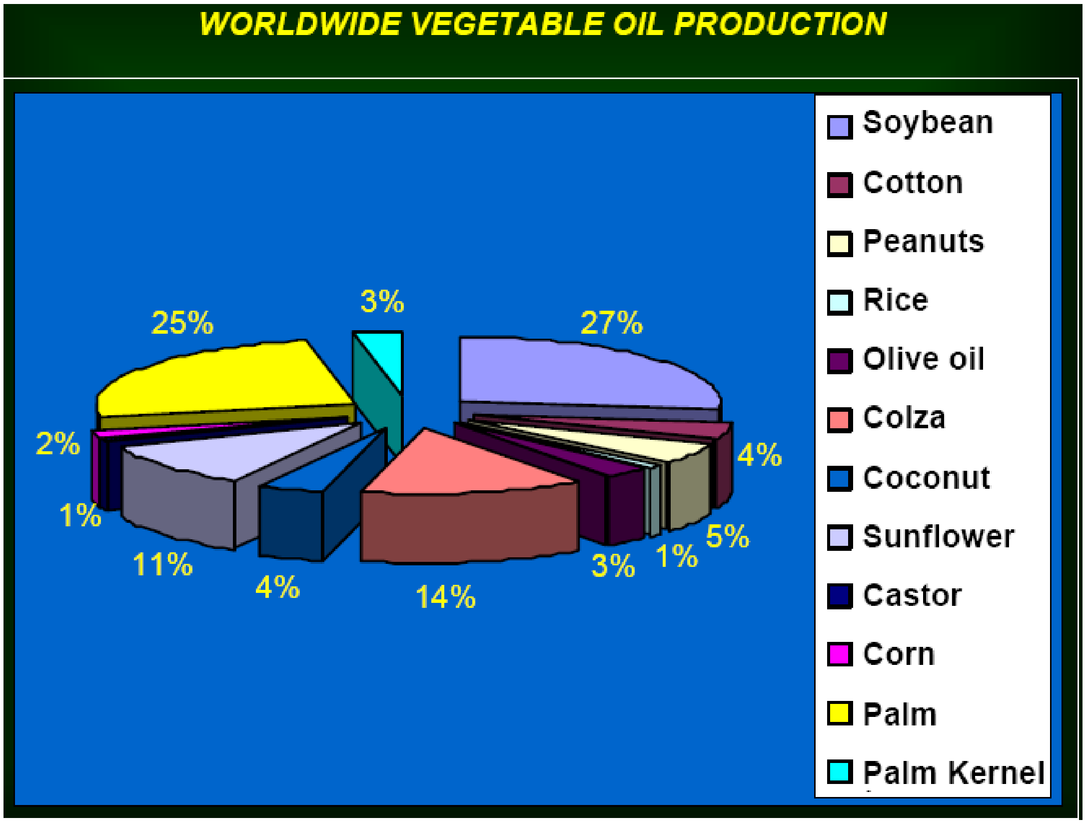
"Biodiesel Production from Vegetable Oils"

I. Introduction

With the recent surges in oil prices has come increasing interest in alternative energy sources as a means for decreasing reliance on petroleum products. Production of bio-fuels such as ethanol and biodiesel are being seriously considered not only as petroleum replacements, but also for environmental and local economic development purposes. Biodiesel feasibility studies have been conducted for Mississippi, Kansas, Missouri, the Southeastern U.S., North Dakota, British Columbia, Minnesota, Georgia, the Inland Pacific Northwest, Seattle, WA, Oregon and Kentucky. Further studies have been conducted on national and international levels, or have focused on specific topics such as emissions, production methods, and markets. Most of these feasibility studies were published since 2000 as interest in biodiesel has grown.

Facts about Biodiesel

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting vegetable oil or animal fat with an alcohol to produce a fatty acid alkyl ester. Production requires a catalyst, such as sodium or potassium hydroxide and produces glycerol as a by product. The approximate proportions of the reaction are: 100 lbs of oil + 10 lbs of methanol → 100 lbs of biodiesel + 10 lbs of glycerol Soybean oil is


WORLDWIDE VEGETABLE OIL PRODUCTION
25%
3%
27%
2%
4%
1%
5%
1%
11%
4%
14%
3%
Soybean
Cotton
Peanuts
Rice
Olive oil
Colza
Coconut
Sunflower
Castor
Corn
Palm
Palm Kernel

the most common feedstock used in U.S. production, while rape seed oil is used in Europe. An important factor in considering which feedstock to use is the stock's free fatty acid (FFA) content. Sources with high FFA content require pretreatment prior to biodiesel production which adds to the cost of production. Biodiesel is most often used as a blended fuel with petroleum diesel, but can be used as a pure fuel. The most common blend is B-20, a mixture of 20 percent biodiesel and 80 percent petroleum diesel. B-100 refers to 100 percent biodiesel. Biodiesel has a lower flashpoint and burns cleaner than petroleum diesel, reducing emissions of nitrogen, carbon monoxide and unburned hydrocarbons. Burning biodiesel or biodiesel blends requires little to no modifications to current engines. Biodiesel has greater lubricating qualities than petroleum diesel and adding even small amounts of biodiesel to poor quality petroleum diesel can increase its lubricating qualities to acceptable levels.

