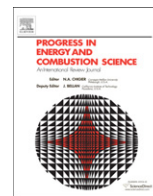




Contents lists available at ScienceDirect

# Progress in Energy and Combustion Science

journal homepage: [www.elsevier.com/locate/pecs](http://www.elsevier.com/locate/pecs)

## Biodiesel and renewable diesel: A comparison<sup>☆</sup>

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### ARTICLE INFO

#### Article history:

Received 17 August 2009

Accepted 18 November 2009

Available online 24 December 2009

#### Keywords:

Biodiesel

Fuel properties

Renewable diesel

### ABSTRACT

The search for alternatives to petroleum-based fuels has led to the development of fuels from various sources, including renewable feedstocks such as fats and oils. Several types of fuels can be derived from these triacylglycerol-containing feedstocks. One of them is biodiesel, which is defined as the mono-alkyl esters of vegetable oils or animal fats. Biodiesel is produced by transesterifying the oil or fat with an alcohol such as methanol under mild conditions in the presence of a base catalyst. Another kind of product that can be obtained from lipid feedstocks is a fuel whose composition simulates that of petroleum-derived diesel fuel. This kind of fuel, probably best termed “renewable diesel”, is produced from the fat or oil by a hydrodeoxygenation reaction at elevated temperature and pressure in the presence of a catalyst. This article discusses in a general and comparative fashion aspects such as fuel production and energy balance, fuel properties, environmental effects including exhaust emissions and co-products. Among the questions that are addressed are if these fuels compete with or complement each other and what the effect of production scale may be.

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### Contents

1. Introduction .....	364
2. Discussion .....	365
3. Conclusions and outlook .....	371
References .....	371

### 1. Introduction

Increasing concerns have caused an intensified search for alternative sources of energy. These concerns include feedstock availability as related to the security of the supply and using domestic energy sources, price volatility and continuing depletion of the reserves of non-renewable petroleum and greenhouse gas emissions. These concerns have been addressed by a variety of legislative and regulatory mandates and incentives around the world which to summarize is beyond the scope of this article.

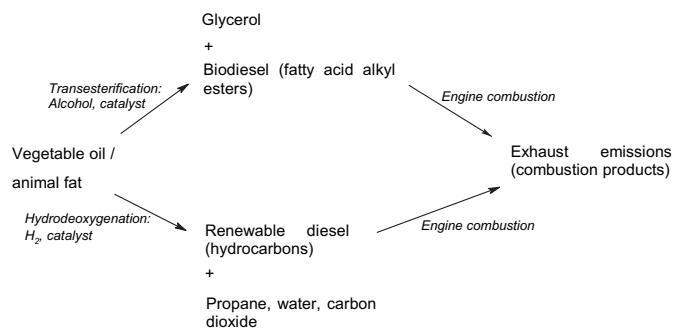
Fuels derived from biological sources, among them lipid materials such as fats and oils, have received increasing attention.

<sup>☆</sup> *Disclaimer:* Product names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

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Different production processes using fats and oils as feedstocks yield fuels with different compositions and properties. The most prominent of these fuels is biodiesel [1,2], which is defined as the mono-alkyl esters of vegetable oils or animal fats, obtained by transesterifying an oil or fat with an alcohol. The major reason for not using a neat vegetable oil as fuel is its high viscosity (usually in the range of 28–40 mm<sup>2</sup>/s), which leads to operational problems in diesel engine including formation of deposits and injector coking due to poorer atomization upon injection into the combustion chamber. Transesterification of the oil reduces the viscosity of the oil to a range (usually 4–5 mm<sup>2</sup>/s) closer to that of petrodiesel. However, a fuel which can be termed “renewable diesel” and whose composition resembles that of petroleum-derived diesel fuel (petrodiesel), has been gaining attention in recent years. Several processes (cracking or pyrolysis, hydrodeoxygenation) can be used to obtain fuels resembling petrodiesel [3], however, this article will emphasize renewable diesel produced by hydrodeoxygenation. Fig. 1 is a flow chart for fuels from triacylglycerol-containing feedstocks from production to engine combustion.



**Fig. 1.** Flow chart for transformation of lipid materials (biodiesel and renewable diesel by hydrodeoxygenation) to products of engine combustion.

This article, which is partially based on a recent short publication [4], will address several issues related to a comparison of these fuels. These issues include terminology, history, fuel composition, production, properties, energy balance, environmental issues and others. Finally, a question that will be addressed is if these two kinds of fuels that can be derived from lipid materials compete with each other or do they complement each other?

## 2. Discussion

**Terminology.** A review of the literature shows that sometimes different terms are used to define the same kind of fuel derived from a triacylglycerol-containing feedstock and, conversely, that one term is sometimes applied to different types of fuels. Therefore, similar to the issue of nomenclature in chemistry, terminology is important in order to define the subjects of discussion and is briefly addressed here.

- *Petrodiesel.* First, the diesel fuel that is derived from petroleum needs to be defined as it is the material the other fuels are compared to. It can be termed “petrodiesel”. Although in almost all literature it is usually called “diesel” or “diesel fuel”, the use of the prefix “petro-” defines its origin in relation to the alternatives that now exist. Commonly applied petrodiesel standards are ASTM D975 [5] in the United States and EN 590 [6] in Europe.
- *Biodiesel.* The term “biodiesel” defines a “fuel comprised of mono-alkyl esters of long-chain fatty acids derived from vegetable oils or animal fats, designated “B100” as formulated in the biodiesel standard ASTM D6751 [7], with the European biodiesel standard EN 14214 [8] referring to fatty acid methyl esters (FAME) as fuel. This fuel is obtained from an oil or fat by a transesterification reaction with glycerol as co-product. It may be argued that, when produced with methanol as alcohol component, the carbon atoms in biodiesel are only approximately 95% “bio”. The reason is that methanol, although it can be obtained from renewable resources, is most commonly derived from non-renewable natural gas. In the case of ethyl esters, biodiesel is completely “bio” as ethanol is commonly derived from renewable resources such as corn and sugarcane. However, the prefix “bio” can be applied to the observation that biodiesel fuel is readily biodegradable. In any case, this definition of biodiesel is generally accepted internationally. More recently, the term “biodiesel” has sometimes been used in the compound phrase “second-generation biodiesel”, usually in conjunction with biodiesel derived from “alternative” feedstocks such as inedible oils or algae. However, this marketing-slogan-like term is misleading and should not be used as it implies that biodiesel derived from such feedstocks

