sub>) and other pollutants in motor exhaust gases compared to petroleum diesel fuel. The main concerns with biodiesel fuel are its relatively high price, instability, and low-temperature properties. The future aims in biodiesel fuel research are improvement of production technology and reduction of the costs of production of plant oil by plant breeding, selection, and gene technology. The low-temperature properties and stability of biodiesel fuel can be improved by additives and genetic engineering of oil plants. The paper includes 250 references.

**Key words:** biodiesel fuel, diesel fuel, plant oils, pollutants, fuel additives.

**Abbreviations.** BDF = biodiesel fuel; CFPP = cold filter plugging point; CP = cloud point; DF = diesel fuel; FAME = fatty acid methyl esters; GLC = gas–liquid chromatography; HPLC = high performance liquid chromatography; OCC = oxidation catalytic converter; PAH = polycyclic aromatic hydrocarbons; PDF = petroleum diesel fuel; PME = plant oil methyl esters; PP = pour point; REE = rapeseed oil ethyl esters; RME = rapeseed oil methyl esters; SME = soybean oil methyl esters; TPM = total particulate matter.

### INTRODUCTION

The research and use of biodiesel fuel (BDF) as an alternative fuel for the diesel engine started in the 1980s. The reason was the petroleum crisis caused by the reduction of petroleum production by OPEC and the resulting price rise. The first attempt was to use neat oils as a DF; however, the high viscosity and solidifying temperature above 0 °C hindered extensive use of these oils. The first who used plant oils in the diesel engine as a fuel was Rudolf Diesel himself in 1900 [1]. In the 1930s and 1940s neat vegetable oils were used as DF from time

---

\* Corresponding author, kann@chemnet.ee

to time, but usually only in emergency situations. The transesterification of triglycerides of plant oils with alcohols gave satisfactory results. Today the main alternative fuel for diesel engines is a mixture of methyl esters of fatty acids (FAME) derived from plant oils.

In the United States, investigations on vegetable oil started as long ago as in 1978 and the research has focused on soybean oil methyl ester (SME) as BDF. Pioneers in this field were Freedman & Pryde [2], Peterson & Hustrulid [3], and also Goodrum [4] in Georgia. In South Africa BDF initiatives were reported in 1981. In Germany and Austria the rapeseed oil methyl ester (RME) was tested in diesel engines for the first time in 1982. In 1985 a small pilot plant was built in Austria and the production of RME using a new technology (ambient pressure and temperature) was started. In 1990 the first farmers' cooperative started commercial production of BDF derived from rapeseed as well as sunflower oil in Austria [5]. Junek & Mittelbach [6] were among organizers in the BDF research in Europe.

The demand for alternative fuels is increasing as the supplies of fossil fuels diminish and therefore their prices rise. The prognosis is that the North Sea oil will run out by 2010 at the latest. The energy demand is growing constantly, and especially dramatically in the non-OECD world, for example in China. The European Commission estimates that biofuels will make up 12% of the market by 2020.

In 1997 the production of BDF was 550 thousand tonnes in Europe (France 250 t, Italy 109 t, Germany 83 t, Czech Republic 45 t, etc.), 10 000 tonnes in Malaysia, and 9000 tonnes in North America. In Europe new projects are estimated for 200 thousand tonnes and in North America 400 thousand tonnes annually [7]. In 2000 the annual production of BDF in Europe was 1 210 000 t (Germany 550 000 t, France 290 000 t, Italy 240 000 t, Belgium 110 000 t, Czech Republic 47 000 t, etc.). The production has increased 2.2 times in three years.

In the 21st century one of the main scientific and political problems is the reduction of the emission of greenhouse gases (mainly carbon dioxide) into the atmosphere (resolutions of the Kyoto congress).

The petroleum diesel fuel (PDF) represented by hexadecane releases 3.1 kg of carbon dioxide per 1 kg of fuel used in combustion. The BDF represented by methyl ester of oleic acid releases 2.7 kg respectively. The carbon dioxide from BDF is fixed by plants and will be recycled in the next generation of crops [8].

It is known that in the case of BDF the amount of pollutants in motor exhaust gases is significantly lower than when petroleum fuel is used: sulphur oxides by 99%, carbon monoxide by 20%, hydrocarbons by 30%, soot by 50%, and particulate matter by 40%.

The acute dermal and oral toxicity of BDF is very low. Its biodegradability is more than 90% within 3 weeks in contact with the ground, but the biodegradability of PDF is much slower. There is a less-global-warming-bonus, which is calculated as CO<sub>2</sub>-avoiding cost of US \$ 0.64 per 1 kg BDF in industrial countries.

The considerable importance of chemically bound oxygen in the BDF such as FAME, also known as plant oil methyl esters (PME), for instance RME and SME,

has the effect of reducing the pollutant concentration in exhaust gases due to better burning of the fuel in the engine. BDF can be used in existing engines. A BDF with 11% oxygen content gives no soot and produces fewer particles, has very good ignitability and better cetane number, good mixing capability with DF, low tendency for coking, good lubrication capability, and the exhaust gases do not poison the oxidation catalyst (no sulphur content in BDF) [9]. The disadvantages of BDF are unpleasant odours when oxidation catalyst of exhaust gases is lacking. It was shown [9] that the sound power is up to 50% lower when BDF is used than in the case of PDF. BDF causes weak aggressiveness against some soft materials (gaskets, lacquers) and an increased content of nitrogen oxides in exhaust gases. The latter will be reduced in modern engines with high-pressure fuel injection systems. The most unpleasant properties of BDF compared with PDF are the higher melting point and the tendency for polymerization because of the content of unsaturated compounds [9].

Although in the early 1980s it was already clear that neat plant oil as BDF is not competitive (higher viscosity, cloud point (CP), cold filter plugging point (CFPP), etc.) with methyl esters of oil, Ryan et al. [10], Tahir et al. [11], Auld et al. [12], Pryde [13], and Romano [14] investigated neat vegetable oils without specific treatment as DF. Tahir et al. [11] and Romano [14] also describe methyl esters of vegetable oil as a DF. The neat plant oils can be used if the injection system of the old tractor engines is reconstructed. It cannot be used in modern direct injection engines.

The situation in the field of BDF research in different countries is given below. In the USA 20% of SME is mixed with PDF, mainly because of price reasons (the taxes on the PDF in the USA are low). In Germany and Austria marked undiluted BDF is in the market and the price of BDF is competitive with PDF if no taxes are levied on BDF. Nowadays Germany has over 600 refuelling stations for BDF.

In the USA the first test with 100% ethyl ester of rapeseed oil (REE) was made by Peterson et al. [8] at the University of Idaho in 1979. The ethyl esters of fatty acids as DF derived from bioethanol have zero greenhouse gas effect, while methyl esters from synthetic methanol obtained from fossil raw material increase the carbon dioxide concentration in the air. Methanol obtained from biomass is even more expensive than bioethanol. Ethanol is also safer to handle than methanol [5]. However, the price of plant oil ethyl esters is higher than that of methyl esters (synthetic methanol is cheaper than bioethanol).

Problems concerning BDF are investigated in many countries. In Austria, as mentioned above, RME as DF has been investigated and used since the beginning of the 1980s [5, 7, 15].

In France the consumption of BDF makes up 1.3% of the total consumption of DF and it is used in blend with PDF [16]. Hillion et al. [17] showed that even 5% blending of PME with PDF gives good results in lubricity of diesel engines and also reduces the pollutant concentration in exhaust gases. In the 1990s the French Government subsidized PME more than 2 French francs per litre [18]. In

1995 France consumed 22.8 Mt of DF and 16.5 Mt of domestic fuel oil. About 900 000 t of DF is consumed per year by the fleets. With a blend of 30% of BDF, this represents almost 300 000 t of BDF. In the Lorraine Region RME blends of 20–90% with fuel oil are used as fuel in local power stations. Thus bioelectricity from RME is being produced [19]. Ecological problems with BDF and PDF were investigated by Poitrat [20].

In Spain oils and transesterified oils as DF based on Jerusalem artichoke were examined [21]. An overview of the situation of BDF in Spain was given by Gomez [22].

In the UK, the quantity of BDF that can be produced from rape would be able to satisfy 5% of the DF demand. If BDF was taxed at 10% of the rate of PDF it would be profitable. The production costs of BDF are 4.56 times higher than those of PDF. Since 1990 about 400 000 ha of oilseed rape has been cultivated annually in the UK and the area has been increased from year to year. It makes up approximately 8% of the available cropland. Although the land base available for oilseed rape cultivation can grow to some extent, the size of biodiesel industry in the UK is limited by the common agricultural policy of the European Union [23]. Increasing the rape cultivation for BDF production will elevate the level of nitrogen residues in the soil. The rape plants are cruciferous plants, which connect the air nitrogen in the soil.

In Italy BDF and its blends in diesel engine were investigated by Rocco et al. [24]. In the Czech Republic 23 BDF manufacturing plants with a total annual output of 72 600 t were in operation or near completion in 1995. The tests with bioethanol showed the heating value of only 35% of that of PDF, but the former had very low smoke and particle emission [25].

Cvengros & Povazanek [26] in Slovakia described a real two-stage low-temperature transesterification process of cold-pressed rapeseed oil with methanol. They presented a fuel blend known as BIONAPHTA MDT, which contains 30 vol % RME and 70 vol % PDF. It is possible to use RME for public transportation in towns, for ship transport, especially on rivers and lakes, and for engines operating in closed spaces (mines, greenhouses, etc.) [26]. Cvengros & Cvengros [27] published a review of BDF in Slovakia.

The esterification of Turkish olive oil with different straight- and branched-chain monoalcohols was investigated by Aksoy et al. [28]. In Turkey 46 000 t of grape seeds may be recovered annually as a by-product of the beverage and fermentation industries. Solvent extraction of this industrial residue may yield 5000 t of grape seed oil per year. Aksoy et al. [29] investigated possibilities of obtaining BDF from this source. The methyl and ethyl esters of this oil can be used directly as DF or blended (10–20%) with PDF [29]. Karaosmanoglu [30] published a review about BDF in Turkey. He and co-workers [31] also studied producing BDF from rapeseed oil of Turkish origin.

In India a review about BDF with 38 references was published by Srivastava & Prasad [32]. Obtaining BDF from minor vegetable oils such as karanja (*Pongamia glabra*) and nahor (*Mesua ferrea*) was also studied in India [33].

In Portugal, similarly to Spain, sunflower oil is the main raw material of BDF. Rapeseed oil is also investigated as a raw material [34].

In Greece sunflower oil and corn oil are the sources for BDF as well as neat oils needed for making blends with PDF [35]. It is interesting to note that in 1998 neat oils were still used. Even 10 vol % BDF (derived from sunflower oil in Greece) blend with PDF reduced significantly black smoke and particulate matter emissions at higher loads compared with PDF. Measurements of metal wear indicated no effect of BDF blends [36].

In Poland BDF was studied by Kotowski & Fechner [37]. In Egypt jojoba oil methyl esters and their blends with PDF and methanol as DF are in highlight [38].

An analysis about the possibilities of biofuels, biogas, bioethanol, and BDF and their production in Croatia was given by Domac and co-workers [39, 40]. Croatia has a significant potential for BDF production from rapeseed oil [41]. BDF has an important role also in Serbia [42].

Sunflower oil 20% and 40% blends with PDF were tested in Rumania in 1996–97 [43]. In Korea bran oil from rice was investigated to produce BDF. For transesterification methanol, ethanol, and butanol were used [44]. In Malaysia palm oil is the main source for BDF [45]. In the region of Maldives locally available coconut oil and coconut oil methyl esters have been tested with success as diesel engine fuels [46]. These plant seed oils have great potential for development as DF or DF extenders [44–47].

Numerous reviews have been published about the properties, production, environmental effects, etc. of BDF [5, 7, 48–55].

## SOURCES

A large variety of plant oils, such as rapeseed, palm, soybean, sunflower, peanut, etc. have been studied as possible sources of BDF. Also microalgae and animal fats have been considered. Neat plant seed oils as diesel engine fuels have been widely investigated and it was found that pure oil is not suitable for long-term use in conventional diesel engines [56]. The use of rapeseed oil is possible if the engine design is modified. ME were found not to cause any environmental or health problems [57]. Neat rapeseed oil and DF blends have been used as DF, but blends of methyl esters are better [58]. Experiments for using neat plant oils and PDF blends as DF were made in Turkey still in 1995 [59], but this way has no prospects.

Rapeseed oil as a source for transesterification to obtain methyl esters (RME) was thoroughly described by Körbitz [5]. Hassett & Hasan successfully tested sunflower oil methyl esters as DF [60]. Kusy [61] transesterified soybean and sunflower oils with ethanol and tested the ethyl ester of soybean oil as fuel for a direct-injection engine in John Deere 4640 tractor.

Maize (*Zea mays*) oil as a source of transesterification to obtain methyl esters to be used as BDF was examined by Son & Verma [62].

Cardoon (*Cynara cardunculus* L.) can be a source of plant oil to produce BDF. Cardoon was already known to the ancient Egyptians, Greeks, and Romans. Today it is growing spontaneously in the countries bordering the Mediterranean, but also in California, Mexico, and South America (Castilian thistle). It is related to artichoke, sunflower, and safflower. Total cultivated biomass production can reach 20–30 t dry matter per ha, including 2000–3000 kg of seeds. The protein content of the seeds is close to 15% and the oil content around 25% [63].

Methyl and ethyl esters of the oil of the seeds of *Jatropha curcas* L., which is a possible energy crop in Nicaragua, have been studied as DF. This is one of the possibilities of enlarging the sources of BDF [64].

From 364 various types of seeds commonly found in Thailand, 21 seed oil methyl esters have cetane index value higher than 60 and could be sources of BDF. Some seeds are waste products of the food industry (papaya, orange, okra, peach, jojoba) and they may have great potential for the development of oils as diesel feedstock [43].

For increasing the raw material resources microalgae could potentially be a source for biological lipids for BDF production [65]. Palm oil and cultured microalgae are potential sources for BDF in Indonesia [66].

Transesterification of beef tallow was investigated by Ma et al. [67, 68] to find new sources for BDF. Transesterified soybean oil and beef tallow as BDF were presented by Muniyappa et al. [69]. A review about beef tallow as BDF source was given by Hanna and co-workers [70–75].

Development of BDF production from feedstocks using frying oils was discussed by Walker [76].

In Austria the amount of the used fats and oils forms approximately 37 000 t per year. Of this amount 59% is produced in households, 35% in restaurants, and 6% in industry [77]. Frying oil is an interesting alternative feedstock for BDF production. The amount of polymers in waste oil is a good indicator of the suitability for BDF production. In the transesterified oil, the polymer content is lower than in the starting oil [78, 79].

Selection and genetical engineering of oil plants is one way to obtain more effective raw material of BDF. In the 1960s the elimination of the content of erucic acid glycerides in rapeseed oil was the first step in the selection of rape plants to obtain edible rape oil. Later (in the 1980s) it was shown that this oil (the canola oil) was also a better raw material for transesterification to produce BDF [80].

Toxicity of erucic acid for rats and pigs was shown by Roine et al. [81]. Elimination (from 50% to 0.2%) of erucic acid (C 22 : 1) was the first step to increase the oleic acid level from 15% to 60% (low (00) rapeseed varieties, which produce the canola oil). The next step was to increase the oleic acid level of the transgenic material to 70.0–72.5%. Nowadays the oleic acid level of 90% has been reached at the expense of linolenic acid and linoleic acid, whose concentration has

been reduced from 10% to 2% and from 22.0% to 2.0%, respectively. This oil is a relatively suitable feedstock for BDF. Today also hybrid varieties are being developed with 15% to 20% more yield than the check varieties [82].

Here the demands for eatable oil and oil as a raw material for BDF are contradictory. The linolenic acid is a valuable component of food. For table oil the rape plant has been treated mutagenically to obtain higher linolenic acid content. For BDF it is necessary to increase the oleic acid content and decrease the linolenic acid content in order to improve the stability of BDF. In the soybean oil as well as in the rapeseed oil an 80% oleic acid content has been reached [83, 84].

Harwood [85] gave a thorough review about the biosynthesis of plant fatty acids and the general base of genetic engineering in this field. It seems that not all aspects of fatty acid and triglyceride biosynthesis can be modified by means of genetic engineering, which will in the future lead to the development of vegetable oil products with greatly improved utility in different applications.

It is possible to obtain by genetic engineering for instance rape plants that produce more lauric acid. The respective oil is called laurate canola (canola – rapeseed oil without erucic acid or low erucic acid content). Laurate canola is more stable against oxidation and polymerization than commodity canola [86]. Another direction in genetic engineering is to increase the content of the short-chain saturated acids, capric acid (C 10:0) and caprylic acid (C 8:0). The methyl esters of these acids have a greater oxygen content and behave better in the combustion process reducing soot and particulate matter emissions in exhaust gases. The melting points are comparable with methyl oleate or lower.