Biodiesel is more susceptible to cold than petroleum based diesel fuel. It will generally start to gel at higher temperatures than #2 diesel fuel. Soybean oilbased biodiesel will form crystals at about 0°C and biodiesel from saturated fats, such as are commonly found in animal fats and greases, can form crystals at higher temperatures. The cetane number of biodiesel is a measurement of the ignition performance of a diesel fuel oil obtained by comparing it to reference fuels in a standardized engine test (ASTM, 1994g). The cetane number for biodiesel should be a minimum of 47; however a cetane number that is too high can lead to engine problems.

ELEMENTARY: What is Biodiesel?

Most trucks and buses and tractors in the United States use **diesel** fuel. Diesel fuel is made from **petroleum**, a **nonrenewable** energy source. Petroleum is a fossil fuel; it takes millions of years to form under the ground, so we can't make more in a short time. We use so much petroleum in the U.S. that we have to buy two-thirds of it from other countries.

When petroleum fuels are burned in vehicle engines, they can pollute the air. If they spill onto the soil or into the water, they can damage the environment for a long time. Petroleum fuels are also **toxic**––they are dangerous for people to handle.

Biodiesel is a fuel made from vegetable oils or animal fats. It is usually made from soybean oil, but it can also be made from corn oil or used restaurant grease and oil. If it is made from restaurant oil, it can smell like french fries. Since biodiesel is made from plant and animal oils, it is a **renewable** fuel. We can raise more plants and animals in a short time to make more biodiesel.

Biodiesel works as well in engines as diesel fuel. In many ways, it is a better fuel, though it is more expensive. Burning biodiesel does not produce as much air pollution as burning petroleum fuels. This means the air is cleaner and healthier to breathe when biodiesel is used. Biodiesel is also **nontoxic**––it is not dangerous to people or the environment and is safe to handle. If biodiesel spills, it is **biodegradable**––it breaks down quickly into harmless substances.

Biodiesel can be used instead of diesel fuel or it can be mixed with diesel fuel. It is usually mixed with diesel fuel as two percent biodiesel or 20 percent biodiesel (B20). Pure biodiesel is called B100. That means it is 100 percent biodiesel. The B stands for biodiesel and the number stands for the percent of biodiesel in the mixture or blend.

Most biodiesel used today is B20, which is 20 percent biodiesel and 80 percent diesel. Many school districts have begun using B20 in their school buses. In Arizona's Deer Valley Unified School District, school buses have driven more than four million miles using biodiesel. Everyone is pleased with the way the buses operate and believe using biodiesel improves the environment and the health of the students and drivers.

Many states, as well as the U.S. Army, Air Force and Department of Agriculture, are using biodiesel to run their buses, garbage trucks, snowplows, and other vehicles. Since biodiesel is not yet available at many public stations, most biodiesel vehicles are in fleets with their own fuel stations.

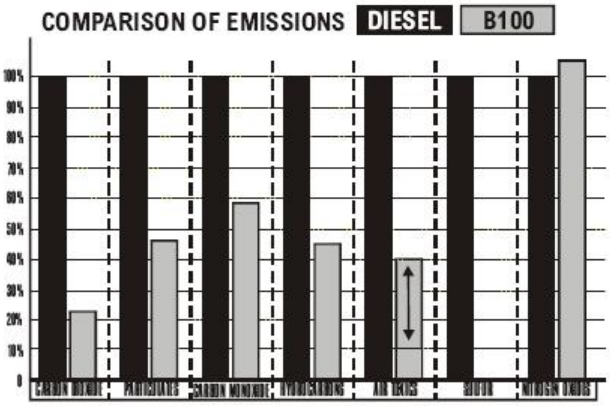
Because of its benefits, the use of biodiesel is growing every year. More public stations are opening and more fleets are switching to biodiesel. As the use of biodiesel grows, farmers are growing more soybeans and other crops to meet the demand. Biodiesel is good for the country and the economy.

Vehicles powered by biodiesel.

Environmental Impacts

Biodiesel is renewable, nontoxic, and biodegradable. Compared to diesel, biodiesel is significantly cleaner burning. It produces fewer air pollutants, less black smoke, and smells better, too.

Biodiesel is made from organic compounds and alcohol. It is no more toxic than table salt. It quickly degrades (breaks down) into natural organic residues if it is spilled. It is often used in boats to protect wildlife and fish hatcheries. In addition, people who use biodiesel find that their hands don't dry out and crack the way they do with diesel.



Distribution of Biodiesel

Today, there are only a few public biodiesel stations in the United States. It is available mainly through bulk suppliers. Because of this, biodiesel is more practical for fleets with their own fueling facilities. As people learn about biodiesel and its benefits, the demand for it will grow. More service stations will install tanks and pumps to provide it to their customers.

Economics of Biodiesel

Today, B100 costs more than diesel; B20 costs 13–22 cents more per gallon. Because it is so clean burning and easy to use, biodiesel is the fastest growing and cheapest alternative fuel for fleet vehicles. Many states are planning to require that every gallon of diesel fuel include two percent biodiesel to improve air quality.