may have superior fuel properties, which is not necessarily the case. For example, biodiesel derived from jatropha contains in the range of 20–25% C<sub>16</sub> and C<sub>18</sub> saturated fatty acid methyl esters and thus possesses poorer cold flow properties than biodiesel derived from soybean or rapeseed (canola) oil, which contain lower amounts of saturated esters. Virtually no literature reports exist on the fuel properties of algae-derived biodiesel” or “jatropha biodiesel” appear preferable. Furthermore, the phrase “second-generation biodiesel” has also been applied to petrodiesel-like fuels derived from biological feedstocks such as lipids and in this case it is even more misleading because the resulting fuel does not even meet the definition of biodiesel as mono-alkyl esters. It may be noted that the terms “first-generation” and “second-generation” biofuels (also applied to fuels other than biodiesel such as ethanol), although not or only ill-defined, have been used in a report by the Food and Agriculture Organization (FAO) of the United Nations [9] but apparently fuel properties were not taken into consideration in the preparation of this report. Furthermore, both biodiesel and renewable diesel are not new concepts as discussed briefly in the section on history and from that perspective also the “generation” terminology is misleading.

- *Renewable diesel.* Besides the aforementioned term “second-generation biodiesel”, the terms “green diesel” and “renewable diesel” have been used interchangeably for petrodiesel-like fuels derived from biological sources. The term “green diesel” is ambiguous because it implies that the resulting fuel itself is “greener” than petrodiesel. While the word “green” may apply to the origin of the fuel and the effect on greenhouse gases, this is not necessarily the case for issues such as biodegradability which is affected by the compositional emulsion of petrodiesel by this fuel. This, however, is not immediately clear. The term “renewable diesel” appears to only imply that the fuel is derived from a renewable resource without any allusions to the nature of the fuel. Therefore, it appears to be the most appropriate term for petrodiesel-like fuels derived from biological sources and will be used in this article. An issue for renewable diesel similar to the origin of methanol when producing methyl esters is the origin of hydrogen, which can be derived from both renewable and non-renewable sources. It may be noted that renewable diesel is also termed “HVO” (hydrotreated vegetable oil) in some technical literature.

**Historical perspectives.** The first documented use of a vegetable oil as fuel for a diesel engine occurred at the Paris World Exposition in 1900, when peanut oil was used to power one of the exhibited diesel engines. The background was the desire of the French government to provide its tropical colonies with an independent source of energy as stated in reports by the inventor of the diesel engine, Rudolf Diesel, himself [10]. Various kinds of petroleum and related materials derived therefrom were the first fuels tested by Rudolf Diesel as documented in his book *Die Entstehung des Dieselmotors* [11]. Numerous reports from the 1920s through the 1940s exist in the literature regarding the use of vegetable oils as diesel engine fuel, often with the theme of providing tropical colonies of European countries with an independent source of fuel [12]. The probably first documented use of a fuel (ethyl esters of palm oil) meeting the present definition of biodiesel is contained in a Belgian patent issued to Chavanne in 1937 [13] with later reports detailing this work [14,15]. The search for alternative sources of energy was then largely dormant until the energy crises of the 1970s and early 1980s sparked renewed interest in this issue. Among the alternative energy sources, vegetable oil-based fuels were reconsidered, with biodiesel in form of esters of sunflower oil to be reported in 1980 [16,17].

Work on the production of hydrocarbon fuels, mainly by a process at that time already termed “cracking”, precedes the aforementioned first documentation of biodiesel. This cracking procedure generally yielded a variety of products including gasoline- and petrodiesel-like fuels. For example, several papers are concerned with the cracking of cottonseed, fish and palm oils [18,19]. The decomposition of cottonseed oil at high temperatures in the presence of hydrogen was described [20]. Other papers published between 1921 and 1927 describe the formation of hydrocarbon fuels in the presence of various catalyst-type materials and from the distillation of fatty acid soaps [21–27]. Work on cracking of various vegetable oils was performed in China in the 1930s [28], with China regarding such fuels as emergency replacements for petroleum-derived fuels during World War II [29,30].

**Fuel composition and properties. Biodiesel.** As mentioned above, biodiesel is defined as the alkyl esters of vegetable oils or animal fats. The fatty acid profile of biodiesel corresponds to that of the parent oil or fat it is obtained from. The major components of biodiesel fuels are straight-chain fatty acids, the most common ones containing 16 and 18 carbon atoms. However, some feedstocks contain significant amounts of fatty acids other than the typical C16 and C18 acids. Such feedstocks include tropical oils (for example, coconut oil) enriched in shorter-chain acids such as lauric acid. Table 1 contains fuel property data [31–38] of some fatty acid methyl esters, also in comparison to alkane components of petrodiesel. Table 2 contains related data from standards. Besides the major fatty ester components, minor constituents of biodiesel include intermediary mono- and diacylglycerols and residual triacylglycerols resulting from the transesterification reaction, residual glycerol and methanol, free fatty acids, sterols as carry-overs from the vegetable oil feedstock as well as sterol glucosides. Glycerol, acylglycerols, free fatty acids and methanol are accordingly limited in biodiesel standards such as ASTM (American Society for Testing and Materials) standard D6751 and the European standard EN 14214 as well as other standards under development around the world.

The composition of a fuel has significant influence on its properties. The cetane number of fatty esters depends on chain length and degree of unsaturation. The presence of polyunsaturated fatty esters is the cause of oxidative stability problems with biodiesel and the presence of higher amounts of saturated fatty esters is the cause of cold flow problems. This is exemplified by methyl stearate possessing a melting of approximately 38 °C and an oxidative

**Table 2**Specifications from standards [5–8] related to data in Table 1.<sup>a</sup>

Specification	Petrodiesel	Biodiesel
Cetane number	40 min [5] 51 min [6] <sup>a</sup>	47 min [7] 51 min [8]
Kinematic viscosity (40 °C; mm <sup>2</sup> /s)	1.9–4.1 [5] 2.0–4.5 [6] <sup>a</sup>	1.9–6.0 [7] 3.5–5.0 [8]
Oxidative stability (h)	–	3 min [7] 6 min [8]
Flash point (°C)	38 min/52 min [5] >55 [6]	93 min; 130 min for alcohol control [7] 120 min [8]
<i>Low-temperature operability:</i>		
Cloud point	Agreement [5] <sup>b</sup> For [6] see footnote c	Report [7]
CFPP <sup>d</sup>	Agreement [5] <sup>b</sup> For [6] see footnote c	Not specified [7] For [8] see footnote c
Cold soak filtration (s)	–	360 max [7]