In genetic engineering a realistic proportion of toxicological, motor-technical, and economic aspects should be considered. Genetic engineering and traditional breeding need to be combined to achieve the goal [87].

Another way to reach the required low-temperature properties and stability of BDF is to use corresponding additives and better technologies.

## PROPERTIES

### The fatty acid content in the triglycerides of plant oil

The fatty acid content in the triglycerides of plant oils and tallow has been studied by a large number of scientists. Some results are given below.

Demirbas [88] investigated 20 Turkish vegetable oils as potential DF sources. The content of the three most interesting fatty acids is presented in Table 1.

**Table 1.** The fatty acid composition in the triglycerides of Turkish oils, % [88]

| Vegetable oil  | C 16:0 | C 16:1 | C 18:0 | C 18:1 | C 18:2 | C 18:3 | Σ    |
|----------------|--------|--------|--------|--------|--------|--------|------|
| Rapeseed       | 3.5    | 0      | 0.9    | 64.1   | 22.3   | 8.2    | 99.0 |
| Soybean        | 13.9   | 0.3    | 2.1    | 23.2   | 56.2   | 4.3    | 100  |
| Sunflower seed | 6.4    | 0.1    | 2.9    | 17.7   | 72.9   | 0      | 100  |

Syassen [9] presented the average content of fatty acids in the triglycerides of “00” rapeseed oil (canola oil) (Table 2).

**Table 2.** The fatty acid composition in the triglycerides of canola oil [9]

| Acid      | Notation | Content, % |
|-----------|----------|------------|
| Palmitic  | C 16:0   | 6          |
| Stearic   | C 18:0   | 1          |
| Oleic     | C 18:1   | 58         |
| Linoleic  | C 18:2   | 24         |
| Linolenic | C 18:3   | 11         |

Capronic acid (C 10:0) and lauric acid (C 12:0) are present only in traces.

The composition of various oils by Wenzel & Lammers [89] is given in Table 3.

**Table 3.** The fatty acid composition in various oils [89]

| Vegetable oil     | The fatty acid content in the triglycerides of oil, % |        |        |        |        |        |        | Σ    | Saturated fatty acids | Multiple unsaturated fatty acids |
|-------------------|---|--------|--------|--------|--------|--------|--------|------|-----------------------|----------------------------------|
|                   | C 14:0  | C 16:0 | C 18:0 | C 18:1 | C 18:2 | C 18:3 | C 22:0 |      |                       |                                  |
| Palm              | 1.1   | 42.7   | 7.9    | 36.1   | 10.6   | 0.2    |        | 98.6 | 52.5                  | 10.8                             |
| Rapeseed (canola) | –   | 4.1    | 0.5    | 63.9   | 21.1   | 10.4   |        | 100  | 4.6                   | 31.5                             |
| Cottonseed        | –   | 19.9   | –      | 20.1   | 53.3   | 1.2    |        | 94.5 | 19.9                  | 54.5                             |
| Sunflower         | –   | 6.2    | 3.6    | 16.8   | 72.0   | 0.1    | 1.1    | 98.7 | 11.1                  | 72.1                             |

The comparative fatty acid composition in triglycerides by Knothe et al. [90] is given in Table 4.

**Table 4.** The fatty acid composition in oils by Knothe et al. [90]

| Oil or fat           | Fatty acid composition, % mass |         |         |         |         |        |
|----------------------|--------------------------------|---------|---------|---------|---------|--------|
|                      | 14:0                           | 16:0    | 18:0    | 18:1    | 18:2    | 18:3   |
| Canola (Rapeseed 00) |                                | 4–5     | 1–2     | 55–63   | 20–31   | 9–10   |
| Soybean              |                                | 2.3–11  | 2.4–6   | 22–30.8 | 49–53   | 2–10.5 |
| Sunflower            |                                | 3.5–6.5 | 1.3–5.6 | 14–43   | 44–68.7 | –      |
| Tallow (beef)        | 3–6                            | 25–37   | 14–29   | 26–50   | 1–2.5   | –      |

Typical fatty acid composition in the triglycerides of various oil sources by Kincs [91] is given in Table 5.

The comparative fatty acid composition in the triglycerides of tallow and soybean oil and in the corresponding esters as well as the properties of these products by Ali et al. [71] are presented in Table 6.



**Table 5.** The fatty acid composition in oils, % [91]

| Fatty acid | Oil     |            |      |         | Fat  |        |
|------------|---------|------------|------|---------|------|--------|
|            | Soybean | Cottonseed | Palm | Coconut | Lard | Tallow |
| Lauric     | 0.1     | 0.1        | 0.1  | 46.5    | 0.1  | 0.1    |
| Myristic   | 0.1     | 0.7        | 1.0  | 19.2    | 1.4  | 2.8    |
| Palmitic   | 10.2    | 20.1       | 42.8 | 9.8     | 23.6 | 23.3   |
| Stearic    | 3.7     | 2.6        | 4.5  | 3.0     | 14.2 | 19.4   |
| Oleic      | 22.8    | 19.2       | 40.5 | 6.9     | 44.2 | 42.4   |
| Linoleic   | 53.7    | 55.2       | 10.1 | 2.2     | 10.7 | 2.9    |
| Linolenic  | 8.6     | 0.6        | 0.2  | 0.0     | 0.4  | 0.9    |

**Table 6.** The fatty acid composition and properties of tallow and soybean oil [71]

| Carbon chain         | Tallow, % | Tallow ester, % | Soybean oil, % | Soybean oil ester, % |
|----------------------|-----------|-----------------|----------------|----------------------|
| C 8:0                |           |                 | 0.04           | 0.07                 |
| C 12:0               |           |                 | –              | 0.36                 |
| C 14:0               | 4.89      | 2.59            | –              | 0.25                 |
| C 16:0               | 28.43     | 23.69           | 10.74          | 9.65                 |
| C 16:1               | 4.63      | 2.96            | –              | –                    |
| C 18:0               | 14.86     | 19.86           | 3.84           | 4.39                 |
| C 18:1               | 44.55     | 48.91           | 20.96          | 23.10                |
| C 18:2               | 2.64      | 1.99            | 56.56          | 53.93                |
| C 18:3               | –         | –               | 7.86           | 8.25                 |
| Saturated            | 48.18     | 46.14           | 14.62          | 14.72                |
| Unsaturated          | 51.82     | 53.86           | 85.38          | 85.28                |
| Technical properties |           |                 |                |                      |
| Melting point, °C    | 45        | 13.5            | –3.5           | –3                   |
| Cloud point, °C      |           | 12              | –9             | –3                   |
| Pour point, °C       |           | 9               | –16            | –7                   |
| Flash point, °C      | 201       | 96              | 174            | 127                  |

### Technical properties and composition of BDF

The properties of FAME by the authors of this paper and Ma & Hanna [92] are presented in Table 7.

The fatty acid composition in tallow and grease esters by Wu et al. [93] is presented in Table 8.

Low-temperature properties of the presented esters compared with PDF and a blend of ethyl tallowate/PDF are given in Table 9.

The low-temperature properties and cetane number of methyl esters by Knothe et al. [90] are presented in Table 10 and the properties of FAME in Table 11.

**Table 7.** The properties of fatty acid methyl esters

| Methyl ester                                   | Boiling point, °C/mmHg             |           | Melting point, °C |       | Flash point, °C | Iodine number <sup>a</sup> , g iodine/100 g |
|--|------------------------------------|-----------|-------------------|-------|-----------------|---|
|  |                                    | [92]      |                   | [92]  |                 |   |
| Myristate<br>(Tetradecanoate)                  | –                                  | 323/760   | –                 | 18.8  |                 |   |
| Palmitate<br>(Hexadecanoate)                   | 164/4<br>~335/760 <sup>b</sup>     | 163–164/4 | 32–34             | 30.6  | 110             | 0   |
| Stearate<br>(Octadecanoate)                    | 181–182/4<br>~350/760 <sup>b</sup> | 181–182/4 | 40–42             | 40–42 | 110             | 0   |
| Oleate<br>(9-Octadecenoate)                    | 218/20<br>~345/760 <sup>b</sup>    | 218/20    | –19.9             | –19.8 | 110             | 85.6  |
| Linoleate<br>(9,12-Octa-<br>decadienoate)      | 192/4<br>~355/760 <sup>b</sup>     | –         | –35               | –     | 110             | 172.4                                       |
| Linolenate<br>(9,12,15-Octa-<br>decatrienoate) | 182/3<br>~355/760 <sup>b</sup>     | –         | –10               | –     | 110             | 292.5                                       |

<sup>a</sup> calculated, <sup>b</sup> according to the nomograph

**Table 8.** The fatty acid content (%) in tallow and grease [93]

| Fatty acid | Ethyl tallowate | Isopropyl tallowate | Ethyl greasate |
|------------|-----------------|---------------------|----------------|
| C 14:0     | 3.38            | 3.40                | 0.72           |
| C 16:0     | 26.97           | 27.09               | 14.33          |
| C 16:1     | 2.29            | 2.39                | 1.33           |
| C 17:0     | 1.22            | 1.26                | –              |
| C 18:0     | 24.56           | 24.31               | 9.22           |
| C 18:1     | 39.06           | 39.00               | 47.01          |
| C 18:2     | 2.53            | 2.55                | 25.27          |
| C 18:3     | –               | –                   | 2.32           |

The iodine number of tallowate esters is between 50 and 60. The ethyl greasate iodine number is approximately 100.

**Table 9.** Low-temperature properties of BDF and PDF [93]

| Fuel                | LTFT, °C | CFPP, °C | CP, °C | PP, °C | T, °C | Gross heat, % |
|---------------------|----------|----------|--------|--------|-------|---------------|
| Ethyl tallowate     | 13       | 12       | 15     | 3      | 17.8  | 87.7          |
| Isopropyl tallowate | 19       | 5        | 9      | 3      | 10.6  | 89.1          |
| Ethyl greasate      | 9        | 0        | 5      | –1     | 9.4   | 88.5          |
| Methyl soyate       | 2        | –3       | 0      | –2     | –     | 88.1          |
| PDF                 | –14      | –27      | –16    | –23    | –8.5  | 100           |
| ET/PDF (20:80)      | –1       | –10      | –6     | –12    | 3.7   | 97.5          |

LTFT – low-temperature flow test, CFPP – cold filter plugging point, CP – cloud point, PP – pour point, T – crystallization onset temperature

**Table 10.** Properties of BDF [90]

| Methyl ester of oil | Cetane number | Cloud point, °C | Pour point, °C |
|---------------------|---------------|-----------------|----------------|
| Rapeseed            | 54.4          | −2              | −9             |
| Soybean             | 46.2          | 2               | −1             |
| Sunflower           | 46.6          | 0               | −4             |
| Tallow              | 58.0–60.0     | 12              | 9              |

**Table 11.** Properties of methyl esters as diesel fuel components by Knothe [90]

| Methyl ester                               | Mol. mass | m.p., °C   | b.p., °C/torr | Cetane No. | Heat of combustion, kcal/mole |
|--|-----------|------------|---------------|------------|-------------------------------|
| Caprylate (C 8:0)<br>(Octanoate)           | 158.24    |            | 193/760       | 33.6       | 1313                          |
| Caproate (C 10:0)<br>(Decanoate)           | 186.30    |            | 224/760       | 47.7       | 1625                          |
| Laurate (C 12:0)<br>(Dodecanoate)          | 214.35    | 5          | 266/766       | 61.4       | 1940                          |
| Myristate (C 14:0)<br>(Tetradecanoate)     | 242.41    | 18.5       | 295/751       | 66.2       | 2254                          |
| Palmitate (C 16:0)<br>(Hexadecanoate)      | 270.46    | 30.5       | 415/747       | 74.5       | 2550                          |
| Stearate (C 18:0)<br>(Octadecanoate)       | 298.51    | 39.1       | 442/747       | 86.9       | 2859                          |
| Oleate (C 18:1)<br>(Octadecenoate)         | 296.49    | −20        | 218.5/30      | 55.0       | 2828                          |
| Linoleate (C 18:2)<br>(Octadecadienoate)   | 294.48    | −35        | 215/30        | 42.2       | 2794                          |
| Linolenate (C 18:3)<br>(Octadecatrienoate) | 292.46    | −57<br>−52 | 109/0.98      | 22.7       | 2750                          |

Comparative fuel properties of PDF and RME by Williamson & Badr [23] are given in Table 12.

**Table 12.** Properties of PDF and RME by Williamson & Badr [23]

| Properties and units                      | Fuel               |         |
|---|--------------------|---------|
|   | No. 2 diesel (PDF) | RME     |
| Heat of combustion, MJ kg <sup>−1</sup>   | 45.2               | 40.5    |
| Heat of vaporization, kJ kg <sup>−1</sup> | 256                | 297     |
| Specific heat, kJ kg <sup>−1</sup> K      | 1.7                | 2.47    |
| Cloud point, °C                           | −10                | −1      |
| Pour point, °C                            | −29                | −9      |
| Flash point, °C                           | 80                 | 170     |
| Cetane number                             | 47.8               | 54.4    |
| Sulphur content, % by mass                | 0.36               | <0.0001 |

Fuel properties of PDF, BDF, and their blend by McDonald & Spears [94] are given in Table 13.

**Table 13.** Fuel properties by McDonald & Spears [94]

|   | D2 (PDF) | BDF    | B30 <sup>a</sup> |
|---|----------|--------|------------------|
| Cetane number                           | 43.2     | 54.7   | 49.1             |
| Heat of combustion, MJ kg <sup>-1</sup> | 42.8     | 37.1   | 40.5             |
| Sulphur, mass %                         | 0.010    | <0.005 | <0.005           |
| Oxygen, mass %                          | 0        | 11.0   | 3.4              |
| Aromatics, mass %                       | 39.0     | 0.0    | 27.3             |
| Kinematic viscosity at 40 °C, cSt       | 2.37     | 3.05   | 2.6              |
| Cloud point, °C                         | -21      | -2     | -17              |
| Flash point, °C                         | 68       | 160    | 77               |

<sup>a</sup> B30 = 30% (by mass) blend of BDF with 70% D2

Tables 14–16 present various properties of DF by Graboski & McCromick [95].

**Table 14.** Heat of combustion for various diesel fuels [95]

| Fuel                  | Relative heat of combustion, % |
|-----------------------|--------------------------------|
| PDF                   | 100                            |
| Soybean methyl ester  | 85                             |
| Rapeseed methyl ester | 86                             |
| Tallow methyl ester   | 89.5                           |

**Table 15.** Low-temperature properties of various diesel fuels [95]

| Fuel                       | Cloud point, °C | CFPP, °C   |
|----------------------------|-----------------|------------|
| PDF                        | -35 to -15      | -10 to -20 |
| Soybean oil methyl ester   | -3.8            | -4.4       |
| Rapeseed oil methyl ester  | -10.8           | 3.6        |
| Sunflower oil methyl ester | -7              | -          |
| Palm oil methyl ester      | 16              | -          |
| Tallow methyl ester        | 9               | 11         |

**Table 16.** Cetane number of diesel fuel [95]

| Fuel                       | Cetane number |
|----------------------------|---------------|
| PDF (US D2)                | 40–52         |
| Soybean oil methyl ester   | 45.7–56.9     |
| Soybean oil ethyl ester    | 48.2          |
| Soybean oil butyl ester    | 51.7          |
| Rapeseed oil methyl ester  | 48.0–61.8     |
| Rapeseed oil ethyl ester   | 64.9          |
| Sunflower oil methyl ester | 49.0          |
| Palm oil methyl ester      | 50.0          |
| Tallow methyl ester        | 58.8          |

Properties of used frying oil methyl ester are given in Table 17.

**Table 17.** Properties of used frying oil methyl ester (UFO-ME) by Sams [96]

| Property           | Unit              | Value  |
|--------------------|-------------------|--------|
| Heat of combustion | MJ/kg             | 36.5   |
| Density at 15 °C   | kg/m <sup>3</sup> | 880    |
| Cetane number      |                   | 49     |
| Viscosity at 40 °C | cSt               | 4.25   |
| Flash point        | °C                | 110    |
| CFPP               | °C                | -5     |
| Sulphur            | % mass            | <<0.01 |

Tables 18–20 give various physical and chemical properties of various DF and relevant US, German, and Austrian standards.