Another benefit of biodiesel is its effect on agriculture. Using biodiesel will require more soybeans and other crops. Farmers will have new crops and markets to keep their farms growing.

Today, the United States imports nearly two-thirds of the petroleum it uses. Biodiesel is a domestic fuel produced in the United States. The growing use of biodiesel can reduce the need to import foreign oil and promote national security.

Biodiesel ferry at Mammoth Cave, KY

Biodiesel bus used by National Park Service

Biodiesel’s cetane number depends on the feedstock used for its production. Energetically, biodiesel has approximately 85 percent of the energy potential of petroleum diesel. When blended with petroleum diesel at levels less than 20% (v/v), these blends generally perform similarly to neat petroleum diesel.

The US Park Service has adopted biodiesel use at many of its parks within the US and thus has kept an extensive database on the fuel’s performance in a wide variety of vehicles. Their data show excellent performance and strong evidence as to the high potential for using biodiesel as a displacement fuel to petroleum. Several original equipment manufacturers (OEMs) are providing warranty coverage for fuels using as much as a B20 fuel blend. In the case of a spill, biodiesel is a fairly environmentally benign chemical that is fully biodegradable. Conversely, petroleum diesel releases into the environmental are a serious threat to the ecosystems receiving these chemicals because many of the components of petroleum diesel are carcinogenic and persistent. Biodiesel must be segregated and handled separately because of its unique physical properties. Biodiesel can be corrosive to rubber materials and liner materials and cannot be stored in concrete lined tanks.

A major by-product in the production of biodiesel is glycerol. Marketing glycerol often dictates the profitability of a biodiesel plant. According to a study from Mississippi State University, identifying and maintaining this market is absolutely critical to a successful biodiesel venture. A potential glut in the glycerol market is of concern to the further development of the biodiesel industry. Current uses for glycerol are many including pharmaceuticals, cosmetics, paints, and toothpaste. The US Biodiesel Board (2003) reports that studies show that the use of biodiesel reduces exotic (derived from outside of the biosphere) carbon dioxide flux into the biosphere by over 75% because of recycling of the carbon dioxide within the biosphere. Carbon monoxide production on a life cycle basis is reduced by approximately 35%.

Emissions Reductions with Biodiesel Blends

Emission Type	**B100**	**B20**	**B2**
Total Unburned Hydrocarbons	-67%	-20%	-2.2%
Carbon Monoxide	-48%	-12%	-1.3%
Particulate Matter	-47%	-12%	-1.3%
Oxides of Nitrogen (NO_X)	+10%	+ 2%***	+0.2%

"When considering the combined benefit of all these reductions, the small increase in nitrogen oxides (NOx) should not overshadow the net environmental gain with biodiesel use in North Carolina. Biodiesel is a viable part of the overall effort to improve our air quality."

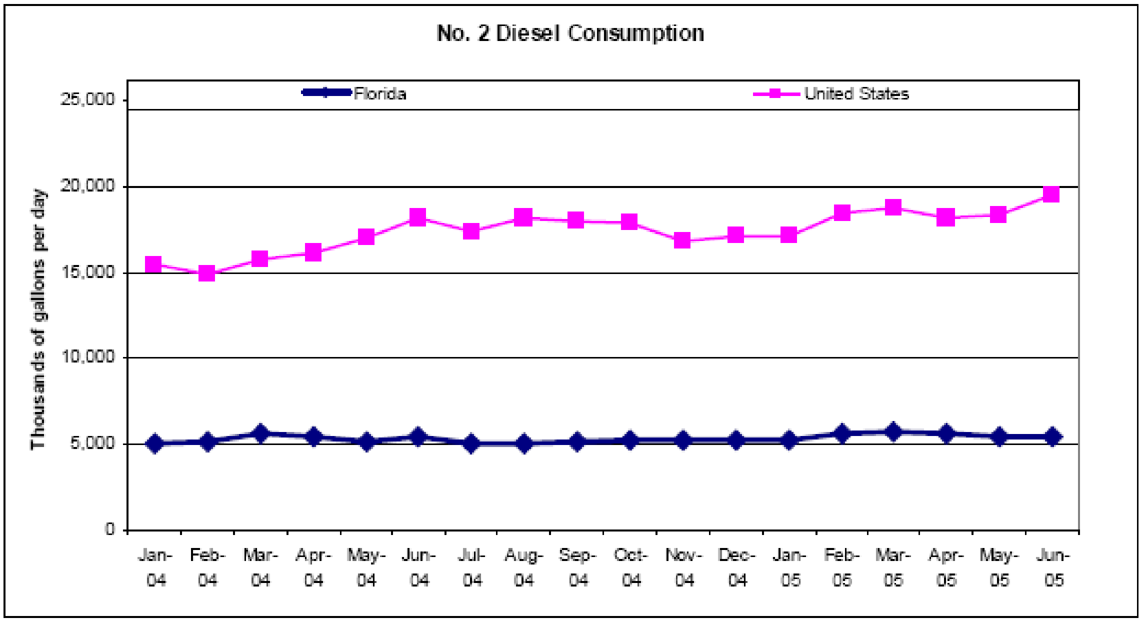
B. Keith Overcash, PE, NC DE&NR, DAQ

Measurements of particulate matter emissions from diesel-run buses indicate a reduction of particulates by over 60%. Soot (black smoke released during rpm increases) within the same tests were reduced by over 80%. Sulfur dioxide and methane releases have been documented to be reduced by over 8% and 3%, respectively. Nitrogen oxide releases were approximately 9% higher than those measured from combustion of petroleum diesel fuel. Wastewater production and hazardous waste generation during processing of biodiesel over petroleum diesel is approximately 80% and 95%, respectively, lower.