<sup>a</sup> Lower values for locations with severe or arctic winter conditions.<sup>b</sup> Low-temperature properties to be agreed upon by purchaser and supplier of fuel due to varying ambient conditions.<sup>c</sup> Depends on location and time of year. For low-temperature testing, both ASTM petrodiesel standards [5,7] refer to the cloud point for low-temperature testing. The ASTM biodiesel standard [7] also prescribes a cold soak filtration test (360 s max).<sup>d</sup> CFPP = cold filter plugging point. LFTF = low-temperature filterability test also in [5].

stability of >24 h as per the test EN 14112 [39] prescribed in the biodiesel standards ASTM D6751 and EN 14214 and methyl linoleate exhibiting a melting point of –43 °C and oxidative stability of 0.94 h as per the test in EN 14112 (Table 1). Thus a tradeoff exists when attempting to solve one of these problems by enriching the fatty ester composition of one kind of fatty ester.

For low-temperature applications of biodiesel the cloud point (CP) is a decisive parameter [40]. It is the temperature at which the first visible crystals form upon cooling a fuel and at which therefore problems such as fuel filter plugging could result. For biodiesel derived from soybean oil the CP is around 0 °C and for biodiesel derived from rapeseed (canola) oil it is only slightly lower. Biodiesel fuels derived from palm oil or animal exhibit significantly higher CP, around 15 °C, due to their content of saturated fatty esters. It may be noted that in connection with low-temperature properties, often the pour point (PP) is reported. The PP is the temperature at which the fuel can no longer be poured freely. Another test related to cold flow properties is the cold filter plugging point (CFPP) which is a filterability test and linearly related to the CP [40].

**Table 1**

Properties of major components of biodiesel and renewable diesel/petrodiesel.

Renewable diesel/petrodiesel				Biodiesel				
Compound	Cetane number	Kinematic viscosity <sup>b</sup> (40 °C; mm <sup>2</sup> /s)	M.P. <sup>c</sup> (°C)	Compound	Cetane number	Kinematic viscosity <sup>b</sup> (40 °C; mm <sup>2</sup> /s)	M.P. <sup>d</sup> (°C)	Oxidative stability <sup>e</sup> (h)
Decane		0.97	–29.6	Methyl decanoate	51.6	1.71	–13.48	>24
Undecane		1.20	–25.5	Methyl laurate	66.7	2.43	4.30	>24
Dodecane	80 [31]	1.46	–9.57	Methyl myristate		3.30	18.09	
Tetradecane		2.09	5.82	Methyl palmitate	85.9 [35]	4.38	28.48	>24
Pentadecane		2.46	9.95	Methyl stearate	101 [35]	5.85	37.66	>24
Hexadecane	100 <sup>a</sup>	2.93	18.12	Methyl oleate	59.3 [35] 55.0 [34]	4.51	–20.21	2.79
Heptadecane		–	22.0	Methyl linoleate	38.2 [35] 42.2 [34]	3.65	–43.09	0.94
Octadecane		–	28.2	Methyl linolenate	22.7 [34]	3.14	–55	0.00
				Methyl erucate	74.2 [36]	7.33	–3.05	

<sup>a</sup> By definition.<sup>b</sup> All kinematic viscosity data from Ref. [32].<sup>c</sup> Data in this column from Ref. [33].<sup>d</sup> Data in this column from Ref. [37].<sup>e</sup> Data in this column from Ref. [38]. Data obtained by EN 14112 (Rancimat) test.

The enhancement of biodiesel fuel properties by modifying/optimizing fatty ester composition is an issue of nascent and ongoing research [41,42]. Esters of palmitoleic acid may be suitable for enrichment in biodiesel due to their low melting point (m.p. of methyl palmitoleate around  $-34\text{ }^{\circ}\text{C}$ ) [37]. Enrichment of saturated esters, especially esters of decanoic acid, may also lead to property improvement. For example, methyl esters of cuphea oil with approximately 65% decanoic acid in the fatty acid profile, display a cloud point around  $-9$  to  $-10\text{ }^{\circ}\text{C}$  [43].

The presence of the ester moiety causes biodiesel to possess inherent lubricity [44,45]. However, minor constituents (impurities) in biodiesel such as free fatty acids and monoacylglycerols contribute largely to the lubricity of low level blends biodiesel with low-lubricity petrodiesel (1–2% biodiesel in petrodiesel) [44,45].

Generally, biodiesel also possesses a higher flash point than petrodiesel. The flash point specification is also lower in petrodiesel standards than in biodiesel standards (Table 2). This is largely a reflection of the boiling points of the individual components. For example, the boiling point of methyl palmitate is  $417\text{ }^{\circ}\text{C}$  and that of methyl decanoate  $224\text{ }^{\circ}\text{C}$ , while that of hexadecane is  $287\text{ }^{\circ}\text{C}$  and that of decane =  $174\text{ }^{\circ}\text{C}$  [33]. In the case of petrodiesel, the branched and lower molecular weight components, which possess lower boiling points, lead to a reduction of the flash point. However, the alcohol used for biodiesel production and remaining in small amounts in the finished product influences the flash point. The environmental issues of biodegradability and influence on exhaust emissions are discussed later in this article.