**Table 18.** Diesel fuel properties by Schäfer [97]

| Diesel fuel  | Iodine number, gI <sub>2</sub> /100 g | Density at 15 °C, kg/m <sup>3</sup> | Heat of combustion, MJ/kg | Viscosity at 40 °C, mm <sup>2</sup> /s | Cetane number |
|--|---------------------------------------|-------------------------------------|---------------------------|--|---------------|
| Methyl esters of rapeseed oil (Europe)             | 114                                   | 882                                 | 37.2                      | 4.2                                    | 60            |
| Methyl esters of sunflower seed oil (South Europe) | 129                                   | 885                                 | 37.1                      | 4.0                                    | 61            |
| Methyl esters of soybean oil (North America)       | 131                                   |                                     | 37.1                      |  | 56            |
| Methyl esters of palm oil (Malaysia)               | 52                                    | 872–877                             | 37.0                      | 4.3–4.5                                | 70.0          |
| Typical petroleum diesel fuel                      | –                                     | 830–840                             | 42.7                      | 2–3.5                                  | 51            |

**Table 19.** US ASTM D 6584 standard for BDF [90]

| Property                    | Unit               | Limits             |
|-----------------------------|--------------------|--------------------|
| Flash point                 | °C                 | min 130.0          |
| Water sediment              | % volume           | max 0.050          |
| Carbon residue, 100% sample | % mass             | max 0.050          |
| Sulphated ash               | % mass             | max 0.020          |
| Kinematic viscosity, 40 °C  | mm <sup>2</sup> /s | 1.9–6.0            |
| Sulphur                     | % mass             | max 0.0015         |
| Cetane number               |                    | min 40             |
| Cloud point                 | °C                 | Report to customer |
| Corrosion on copper         |                    | No. 3 max          |
| Acid number                 | mgKOH/g            | max 0.80           |
| Free glycerin               | % mass             | max 0.020          |
| Total glycerin              | % mass             | max 0.240          |

In the US ASTM standard for BDF the iodine number is not standardized

**Table 20.** The standards of Austria and Germany on diesel fuel and biodiesel fuel fatty acid methyl esters (FAME)

| Properties                        | Unit                   | Diesel fuel                            | FAME              |                     |
|-----------------------------------|------------------------|--|-------------------|---------------------|
|                                   |                        |  | Austria ON C 1191 | Germany DIN E 51606 |
| Density 15 °C                     | kg/m <sup>3</sup>      | 820–845                                | 850–890           | 875–900             |
| Viscosity 40 °C                   | mm <sup>2</sup> /s     | summer<br>2.0–4.5<br>winter<br>1.5–4.0 | 3.5–5.0           | 3.5–5.0             |
| Flash point                       | °C                     | min 55                                 | min 100           | min 110             |
| CFPP summer                       | °C                     | max –15                                | max 0             | max 0               |
| CFPP medium                       | °C                     |  |                   | max –10             |
| CFPP winter                       | °C                     | max –26                                | max –15           | max –20             |
| Total sulphur                     | % mass                 | max 0.035                              | max 0.02          | max 0.01            |
| CCR <sup>a</sup>                  | % mass                 | max 0.30                               | max 0.05          | max 0.05            |
| Cetane number                     |                        | summer min 51<br>winter min 49         | min 49            | min 49              |
| Water                             | mg/kg                  | free of visible                        | free of visible   | max 300             |
| Total solids                      | mg/kg                  | free of visible                        | free of visible   | max 20              |
| Ash                               | % mass                 | max 0.01                               | max 0.02          | max 0.01            |
| Oxidation stability               | g/m <sup>3</sup>       | max 25                                 | to be mentioned   | to be mentioned     |
| Lubricity                         | nm                     | max 460                                | –                 | –                   |
| Neutralization number             | mgKOH/g                | 0.08                                   | max 0.8           | max 0.5             |
| Iodine number                     | gI <sub>2</sub> /100 g | –                                      | max 120           | max 115             |
| Corrosion on Cu<br>(3 h at 50 °C) |                        | No. 1                                  |                   | No. 1               |
| Phosphorous                       | mg/kg                  | –                                      | max 20            | max 10              |
| Methanol content                  | % mass                 | –                                      | max 0.20          | max 0.3             |
| Monoglycerides                    | % mass                 | –                                      |                   | max 0.8             |
| Diglycerides                      | % mass                 | –                                      |                   | max 0.4             |
| Triglycerides                     | % mass                 | –                                      |                   | max 0.4             |
| Free glycerin                     | % mass                 | –                                      | max 0.02          | max 0.02            |
| Total glycerin                    | % mass                 | –                                      | max 0.24          | max 0.25            |
| Aromatic hydrocarbons             | % vol.                 | Winter max 11                          | –                 | –                   |
| Polycyclic aromatic hydrocarbons  | % vol.                 | Summer max 11                          | –                 | –                   |
| Distillation at 250 °C            | % vol.                 | max 65                                 | –                 | –                   |
| at 350 °C                         | % vol.                 | min 85                                 | –                 | –                   |
| 95% vol.                          | °C                     | Summer<br>max 360                      | –                 | –                   |
| 95% vol.                          | °C                     | Winter<br>min 340                      | –                 | –                   |

<sup>a</sup> CCR – Conradson carbon residue

### **The cetane number**

Klopfenstein [98] found that for the methyl esters the cetane numbers increased in a nonlinear relation with the chain length of the acid. Cetane numbers of esters also increase when the fatty acid is kept constant but the molecular mass of the alcohol increases. The fatty acid ester of the transesterified plant oil with the lowest molecular mass, the methyl octanoate, has the cetane number 33.6. The minimum cetane number allowed for DF is 40.

The cetane number is higher for saturated compounds compared with unsaturated compounds: methyl octadecanoate 86.9, methyl octadecenoate 55.0, methyl octadecadienoate 42.2, and methyl octadecatrienoate 22.7. The cetane number of fatty alcohol is also higher than of the corresponding methyl ester. For example, the cetane number value of 1-tetra-decanol ( $C_{14}$  alcohol) is 80.8 and for methyl myristate ( $C_{14}$  acid methyl ester) it is 66.2 [90].

In fatty compounds, correlations exist between the cetane number and the number of  $CH_2$  groups [99]. The cetane number increases for PME from C 22 : 3 to C 16 : 0 [6], here on the one hand unsaturation and saturation and, on the other, the number of  $CH_2$  groups play a role. Knothe et al. [100] suppose that the low cetane number of the intermediary precombustion species may constitute a possible partial explanation why the more unsaturated fatty compounds have a relatively low cetane number.

### **Low-temperature properties**

The low-temperature properties of BDF are especially important in northern countries. The melting point of fatty acid methyl esters drops significantly from C 16 : 0 to C 18 : 3.

In very cold areas ethanol is sometimes added to DF in winter to prevent ice from plugging fuel lines and filters. The maximum amount of ethanol added is 1.25 mL per 1 L of fuel [101]. The simplest method to improve low-temperature properties of BDF is to use blends of PDF and BDF. A 70 : 30 PDF : SME blend has a CP of  $-17^{\circ}C$  and SME of  $-2^{\circ}C$  [90].

By cooling or winterizing it is possible to remove the high melting compounds. The mixture of methyl esters is cooled so that the high melting compounds crystallize and the CFPP falls to  $-40^{\circ}C$ . The winterized RME mixture has a higher iodine number than the native RME while the saturated methyl esters are removed by crystallization [102]. Methyl soyate has a crystallization onset temperature of  $3.7^{\circ}C$ . By removing saturated esters (palmitate) by winterization, that is with step-wise cooling, a yield of 86% methyl esters of a low-palmitate soybean oil with crystallization onset temperature of  $-6.5^{\circ}C$  was obtained [103, 104].

Low-temperature flow properties can be improved (see Table 21) for instance with the following composition:

Winterflow (Starreon Corp) – a mixture of light and heavy petroleum naphtha, trimethyl benzene isomers, propylene glycol ether, xylene, hydroxyethylated aminoethyl amide, cumene, and ethyl benzene.

DFI-200 (Du Pont Chemical) – a mixture of severely hydrated light naphthenic distillates and ethylene–vinyl acetate copolymers [105].

**Table 21.** Low-temperature properties [105]

| Fuel                       | CP, °C | PP, °C | CFPP, °C | LTFT, °C |
|----------------------------|--------|--------|----------|----------|
| SME (soybean methyl ester) | 0      | –2     | –3       | 2        |
| SME+DFI-200 (2000 ppm)     | –1     | –16    | –4       | –4       |
| SME+Winterflow(2000 ppm)   | –1     | –17    | –2       | –4       |
| Winterized SME             | –20    | –21    | –17      | –16      |

Pour-point depressants are also Lubrizol 5972 and Edenor 2661 [106].

Lee et al. [107] transesterified oils and fats using branched-chain alcohols, such as isopropyl or 2-butylalcohols to reduce the crystallization temperature of biodiesel. The crystallization temperatures of isopropyl and 2-butyl esters of soybean oil were 7–11 and 12–14°C lower than that of SME, respectively [90].

On the other hand, when the melting point of the mixture is lowered by winterizing for instance up to CFPP = –36°C then the iodine number can rise to 115, increasing thus the tendency of polymerization.

Also low molecular mass triglycerides (C 4:0, C 6:0, C 8:0, C 10:0) as DF improve the low-temperature properties as Goodrum & Eiteman [108] established.

The key in promoting the use of RME across Europe is its low-temperature performance, which is measured by its CFPP [109]. The requirement is for the CFPP to reach –20°C. Pure BDF has a pour point of only –12°C, a CFPP of –8°C, and it freezes at –13.6°C. This problem has been resolved with high-oleic rapeseed oil with oleic acid content of 80% obtained by genetic engineering; the methyl esters of such rapeseed oil have very good oxidative stability and good low-temperature properties. The 00 rapeseed oil has oleic acid esters content of 55–60%. In high oleic sunflower oil the oleic acid esters content has reached 80–87%.

The patent literature presents many additives for PDF and BDF for improving the low-temperature properties, for instance carboxy containing inter polymers [110], styrene-maleic anhydride copolymer [111], alkyl methacrylate copolymer [112], polymethacrylates [113, 114], copolymers of lower olefins and vinyl esters [115], ethylene-vinylester (acetate) copolymers [116–118], unsaturated fatty acids [119], etc.

### **The iodine number of BDF**

Unsaturation of the fatty acids is the main factor causing formation of engine deposits through polymerization of BDF, especially with linolenic acid methyl ester with an iodine number of 292.5. We suggest that it is better to limit the



amount of higher unsaturated fatty acids (e.g. linolenic acid) than to limit the degree of unsaturation by means of genetic engineering.

The iodine number of BDF in oil methyl esters is presented in Table 22.

**Table 22.** The iodine number of methyl esters of oils

| BDF                             | Iodine number |
|---------------------------------|---------------|
| Soybean oil methyl ester (SME)  | 133.2         |
| Rapeseed oil methyl ester (RME) | 97.4          |
| Sunflower oil methyl ester      | 125.5         |

RME has the best stability

It has been suggested that a fuel with the iodine number greater than 115 is not acceptable because of excessive carbon deposits. Therefore soybean and sunflower oil methyl esters are used only in blends with PDF (20–30% BDF) [95].

In the United States a working group was formed to evaluate methods of testing BDF stability. This effort will be summarized in an appendix of the US standard ASTM for BDF, which is similar to that contained in the ASTM D975 [120]. Samples of BDF were used with an iodine number from 100 to 180 for testing in diesel engine. Increasing deposits with increasing iodine number were found at piston rings of engine [121]. On the other hand, Prankel et al. [122] showed that a BDF with a high iodine number, camelina oil methyl esters with a 37% content of linolenic acid and iodine number of 150, can be used as DF without formation of deposits in the engine.

It is possible to increase the stability of BDF with additives. Hydroquinone and *tert*-butylhydroxytoluene as stabilizers of BDF are recommended [123]. The oxidative stability of methyl soyate was investigated by Dunn [124]. *tert*-Butylhydroquinone and  $\alpha$ -tocopherol were found to be effective antioxidants.

### The viscosity of BDF

The viscosity of BDF reduces considerably with the increase in unsaturation. Contamination with small amounts of glycerides significantly effects the viscosity of BDF. However, other properties at low temperature (CP, PP, CFPP) are more significant for BDF than the viscosity. The viscosity is satisfactory for all types of BDF, but it must be observed that viscosity is in correlation with the flow properties at low temperature [125]. Coconut:canola and peanut:canola oil mixtures were transesterified. Viscosity and surface tension were found to decrease with the increase in saturated fatty acids of carbon numbers from 8 to 18 [126]. The BDF 75, 50, and 20% blends with PDF indicate qualitatively similar temperature-dependent behaviour (viscosity) with neat PDF [127]. The neat BDF and blends of BDF and PDF have higher kinematic viscosity than PDF, but they behave in diesel engine similar to PDF [128].

### **Corrosion problems of BDF**

BDF may cause corrosion in the diesel engine. SME and their blends with PDF exhibited severe corrosion with copper containing metals and reduced swelling was observed in many elastomers [129]. On the other hand, an agricultural tractor with an unmodified diesel engine has been running 13 years on BDF (RME) and this fuel has caused no problems [130].

Water content in BDF may cause corrosion in the injection system and promote the life of microorganisms in fuel. BDF containing over 0.02% glycerin and (or) glycerides may also cause corrosion [131]. On the other hand, an emulsion of water and vegetable oils is patented as DF that inhibits corrosion, improves cetane number, and is useable as a freezing-protecting agent [132]. Graboski & McCromick [95] showed that a low water content in the diesel fuel has a role as a combustion promoter. The solubility of water in pure SME is 1.5 g per 1 kg of SME, in the blend B-20 only 40–60 mg of water per 1 kg is dissolved. Monoglycerides, glycerol, and free fatty acids corrode bearing metals and valve deposits may occur. BDF as a solvent can dissolve elastomers and lead to fuel filter and injector plugging. Nitrile rubber, high-density polyethylene, and polypropylene all change physical properties of gaskets. For BDF fluorinated elastomers are the most resistant [129].

### **The lubricity of BDF**

BDF has good lubricity for the diesel engine compared with PDF. Fuel lubricity is important in the fuel pumps in diesel motors. Methyl esters of soybean oil, rapeseed oil, and sunflower oil and their blends with PDF have better lubricity than neat PDF. When BDF is used, the lubricity of DF is not a problem. The lubricity of BDF is imparted to blends at levels above 20 vol % [95]. Karonis et al. [133] showed that in all cases methyl esters of sunflower oil and olive oil are added to PDF in concentrations from 0.25 to 10 vol % noticeable decreases in engine wear occur when compared with neat PDF. Mixing up to 5% PME in DF was authorized in France in 1995. This makes the fuel sulphur content lower and lubricity better. The presence of mono- and diglycerides in the range of 100 to 200 ppm provides sufficient antiwear capacity [17].

### **The phosphorus content of BDF**

Phosphorus content in the compounds in BDF is not a very essential problem although its maximum allowed level is 20 mg per 1 kg of BDF. PDF has no phosphorus containing compounds. The methyl esters obtained from cold pressing of rapeseeds and transesterification with methanol contain 1 mg kg<sup>-1</sup> phosphorus. The use of film evaporation for distilling raw RME leads to a phosphorus level in the distillate lower than 0.1 mg kg<sup>-1</sup> [134].

## The toxicity of BDF

The toxicity of BDF is very low. LD<sub>50</sub> values for RME and rapeseed oil ethyl ester (REE) are higher than 5000 mg kg<sup>-1</sup> when administered once orally and higher than 2000 mg kg<sup>-1</sup> administered once for 24 h to the clipped, intact skin of male and female albino rats. LC<sub>50</sub> values for acute aquatic toxicity with *Daphnia magna* in ppm are 3.7 for table salt, 1.4 for PDF (D-2), and 23 for RME. RME is 6.2 times less toxic than table salt. It has no acute oral and dermal toxicity, oral LD<sub>50</sub> value determined by Williamson & Badr [23] was 17.4 g kg<sup>-1</sup>. BDF is biodegradable within 3 weeks at 99% in water and soil [135]. It is interesting to mention that the RME stored 24 months gave a decrease of 3.2% in smoke emission [136, 137]. Biodegradability tests showed that REE and RME degrade more rapidly than sugar. The esters were degraded by 90% after 23 days. DF was degraded by 26% after 23 days [138]. The toxicity of motor exhaust gases from BDF is lower than that from PDF. Bünger et al. [139] tested the mutagenic and cytotoxic effects of extracts from particulate matter of BDF and PDF emissions in the *Salmonella typhimurium*/mammalian microsome using strains TA 97a, TA 98, TA 100, and TA 102. A higher mutagenic potency of PDF compared to BDF (RME) was shown. This is due to the lower content of polycyclic aromatic compounds in emissions of RME. The toxicity of the established cell line L 929 (mouse lung fibroblasts) was investigated. The mutagenic effects of the particle extracts were positively correlated to the content of polycyclic aromatic compounds, particularly to picene, phenanthrene, 2-methyl-anthracene, 3-methyl-phenanthrene, and fluoranthene [139].