Diesel Demand

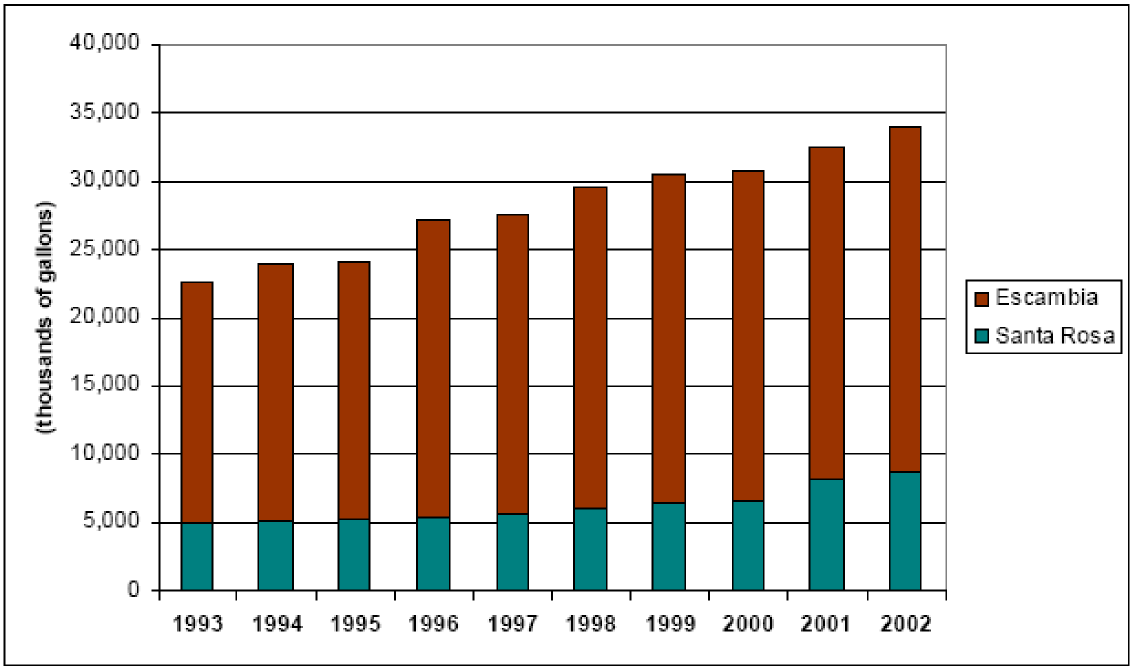
According to the Energy Information Administration (EIA), on average some 20 million gallons of No. 2 diesel fuel are consumed daily in the United States, with over 5 million gallons of that occurring in the state of Florida. See Figure 1.

Figure 1 - Diesel Consumption in U.S. and Florida



In the two-county Pensacola region, nearly 35 million gallons of No. 2 diesel fuel was consumed in 2002. See Figure 2.