*Fuel composition and properties. Petrodiesel and renewable diesel.* Petrodiesel is a very complex mixture, with the “ideal” components being straight-chain alkanes (Table 1). Indeed, hexadecane (trivial name “cetane”) is the high-quality reference compound on the cetane scale, a concept similar to the octane number used for gasoline, and which is related to the ignition quality of a diesel fuel. Besides such alkanes, branched alkanes and aromatic compounds (with one or more aromatic rings) with alkyl side chains are common constituents of petrodiesel. Branched compounds, however, exhibit lower cetane numbers as exemplified by highly branched 2,2,4,4,6,8,8-heptamethylnonane being the low-quality reference compound on the cetane scale but possess lower melting points. Alkylaromatics and alkylcycloalkanes also possess low melting points and lower cetane numbers which increase with increasing side chain length [31,46]. The sulfur-containing compounds that are removed from petrodiesel in the now common ultra-low sulfur diesel (ULSD) fuels are dibenzothiophenes with alkyl (usually methyl) substituents. The hydrodesulfurization process that yields ULSD fuels also removes minor oxygen- and nitrogen-containing compounds, which had been responsible for the lubricity of petrodiesel [47]. Thus ULSD fuels possess poor lubricity. Adding biodiesel at levels of 2% or above restores the lubricity, although lubricity additives (which in some cases may be also based on lipid feedstocks) can also achieve lubricity improvement. Renewable diesel fuels simulate petrodiesel, the goal being especially to enrich these fuels in long-chain alkanes, which, as mentioned above, are “ideal” components of petrodiesel. If renewable diesel consists mainly of long-chain alkanes, then this fuel will have a high cetane number (Table 1), however, if it contains large amounts of shorter-chain and isomerized species, the cetane number will be lower. The cetane number of renewable diesel has been stated to be high ( $>70$ ) [48–52]. For improved low-temperature properties, long-chain alkanes are less desirable and shorter-chain and isomerized compounds are desirable. The cloud point of a renewable diesel investigated for exhaust emissions testing was given as  $7\text{ }^{\circ}\text{C}$  [51] but has been usually stated to be between  $-5$  and  $-25$  or  $-30\text{ }^{\circ}\text{C}$  [48–52] with the exact value depending on the “severity” of the production process or

“additional catalytic processing” [49–51]. It appears likely that renewable diesel with better cold flow properties would exhibit lower CN as the smaller (and/or branched) molecules necessary for improved cold flow have lower CN. No report seems to be available yet on renewable diesel being tested according to the petrodiesel standards ASTM D975 or EN 590 or jet fuel specifications such as ASTM D1655 [53].

*Fuel production.* Both biodiesel and renewable diesel require a co-reagent and catalysts to obtain the desired product from the feedstock. In case of biodiesel, the co-reagent is an alcohol (most commonly methanol to give the methyl esters) and in case of renewable diesel it is hydrogen in order to saturate double bonds and replace oxygen. In the case of biodiesel, the catalyst is most commonly sodium alkylate (methylate in case of methanol) or sodium or potassium hydroxide (alkylates are preferable to hydroxides) and in the case of renewable diesel various catalysts depending on the exact nature or desired products in case of renewable diesel. However, the process termed hydrodeoxygenation has probably found the most attention for renewable diesel.

*Fuel production. Biodiesel.* Biodiesel is produced from the triacylglycerol-containing material by means of a transesterification reaction. Typical conditions when using methanol are a molar ratio alcohol:vegetable oil of 6:1,  $60\text{--}65\text{ }^{\circ}\text{C}$ , 1 h, and ambient pressure in the presence of hydroxide or, more effectively, alkoxide catalyst [54]. An alkoxide catalyst is more effective than hydroxide because water according to the reaction  $\text{ROH} + \text{XOH} \rightarrow \text{H}_2\text{O} + \text{ROX}$  ( $\text{R} = \text{alkyl}$ ,  $\text{X} = \text{Na}$  or  $\text{K}$ ) cannot be formed. The presence of water can cause incomplete reaction, leaving, for example, monoacylglycerols in the mixture, and promotes the formation of free fatty acids. Therefore, the feedstock should also be as free of water and free fatty acids as possible [54]. Thus, a refined vegetable oil is advantageous for biodiesel production compared to a crude vegetable oil. Besides these “classical” conditions, numerous variations of the transesterification reaction exist, including application of enzymatic and heterogeneous catalysts [55–77]. Enzymatic catalysis offers the benefits of reduced or eliminated pretreatment of lower-quality or high free fatty acid feedstocks, versatility regarding the alcohol used and higher quality glycerol but is more expensive and exhibits lower reaction rates. Overall, the “classical” conditions indicated above are still largely applied as this process is relatively mild, rapid and high-yielding. If a lower-quality feedstock with high acid value, for example used frying oil, serves as feedstock, an acid pre-treatment may be required before carrying out the base-catalyzed transesterification reaction [78]. The procedure used for industrial production of biodiesel is very similar to that used on a laboratory scale.

*Fuel production. Renewable diesel.* The synthesis of renewable diesel on a laboratory scale has been described in numerous publications. While some papers discuss concerned with the technical-scale production of renewable diesel [48,49,79–81], no details on the nature of the process or the catalysts are offered, likely for proprietary reasons, except for commentaries such as a reference to using “conventional hydrotreating catalysts” [79]. The stated lower cost of this processing vs. transesterification [79] is thus difficult to substantiate. In any case, it appears likely that catalyst systems and conditions resembling those on a laboratory scale as discussed below are applied.

Several catalyst systems can be applied to obtain petrodiesel-like fuels from triacylglycerol feedstocks. Cracking or pyrolysis is often promoted by zeolite catalysts, a process probably first reported in 1979 [82], while hydrotreating (hydrodeoxygenation) is accomplished with catalysts such as  $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$  or  $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ . Cracking will generally lead to shorter-chain hydrocarbon products while hydrodeoxygenation will generally lead to



saturated longer-chain alkanes from which the ester moiety has been removed (for example, formation of C<sub>17</sub> compounds such as heptadecane from C<sub>18</sub> fatty esters). Cracking or pyrolysis is accomplished at elevated temperatures (300–400 °C) at normal pressure without the presence of hydrogen. Hydrodeoxygenation requires both elevated temperatures and elevated pressure as well as the presence of hydrogen.

Cracking or pyrolysis (atmospheric pressure, elevated temperatures in the range of 350–400 °C) [3,83] usually leads to the production of gasoline and diesel-like fuels from one reaction. It was discussed as one of four solutions (besides pyrolysis and transesterification, these are blending with petrodiesel and use of microemulsions; note that renewable diesel may now be considered a fifth solution) to the viscosity problem of lipid feedstocks [84]. The classes of compounds obtained from catalytic cracking and pyrolysis are linear and cyclic alkanes, alkenes, aldehydes, ketones and carboxylic acids [3,84]. Catalysts usually have been zeolites such as HZSM,  $\beta$ -zeolite and USY [3]. Base catalysts such as Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were reported to reduce the amounts of carboxylic acids and aldehydes formed during pyrolysis, thus reducing corrosiveness and improving cold flow [85]. Kinetic modeling of the cracking of used palm oil and palm oil fatty acids was reported [86]. With the multitude of products formed, better understanding of the reaction is necessary [3]. Depending on the reaction conditions, product fuels more in the diesel or gasoline range can be obtained [83]. Recently, an ASTM standard (D7544) for pyrolysis oils was issued [87]. Overall, cracking and pyrolysis currently does not appear to be the most promising approach to obtain high yields of a product suitable as diesel fuel.