## PREPARATION METHODS

### Transesterification with catalysts

Plant oils have high viscosity and they are unstable because of polymerization. Therefore plant oils may be used as DF by dilution, microemulsification, pyrolysis, and transesterification. The last is the most promising method. The first transesterification of coconut oil was carried out by Haller & Youssoufin [140] at the beginning of the 20th century. The coconut oil was transesterified with methanol containing 2% hydrogen chloride. The product was a mixture of fatty acid (oleic, palmitic, etc.) methyl esters.

Although the transesterification products of triglycerides were applied as DF only in the 1980s, the transesterification was first patented in the United States already in 1945. According to this patent, 224 part/min of refined coconut oil and 96 part/min of ethanol containing 0.75% of NaOH were reacted for about 10 min at 100°C. In the preheater the ethanol was separated at 110°C. Then the glycerol was separated and the ester layer was washed and distilled under vacuum [141].

A transesterification process for further preparation of detergents was patented by Bradshaw & Meuly [142]. The oils were transesterified at 25–100°C, 1.10–1.75

alcohol equivalents, and 0.1–0.5% catalyst by weight of oil. The continuous transesterification process was patented by Trent already in 1945 [143]. For high acid oils alkali- and then acid-catalysed transesterification was used by Sprules & Price [144]. The free fatty acids were neutralized with alkali, then the triglycerides were converted to esters, alkali catalyst was neutralized, and the free fatty acids were esterified. The mixture was neutralized with calcium carbonate, filtered, and methanol was distilled over; after that the glycerol was separated and the esters were distilled under vacuum. In the patent of Smith from 1949 [145] the molar ratio of methanol and oil was from 6:1 to 12:1, the reaction temperature range was 20–35°C, and NaOH as catalyst by weight of 0.005–0.35% of oil was used.

In 1981 the transesterification of sunflower and soybean oils to fatty esters was carried out by Freedman et al. [146]. The reaction temperature was 32–60°C. At 45°C the methyl esters were produced in an hour with a yield of 97%. The molar ratio of methanol and sunflower oil was from 4:1 to 6:1. With all alcohols (methanol, ethanol, and *n*-butanol) a good yield was obtained. Alkaline and acidic catalysts were used, but the alkaline catalysts were more effective than the acidic. The optimum conditions for transesterification of vegetable oils (cottonseed, peanut, soybean, and sunflower) were worked out by Freedman et al. [147]. The transesterification with an alkali catalyst (either NaOH or methoxide) at temperatures >60°C and molar ratio of alcohols and oils 6:1 was complete in 1 h. At 32°C the vegetable oils were 99% transesterified in 4 h with an alkali catalyst, by acid catalysis the reaction rate was much slower.

The transesterification of soybean oil and other triglycerides with alcohol in the presence of catalyst and the kinetics of the process were investigated by Freedman et al. [147]. Schwab et al. [148] used for transesterification with methanol a 6:1 molar ratio and 1% of sodium hydroxide in methanol. After 4 h conversion to ester at 32°C the reaction yield was 98%. The CP and PP of methanyl soyate were 2 and –1 °C and of butyl soyate –3 and –7 °C, respectively.

An inexpensive and simple method for the transformation of large quantities of rape oil into its methyl esters was carried out by Mittelbach et al. [149, see also 6].

Transesterification of plant oils or animal fats with aliphatic alcohols in the presence of potassium hydroxide as catalyst at ambient conditions and the separation of the phases by a coalescence filter was patented by Mittelbach & Junek [150]. After transesterification the ester phase can pass through a column with cation exchanger (Amberlite IR 120). The product obtained was used successfully in diesel engines [151].

In an Austrian patent [152] after separation of glycerol from the ester phase it was treated after neutralization with Fuller's earth or silica gel and then the esters were distilled at reduced pressure. The transesterification product after the glycerol separation can be treated with water steam at a pressure of 3 bars [153].

Numerous patents have been issued for transesterification with alkali catalysts (sodium hydroxide, potassium hydroxide, etc.) [151–159]. A continuous process for transesterification of triglycerides to methyl esters was investigated with a high-shear mixer by Nouredini et al. [160]. The reaction time was 6 to 8 min. Molar

ratios of methanol to oil were 8:1 to 6:1, catalyst concentration was 0.1%, and mixing speed 3600 rpm, the reaction temperature was 80°C [160]. A transesterification process with a very intensive mixing (turbolater, dynamic emulgator, ultra-sound, etc.) has been also patented. In this process the reaction product emulsion is separated by membrane technology [161]. Also acid catalysts are used in the transesterification process, especially when the mixture of triglycerides contains free fatty acids, for instance frying oils, waste oils, etc. Mostly sulphuric acid is used.

Nimcevic et al. [162] prepared rapeseed oil esters with higher alcohols. Propyl and butyl esters were obtained only under acid catalysis. Isopropyl and isobutyl alcohols reacted more slowly than their linear isomers, while *tert*-butyl alcohol did not react at all [163].

Transesterification of triglycerides and esterification of fatty acids with methanol in the presence of acid catalysts such as alkyl, aryl, or alkylaryl-sulphonic acids (*p*-toluenesulphonic acid) at a temperature from 59 to 89°C in a continuously working reaction apparatus was patented by Tanaka et al. [164]. Plant oils containing free fatty acids are transesterified with methanol in the presence of a sulphonated ion exchange catalyst [165].

Several methods have been patented in which the catalyst (mostly an alkali methanol solution) is added to the reaction mixture in two steps [166–172]. In Austria a method of transesterification in two steps at temperatures from 50 to 100°C is patented. The product, FAME, is distilled in vacuum and then frozen at –20°C and centrifugated [167]. Wimmer [168] presented a method for transesterification of natural oils and fats with the KOH solution in methanol added in two steps and after separation of the glycerol the rapeseed oil methyl esters used without further purification as DF. Also heterogenic catalytic processes are used for transesterification of triglycerides. Peterson & Scarrah [173] were the first to examine heterogeneous catalysis of transesterification of vegetable oils. CaO, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, NaAlO<sub>2</sub>, Zn, Cu, Sn, Pb, ZnO, and anion exchange resin Dowex 2XS as catalysts were tested mainly at 60–63°C. Transesterification of rapeseed oil with methanol was carried out. The best catalysts among those tested were CaO and MgO, but alkali hydroxide catalysts are better. Transesterification over Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> catalysts at 160–400°C and <400 bar is patented by Hofman [174]. Calcium acetate and barium acetate [175] as well as aluminates and silicates of zinc, titane, and tin [176] at 180–250°C have been used as catalysts. A process is patented in which the triglycerides or free fatty acids with an alcohol stream are led into an introduced critical fluid medium at critical conditions over an acidic or basic catalyst. Carbon dioxide or hydrocarbon gases [177] are used as critical fluid solvents.

### **Transesterification without a catalyst**

A new interesting method for transesterification of triglycerides without a catalyst in a methanol solution was developed by Diasakou et al. [178]. In this

method the reaction temperature is at first 220–235 °C. Saka & Padau [179] carried out a process in the batch reactor at 380 °C and 20 MPa with a molar ratio of 1 to 42 of oil to methanol with reaction time of 120 s. The yield was close to the theoretical value. The purification of the product was simple. Saka and Kusdiana [180, 181] investigated a transesterification process of rapeseed oil in supercritical methanol without using any catalyst. The reaction conditions were: temperature 350–400 °C, pressure 45–65 MPa, rapeseed oil to methanol molar ratio 1:42, reaction time 240 s. The reaction temperature of 350 °C was found to be the best condition. The process in supercritical methanol is also patented [182, 183].

### **Transesterification with biochemical catalysts**

Several investigations have been made in the field of biochemical catalysis of the transesterification reaction of triglycerides with alcohols but we are of the opinion that these processes are nowadays economically less effective than chemical catalysis. Using lipases as catalysts for the ethanolysis of sunflower oil Mittelbach achieved a satisfactory yield [184]. Shaw et al. [185] reported high degrees of alcoholysis of triglycerides in a solvent-free system in lipase catalysed ethanolysis and 2-propanolysis. Also methods of alcoholysis of triglycerides by immobilized lipase have been described. Jackson & King [186] carried out direct methanolysis of triglycerides in flowing supercritical carbon dioxide. This combined extraction reaction process is performed at 17.2 MPa and 50 °C. Direct methanolysis of soy flakes gives FAME at similar yields. Haas & Scott [187] investigated three lipases (Lipozyme 1M 20, Amano PS-30, Amano CE) for synthesizing FAME via the alcoholysis of soy triglycerides and phosphatidylcholine in PDF. This work establishes the feasibility of using DF as a solvent for enzymatic synthesis of ethyl esters from triglycerides and phospholipids. Thus it is possible to apply this reaction to the synthesis of BDF from low-value materials, such as soapstock, that are rich in these lipids and in related compounds. The product can be used directly as DF. An immobilized lipase was used to catalyse the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of >98% [186]. It is possible to produce fatty acid triglycerides from whey with yeast *Cryptococcus curvatus* and from the triglycerides chemically methyl esters that can be used as BDF [188]. Wu et al. [189] catalysed transesterification of recycled restaurant greases with 95% ethanol by PS-30 lipase; the optimal reaction conditions were 38.4 °C, 2.5 h, and 13.7 mass % lipase.

Kaieda et al. [190] developed a new enzymic method of synthesizing methyl esters from plant oil and methanol in the presence of lipase from *Rhizopus oryzae*. The catalysis of the methanolysis of soybean oil was possible in the presence of 4–30 mass % water. The lipase was inactive in the absence of water. In this process the oil is first hydrolysed to free fatty acids and then the fatty acids are esterified with methanol. The methyl ester content in the reaction mixture reached 80–90%.

Watanabe et al. [191] studied a two-step continuous methanolysis process of vegetable oils in the presence of unactivated immobilized *Candida antartica* lipase. The lipase could be used for 70 cycles without any decrease in the conversion. Enzymatic alcoholysis of vegetable oil in supercritical carbon dioxide was examined also by Oliveira & Oliveira [192]. They carried out ethanolysis of palm kernel oil in supercritical carbon dioxide catalysed by two commercial lipases in the temperature range of 40–70°C at 60 to 200 bar and oil and ethanol molar ratios from 1:3 to 1:10. Samukawa et al. [193] investigated immobilized *Candida antartica* lipase enzyme (Novozym 435) on methanolysis of soybean oil for BDF production. When preincubated Novozym 435 was used the methyl ester yield was over 97% within 3.5 h by stepwise addition of 0.33 molar equivalent of methanol at 0.25–0.4 h intervals. A lipase process in which alcohol concentration in the esterification process is kept lower than the lipase inhibitory concentration is patented [194].

### **Transesterification *in situ***

Harrington & D'Arcy-Evans [195] were the first to work out a method of transesterification of sunflower oil *in situ* (alcoholysis of the sunflower oil seeds) with methanol in the presence of sulphuric acid. Yield improvements of more than 20% were obtained. In the *in situ process* of transesterification the plant seeds were extracted and alcoholysed in the same apparatus in the presence of a conventionally acidic catalyst. Methanol is a poor solvent for soybean oil and therefore the yield of methyl esters is low in *in situ* alcoholysis. Ethyl, propyl, and butyl esters with the corresponding alcohols can be obtained in high yields in *in situ* alcoholysis of soybean oil from soybeans [196]. Harrington & D'Arcy-Evans [195] obtained significantly greater yields in *in situ* alcoholysis of sunflower oil with acidified methanol than those obtained from the conventional reaction with pre-extracted or pressed oil from seeds. Silver-Marinkovic & Tomasevic [197] also transesterified the oil in sunflower seeds *in situ*. The sunflower seeds were macerated with methanol (1.32 mass part of seeds per 1 volume part of methanol). Then from 2 to 3.5 volume part of methanol and 0.03–0.19 volume part of concentrated sulphuric acid were added and the mixture was heated under reflux and mixing for 1–4 h. Good quality of esters was obtained when 200:1 or higher molar ratio of methanol and oil in seeds was used. However, methanolysis with 300:1 molar ratio was essentially complete in an hour at 60°C and in 4 h at 30°C. Reaction times of 18–69 h have been reported for acid catalyst transesterification of vegetable oil by Freedman & co-workers [2, 147]. The reaction mixture was filtrated and methanol evaporated. The product quality was the same as in customary transesterification, but the CP was slightly lower than in the case of conventional methods. The *in situ* process has not yet been technologically realized.

### **Hydrotreatment process**

Wong, Stumborg, and Hogan [198–200] have developed a catalytic hydro-treatment process of vegetable oils or fats. They examined conversion of the oil into a 60–90 cetane number middle distillate. This product can be used neat as a DF or as a blending agent for ordinary DF. This BDF has shown lower emissions of particulates, carbon monoxide, and hydrocarbons compared with PDF. By the authors the advantages of hydroprocessing over transesterification in the Canadian context include lower processing costs. Problems may be cold flow properties. By our calculations the hydroprocessing costs are higher than those of the transesterification process.

### **The byproducts of transesterification**

A byproduct of the transesterification of triglycerides, glycerol, was also used to obtain useful compounds for BDF. In this field some methods have been patented. Free fatty acids are obtained from triglycerides by hydrolysing. The fatty acids are esterified with isobutene and isobutene is also used to etherify glycerol. Glyceryl ethers in the blend of fatty acid isobutyl esters have lower viscosity and better low-temperature properties than the methyl ester mixture of fatty acids obtained from the transesterification process [201].

In the patents of Nouredini [202, 203] the product of transesterification of triglycerides with methanol in the presence of a homogeneous basic catalyst, the glycerol phase was passed after separation through an ion exchanger. From the resulting neutral product methanol was removed and glycerol was reacted with isobutene in the presence of a strong acid catalyst to produce glycerol ethers. The glycerol ethers were added to the upper phase (methyl ester phase) to provide BDF with reduced viscosity and CP. Isoamylene as an etherifying agent was also used [203]. The realization of these methods depends on the demand and price of glycerol in the market. Many blends of BDF and PDF have been patented for improving the lubricity of PDF and low-temperature properties of BDF, as well as for reducing the pollutant concentration in the emissions of PDF. For instance methyl, ethyl, and isopropyl esters of fatty acids and even plant oils are added to PDF and fuel oil [204, 205].

### **Blends and additives**

Blends with fuel oil and alkyl, alkenyl, or phenyl ester of fatty acids have been patented as DF [206].

A method for preparing additives to PDF from used oils and fats includes transesterification in a ketone solvent in the presence of sulphuric acid [207]. Lubricant additives for DF containing hydrocarboxylic and fatty acids (carbon oil) and their  $C_1$ – $C_{10}$  aliphatic alcohol esters are also patented [208]. Fatty acids from oils are esterified also with pentaerythritol (220°C 5 h) to obtain additives of PDF [209].



Waste oils from cooking and frying contain free fatty acids and therefore usually acidic catalysts are used for transesterification. Nevertheless, also a method for transesterification of waste cooking oils with an alkali catalyst is patented [210]. For the esterification of free fatty acids present in residual used fats only an acidic catalyst with methanol was used by Dimming et al. [211] to avoid the formation of insoluble salts with fatty acids. Various substituted benzene sulphonic acids were found to be good catalysts for this process.

In Spain the process of BDF production was optimized by the application of the factorial design and response surface method. Different types of catalysts (acid and basic, homogeneous and heterogeneous, zirconium based, and an immobilized lipase) for sunflower oil and rapeseed oil with methanol were examined. Optimum conditions for the production of methyl esters of sunflower oil were found to be mild temperatures (20–50°C) and high catalyst concentrations (1.3%). The largest conversion was obtained with sodium hydroxide as catalyst [212, 213]. The base-catalysed transesterifying process of vegetable oils can be intensified with continuous centrifugation of the reaction product [214].

## EMISSIONS

### General

Biodiesel exhaust emissions have been reported in numerous publications [215–238]. Tables 23–26 present comparisons of exhaust emissions from BDF and PDF by several authors. Results of Mittelbach et al. [215] are given in Table 23.

**Table 23.** Exhaust emissions from BDF compared with PDF (100%)

| CO     | HC     | PAH    | NO <sub>x</sub> | Particulates | Smoke  |
|--------|--------|--------|-----------------|--------------|--------|
| 34–90% | 30–77% | 40–90% | 84–125%         | 70–120%      | 43–55% |

HC – hydrocarbons

PAH – polycyclic aromatic hydrocarbons

The differences are independent of the engine design. Results of an experiment with palm oil methyl esters (PME), 50/50 blend of PME and PDF, RME, and PDF (100%) published by Schäfer [216] are given in Table 24.