Figure 2 - Pensacola MSA diesel consumption



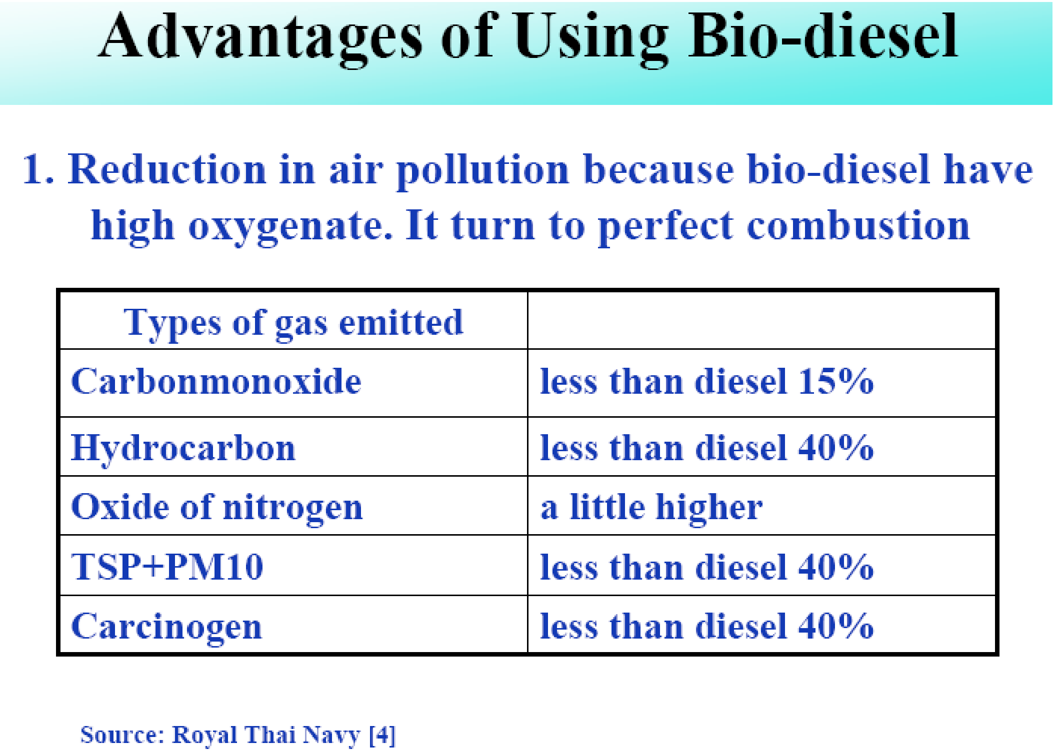
Source: Florida Department of Revenue

Prices for Number 2 diesel fuel in the U.S. increased 73 percent between January, 2003 and November, 2005.

The Role of the U.S. Soybean Farmer in the Development of the North American Biodiesel Industry Michael Mc Cranie The National Biodiesel Board and Foundation (NBB/NBF) are dedicated to creating a market for biodiesel in the United States. NBB/NBF has established itself as the creator of the biodiesel market in the United States. It cannot and will not be able to sell fuel, but will continue to be an integral part of the overall exchange of information for the biodiesel commercialization effort, which includes feedstock providers, government agencies, customers, engine manufacturers, fuel providers, and other interested parties.

The NBB/NBF implements programs and activities relating to market development, education, regulations, and demonstrations regarding biodiesel under the direction of farmer directors with funds provided by soybean producers through the soybean check off and related industries. This presentation will detail the important role that the US soybean farmer played in the advancement of the US biodiesel industry. In addition, the role of “new generation” cooperatives will be discussed as a method for producer involvement in the biofuels industry. The Potential of the Oilseeds Industry in MERCOSUR: The Role played by Brazil and Argentina in Providing Vegetable Oils to Meet the Potential Demand for Biodiesel Pablo G. Adreani. The major players in the development Of the oilseeds industry in MERCOSUR are Argentina and Brazil. There has been an evolution of soybean crushing in Brazil during the last decade. During the 1996/97 crop year, 2 1,600,OOO metric tons were crushed, the highest crush ever recorded by the Brazilian industry, compared with a crush of I3,774,000 tons in the year 1983. In OdY 12 years, the crushing industry increased by over 56%. During 97/98 a total of 18.8 million tOnS of soybeans were crushed, resulting in a production of 14,900,OOO tons of soybean meal (79.3%) and of 3,600,OOO tons of soybean oil (19.1%). The domestic disappearance of soybean meal has been estimated at 5,500,OOO tons, and exports were estimated at 9,800,OOO tons. Domestic disappearance of soybean oil is estimated at 2,750,OOO tons and exports at I ,050,OOO tons. Imports were around 300,000 tons of meal and 200,OO tons of oil. There has also been an evolution of the soybean crushing industry in Argentina during the last decade. The growth in capacity of Argentina has been accompanied by a strong and sustained increase on the supply side. Area and production of soybeans has been increasing continuously since the beginning of the crop in Argentina. Only 12 years ago the area planted to soybeans stood at 3.3 million hectares, compared with 7. I millon hectares planted during the current crop year 1997/98, for an increase of 115 % that turned the area planted to soybeans into the major planted crop in Argentina. By the same token, production increased from 7.1 million tons to almost I8 million tons during the current harvest. The increase comes to 153% due to the improvements in production techniques and the increase in average yields nationally.

The Importance of Diesel Fuel Substitutes from Non-Edible Seed Oils due to the limited availability of agricultural area leading to competition with the food industry as well as the current relatively high price for vegetable oils, it is important to look for alternative feed stocks for biodiesel production. There are two possible routes to overcome that issue, both using feedstocks which are not suitable for nutritional purposes. On the one hand, waste oils and fats - such as used frying oil or animal fat like tallow or lard - can be used as feedstock. On the other



Advantages of Using Bio-diesel

1. Reduction in air pollution because bio-diesel have high oxygenate. It turn to perfect combustion

Types of gas emitted	
Carbonmonoxide	less than diesel 15%
Hydrocarbon	less than diesel 40%
Oxide of nitrogen	a little higher
TSP+PM10	less than diesel 40%
Carcinogen	less than diesel 40%

Source: Royal Thai Navy [4]

Biodiesel Customers

US Dept of Defense - DLA
National Forest Service
US Department of Energy - Green Parks
US Postal Service
ODOT, IDOT, VDOT, MODOT, NJDOT etc…
Five Seasons Transit – Cedar Rapids
New Jersey Transit
General Services Administration
Omaha Public Power District
Georgia Power
Commonwealth Edison
Deer Valley & Paradise Valley School Districts, Phoenix, AZ
MORE THAN 1,000 FLEETs

hand, seed oils - which cannot be used for food production due to the content of natural poisonous compounds - are ideal for industrial use.

Biodiesel: fuel of the future?