Hydrodeoxygenation is a process by which a feedstock that contains double bonds and oxygen moieties is converted to hydrocarbons by saturation of the double bonds and removal of oxygen (decarboxylation, decarbonylation, dehydration). Thus the reaction requires hydrogen. Decarboxylation of unactivated carboxylic acids, although exothermic, requires high transition state energies [88], which is reflected in reaction conditions such as elevated temperature and pressure. The types of catalysts most commonly discussed in the literature are NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (for example, see [89–101]) but catalysts with differing metals and/or supports such as CoMo/C [93,102,103], CoMo/Si [93] Rh/Al<sub>2</sub>O<sub>3</sub> [104,105], Pd/SiO<sub>2</sub> [88], reduced Ni/SiO<sub>2</sub> [89], Pd/C [106–108], Pt/C [104] and others have also been used. The NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts refer to metal oxides (NiO, MoO<sub>3</sub>, etc.) supported on alumina. The catalysts have been typically sulfided with elemental sulfur or H<sub>2</sub>S (H<sub>2</sub>S/H<sub>2</sub>) as this increases the activity of the catalysts, forming metal sulfides [94]. Partial pressure of H<sub>2</sub>S during the reaction can preserve the catalytic sites [103]. In more recent reports, dimethyl disulfide (DMDS) has been applied in reactions using rapeseed, cottonseed and raw sunflower oils as feedstocks [99–101].

Water formed during hydrotreating itself may decrease activity in the reaction [3,95], although the effect was stated to be weak [92]. Reaction metallurgy makes it difficult to process vegetable oils with high acidity in standard hydrotreating reactors [3]. Therefore, it appears that some of the same quality constraints that affect the production of biodiesel by transesterification also influence the production of renewable diesel by hydrodeoxygenation.

Catalysts can possess different activities depending on the structure of the feedstock [97]. NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a higher decarboxylation activity than CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [91] with hydrogenation of carboxylic groups requiring temperatures around 300 °C [91]. Carboxylic acids and esters react at similar rates with similar reactivity [91]. Alumina-supported catalysts exhibited higher rates of decarboxylation and deesterification compared to carbon and silica, although the overall effect is complex [91]. The acidity of the

support influences the formation of active sites for decarboxylation and hydrogenation of carboxyl groups [93].

Ammonia depresses the activity of NiMo and CoMo catalysts for the conversion of carboxylic and methoxy groups, but not ketones [92]. Hydrogen sulfide depresses the activity on NiMo but not CoMo in the case of ketones. However, H<sub>2</sub>S enhances the conversion of ester groups [92,95] and is more effective than CS<sub>2</sub> [109]. Therefore, NH<sub>3</sub> and H<sub>2</sub>S can be used to control hydrotreating.

The reaction conditions and the composition of the feedstock can be used to control the nature of the product. More unsaturated feedstocks led to greater formation of cycloalkanes and alkylbenzenes with only comparatively small amounts of shorter-chain alkanes [90]. More saturated feedstocks led to alkanes with the one less or the same number of carbons than in the original fatty acid chains [90].

The hydrodeoxygenation of vegetable oils produces alkanes with one carbon atom less than the fatty acid chains, although the exact nature of the product mix depends on reaction conditions. Thus, a vegetable oil consisting of the typical C<sub>16</sub> and C<sub>18</sub> fatty acids would yield C<sub>15</sub> and C<sub>17</sub> alkanes. The straight-chain alkanes can undergo isomerization and cracking for production of fuels more suitable for aviation purposes [3]. The yield of straight-chain alkanes decreases at temperatures >350 °C [3,98]. At higher temperatures, the alkanes undergo cracking and isomerization [3,98]. The presence of heavy vacuum oil (from petroleum) can increase the yield of straight-chain alkanes as was demonstrated for mixtures of 5% sunflower oil with 95% HVO with other reaction conditions of 300–450 °C at 50 atm [98].

It has been implied [98] that an advantage of renewable diesel vs. biodiesel is that for renewable diesel no dedicated production facility is required as the feedstock can be processed in the petrochemical production stream. On the other hand, another report states [81] that it is more cost-effective to construct a dedicated unit for processing of vegetable oils. The hydrodeoxygenation apparently competes with the hydrodesulfurization applied to obtain ultra-low sulfur petrodiesel [81].

*Methanol vs. hydrogen.* The issue of amounts of methanol vs. hydrogen used for producing biodiesel resp. renewable diesel is affected by the nature of the feedstock. For biodiesel, the average molecular weight of the feedstock plays a role in order to maintain the 6:1 molar ratio of alcohol/vegetable oil. For renewable diesel, the fatty acid profile plays a role since the level of saturation of the fatty acid chains can influence the amount of hydrogen consumed. Thus, highly saturated feedstocks such as palm oil and animal fats appear to offer advantages in terms of reduced hydrogen requirements and thus reduced production costs as the expenses for hydrogen may be significant, especially when longer hydrocarbon chains in the product are acceptable. This aspect may play a role in reports that a commercial producer of renewable diesel is using palm oil and animal fats as feedstock [110,111]. This may be different when products with good low-temperature properties are desired, for example, in aviation fuels. For example, a renewable diesel blended with aviation fuel was largely (84%) obtained from camelina oil as feedstock [112]. Camelina oil contains a relatively high amount of unsaturated fatty acid chains (27–40% C18:3) [113], thus offering more cleavage sites to produce hydrocarbons as they are necessary for the low-temperature requirements of aviation fuels. Some oils from algae may also contain high amounts of unsaturated chains [114] and fuel derived from this feedstock has also been reported for use in aviation [115]. Linseed oil (around 47% C18:3 [110]) may therefore also be suitable.

On the other hand, biodiesel is usually the methyl esters of vegetable oils or animal fats, thus methanol is used for biodiesel production. Although methanol can be obtained from renewable resources, it is usually derived from natural gas, a non-renewable

resource. Thus, as mentioned above, for fatty acids containing 16 or 18 carbons, the carbons in biodiesel are approximately 95% derived from a renewable resource, the oil or fat. This is different for biodiesel derived from ethanol. Relatedly, the hydrogen used in the hydrotreating process, although also obtainable from renewable resources, is usually not obtained from a renewable resource, namely from natural gas by steam reforming.