**Table 24.** Pollutants of BDF vs PDF (100%)

|               | Pollutant in exhaust gases, % |       |       |                 |
|---------------|-------------------------------|-------|-------|-----------------|
|               | CO                            | HC    | Smoke | NO <sub>x</sub> |
| PME           | 61                            | 91    | 24    | 104             |
| 50/50 PME/PDF | 74                            | 90    | 58    | 99              |
| RME           | 88–117                        | 50–53 | 28–42 | 106–119         |

Reduction in black smoke is approximately 60–75% for vegetable oil esters. There is less engine wear with PME operation, which can be easily explained by the very low smoke emissions of PME. The soot particulates in the lubricating oil are hard and therefore cause wear. From the components of the transesterified plant oils methyl palmitate is the most effective ester in achieving reduction of hydrocarbons and particulates in exhaust emissions. Particulate emission reduction can be attributed to oxygen content in esters and lack of aromatic hydrocarbons [217].

The pollutants emission by Kordesch [218] is given in Table 25.

**Table 25.** Emission of pollutants by Kordesch [218]

| DF         | Pollutants, g/kWh |      |                 | Pollutants, g/h |       |                 |
|------------|-------------------|------|-----------------|-----------------|-------|-----------------|
|            | CO                | HC   | NO <sub>x</sub> | CO              | HC    | NO <sub>x</sub> |
| PDF        | 1.03              | 0.23 | 7.37            | 48.80           | 10.82 | 347.62          |
| RME        | 0.92              | 0.14 | 7.65            | 41.04           | 6.24  | 341.97          |
| RME/PDF, % | 89.3              | 60.9 | 103.8           | 84.1            | 57.7  | 98.4            |

Krahl et al. [219] compared the pollutant concentrations of PDF (100%) and RME, their data are presented in Table 26.

**Table 26.** Pollutant average concentrations in RME compared with PDF [219]

|     | Pollutant                             |   |                 |                     |      |
|-----|---------------------------------------|---|-----------------|---------------------|------|
|     | CO                                    | HC                                      | NO <sub>x</sub> | Particulates        | Soot |
| RME | 90% <sup>a</sup><br>100% <sup>b</sup> | 70% <sup>a</sup><br>80–90% <sup>b</sup> | 110%            | 60–80% <sup>a</sup> | 60%  |

  

|     | Pollutant |           |             |         |
|-----|-----------|-----------|-------------|---------|
|     | PAH       | Aldehydes | Aromatic HC | Benzene |
| RME | 65%       | 120%      | 60%         | 70%     |

<sup>a</sup> indirect injection

<sup>b</sup> direct injection

Predominant limits are: CO 30–90%; HC 50–80%

It was shown by Krahl et al. [219] that in *in vitro* tests the mutagenic effect of PDF is 2 to 6 times higher compared to RME. This is due to the lower content of PAH and soot in RME exhaust gases.

Peterson & Reece [220] studied in the truck 5.9 turbocharged direct injection diesel engine RME and REE (rapeseed oil ethyl esters) emissions. RME reduced hydrocarbons 52.4%, carbon monoxide 47.6%, and nitrogen oxides 10.0% compared to PDF as the control fuel. Compared to RME REE reduced hydrocarbons 8.7%, carbon monoxide 4.3%, and nitrogen oxides 3.4% more.

The use of PME is especially promising for river and lake ship engines: the degradability of the RME in water is 99.6% but for the PDF approximately 28%. As Womac et al. [221] showed use of BDF reduced significantly the carbon monoxide emission from marine diesel engine. Soot was also reduced by using BDF (SME). It is interesting to mention that BDF produced greater power than PDF only when the engine was operated at full throttle at speeds less than 2650 rpm [221]. The diesel-electric buses tested with BDF had very low emission levels [222].

### **Emissions of hydrocarbons, particulates, and soot**

The boiling curve of PDF increases steadily in a range between 200 and 340°C. Methyl esters of rapeseed, soybean, and sunflower oil have boiling curves within the range 320–350°C. Vegetable oil esters are evaporated at the beginning of the combustion without decomposing and that is one of the reasons of the lower emission of hydrocarbons [95].

For neat RME and REE specific PAH emissions decrease by 37% and 54%, respectively. The PAH reduction was in the range 20–30% for B-50 blends. Emissions of phenanthrene, pyrene, and benzanthracene were by 20–40% less for BDF than for PDF [96].

The mean concentration of benzo[*a*]pyrene in the exhaust gases was determined to be 35 ng/m<sup>3</sup> for RME and 215 ng/m<sup>3</sup> for PDF [223].

PDF emissions increase lung cancer risk. BDF emissions contain less soot mass than PDF and a greater portion of BDF soot is soluble and less mutagenic than PDF soot. The future of BDF will be limited more by economic factors than by health concerns although it might be vice versa. Between 1957 and 1993 epidemiological studies focused on lung cancer risk from PDF emissions.

Soot emission from engine starting for PDF US D-2 is 0.16 g/km, for Austrian DF 0.14 g/km, and RME 0.06 g/km. The BDF produces less soot under cold start conditions than under hot start conditions. Bacterial mutagenicity of the soot extract of RME on *Salmonella* TA-98 and TA-100 is 3.5 times lower compared to PDF [224].

In an indirect injection diesel engine a soybean fatty-acid monoester as BDF and an oxidation catalytic converter (OCC) were operated in an underground mine. Emissions with PDF and BDF with and without OCC were compared. The solid portion of the total particulate matter (TPM) and the PAH content were lower with the BDF. Vapour-phase PAH emissions were reduced up to 90% and particle and vapour-phase associated mutagenic activity was reduced over 50% with both fuels when the OCC was used [225].

Emission test results showed that the heavy trucks fuelled by B35 (35% BDF and 65% PDF) emit significantly lower amounts of particulate matter and moderately less carbon monoxide and hydrocarbons compared with PDF (USA D-2). NO<sub>x</sub> emissions were generally at the same level [226].

A blend of 50% SME with PDF (D-2) provided a reduction of 37% in the carbon portion of the particulates and 25% in the TPM. The 50% blend of isopropyl ester and 50% PDF gave a 55% reduction in carbon and 28% reduction in TPM emissions [227]. A DF blend that contains 10–20 vol. % of isoolefinic fractions from manufacturing polypropylene or polybutylene (150–300°C) in addition to FAME is patented. The fuel generates only a small amount of smoke [228].

A high oxygen content of some diesters seems to be an extra advantage in ignition quality of blends with gas oil in diesel engine. The oxygen–carbon ratio of fuel affects significantly particulate emissions; the ratio ought to be higher than 0.2. Due to their high oxygen content, many diesters of dicarboxylic acids offer the additional advantage of reducing particulate emissions [229], but these esters cannot be prepared from renewable raw materials.

Inhaled particles extract is mutagenic because of the PAH content. Inhaled particles of PDF exhaust have been implicated as causative agents for lung tumour in laboratory rats after long-term exposure. BDF results in less particulate emissions and lower PAH concentrations. On the other hand, more NO<sub>x</sub> emissions and higher concentrations of aldehydes (formaldehyde, acrolein) increase the toxicity of the emissions of BDF [230].

An essential direction in the field of BDF research is reduction of the content of nitrogen oxides and aldehydes in the fuel emissions. Two main ways are (1) improvement of the design of engines and (2) improvement of the composition of fuel by developing new effective additives.

### **Emission of nitrogen oxides**

Sometimes emissions of nitrogen oxides are higher for BDF than for PDF, but not always. The relationship depends on the engine and operating conditions. For instance, a feed start set 5 degrees later reduces NO<sub>x</sub> values by 25% due to the lower gas temperature level, at the same time causing impermissible levels of soot with DF. The higher the development of a diesel engine the better suited it will be for BDF operation [231].

Californian DF was compared with neat BDF, and with a blend containing 80% Californian DF and 20% BDF. The BDF and BDF blends produced generally lower total hydrocarbons and carbon monoxide emissions than Californian DF. Slightly higher NO<sub>x</sub> emissions were found for the noncatalyst vehicles on neat BDF [232]. On the other hand Purcell et al. [233] showed that in the case of SME NO<sub>x</sub> emission from diesel engine does not increase when a modern diesel oxidation catalyst is used.

It was shown that increasing the cetane number can reduce the nitrogen oxide emissions [96].

NO<sub>x</sub> and smoke concentrations are lower for emulsified neat rapeseed oil in gas oil than those of gas oil [234]. Saturated synthetic esters and their blends with PDF showed the smallest increase in NO<sub>x</sub> emissions compared with low palmitic

acid containing soybean esters and their blends with PDF. The blends with saturated synthetic esters provided a faster burning rate and a better emission reduction than the soybean ester blends [235].

The water content in fuel can reduce  $\text{NO}_x$  emission and particulates in the exhaust gases. The water content in fuel reduces the burning temperature and correspondingly the formation of  $\text{NO}_x$  from nitrogen [236]. Crookes et al. [237] showed that the biofuel with water emulsified vegetable oil reduces levels of both soot and nitrogen oxides in exhaust gases of diesel engine. The biofuel with water emulsified vegetable oil even reduces the emissions [237].

BDF, BDF blends (20% BDF), and also synthetic DF from Fischer-Tropsch process produce generally lower total hydrocarbon and carbon monoxide emissions than PDF (Californian). Nitrogen oxides emissions are comparable with the Californian PDF or only slightly higher [232].

### **Emission of aldehydes**

The content of aldehydes in the BDF exhaust gases is approximately 50% higher compared with PDF; with catalyst for exhaust gases, oxycat, it is possible to reduce it considerably [97]. It was found that total aldehydes for direct injection engines generally increased with BDF by 0 to 75% independently of test cycle [96]. Schäfer reported the results of a study by Mercedes Benz using palm oil esters. Compared to PDF, all aldehydes, except acrolein, decreased. The increase in acrolein was attributed to glycerol in the fuel [97].

## **ANALYTICAL METHODS**

A quantitative method, thin layer and gas-liquid chromatography (GLC), for analysing mixtures containing fatty esters and tri-, di-, and monoglycerides obtained by the transesterification of vegetable oils was reported by Freedman et al. [238] in 1984. Two years later Freedman et al. [239] reported a quantitative method of capillary GLC analysis of transesterified soybean oil. Prior to the analysis, mono- and diglycerides were silylated with N,O-bis(trimethylsilyl)tri-fluoroacetamide. The temperature program was from 160 to 350°C and a 1.8 m × 0.32 mm SE-30 fused silica column was used.

The quality of BDF is limited by the content of free glycerol and methanol. Mittelbach et al. [240] worked out a GLC method for determination of free glycerol and methanol in BDF.

Separation of all classes of acylglycerols from FAME is achieved by liquid chromatography after acetylation of the hydroxyl groups. The acylglycerol fraction is transferred online to the gas chromatograph using the loop-type interface and concurrent eluent evaporation [241].

Holcapek et al. [242] developed a high performance (pressure) liquid chromatography (HPLC) method for analysis of products of transesterification of

triglycerides. Detection was carried out with UV at 205 nm, evaporative light scattering, mass spectrometry, and combined linear gradient with aqueous organic and nonaqueous mobile phase steps (acetonitrile/water and acetonitrile/2-propanol/hexane) were used.

The determination of the content of free glycerol traces in esters derived from vegetable oils is possible by HPLC combined with pulsed amperometric detection (HPLC–PAD). The limit of detection is 1 ppm (1 µg/g) [243]. A quality control method of RME by the determination of acyl conversion was worked out by Cvengros & Cvengrosova [244]. A method for the determination of the neutralization rate for BDF products was developed by Komers et al. [245].

### **ECONOMIC ASPECTS OF USING BDF**

Soybean oil is of primary interest as a source of BDF in the United States. Soybean oil is on the order of \$ 2–3 per gallon compared to \$ 0.50–0.60 for PDF. In the USA taxes on fuels are low. In most European countries fuels are so heavily taxed that tax incentives have to be applied to encourage the use of BDF [96].

In 1997, the DF consumption in Germany was 26 Mio t and the production of RME (BDF) was 83 000 t (0.3%). In 2000 the production of BDF in Germany was nearly 2% of the whole DF consumption. The price of DF without taxes in Germany was 0.3 DM/L while rapeseed oil price was 2.3 DM/L (1997). The maximum possible production of RME in Germany is 4 Mio t, 15% from the DF consumption.

The price of RME can be reduced by opening new markets for rape protein isolates and concentrates. The technology of shelling rapeseed before further processing will probably be utilized [246]. It is necessary to increase the productivity of oil seed production. The average yield of industrial oilseed rape in the European Union is 2.36 t per ha. In the UK the average yield obtained in winter double-low oilseed rape varieties is 3.6 t per ha. It is reported that 1 t of rapeseed produces 0.37 t of RME, 0.58 t of rape meal, and 0.04 t of glycerol [23].

In the USA, seed yields in excess of 5.6 t per ha have been achieved in experimental trials of new oilseed rape varieties [247]. Different authors give the energy input:output ratio for the use of RME as a fuel in diesel engines from 1:18 to 1:5 (in MJ ha<sup>-1</sup>). It is suggested that an input:output energy ratio for RME production of 1:7.6 could be achieved in the future if oilseed rape straw is used as a by-product. Most favourable input:output energy ratio of 1:10.2 can be reached if RME, rape meal, glycerol, and straw are utilized [248].

The price of feedstock (plant oil) and the yield of transesterification and BDF are the most important components in the price of BDF [249].

In Scotland the RME production was found to be sustainable under all but the worst conditions (i.e. lowest seed yield, highest pesticide applications, etc.). Utilization of rape meal improved greatly the energy ratio. Glycerol utilization

had relatively little effect on the energy balance while the use of straw resulted in a net energy gain from the production of RME under all scenarios also in worst conditions [250].

## CURRENT SITUATION AND PROSPECTS IN ESTONIA

In 2001 rapeseeds were grown in Estonia on 28 800 ha with a total production of 38 900 t (Estonian Ministry of Agriculture). It is possible to cultivate rape on 60 000 ha. Assuming that the yield is 2.4 t/ha, the annual production would be 144 000 t of rapeseeds. The production of table rapeseed oil uses approximately 60 000 t of rapeseeds. Thus it would be possible to produce 31 000 t RME from the remaining 84 000 t.

If the 270 000 ha of arable land currently out of use was used for rape cultivation in six year rotation, it would be possible to produce additionally RME as presented in Table 27.

**Table 27.** A very optimistic prognosis of RME production in Estonia

| Yield of seeds,<br>t/ha | Seeds, t/year<br>(6-year rotation) | RME,<br>t/year |
|-------------------------|------------------------------------|----------------|
| 1.5                     | 67 500                             | 25 000         |
| 2.4                     | 108 000                            | 40 000         |
| 5.6                     | 252 000                            | 93 000         |

The actual yield of rapeseeds in Estonia is today 1.5 t/ha; in Central Europe the average yield is 2.4 t/ha. The yield of 5.6 t/ha is possible after breeding and genetic engineering of rape plants.

The prognosis above is a very optimistic one and may not be realistic, taking into consideration possibilities of increasing the production of other crops instead.

In 2000 the DF consumption in Estonia was 330 000 t. The production of RME in Estonia is possible only without or with a very low excise tax.

## SUMMARY

In this paper the BDF sources, properties, preparation methods, emissions in exhaust gases by using BDF, analytical methods, and economic aspects are discussed.

The main advantage of BDF over PDF is the reduction of greenhouse gases (carbon dioxide which is in recirculation). Using 1 kg of BDF reduces the carbon dioxide emission by 2.8 kg on an average. Compared with PDF the use of BDF reduces the concentration of pollutants in motor exhaust gases: sulphur dioxide practically completely, carbon monoxide on the average 20%, hydrocarbons on

the average 30%, soot and particulate matter 40–50%. Because of a lower concentration of polycyclic aromatic hydrocarbons in the emissions of BDF the emissions are many times less carcinogenic than those of PDF. The lubricity properties of BDF inhibit the motor wear.

The main concern with BDF is its high price, which is 3–8 times higher than that of the PDF. The future tasks in the BDF research are to find ways to reduce the costs of the production of plant oil by improving plant breeding, and using gene technology and selection.

The low-temperature properties and stability of BDF are worse than those of PDF. Nitrogen oxide and aldehyde concentration in the motor emissions of BDF may be higher compared with PDF. The low-temperature properties of BDF can be improved by additives and genetic engineering of oil plants. The stability of BDF can be improved also by adding substances that reduce the polymerization process of unsaturated compounds of BDF. With gene engineering of oil plants it is also possible to obtain oil containing less unstable compounds.

The higher concentration of nitrogen oxides and also aldehyde in the exhaust gases is mainly a physical problem of the engine rather than a chemical problem of the fuel. It is possible to reduce the concentration of these compounds in emissions with relevant additives in the BDF.