The Hindu - 03 Aug 06

Biodiesel resources can provide energy security WITH THE upsurge in economic activities, India is consuming over a whopping 127 million tonnes of crude oil a year and is forced to import about 70 per cent of its needs. The current yearly consumption of diesel alone is approximately 40 million tonnes in India constituting about 40 per cent of all petro-products.

In the current scenario, exploring energy alternatives in the form of bio-fuels, namely, ethanol and biodiesel assumes top priority. Biodiesel, derived from the plants (bearing oils) like sunflower, rapeseed, canola or Jatropha Curcas, can be used as a substitute or an additive to diesel. Biodiesel can provide power similar to conventional diesel and thus can be used in diesel engines. Biodiesel is non-toxic and environment friendly as it produces substantially less carbon monoxide and the combustion gases contain no sulphur dioxide and unburnt hydrocarbons.

Cancer Risk Reduced

Because of these properties cancer risks and neonatal defects are reduced. Biodiesel mixed (5-20 per cent) with conventional diesel can extend engine life. It has good potential for rural employment generation. Considering all the options in India, Jatropha Curcas has been identified as the most suitable source due to its lower gestation period. While the seeds are used for oil extraction, other parts of the plant, that is, leaves, bark and the like, can be used for organic dyes, medicines, biogas and the like. Originating in the Caribbean islands, jatropha has spread as a valuable hedge plant to Africa, Asia and India. It grows in a variety of agro-climatic conditions. Thus it ensures a reasonable production of seeds with little inputs.

Intercropping

Intercropping of jatropha with lemon grass, turmeric, ashwagandha and the like has been found to be an economically viable option when compared with monocropping. Since jatropha is not suitable for forage, fence farming is also an attractive option. Plantation of saplings from the seeds rather than vegetative propagation is a better option for the dry areas.

The plantation of saplings (4 months old) should be carried out before the rains. As the growth and canopy coverage are more in fertile soil, the plants occupy more area when compared with dry land cultivation.

While the plantation pitch for jatropha could be 1.5 x 1.5m in lighter/dry lands, a spacing of 2.0 x 2.0m would be required in fertile soil resulting in 2,500 plants/hectare. For intercropping, a spacing of 3m should be maintained between the rows for inter-cultivation and ploughing required for vegetables and flowers. For better growth, the plants require irrigation for the first two years. The plants require pruning after they grow over 1.0 m in height.

Effective Yield

The jatropha plant bears fruits from the 2nd year after its plantation and the economic yield stabilises from the 4th or 5th year onwards. The plant may live for more than 50 years with an average effective yielding time of 50 years. The economic yield can be considered as 0.75-2.00kg/plant and 4.00-6.00 tonnes per hectare per year depending on the agro-climatic zone and agricultural practices. The cost of plantation has been estimated as Rs.20,000 a hectare, inclusive of plant material, maintenance for one year, training, overheads and the like. A selling price of jatropha seeds at Rs.12 a kg would be an economically attractive proposition for farmers.

Oil from jatropha seeds (oil content: 35 per cent on average) can be extracted by using a screw press for further processing into biodiesel by the transesterification route. Transesterification is the process of converting the raw vegetable oil into biodiesel. The process involves displacement of alcohol from an ester by another alcohol (methanol is used commonly).

Return on investment

For an optimal capacity of 10,000 TPA of biodiesel, the capital cost for oil extraction and transesterification would be Rs.20,000/tonne capacity. The return on investment (ROI) has been arrived at 15 per cent pre tax on the capital cost.

The efficient storage of biodiesel resources can provide energy security to the country. Biodiesel can safely be stored for up to 6 months. The existing storage facilities and infrastructure for petrol and diesel can be used for the biodiesel with minor alterations

12 million jobs

India has vast stretches of degraded land, mostly in areas with adverse agro-climatic conditions, where species of jatropha can be grown easily. Considering 10 million plantation on both sides along the railway tracks, 1,26,000 hectares can be cultivated with jatropha. Use of 11 million hectares of wasteland for jatropha cultivation can lead to generation of a minimum of 12 million jobs. Production of bio-fuel from plant materials is a major step toward harnessing one of the world's most-prevalent, yet least-utilised renewable energy resources. India, with its huge waste/non-fertile lands, has taken a well-noted lead in jatropha cultivation and commercial production is what the industries have to focus on for sustainable development.