**Energy balance.** For fuels derived from vegetable oils or other lipid feedstocks, it can be assumed that the energy input is largely identical until the point of fuel production. An issue affecting this, however, is the quality of the feedstock needed for fuel production as refining of vegetable oils. The base-catalyzed transesterification for producing biodiesel is best carried out with refined vegetable oils. However, the production of renewable diesel is also somewhat sensitive to this issue as mentioned above, although it may not play a significant role if the lipid feedstock is treated at low levels together with petroleum. Overall, any significant differences in the energy balance of biodiesel and renewable diesel appear to arise from the production process and the energy content of the product.

The issue of the energy balance is affected by the energy necessary for producing the alcohol and hydrogen as well as the catalysts necessary for the production process. It is further complicated by the fact that alcohol and hydrogen amounts can depend on the feedstock (as shown by the fatty acid profile) and as discussed above in the sections on production. In the case of biodiesel esters other than methyl can be produced, altering the energy balance as the production of each alcohol has its own energy requirements. In the case of renewable diesel the amount of hydrogen used can depend on the eventual use of the desired product, which influences its composition and production. For example, if renewable diesel is to undergo further cracking and isomerization to aviation fuel, this may influence the energy balance.

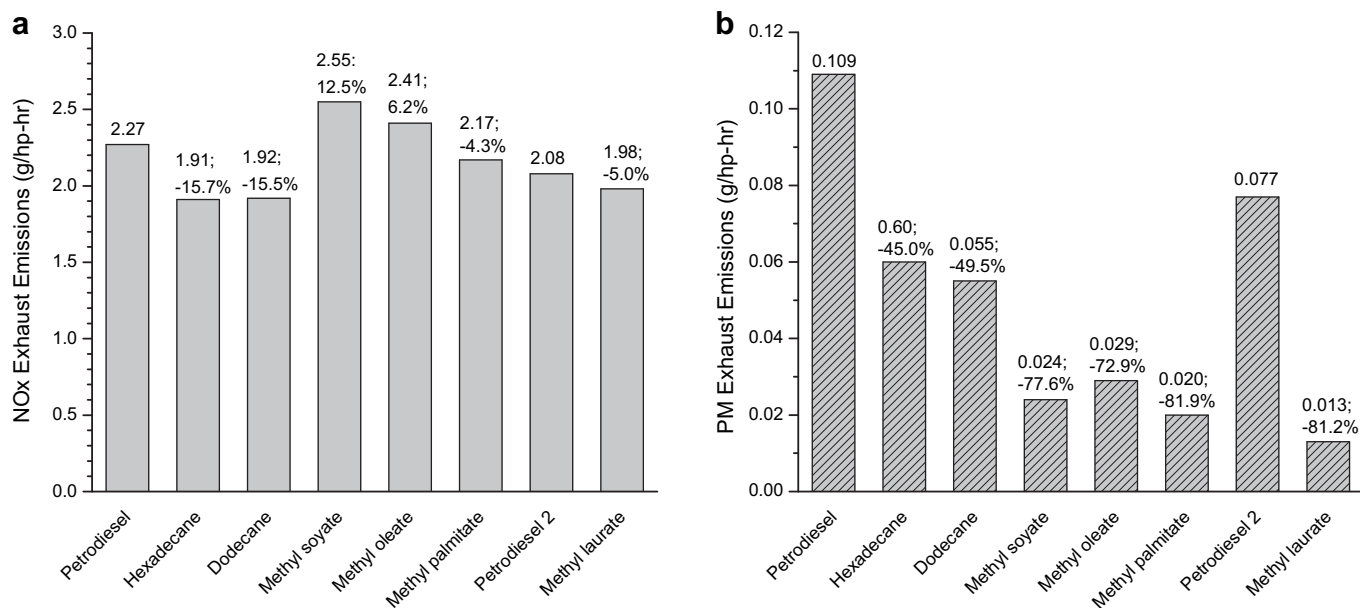
Most recently, the energy balance for biodiesel has been assessed to be about 4.5:1, an increase from previous studies [116]. To this author's knowledge, no information on the energy balance of renewable diesel is currently available. It has been stated in a life-cycle analysis of renewable diesel vs. biodiesel that the fossil energy consumption for renewable diesel is lower than for biodiesel [82] but no details on how this conclusion is reached are presented. However, the more severe reaction conditions for producing renewable diesel discussed above raise the possibility that it is less favorable. The greater amount of energy required for producing renewable diesel is reflected in the greater heat of combustion of renewable diesel, i.e., in the storage of energy in the fuel necessary for producing it. For example, the heat of combustion as calculated from the enthalpy of formation (higher heating value) of hexadecane is 47,247 kJ/kg whereas that of methyl palmitate is 39,449 kJ/kg [38]. Another issue to consider is that glycerol is formed "free" when producing biodiesel, not requiring a multi-step, energy-intensive process using propene as starting material.

Mass balance also affects the energy balance. To illustrate this, a hypothetical case of conversion of triolein to methyl oleate by transesterification or to heptadecane by hydrodeoxygenation can be used (similar calculations can be performed for other materials with similar results). The synthesis of methyl oleate (molecular weight 296.485) utilizes both the original fatty acid chain and the alcohol, formally leading to retention of the carbon "lost" by cleavage of glycerol. In hydrodeoxygenation, the synthesis of heptadecane (molecular weight 240.475) requires hydrogen to saturate the double bond but with loss of a carbon from the original fatty acid chain through decarboxylation and without retention of the "glycerol" carbon. Thus, on a weight basis, hydrodeoxygenation yields approximately only 81% of the yield from biodiesel production, which, when taking density (approximately 0.875 g/cm<sup>3</sup> for methyl oleate, 0.77 g/cm<sup>3</sup> for heptadecane) into account (giving volume

basis), increases to approximately 92%. This observation also relates to the energy content (kJ/kg) as discussed above. For 1 kg, 3.372 mol of methyl oleate equal are required and 4.158 mol of heptadecane, leading again to a mass balance 81% of heptadecane compared to methyl oleate. As a result, correspondingly more feedstock is required to produce heptadecane from triolein than methyl oleate. The higher energy content of alkanes in renewable diesel vs. methyl esters in biodiesel of approximately 15–20% (weight basis) is thus offset by the greater amount of feedstock required to "achieve" this higher energy content.