Although the substitution of PDF by BDF may be an essential factor in reducing the greenhouse effect, the authors of this paper are of the opinion that complete substitution is not realistic today. It has been calculated that the sown acreage for the production of oil plants in the world can cover approximately 20% of the consumption of DF. Therefore the use of neat BDF is suitable only in city buses and in river and lake ships where the pollution problems are very critical. In other cases it is expedient to use blends of PDF and BDF. It is possible that in ten or twenty years the use of BDF may be profitable without special tax policy. The price of petroleum will be so high that using BDF will become profitable. Algae can be a source for increasing the role of BDF.

It is the opinion of the authors of this paper that the unsuitable properties of BDF such as instability and relatively high CFPP may be improved by using appropriate additives.

Many authors suppose that any water content in DF is harmful. The authors of this paper have results showing that suitable additives in DF inhibit the growth of biological objects and the corrosion caused by water in the fuel blend. Stabilization of water and PDF or BDF blends with additives is not a problem now. Furthermore, water in DF reduces the concentration of pollutants (especially NO<sub>x</sub>) in motor exhaust gases.

## REFERENCES

1. Diesel, R. *Die Entstehung des Dieselmotors*. Springer-Verlag, Berlin, 1913.
2. Freedman, B. & Pryde, E. H. Fatty esters from vegetable oils for use as a diesel fuel. *ASAE Publ.*, 1982, (4–82, *Veg. Oil Fuels*), 117–122.



3. Peterson, C. L. & Hustrulid, T. Carbon cycle for rapeseed oil biodiesel fuels. *Biomass Bioenergy*, 1998, **14**, 2, 91–101.
4. Goodrum, J. W. Review of biodiesel research at University of Georgia. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 128–135.
5. Körbitz, W. The biodiesel market today and its future potential. In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 3–12.
6. Junek, H. & Mittelbach, M. Verfahren und Vorrichtung eines als Kraft-bzw Brennstoff geeigneten Fettsäureestergemisches. DE OS 3727981 (1988).
7. Körbitz, W. Biodiesel production in Europe and North America, an encouraging prospect. *Renewable Energy*, 1999, **16**, 1078–1083.
8. Peterson, C. L., Reece, D. L., Thompson, J. C., Beck, S. M. & Chase, G. Ethyl ester of rapeseed used as a biodiesel fuel – a case study. *Biomass Bioenergy*, 1996, **10**, 5/6, 331–336.
9. Syassen, O. Diesel engine technologies for raw and transesterified plant oils as fuels: desired future qualities of the fuels. In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 47–63.
10. Ryan, T. W., Callahan, T. J. & Dodge, L. G. Characterization of vegetable oils for use as fuels in diesel engines. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 70–81.
11. Tahir, A. R., Lapp, H. M. & Buchanan, L. C. Sunflower oil as a fuel for compression ignition engines. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 82–91.
12. Auld, D. L., Bettis, B. L. & Peterson, C. L. Production and fuel characteristics of vegetable oil from oilseed crops in the Pacific Northwest. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 92–100.
13. Pryde, E. H. Vegetable oil standards. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 101–105.
14. Romano, S. Vegetable oils – a new alternative. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 106–116.
15. Worgetter, M., Prankel, H. & Rathbauer, J. Biodiesel in Austria. An overview. In *Proc. Biomass Conf. Am. 3rd*, 1997, Vol. 2, 1043–1053.
16. Veermersh, G. Development of the diester activity in France. *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 177–182.
17. Hillion, G., Montagne, X. & Marchard, P. Methyl esters of plant oils used as additives or organic fuel. *Lipids*, 1999, **6**, 5, 435–438.
18. Sourie, J. C., Hautcolas, J. C., Bonnafous, P. & Gaouyer, J. P. The costs of liquid biofuels in the French context. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 305–308.
19. Mauguin, P., Poitrat, E., Gaoyer, J.-P., Charonnat, C. & Gosse, G. Production of bioelectricity from rape methyl ester (RME). In *Biomass Energy Environ., Proc. Eur. Bioenergy Conf., 9th*, 1996, Vol. 2, 1435–1440.
20. Poitrat, E. Ecological assessment of rapeseed methyl ester comparison with mineral fuel (life cycle analysis). In *Proc. Eur. Biomass Conf., 8th*, 1994. 1995, Vol. 2, 1081–1093.
21. Lopez Sastre, J. A., Guijosa, L. & Sanz, J. M. Vegetable oils as ecologically acceptable fuels. *Energia* (Madrid), 1995, **21**, 5, 71–76. C.A. 124: 150703z.
22. Gomez Herrera, C. Fatty acid methyl esters as diesel fuel. *Grasas Aceites* (Madrid), 1995, **46**, 2, 121–129. C.A. 124: 33576z.
23. Williamson, A.-M. & Badr, O. Assessing the viability of using rape methyl ester (RME) as an alternative to mineral diesel fuel for powering road vehicles in the UK. *Appl. Energy*, 1998, **59**, 2–3, 187–214.
24. Rocco, V., Montanari, R., Prati, M. V. & Senatore, A. Analysis of particulate emitted from an IDI turbocharged small diesel engine fueled with biofuels and their blend. In *ICE (Am. Soc. Mech. Eng.) Proc. 17th Conf. ASME*. 1995, 25, 1–10.
25. Kara, J., Prokorny, Z. & Andert, D. Biomass utilization to energetic purposes in the Czech Republic. In *Biomass Energy Environ., Proc. Eur. Bioenergy Conf., 9th*, 1996, Vol. 3, 1817–1822.
26. Cvangros, J. & Povazanec, F. Production and treatment of rapeseed oil methyl esters as alternative fuels for diesel engines. *Bioresour. Technol.*, 1996, **55**, 2, 145–152.

27. Cvengros, J. & Cvengros, M. Alternative fuels for diesel engines from vegetable oils and animal fats. *Pet. Coal*, 1995, **37**, 2, 25–28.
28. Aksoy, H. A., Kahraman, L., Karaosmanoglu, F. & Civelekoglu, H. Evaluation of Turkish sulfur olive oil as an alternative diesel fuel. *J. Am. Oil Chem. Soc.*, 1988, **65**, 936–938.
29. Aksoy, H. A., Becerik, I., Karaosmanoglu, F., Yatamaz, H. C. & Civelekoglu, H. Utilization prospects of Turkish raisin seed oil as an alternative fuel. *Fuel*, 1990, **69**, 600–603.
30. Karaosmanoglu, F. Vegetable oil fuels: a review. *Energy Sources*, 1999, **21**, 3, 221–231.
31. Karaosmanoglu, F., Akdag, A. & Cigizoglu, K. B. Biodiesel from rapeseed oil of Turkish origin as an alternative fuel. *Appl. Biochem. Biotechnol.*, 1997, **61**, 3, 251–265.
32. Srivastava, A. & Prasad, R. Triglycerides-based diesel fuels. *Renew. Syst. Energy Rev.*, 2000, **4**, 2, 111–133.
33. Bhattacharyya, R. Biodiesel from minor vegetable oils like karanja oil and nahor oil. *Fett/Lipid*, 1999, **101**, 10, 404–406.
34. Ferreira-Dias, S., Coneia, A. C., Mazumbe, J. V., Laurencio, E. V. & Regato, J. E. Rapeseed as an alternative crop non-food uses in Portugal. In *Biomass, Proc. Biomass Conf. Am.*, 4th, 1999, Vol. 1, 343–348.
35. Fragioudakis, K., Teas, C., Sakellaropoulos, F., Zannikos, F., Stournas, S. & Lois, E. Adding biodiesel corn oil and sunflower oil to diesel fuel: the impact on the performance of conventional road vehicles. *J. Inst. Energy*, 1998, **71**, 488, 126–136.
36. Serdari, A., Fragioudakis, K., Teas, C., Zannikos, F., Stournas, S. & Louis, E. Effect of biodiesel addition to diesel fuel on engine performance and emissions. *J. Propul. Power*, 1999, **15**, 2, 224–231.
37. Kotowski, W. & Fechner, W. Conversion of vegetable oils to diesel fuel. *Karbo*, 1999, **44**, 2, 69–74. C.A. 131: 90083e.
38. Radwan, M. S., Dandoush, S. K., Selim, M. Y. E. & Kader, A. M. A. Biodiesel fuel. *Soc. Automot. Eng.*, 1997, SP-1298, 61–71.
39. Domac, J. Biofuels production possibilities in the Republic of Croatia. *Naphtha*, 1998, **49**, 5, 159–166.
40. Kricka, T., Domac, J. & Jukic, Z. Biodiesel fuel production in Croatia. *Naphtha*, 1999, **50**, 10, 337–342.
41. Siler-Marinkovic, S. S., Tomasevic, A. V., Mojavic, L. V. & Petrovic, S. D. Optimization of methanolysis of vegetable oils. I. Effect of process parameters. *Hem. Ind.*, 1996, **50**, 7–8, 303–307. C.A. 125: 252758j.
42. Vukas, S., Groic, S. & Ilic, D. Influence of biodiesel fuel on diesel engine parts and motor oil. *J. Balk. Tribol. Assoc.*, 1998, **4**, 3–4, 253–261. C.A. 131: 132040w.
43. Radu, R. & Mircea, Z. The use of sunflower oil in diesel engine. *Soc. Automot. Eng.*, 1997, SP-1298, 105–111.
44. Bak, Y.-C., Choi, J.-H., Kim, S.-B. & Kang, D.-W. Production of bio-diesel fuels by transesterification of rice bran oil. *Korean J. Chem. Eng.*, 1996, **13**, 3, 242–245.
45. Choo, Y. M., Ma, A. N. & Ong, A. S. H. Biofuels. In *Lipid Technology and Application* (Gunstone, F. D. & Padley, F. B., eds.). Dekker, New York, 1997, 771–785.
46. Shaheed, A. K. & Swain, D. Combustion analysis of coconut oil and its methyl esters in a diesel engine. In *IMEchE. Conf. Trans.*, 1998, 287–297.
47. Kalayasiri, P., Jeyashoke, N. & Krisnangkura, K. Survey of seed oil for use as diesel fuels. *J. Am. Oil Chem. Soc.*, 1996, **73**, 471–474.
48. Harrington, K. J. Chemical and physical properties of vegetable oil esters and their effect on diesel fuel performance. *Biomass*, 1986, **9**, 1, 1–17.
49. Krah, J., Munack, A., Bahadir, M., Schumacher, L. & Elser, N. Utilization of rapeseed oil, rapeseed oil methyl ester or diesel fuel: exhaust gas emissions and estimation of environmental effects. *Soc. Automot. Eng.*, 1996, SP-1208, 311–330.
50. Gutsche, B. Technology of methyl ester production and its application as biodiesel. *Fett/Lipid*, 1997, **99**, 12, 418–427.
51. Dunn, R. O., Knothe, G. & Bagby, M. O. Recent advances in the development of alternative diesel fuel from vegetable oils and animal fats. *Recent Res. Dev. Oil Chem.*, 1997, 1, 31–56.

52. Foglia, T. A., Nelson, L. A., Marmer, W. N., Knothe, G. H., Dunn, R. O. & Bagby, M. O. Improving the properties of vegetable oils and fats for use as biodiesel. In *Proc. World Conf. Oilseed Edible Oils Process* 1996. 1998, Vol. 1, 121–125.
53. Bagby, M. O. Products from vegetable oils: two examples. *ACS Symp. Ser.*, 1996, **647**, 248–257.
54. König, J. W. J. Biodiesel, an environmental blessing or biodegradation. Headache for long term storage. In *Proc. Int. Conf. Stab. Handl. Liq. Fuels, 6th, 1997*. 1998, Vol. 2, 833–850.
55. Borgelt, S. C., Kolb, T. S. & Schumacher, L. G. Biodiesel: world status. In *Proc. Altern. Energy Conf.*, 1994, 67–76.
56. Ryan, T. W., Dodge, L. G. & Callahan, T. J. The effects of vegetable oil properties on injection and combustion in two different diesel engines. *J. Am. Oil Chem. Soc.*, 1984, **61**, 1610–1619.
57. Krah, J., Seidel, H. & Bemger, J. Exhaust gas emissions and effects on environment and human health of rapeseed oil based fuels. In *Biomass Energy Environ., Proc. Env. Bioenergy Conf., 9th, 1996*, Vol. 3, 1657–1661.
58. Nwafor, O. M. I. & Rice, G. Performance of rapeseed oil blends in a diesel engine. *Appl. Energy*, 1996, **54**, 4, 345–354.
59. Ozaktas, T., Cigizoglu, K. B. & Karaosmanoglu, F. Plant oils as diesel fuel. *Energy Sources*, 1997, **19**, 2, 173–181.
60. Hassett, D. J. & Hasan, R. A. Sunflower oil methyl ester as diesel fuel. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 127–137.
61. Kusy, P. F. Transesterification of vegetable oils for fuels. *ASAE Publ.*, 1982 (4–82, *Veg. Oil Fuels*), 127–137.
62. Son, R. & Verma, S. R. Preliminary studies on methyl ester of maize oil as alternative fuel in compression ignition engine. *J. Res.*, 1999, **35**, 1/2, 67–72.
63. Encinar, J. M., Gonzalez, J. F., Sabio, E. & Ramiro, M. J. Preparation and properties of biodiesel fuel from *Cynara cardunculus* L. oil. *Ind. Eng. Chem. Res.*, 1999, **38**, 2927–2931.
64. Foidl, N., Foidl, G., Sanchez, M., Mittelbach, M. & Hackel, S. *Jatropha curcas* L. as a source for the production of biofuel in Nicaragua. *Bioresour. Technol.*, 1996, **58**, 1, 77–82.
65. Roessler, P. G., Brown, L. M., Dunahay, T. G., Heacox, D. A., Jarvis, E. E., Schneider, J. C. & Zeiler, K. G. Genetic engineering approaches for enhanced production of biodiesel from microalgae. *ACS Symp. Ser.*, 1994, **566**, 255–270.
66. Rahman, M. Biodiesel, a promising substitute energy for Indonesia. *Lembaran Publ. Lemigas*, 1995, **29**, 1, 33–38. C.A. 124: 150710z.
67. Ma, F., Clements, L. D. & Hanna, M. A. Biodiesel fuel from animal fats. Ancillary studies on transesterification of beef tallow. *Ind. Eng. Chem. Res.*, 1998, **37**, 3768–3771.
68. Ma, F., Clements, L. D. & Hanna, M. A. The effect of mixing on transesterification of beef tallow. *Bioresour. Technol.*, 1999, **69**, 3, 289–293.
69. Muniyappa, P. R., Brammer, S. C. & Nouredini, H. Improved conversion of plant oils and animal fats into biodiesel and co-product. *Bioresour. Technol.*, 1996, **56**, 1, 19–24.
70. Ali, Y. & Hanna, M. A. In-cylinder pressure characteristics of a D.I. heavy duty diesel engine on biodiesel fuel. *Soc. Automot. Eng.*, 1997, SP-1247, 143–151.
71. Ali, Y., Hanna, M. A. & Cuppett, S. L. Fuel properties of tallow and soybean oil esters. *J. Am. Oil Chem. Soc.*, 1995, **72**, 1557–1564.
72. Hanna, M. A., Ali, Y., Cuppett, S. L. & Zheng, D. Crystallization characteristics of methyl tallowate and its blends with ethanol and diesel fuel. *J. Am. Oil Chem. Soc.*, 1996, **73**, 759–763.
73. Zheng, D. & Hanna, M. A. Preparation and properties of methyl esters of beef tallow. *Bioresour. Technol.*, 1996, **57**, 2, 137–142.
74. Ali, Y. & Hanna, M. A. Beef tallow as a biodiesel fuel. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd, 1996*, 59–72.
75. Hanna, M. A. & Ali, Y. Fuel properties of methyl esters of beef tallow. *Recent Res. Dev. Oil. Chem.*, 1997, 1, 309–320.