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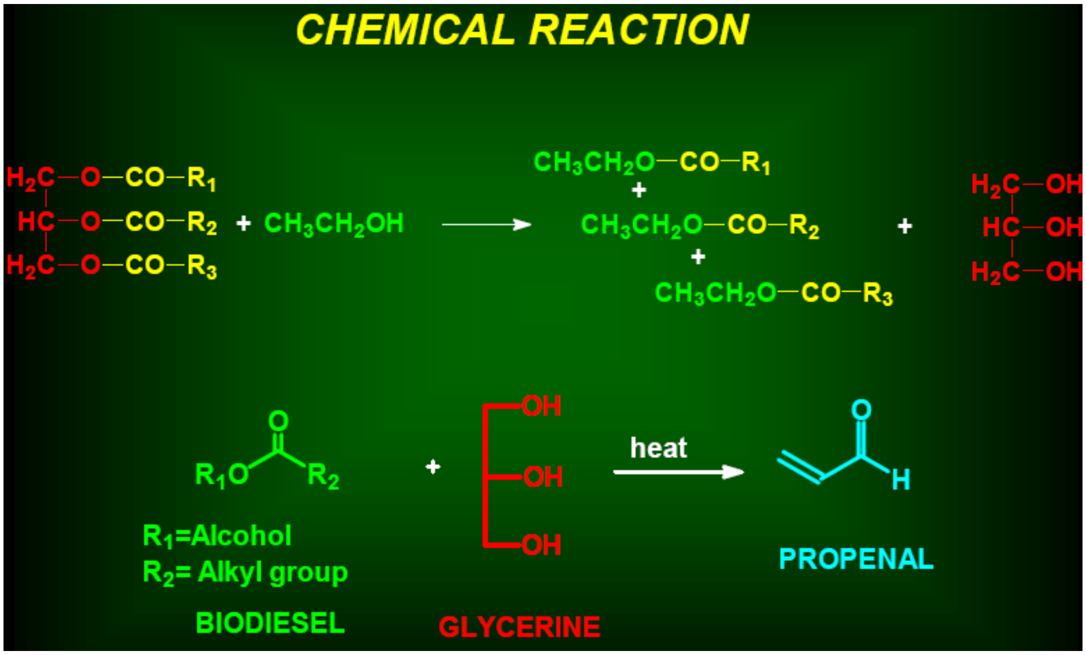
Department of Science & Technology, New Delhi.

II.Transesterification of Vegetable Oils

The transesterification of vegetable oils[1-98] with methanol as well as the main uses of the fatty acid methyl esters are reviewed. The general aspects of this process and the applicability of different types of catalysts (acids, alkaline metal hydroxides, alkoxides and carbonates, enzymes and non-ionic bases, such as amines, amidines, guanidines and triamino (imino) phosphoranes) are described. Special attention is given to guanidines, which can be easily heterogenized on organic polymers. However, the anchored catalysts show leaching problems. New strategies to obtain non-leaching guanidine-containing catalysts are proposed. Finally, several applications of fatty acid esters, obtained by transesterification of vegetable oils, are described.\

General Aspects of Transesterification

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Scheme 1)1. In this review, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst



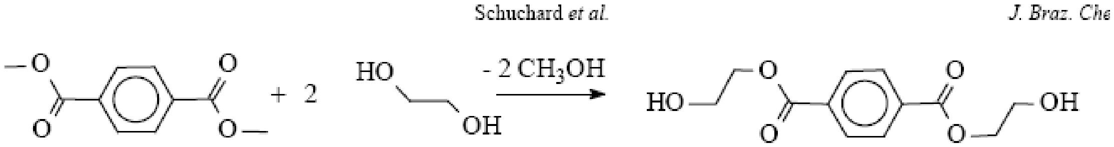
CHEMICAL REACTION

$H_2C-O-CO-R_1$
$HC-O-CO-R_2$ + CH_3CH_2OH ⟶ $CH_3CH_2O-CO-R_1$ + $CH_3CH_2O-CO-R_2$ + $CH_3CH_2O-CO-R_3$ + H_2C-OH, $HC-OH$, H_2C-OH
$H_2C-O-CO-R_3$

R_1=Alcohol
R_2= Alkyl group

BIODIESEL + GLYCERINE $\xrightarrow{\text{heat}}$ PROPENAL

(typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess. The applicability of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds1. An example is the production of PET (polyethylene terephthalate), which involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst (Scheme 2)2



Furthermore, a large number of acrylic acid derivatives is produced by transesterification of methyl acrylate with different alcohols, in the presence of acid catalysts3-6. If the alcohol and the ester groups are present in the same molecule simple lactones7,8 or macrocycles9-10 are formed by an intramolecular transesterification, as shown

$$\mathrm{RCOOR'} + \mathrm{R''OH} \xrightleftharpoons{catalyst} \mathrm{RCOOR''} + \mathrm{R'OH}$$

Scheme 1. General equation for a transesterification reaction.

in Scheme 3. Further transesterification reactions can be found in the literature, in which metal alkoxides11-16, aluminum isopropoxide17-19, tetraalkoxytitanium compounds20- 22 and organotin alkoxides23,24 are applied as catalysts.

Transesterification of Vegetable Oils

In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol25,26 (Scheme 4). The overall process is a sequence of three consecutive and reversible reactions, in which di and monoglycerides are formed as intermediates26. The stoichiometric reaction requires 1 mol of a triglyceride and 3 mol of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several aspects, including the type of catalyst (alkaline or acid), alcohol/ vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on