**Environmental issues. Combustion and emissions.** One of the prime issues when operating a diesel engine on a fuel is that of exhaust emissions. It is well-known that operating a diesel engine on biodiesel leads to increased NO<sub>x</sub> exhaust emissions of about 10% compared to petrodiesel. However, the three other kinds of regulated exhaust emissions, particulate matter (PM), hydrocarbons (HC) and carbon monoxide are significantly reduced by the use of biodiesel. Furthermore, new exhaust emissions control technologies such as various catalysts or selective catalytic reduction (SCR) used in conjunction with newer engines likely cause the NO<sub>x</sub> and PM exhaust emissions of any bio- or petrodiesel fuel to meet regulatory standards so that the differences discussed here will likely continuously decrease and lose significance with time. Previous literature discusses work conducted through the late 1990s regarding the effect of biodiesel on exhaust emissions [117], a report summarizing the results of numerous exhaust emissions tests conducted through about 2002 can be found on the website of the U.S. Environmental Protection Agency report no. 420-P-02-001 [118] and a newer summary is also available [119].

It is of interest to assess the effect of individual components of biodiesel and renewable diesel on regulated exhaust emissions, which are nitrogen oxides (NO<sub>x</sub>), particulate matter (PM), hydrocarbons (HC) and carbon monoxide. In this connection, it is of interest to assess the effect of neat components on exhaust emissions. Work conducted with a 2003 model year engine (14 L, six-cylinder, turbocharged, intercooled, exhaust gas recycling) showed that biodiesel and its components lowered PM more than neat alkanes such as hexadecane or dodecane, with PM reduced about 73–83% by biodiesel and its components vs. a petrodiesel fuel while the neat alkanes achieved reductions around 45–50% [120]. NO<sub>x</sub> exhaust emissions were increased by 12.5% using methyl soyate, about 6% with technical grade oleate and slightly reduced (4–5%) with the saturated esters methyl palmitate and methyl laurate. Hexadecane and dodecane reduced NO<sub>x</sub> by 15–16% vs. the petrodiesel fuel. These results are depicted in more detail in Fig. 2. Results for HC were strongly chain-length dependent, with alkanes performing better than biodiesel or its components (hexadecane –62.1%, dodecane –1.6%, methyl soyate –44.4%, methyl oleate –54.6%, methyl palmitate –29.2%, methyl laurate +13.2% vs. petrodiesel reference fuel) [120]. On the other hand, regarding CO exhaust emissions were decreased more strongly by biodiesel and its components than by alkanes (hexadecane –27.7%, dodecane –15.0%, me soyate –25.0%, me oleate –49.0%, me palmitate –43.1%, me laurate –28.8% vs. petrodiesel) [120]. Thus, biodiesel performs significantly better than renewable diesel in terms of PM and CO exhaust emissions, with renewable diesel having an advantage in terms of NO<sub>x</sub> exhaust emissions and apparently a slighter advantage for HC exhaust emissions. The effect of compound structure such as double bond and chain length on exhaust emissions of biodiesel was also investigated by other researchers with similar results [121,122]. In emission tests comparing renewable diesel with other fuels [50–52] using a petrodiesel fuel meeting the European petrodiesel standard EN 590 [6], it was shown that renewable possesses benefits in terms of all regulated exhaust emissions. It was reported that NO<sub>x</sub> exhaust emissions are 7–14%



**Fig. 2.** a) NO<sub>x</sub> exhaust emissions of petrodiesel, biodiesel and some neat components thereof. Data from Ref. [114]. The inscribed numbers show the level of these exhaust emission species and the numbers in parentheses indicate fuel consumption changes for the other fuels relative to petrodiesel. Petrodiesel 2 refers to a second test of the petrodiesel reference fuel relating only to methyl laurate due to a new turbocharger on the test engine [114]. b) Particulate matter exhaust emissions of petrodiesel, biodiesel and some neat components. Data from Ref. [114]. The inscribed numbers show the level of these exhaust emission species and the numbers in parentheses indicate fuel consumption changes for the other fuels relative to petrodiesel. For an explanation of “Petrodiesel 2”, see caption for Fig. 2a.

with renewable diesel compared to the EN 590 reference fuel, PM 28–46% reduced, CO 5–78% and HC 0–48% [50,51]. The mutagenicity of exhaust emissions of both biodiesel and renewable diesel has also been investigated [52,123–127]. Generally, biodiesel has been reported to have benefits in early studies [123,124]. More recently, renewable diesel has also been reported to have beneficial effects [52] and petrodiesel meeting the EN 590 requirements had effects similar to biodiesel [125–127]. The number of particles is reduced with biodiesel, also in comparison to petrodiesel and renewable diesel [52].

**Environmental issues. Biodegradability and sulfur.** Biodegradability studies of biodiesel vs. petrodiesel have shown that generally biodiesel decomposes more readily when exposed to the relevant conditions and micro-organisms, which includes the effect of higher amounts of biodiesel in blends with petrodiesel promoting biodegradation [128–132]. However, *n*-alkanes decomposed at approximately the same rate as fatty acid methyl esters [133]. This implies that branched alkanes and other hydrocarbons do not biodegrade as readily as biodiesel and *n*-alkanes. It may be noted that no comparative studies of the biodegradability of biodiesel vs. renewable diesel have been performed yet but it appears reasonable to assume that renewable diesel will perform very similar to petrodiesel in this respect considering their compositional similarities but with some dependence on fuel composition. Renewable diesel consisting largely of *n*-alkanes may have benefits in terms of biodegradability compared to petrodiesel or renewable diesel containing significant amounts of non-straight-chain hydrocarbons.

Most biodiesel fuels have low sulfur content, meeting specification in biodiesel standards (0.05 mass% in ASTM D6751), as most feedstocks contain only small amounts. Sulfur in biodiesel could arise in case of rapeseed (glucosinolates) or faunal feedstocks due to contact with meat or bone. However, in most cases this does seem to be an issue. Similarly, renewable diesel also appears to be low in sulfur content.