76. Walker, K. C. Development in feedstocks available for biodiesel production. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 165–169.
77. Mittelbach, M. The high flexibility of small scale biodiesel plants production of methyl esters in high quality using various feedstocks. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 183–187.
78. Mittelbach, M. & Enzelsberger, H. Transesterification of heated rapeseed oil for extending diesel fuel. *J. Am. Oil Chem. Soc.*, 1999, **76**, 545–550.
79. Mittelbach, M. & Tritthart, P. Diesel fuel derived from vegetable oils. III. Emissions test using methyl esters of used frying oil. *J. Am. Oil Chem. Soc.*, 1988, **65**, 1185–1187.
80. Stefanson, B. R. & Hongen, F. W. Selection of rape plants (*B. napus*) with seed oil practically free from erucic acid. *Can. J. Plant Sci.*, 1964, **44**, 359–364.
81. Roine, P. E., Uksila, H., Teir, H. & Rapola, J. 1960. Histopathological changes in rats and pigs fed rapeseed oil. *Z. Ernährungswiss.*, 1960, **1**, 1, 118–124.
82. Frauen, M. Breeding of high-oleic-acid rapeseed (HOAR). In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 240–245.
83. Rakow, G. Selection auf Linol- und Linolensäuregehalt in Rapssamen nach Mutagener Behandlung. *Z. Pflanzenzücht.*, 1973, **69**, 1, 62–82.
84. Röbbelen, G. & Nitsch, A. Genetical and physiological investigations on mutants for polyenoic fatty acids in rapeseed. *Z. Phlanzenzücht.*, 1975, **75**, 2, 93–105.
85. Harwood, J. L. Recent advances in the biosynthesis of plant fatty acids. *Biochim. Biophys. Acta*, 1996, **1301**, 7–56.
86. Sovero, M. Modification of fatty acids by genetic engineering. In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 233–239.
87. Geller, D. P., Goodrum, J. W. & Campbell, C. C. Rapid screening of biologically modified vegetable oils for fuel performance. *Trans. ASAE*, 1999, **42**, 859–862.
88. Demirbas, A. Fuel properties and calculation of higher heating values of vegetable oils. *Fuel*, 1998, **77**, 1117–1120.
89. Wenzel, G. & Lammers, P. S. Boiling properties and thermal decomposition of vegetable oil methyl esters with regard to their fuel suitability. *J. Agric. Food Chem.*, 1997, **45**, 4748–4752.
90. Knothe, G., Dunn, R. O. & Bagby, M. O. Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. *ACS Symp. Ser.*, 1997, **660**, 172–208.
91. Kincs, F. R. Meat fat formulation. *J. Am. Oil Chem. Soc.*, 1985, **62**, 815–818.
92. Ma, F. & Hanna, M. A. Biodiesel production: a review. *Biores. Technol.*, 1999, **70**, 1, 1–15.
93. Wu, W.-H., Foglia, T. A., Marmer, W. N., Dunn, R. O., Gaering, C. E. & Briggs, T. E. Low-temperature property and engine performance evaluation of ethyl and isopropyl esters of tallow and grease. *J. Am. Oil Chem. Soc.*, 1998, **75**, 1173–1178.
94. McDonald, J. & Spears, M. W. Biodiesel: effects on exhaust constituents. In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 141–160.
95. Graboski, M. S. & McCromick, R. L. Combustion of fat and vegetable oil derived fuels in diesel engine. *Prog. Energy Comb. Sci.*, 1998, **24**, 1, 125–164.
96. Sams, T. Exhaust components of biofuels under real world engine conditions. In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 64–78.
97. Schäfer, A. Vegetable oil fatty acid methyl esters as alternative diesel fuels for commercial vehicle engines. In *Plant Oils as Fuels. Proc. Symp. 1997*. Springer-Verlag, 1998, 29–46.
98. Klopfenstein, W. E. Effect of molecular weights of fatty acid esters on cetane numbers as diesel fuels. *J. Am. Oil Chem. Soc.*, 1985, **62**, 1029–1031.
99. Knothe, G., Bagby, M. O. & Ryan, T. W. The influence of various oxygenated compounds on the cetane numbers of fatty acids and esters. In *Proc. Liq. Fuel Conf., 3rd*, 1996, 54–58.
100. Knothe, G., Bagby, M. O. & Ryan, T. W. Precombustion of fatty acids and esters of biodiesel. A possible explanation for differing cetane numbers. *J. Am. Oil Chem. Soc.*, 1998, **75**, 8, 1007–1013.
101. Kirk-Othmer. *Encyclopedia of Chemical Technology*. Third edn. John Wiley & Sons, New York, 1978, Vol. 11.

102. Rathbauer, J. Fatty acid methyl esters (FAME) as special winter fuel. In *Proc. Eur. Biomass Conf., 8th, 1994*, 1995, Vol. 2, 1174–1177.
103. Lee, I., Johnson, L. & Hammond, E. G. Reducing the crystallization temperature of biodiesel by winterizing methyl soyate. *J. Am. Oil Chem. Soc.*, 1996, **73**, 631–636.
104. Angelrot, D. Method for producing fractions of methyl esters of C<sub>11</sub>–C<sub>20</sub> fatty acids with low cloud point. FR Pat. 2763939 (1998). C.A. 130: 140768j.
105. Dunn, R. O. Thermal analysis of alternative diesel fuels from vegetable oils. *J. Am. Oil Chem. Soc.*, 1999, **76**, 109–115.
106. Bachler, A., Wörgetter, M. & Rathbauer, J. Separation of fatty acid ester mixtures. AT Pat. 404137 (1998). C.A. 130: 140767h.
107. Lee, I., Johnson, L. & Hammond, E. G. Use of branched-chain esters to reduce the crystallization temperature of biodiesel. *J. Am. Oil Chem. Soc.*, 1995, **72**, 1155–1160.
108. Goodrum, J. W. & Eiteman, M. A. Physical properties of low molecular weight triglycerides for the development of biodiesel fuel. *Bioresour. Technol.*, 1996, **56**, 1, 55–60.
109. Harold, S. Industrial vegetable oils: opportunities within the European biodiesel and lubricant markets. Part 1. Technology and applications. *Lipid Techn.*, 1997, **9**, 2, 33–38.
110. Lal, K., Dishong, D. M. & Dietz, J. G. Pour point depressants for high monosaturated vegetable oils and for high monosaturated vegetable oils/biodegradable base and fluid mixtures. EP 604125 (1994).
111. Lal, K. Pour point for industrial lubricants containing mixtures of fatty acid esters and vegetable oils. US Pat. 5338471 (1994).
112. Majerczak, V. A. Pour point depression of heavy cut methyl esters via alkyl methacrylate copolymer. GB Pat. 2331761 (1999).
113. Demmering, G., Schmid, K., Bonagard, F. & Wittich, L. Mischungen von Fettsäureniedrigalkylestern mit verbesserten Kältestabilität. DE OS 4040317 (1992), EP 563070 (1995).
114. Bömke, M. & Pennewiss, H. Verfahren zur Herstellung von Kompositionen mit verbessertem Tieftemperaturverhalten. EP 543356 (1993).
115. Krull, M. & Reimann, W. Procedure for improving cold flow properties of fuel oils. EP 931824 and 931825 (1999).
116. Davies, B. W., Lewtas, K. & Lombardi, A. Oil additives and compositions. PCT WO 94/10267, EP 665873B1 (1996).
117. Lewtas, K. & Block, D. Additives for oils. PCT WO 93/18115, EP 629231B1 (1999).
118. Müller, M., Pennewiss, H. & Jenssen, D. Additive für Dieselmotoren. EP 406684B1 (1998).
119. Kishida, M., Nomura, T. & Matsuie, H. Fuel oil additives and fuel oil compositions containing mono- and diunsaturated fatty acids. Jpn. Kokai 11236581 (1999). C.A. 131: 187244w.
120. Stavinocha, L. L. & Howell, S. Potential analytical methods for stability testing of biodiesel and biodiesel blends. *Soc. Automot. Eng.*, 1999, SP-1482, 79–93.
121. Prankel, H. & Wörgetter, M. Influence of the iodine number of biodiesel on the engine performance. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 191–196.
122. Prankel, H. & Wörgetter, M. & Rathbauer, J. Technical performance of vegetable oil methyl esters with high iodine number. In *Biomass, Proc. Biomass Conf. Am., 4th*, 1999, Vol. 1, 805–810.
123. Fabisz, E. & Morawski, I. Stabilization of methyl esters of fatty acids from rape oil. *Przem. Chem.*, 1999, **78**, 5, 175–176. C.A. 131: 132159s.
124. Dunn, R. O. Analysis of oxidative stability of methyl soyate by pressurized differential scanning calorimetry. *Trans. ASAE*, 2000, **43**, 1203–1208.
125. Allen, C. A. W., Watts, K. C., Ackman, R. G. & Pegg, M. J. Predicting the viscosity of biodiesel fuels from their fatty acid ester composition. *Fuel*, 1999, **78**, 1319–1326.
126. Allen, C. A. W., Watts, K. C. & Ackmann, R. G. Properties of methyl esters of interesterified triglycerols. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 73–82.
127. Tat, M. E. & Van Gerpen, J. H. The specific gravity of biodiesel and its blends with diesel fuel. *J. Am. Oil Chem. Soc.*, 2000, **77**, 115–119.

128. Tat, M. E. & Van Gerpen, J. H. The kinematic viscosity of biodiesel and its blends with diesel fuel. *J. Am. Oil Chem. Soc.*, 1999, **76**, 1511–1513.
129. Bessee, G. B. & Fey, J. P. Compatibility of elastomers and metals in biodiesel fuel blends. *Soc. Automot. Eng.*, 1997, SP-1274, 221–232.
130. Krah, J., Bunge, J., Jeberien, H.-E., Prieger, K., Schutt, C., Munack, A. & Bahadir, M. Analysis of biodiesel exhaust emission and determination of environmental and health effects. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 149–165.
131. Kossmehl, S.-O. Biodiesel als Kraftstoff für Volkswagen-Dieselmotoren. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 217–224.
132. Wolf, G. Motor fuel for diesel engines suitable for operation with difficultly combustible fuels. DE OS 19904194 (1999). C.A. 131: 132259z.
133. Karonis, D., Anastopoulos, G., Lois, E., Stournas, S., Zannikos, F. & Serdari, A. Assessment of the lubricity of Greek road diesel and the effect of the addition of specific types of biodiesel. *Soc. Automot. Eng.*, 1999, SP-1461, 1–6.
134. Cvenegros, J., Pavlovicova, A., Gladisova, G. & Cerny, J. Rape seed oil methyl esters with low phosphorus content. *Fett/Lipid*, 1999, **101**, 7, 261–265.
135. Theil-Gangl, A. Risk reduction for transports and engines in environmental sensitive areas. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 273–284.
136. Thompson, J. C., Peterson, C. L., Reece, D. L. & Beck, S. M. Two-year storage study with methyl and ethyl esters of rapeseed. *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 104–114.
137. Thompson, J. C., Peterson, C. L., Reece, D. L. & Beck, S. M. Two-year storage study with methyl and ethyl esters of rapeseed. *Trans. ASAE*, 1998, **41**, 931–939.
138. Reece, D. L., Zhang, X. & Peterson, C. L. Environmental and health effects of biodiesel. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 166–176.
139. Bünger, J., Krah, J., Franke, H.-U., Munack, A. & Hallien, E. Mutagenic and cytotoxic effects of exhaust particulate matter of biodiesel compared to fossil diesel fuel. *Mutat. Res.*, 1998, **415**, 1–2, 13–23.
140. Haller & Yousoufin. – *Compt. Rend*, 1906, **143**, 805. *Beilsteins Handbuch*. Springer-Verlag, 1920, Vol. 2.
141. Allen, H. D., Rock, G. & Kline, W. A. Process for treating fats and oils. US Pat. 2383579 (1945).
142. Bradshaw, G. B. & Meuly, W. C. Preparation of detergents. US Pat. 2360844 (1944).
143. Trent, W. R. Process of treating fatty glycerides. US Pat. 2383632 (1945).
144. Sprules, F. J. & Price, D. Production of fatty esters. US Pat. 2366494 (1945).
145. Smith, M. K. Process of producing esters. US Pat. 2444486 (1949).
146. Freedman, B., Pryde, E. H. & Mounts, T. L. Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.*, 1984, **61**, 1638–1643.
147. Freedman, B., Betterfield, R. & Pryde, E. H. Transesterification kinetics of soybean oil. *J. Am. Oil Chem. Soc.*, 1986, **63**, 1375–1380.
148. Schwab, A. W., Bagby, M. O. & Freedman, B. Preparation and properties of diesel fuels from vegetable oils. *Fuel*, 1987, **66**, 1372–1378.
149. Mittelbach, M., Woergetter, M., Pernkopf, J. & Junek, H. Diesel fuel derived from vegetable oils: preparation and use of rape oil methyl ester. *Energy Agric.*, 1983, **2**, 4, 369–384.
150. Mittelbach, M. & Junek, H. Verfahren zur Herstellung eines Fettsäureestergemisches aus Abfallfetten bzw. Ölen und Verwendung dieses gemisches als Kraft.-bzw Brennstoff. Austrian Pat. 388743B (1989).
151. Germani, M. M. G. Verfahren zur Herstellung von Alkylestern aus Pflanzenölen. DE OS 4324875 (1994).
152. Wimmer, T. Verfahren zur Herstellung von Fettsäureestern niederer Alkohole. Austrian Pat. 394374B (1992).
153. Leodolter, A. Verfahren zur Reinigung von rohen Pflanzenölestern. Austrian Pat. 398777 (1995).

154. Suzuki, H., Suzuki, A. & Suzuki, K. Manufacture of fatty acid methyl esters useful for diesel fuels. Jpn. Kokai 07310090 (1995). C.A. 124: 294088a.
155. Someya, A. Refinery method for waste edible oils as raw materials for recovery of diesel fuels, glycerin and substitute fuels for heavy-oil burners. Jpn. Kokai 09235573 (1997). C.A. 127: 265530v.
156. Iwakura, K. & Sohda, H. Manufacture of fatty acid esters and their uses for diesel fuels and fuel additives. Jpn. Kokai 2000 144172. C.A. 132: 349266e.
157. Billenstein, S., Kukla, B. & Stühler, H. Verfahren zur Herstellung von Fettsäureestern kurzkettiger Alkohols. DE PS 3421217 (1985), EP 164643B1 (1989).
158. Lepper, H. & Friesenhagen, L. Fettsäuren Methylestern. DE PS 3444893 (1986).
159. Sankaran, V. Transesterification of triglycerides. US Pat. 4966876 (1990).
160. Nouredini, H., Harkey, D. & Medikonduru, V. A. Continuous process for the conversion of vegetable oils into methyl esters of fatty acids. *J. Am. Chem. Soc.*, 1998, **75**, 1775–1783.
161. Ergun, N. & Panning, P. Method for producing fatty acid methyl ester and equipment for realizing the same. PCT WO 99/26913.
162. Nimcevic, D., Pentigam, R., Worgetter, M. & Gapes, J. R. Preparation of rapeseed oil esters of lower aliphatic alcohols. *J. Am. Oil Chem. Soc.*, 2000, **77**, 275–280.
163. Sunderbrink, T. Kraftstoff für hochverdichtende selbstzündende Motoren. EP 716139 (1996).
164. Tanaka, Y., Okabe, A. & Ando, S. Method for the preparation of a lower alkyl ester of fatty acids. US Pat. 4303590 (1981).
165. Hock, O. S., May, Ch. Y., Yoo, C. K. & Nasir, A. B. S. Production of alkyl esters from oils and fats containing varying amount of free fatty acids. AU 626014 (1992).
166. Dimming, T., Radig, W., Haupt, J. & Dittmar, T. Verfahren zur Herstellung von Fettsäuremethylestern aus Triglyceriden und Fettsäuren. DE OS 19908978 (2000).
167. Gaskoks-Vertrieb, Wien. Verfahren und Vorrichtung zur Herstellung von Fettsäureestern und deren Verwendung. Austrian Pat. 387399 (1989).
168. Wimmer, T. Transesterification process for the preparation of C<sub>1</sub>–C<sub>5</sub>-alkyl fatty esters from fatty glycerides and monovalent lower alcohols. PCT WO 92/009268.
169. Klok, R. & Mulder, C. W. Process for producing fatty-acid lower-alkyl monoesters. EP 391485 (1993).
170. Wimmer, T. Process for preparing fatty acid esters of short-chain monohydric alcohols. PCT WO 93/09212.
171. Enchelmaier, H. & Rasehorn, H.-J. Verfahren und Vorrichtung zur Herstellung von Rapsmethylester. DE OS 4238195 (1994).
172. Foidl, N. Verfahren zur Herstellung von Fettsäurealkylestern. PCT WO 97/00234.
173. Peterson, G. R. & Scarrah, W. P. Rapeseed oil transesterification by heterogeneous catalysis. *J. Am. Oil Chem. Soc.*, 1984, **61**, 1593–1597.
174. Hofman, P. Verfahren zur Herstellung von Carbon-säurealkylestern, insbesondere Fettsäurealkylestern, und deren Verwendung als Dieselmotorkraftstoff. DE OS 3512497 (1986), EP 198243B1 (1988).
175. Basu, H. N. & Norris, M. E. Process for production of esters for use as a diesel fuel substitute using a non-alkaline catalyst. US 5525126 (1996).
176. Stern, R., Hillion, G. & Rouxel, J.-J. Procédé de fabrication d'esters de corps et les esters de haute pureté obtenus. EP 924185 (1999).
177. Ginosar, D. M. & Fox, R. V. A process for producing biodiesel, lubricants, and fuel and lubricant additives in a critical fluid medium. PCT WO 00/05327.
178. Diasakou, M., Louloudi, A. & Papayannakos, N. Kinetics of the non-catalytic transesterification of soybean oil. *Fuel*, 1998, **77**, 1297–1302.
179. Saka, S. & Padau, K. Transesterification of rapeseed oils in supercritical methanol to biodiesel fuel. In *Biomass, Proc. Biomass Conf. Am. 4th*, 1999, Vol. 1, 797–801.
180. Saka, S. & Kusdiana, D. Biodiesel fuel from rapeseed oil as prepared in supercritical methanol. *Fuel*, 2001, **80**, 225–231.
181. Kusdiana, D. & Saka, S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol. *Fuel*, 2001, **80**, 693–698.