**Plant cultivation.** Another issue which affects biodiesel and renewable diesel in the same manner is environmental impact in terms of plant cultivation. For example, in connection with palm

oil-derived biodiesel the issue of deforestation of tropical rain forests for the sake of extending palm production has raised concerns for biodiesel. The resulting palm oil was reportedly to be largely used for biodiesel production. Thus, it was stated that biodiesel from palm oil may have a negative carbon footprint. The same observation holds, of course, for renewable diesel derived from palm oil, therefore biodiesel and renewable diesel do not differ in this respect. Issues raised for other vegetable oils, such as use of fertilizer, would also apply to biodiesel and renewable diesel in similar fashions.

**Food vs. fuel issue.** Similar to plant cultivation, this issue affects biodiesel and renewable diesel in the same manner. The only aspect may be which fuel would be produced in greater amounts from edible oils. The fuel with the greater production would likely have the greater impact in form of increasing vegetable oil prices.

**Economics.** It can be assumed that the economics of biodiesel vs. renewable diesel are largely identical to the point of production as both processes can utilize the same feedstock. As is well-known for biodiesel, the higher cost of lipid feedstock vs. petroleum, translating into higher fuel costs, has been a major impediment to biodiesel commercialization. This aspect obviously also holds for renewable diesel. However, a full economic comparison of biodiesel vs. renewable diesel is rendered difficult because of the current lack of hard data concerning especially the production of renewable diesel. Differences in the economics can therefore be largely attributed to the production process and post-production distribution.

Some of the factors affecting production and thus cost are feedstock quality and its potential impact on process conditions, the fatty acid profile of the feedstock, and, for renewable diesel, the conditions of the process needed to obtain a product with the desired cold flow properties. Another aspect is the commingling of lipid feedstock and petroleum feedstock. In this case it is not clear, again as no data are available, if this may affect the economics of the process because it is not unreasonable to surmise that changes to the production process may be necessary. On the other hand, commingling simplifies post-production distribution of the

renewable portion of the resulting fuel as it does not require any separate handling.

Another issue affecting the overall economics is that of the co-products, glycerol (discussed below) in the case of biodiesel and propane in the case of renewable diesel. The excess of glycerol from increasing biodiesel production has affected the glycerol market, leading to efforts to find new and/or improved uses of this material. Glycerol is a more versatile commodity than propane as it can be used in the manufacture of a variety of products (see discussion below), potentially affecting other markets and an aspect that may affect overall economics of biodiesel and thus of biodiesel vs. renewable diesel.

**Glycerol.** The production of biodiesel is accompanied by the formation of glycerol. Glycerol obtained from biodiesel production does not require any further processing except purification. In times (late 1980s to early 1990s) before the increased production of biodiesel, approximately 25% [134] to 30% [135] of glycerol had been produced from propene, largely via the petrochemical route propene → allylchloride → epichlorohydrin (1-chloro-2,3-epoxypropane) → (hydrolysis to) glycerol. Compared to the transesterification reaction, the multi-step process using the petrochemical route is obviously more complex, energy-consuming and requires a dedicated production facility.

The increased supply of glycerol from biodiesel production has led to significant changes to the glycerol market, including closure of facilities producing glycerol from petroleum. Therefore, the use of triacylglycerol feedstocks for renewable diesel production has occasionally been advertised under the aspect of avoiding this problem. However, in the case that should renewable diesel be the major fuel derived from lipid materials, the supply of glycerol from these feedstocks would dwindle or become non-existent in the extreme case. Thus dedicated production facilities for glycerol from petroleum may become necessary again, perhaps by re-opening closed facilities, making the source of glycerol less “green”. The tradeoff therefore appears to be excess, lower-priced glycerol from a renewable feedstock vs. less, higher-priced glycerol from petroleum.

Classical applications of glycerol have been in personal care products (soaps, cosmetics, hair care, toothpaste), pharmaceuticals, sweetener in candies and cakes [134–136]. It appears unlikely that additional glycerol due to biodiesel production would find application in these areas [136]. Therefore, additional applications must be explored. These applications include glycerol esters, glycerol ethers, acetals and ketals, epoxides, aldehydes, ketones, oxidation and dehydration products, as well as 1,2- and 1,3-propanediol [136–138]. In some cases, using glycerol would simplify the process of obtaining useful chemicals such as the diols and epichlorohydrin, in the latter case reversing the petrochemical process and possessing several technical advantages in comparison [131].

### 3. Conclusions and outlook

As the above discussion shows, the issue of biodiesel and renewable diesel is complex. Both biodiesel and renewable diesel possess advantages in terms of carbon renewability compared to petrodiesel but there are advantages and disadvantages to either in terms of fuel properties, environmental issues and energy balance. There is only a limited amount of feedstock available to satisfy potential demand for both fuels. Despite all efforts to develop additional feedstocks, this will likely remain an issue in the future. Therefore, a significant question appears to be if biodiesel and renewable diesel compete with or complement each other. Either fuel can only replace a few percent of the petrodiesel market. A possible aspect is if the use of these fuels should be concentrated in areas where the most benefit is derived from either. In case of

biodiesel, this would be taking advantage of environmental benefits and in case of renewable diesel this would be taking advantage of improved cold flow properties mainly for aviation purposes, provided the renewable diesel is of the kind largely composed of smaller and isomerized molecules.

Renewable diesel has been promoted under the aspect of being a “premium” diesel fuel with, for example, a very high cetane number (which would be a result of the high content of longer-chain alkanes, thus depending on the composition and intended use). A question that arises in this connection is if this premium diesel fuel should be blended with conventional petrodiesel. Blending with conventional petrodiesel would cause the advertised properties to be “lost” as there would be only a marginal improvement of the properties of petrodiesel as a result of the relatively small amounts of the “premium” renewable diesel fuel being available. The other alternative would be to use renewable diesel neat. There appears to be some environmental benefits to renewable diesel vs. petrodiesel, which would be “lost” when blending but would be more available in the neat form. However, the environmental benefits of renewable diesel appear to be less compared to biodiesel. Blending petrodiesel (as ULSD) with biodiesel offers the benefit of restoring lubricity to petrodiesel, although lubricity additives, which may also be lipid-based, can also restore lubricity. A question is, however, if the environmental benefits of biodiesel should promote its use (in the neat form) in environmentally sensitive areas.

Concerns have been raised in the past regarding the impact of biofuel production on the prices of agricultural commodities. While this effect may not be fully clear, an issue with potential impact could be production scale, i.e., would more biodiesel or more renewable diesel be produced.

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