182. Sasaki, T., Suzuki, T. & Okada, F. Method for preparing fatty acid esters and fuel comprising fatty acid esters. EP 985654 (2000).
183. Shiro, S. Manufacture of fatty acid monoesters for diesel fuel. Jpn. Kokai 2000 204392. C.A. 133: 121966t.
184. Mittelbach, M. Lipase catalyzed alcoholysis of sunflower oil. *J. Am. Oil Chem. Soc.*, 1990, **67**, 168–170.
185. Shaw, J.-F., Wang, D.-L. & Wang, Y. J. Lipase-catalyzed ethanolysis and isopropanolysis of triglycerides with long-chain fatty acids. *Enzyme Microb. Technol.*, 1991, **13**, 544–546.
186. Jackson, M. A. & King, J. W. Methanolysis of seed oils in flowing supercritical carbon dioxide. *J. Am. Oil Chem. Soc.*, 1996, **73**, 353–356.
187. Haas, M. J. & Scott, K. M. Diesel fuel as a solvent for the lipase-catalyzed alcoholysis of triglycerides and phosphatidylcholine. *J. Am. Oil Chem. Soc.*, 1996, **73**, 1498–1503.
188. Sylđatk, Ch., Reuss, M., Daniel, A. & Otto, R. Verfahren zur biotechnischen Herstellung von Fettsäuremethylestern (“Biodiesel”) auf Molkebasis. DE OS 19838011 (1999).
189. Wu, W. H., Foglia, T. A., Marmer, W. N. & Philips, J. G. Optimizing production of ethyl esters of grease using 95% ethanol by response surface methodology. *J. Am. Oil Chem. Soc.*, 1999, **76**, 517–521.
190. Kaieda, M., Samukawa, T., Matsumoto, T., Ban, K., Kondo, A., Shimada, Y., Noda, H., Nomoto, F., Ohtsuka, K., Izumoto, E. & Fukuda, H. Biodiesel fuel production from plant oil catalyzed by *Rhizopus oryzae* lipase in a water-containing system without an organic solvent. *J. Biosci. Bioeng.*, 1999, **88**, 627–631.
191. Watanabe, Y., Shimada, Y., Sugihara, A., Noda, H., Fukuda, H. & Tominaga, Y. Continuous production of biodiesel fuel from vegetable oil using immobilized *Candida antarctica* lipase. *J. Am. Oil Chem. Soc.*, 2000, **77**, 355–360.
192. Oliveira, J. V. & Oliveira, D. Kinetics of enzymatic alcoholysis of palm kernel oil in supercritical CO<sub>2</sub>. *Ind. Eng. Chem. Res.*, 2000, **39**, 4450–4454.
193. Samukawa, T., Kaieda, M., Matsumoto, T., Ban, K., Kondo, A., Shimada, Y., Noda, H. & Fukuda, H. Pretreatment of immobilized *Candida antarctica* lipase for biodiesel fuel production from plant oil. *J. Biosci. Bioeng.*, 2000, **90**, 180–183.
194. Shimada, Y., Watanabe, Y., Segihara, A., Tominaga, Y., Fukuda, H. & Noda, H. Process for producing biodiesel fuel lower alcohol ester. PCT WO 00/12743.
195. Harrington, K. J. & D’Arcy-Evans, C. A comparison of conventional and *in situ* methods of transesterification of seed oil from a series of sunflower cultivars. *J. Am. Oil Chem. Soc.*, 1985, **62**, 1009–1013.
196. Kildiran, G., Yücel, S. Ö. & Türkay, S. *In situ* alcoholysis of soybean oil. *J. Am. Oil Chem. Soc.*, 1996, **73**, 225–228.
197. Silver-Marinkovic, S. & Tomasevic, A. Transesterification of sunflower oil *in situ*. *Fuel*, 1998, **77**, 1389–1391.
198. Wong, A. & Hogan, E. A green approach for the production of bi-cetane enhancer for diesel fuels. In *Biomass, Proc. Biomass Conf. Am.*, 4th, 1999, Vol. 1, 837–841.
199. Stumborg, M., Wong, A. & Hogan, E. Hydroprocessed vegetable oils for diesel fuel improvement. In *Liq. Fuels, Lubr. Addit. Biomass, Proc. Altern. Energy Conf.*, 1994, 157–165.
200. Stumborg, M., Wong, A. & Hogan, E. Hydroprocessed vegetable oils for diesel fuel improvement. *Bioresour. Technol.*, 1996, **56**, 1, 13–18.
201. Bradin, D. S. Biodiesel fuel. US Pat. 5578090 (1996).
202. Noureddini, H. Process for producing biodiesel fuel with reduced viscosity and cloud point below 32 °F. US Pat. 6015440 (2000).
203. Noureddini, H. System and process for producing biodiesel fuel with reduced viscosity and cloud point below thirty-two (32) degrees Fahrenheit. US Pat. 6174501 (2001).
204. Weiss-Schur, G. & Welzel, W. Treibstoffgemisch und seine Verwendung. DE PS 4135294 (1993).
205. Johanson, L. A. & Hammond, E. G. Soybean oil ester fuel blends. US 5520708 (1996).
206. Koseki, K., Ueno, H. & Ito, T. Fuel oil compositions containing ester compounds for diesel engines. Jpn. Kokai 09194859 (1997). C.A. 127: 137981f.



207. Kramaschke, V. Dieselkraftstoffsubstitut und Verfahren zu dessen Herstellung. EP 937767 (1999).
208. Uta, K., Ono, H., Fuchigami, M. & Muto, T. Lubricant additives for low-sulfur light oils as diesel engine fuels. Jpn. Kokai 11228977 (1999). C.A. 131: 172532q.
209. Kikawa, H., Itai, E., Kanae, K. & Inagaki, T. Light oil additives and light oil compositions for diesel fuels. Jpn. Kokai 11228978 (1999). C.A. 131: 172533r.
210. Hayafuji, S., Shimizu, T., Wang, S.-S. & Zaima, H. Manufacture method of diesel fuel oils from waste cooking oils. Jpn. Kokai 10245586 (1989). C.A. 129: 291805z.
211. Dimming, Th., Haupt, J., Radig, W. & Dittmar, Th. Biodiesel–diesel fuel substitute from vegetable oils and native recycling products. *Freiberg. Forschungsh. A*, 1999, A 852 (Neue Erkenntnisse zur Stofflichen Nutzung von Nachwachsenden Rohstoffen), 34–60.
212. Coteron, A., Vicente, G., Martinez, M. & Aracil, J. Biodiesel production from vegetable oils. Influence of catalysts and operating conditions. *Res. Devel. in Oil Chem.*, 1997, 1, 109–114.
213. Vicente, G., Coteron, A., Martinez, M. & Aracil, J. Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. *Ind. Crops Prod.*, 1998, 8, 1, 29–35.
214. Boocock, D. G. B., Konar, S. K., Mao, V. & Sidi, H. Biodiesel: transesterification of vegetable oils revisited: a method for increasing base-catalyzed methanolysis rates. In *Proc. Eur. Biomass Conf., 8th, 1994*, 1995, Vol. 2, 1192–1197.
215. Mittelbach, M., Tritthart, P. & Junek, H. Diesel fuel derived from vegetable oils II: emission tests using rape oil methyl ester. *Energ. Agric.*, 1985, 4, 2, 207–215.
216. Schäfer, A. Biodiesel as an alternative fuel for commercial vehicle engines. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 233–244.
217. Schmidt, K. & Van Gerpen, J. The effect of biodiesel fuel composition on diesel combustion and emissions. *Soc. Automot. Eng.*, 1996, SP-1181, 113–124.
218. Kordesch, V. Modern diesel engines for the marine sector. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 247–252.
219. Krahel, J., Bünger, J. & Munack, A. Biodiesel exhaust emissions and determination of their environmental and health effects. In *Plant Oils as Fuels. Proc. Symp., 1997*. Springer-Verlag, 1998, 104–122.
220. Peterson, C. & Reece, D. Emissions characteristics of ethyl and methyl ester of rapeseed oil compared with low-sulfur diesel control fuel in a chassis dynamometer test of a pickup truck. *Trans. ASAE*, 1996, 39, 805–816.
221. Womac, A. R., Strange, R. J., Crouch, J. A. & Easterly, C. Power emissions and bioresponse of biodiesel in marine environment. In *Liq. Fuel Ind. Prod. Renewable Resour., Proc. Liq. Fuel Conf., 3rd*, 1996, 177–190.
222. Karman, D., Kuhl, M. & Rideout, G. Exhaust emissions from alternatively-fueled vehicles. In *Environ. Res. Forum*, 1997, 7–8, 139–144.
223. Mauderly, J. L. Health issues concerning inhalation of petroleum diesel and biodiesel exhaust. In *Plant Oils as Fuels. Proc. Symp., 1997*. Springer-Verlag, 1998, 92–103.
224. Eckl, P. M., Leikermosen, P., Wörgetter, M., Prankel, H. & Wurst, F. The mutagenic potential of diesel and biodiesel exhaust. In *Plant Oils as Fuels. Proc. Symp., 1997*. Springer-Verlag, 1998, 123–140.
225. Bagley, S. T., Gratz, I. D., Johnson, J. H. & McDonald, J. F. Effects of an oxidation catalytic converter and a biodiesel fuel on the chemical, mutagenic, and particle size characteristics of emissions from diesel engine. *Environ. Sci. Technol.*, 1998, 32, 1183–1191.
226. Wang, W. G., Lyons, D. W., Clark, N. N., Gantam, M. & Norton, P. M. Emissions from nine heavy trucks fueled by diesel and biodiesel blend with engine modification. *Environ. Sci. Technol.*, 2000, 34, 933–936.
227. Chang, D. Y., Van Gerpen, J. H., Lee, I., Johnson, L. A., Hammond, E. & Marley, S. J. Fuel properties and emissions of soybean oil esters as diesel fuel. *J. Am. Oil Chem. Soc.*, 1996, 73, 1549–1555.

228. Stalmach, F. Fuel for diesel engines with decreased formation of harmful emissions. Czech. Rep. CZ 283754. C.A. 131: 76129t.
229. Serdari, A., Lois, E. & Stournas, S. Impact of esters of mono- and dicarboxylic acids on diesel fuel quality. *Ind. Eng. Chem. Res.*, 1999, **38**, 3543–3548.
230. Oberdörster, G. Toxicological and environmental aspects related to the use of plant oils as fuels. In *Plant Oils as Fuels. Proc. Symp.*, 1997. Springer-Verlag, 1998, 89–91.
231. Sams, T. Use of biofuels under real world engine operation. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 225–231.
232. Durbin, T. D., Collins, J. R., Norbeck, J. M. & Smith, M. R. Effects of biodiesel, biodiesel blends and a synthetic diesel on emissions from light heavy-duty diesel vehicles. *Environ. Sci. Technol.*, 2000, **34**, 349–355.
233. Purcell, D. L., McClure, B. T., McDonald, J. & Basu, H. N. Transient testing of soy methyl ester fuels in an indirect injection, compression ignition engine. *J. Am. Oil Chem. Soc.*, 1996, **73**, 381–387.
234. Hamasaki, K., Kinoshita, E., Nakamura, T., Kanuda, A. & Oyama, T. Rapeseed oil fuel properties for diesel engines. *Kagoshima Daigaku Kogakubu Kenkyn Hokoku*, 1997, **39**, 23–28. C.A. 127: 333970r.
235. Chang, D. Y. Z. & Van Gerpen, J. H. Fuel properties and engine performance for biodiesel prepared from modified feedstocks. *Soc. Automot. Eng.*, 1997, SP-1274, 153–172.
236. Gong, J.-S. & Fu, W.-B. A study on the effect of more volatile fuel on evaporation and ignition for emulsified oil. *Fuel*, 2001, **80**, 437–445.
237. Crookes, R. J., Kiannejad, F. & Nazha, A. A. Systematic assessment of combustion characteristics of biofuels and emulsions with water for use as diesel engine fuels. *Energy Convers. Mgm.*, 1997, **38**, 1785–1795.
238. Freedman, B., Pryde, E. H. & Kwolek, W. F. Thin layer chromatography/flame ionization analysis of transesterified vegetable oils. *J. Am. Oil Chem. Soc.*, 1984, **61**, 1215–1220.
239. Freedman, B., Kwolek, W. F. & Pryde, E. H. Quantitation in the analysis of transesterified soybean oil by capillary gas chromatography. *J. Am. Oil Chem. Soc.*, 1986, **63**, 1370–1375.
240. Mittelbach, M., Roth, G. & Bergmann, A. Simultaneous gas chromatographic determination of methanol and free glycerol in biodiesel. *Chromatographia*, 1996, **42**, 7/8, 431–434.
241. Lechner, M., Bauer-Planck, C. & Lorbeer, E. Determination of acylglycerols in vegetable oil methyl esters by online normal phase LC–GC. *J. High Resolut. Chromatogr.*, 1997, **20**, 11, 581–585.
242. Holcapek, M., Jandera, P., Ficher, J. & Prokes, B. Analytical monitoring of the production of biodiesel by high-performance liquid chromatography with various detection methods. *J. Chromatogr., A.*, 1999, **858**, 1, 13–31.
243. Lozano, P., Chirat, N., Graille, J. & Pioch, D. Measurement of free glycerol in biofuels. *Fresenius' J. Anal. Chem.*, 1996, **354**, 319–322.
244. Cvengros, J. & Cvengrosova, Z. Quality control of rapeseed oil methyl esters by the determination of acyl conversion. *J. Am. Oil Chem. Soc.*, 1994, **71**, 1349–1352.
245. Komers, K., Skopal, F. & Stloukal, R. Determination of the neutralization number for biodiesel fuel production. *Fett/Lipid*, 1997, **99**, 2, 52–54.
246. Schöpe, M. Economic aspects of biodiesel production in Germany. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 311–316.
247. Peterson, C. L., Auld, D. L. & Thompson, J. C. Experiments with vegetable oil expression. *Trans. ASAE*, 1983, **26**, 1298–1302.
248. Devitt, M., Drysdale, D. W., McGillivray, I., Norris, A. J., Thompson, R. & Twidell, J. W. Biofuel for transport: an investigation into the viability of RME as an alternative to diesel fuel. *Int. J. Amb. Energy*, 1993, **14**, 4, 195–218.
249. Koncar, M. Criteria for the development and selection of low cost and high quality technologies for biodiesel. In *2nd European Motor Biofuels Forum, Graz, Austria*, 1996, 171–176.
250. Batchelor, S. E., Booth, E. J. & Walker, C. Energy analysis of rape methyl ester (RME) production from winter oilseed rape. *Ind. Crops Prod.*, 1995, **4**, 3, 193–202.

## **Edusammud biodiislikütuse uurimisel**

Jüri Kann, Heino Rang ja Jüri Kriis

On esitatud põhjalik analüütiline ülevaade biodiislikütuse toorme, omaduste, valmistamismeetodite, tootmise, heitgaaside, analüüsimeetodite ja ökonoomiliste aspektide kohta.

Biodiislikütuse kasutamise eelis on kasvuhoonegaaside (eelkõige CO<sub>2</sub>) ja õhku reostavate ainete koguste vähenemine võrreldes naftast saadava diislikütusega. Probleeme põhjustavad aga biodiislikütuse suhteliselt kõrge hind, ebastabiilsus ja voolavus madalatel temperatuuridel. Biodiislikütuse hinna alandamine on võimalik tootmistehnoloogia parandamise ja taimeõlide tootmiskulude vähendamisega õlitaime sordiaretuse ja geenitehnoloogia abil. Biodiislikütuse stabiilsust ja omadusi madalatel temperatuuridel saab parandada lisanditega, aga ka sordiaretuse ja geenitehnoloogia abil uute õlitaimesortide saamisega.

Artiklis on refereeritud 250 kirjandusallikat.