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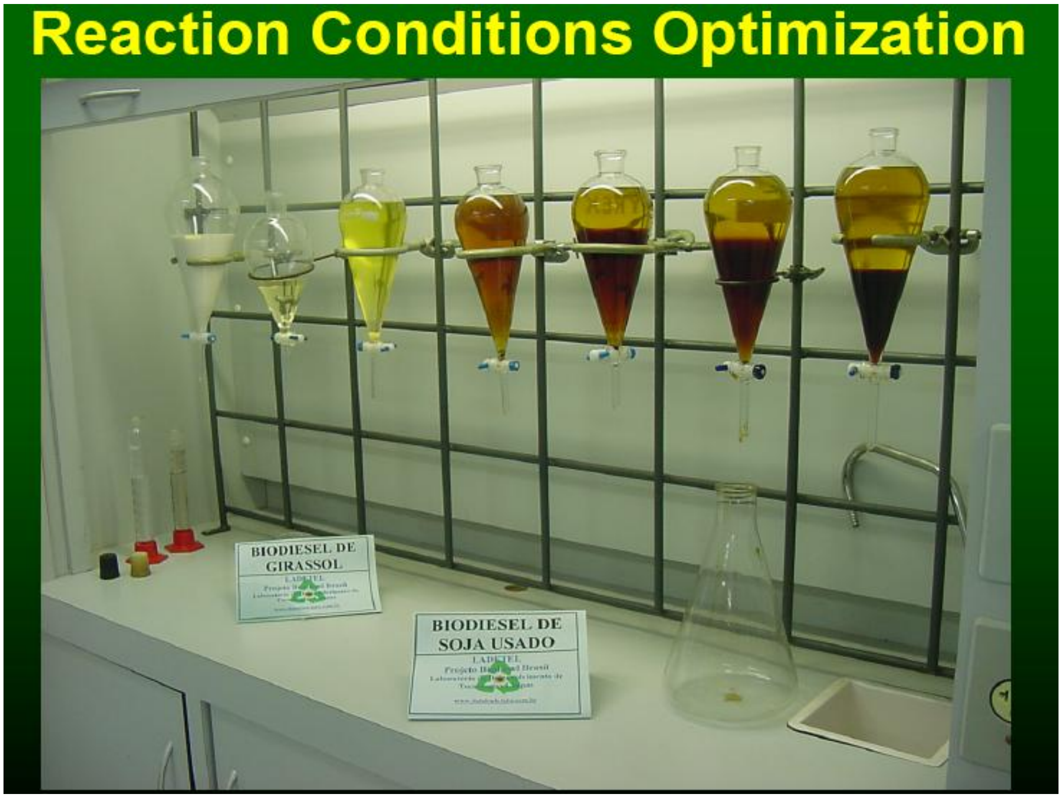
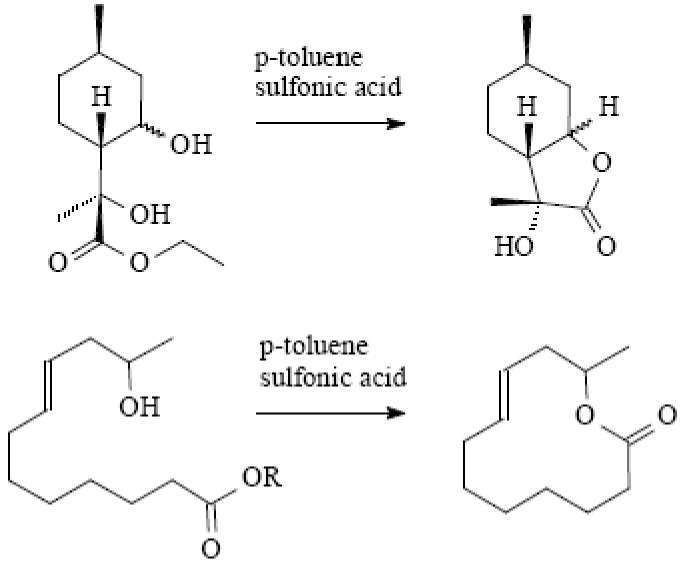


Reaction Conditions Optimization

the course of the transesterification and will be discussed below, based on the type of catalyst used.

Acid-Catalyzed Processes

The transesterification process is catalyzed by BrØnsted acids, preferably by sulfonic27 and sulfuric acids26,28,29.These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 h to reach complete conversion30. Pryde *et al*.26 showed that the methanolysis of soybean oil, in the presence of 1 mol% of H2SO4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively. The alcohol/vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the other hand,



Scheme 3. Examples of intramolecular transesterification reactions, forming lactones or macrocycles.

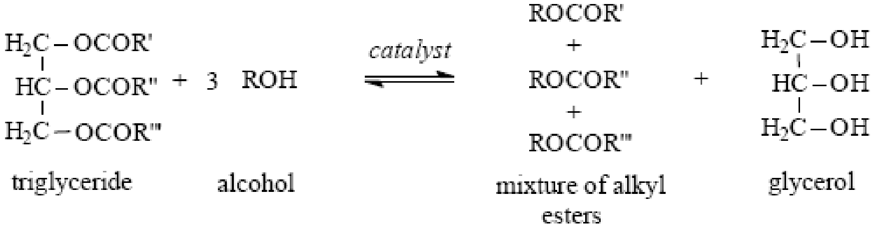
Scheme 3. Examples of intramolecular transesterification reactions, forming lactones or macrocycles.

an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/ oil ratio has to be established empirically, considering each individual process. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Scheme 5, for a monoglyceride.

However, it can be extended to di- and triglycerides31. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H+. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

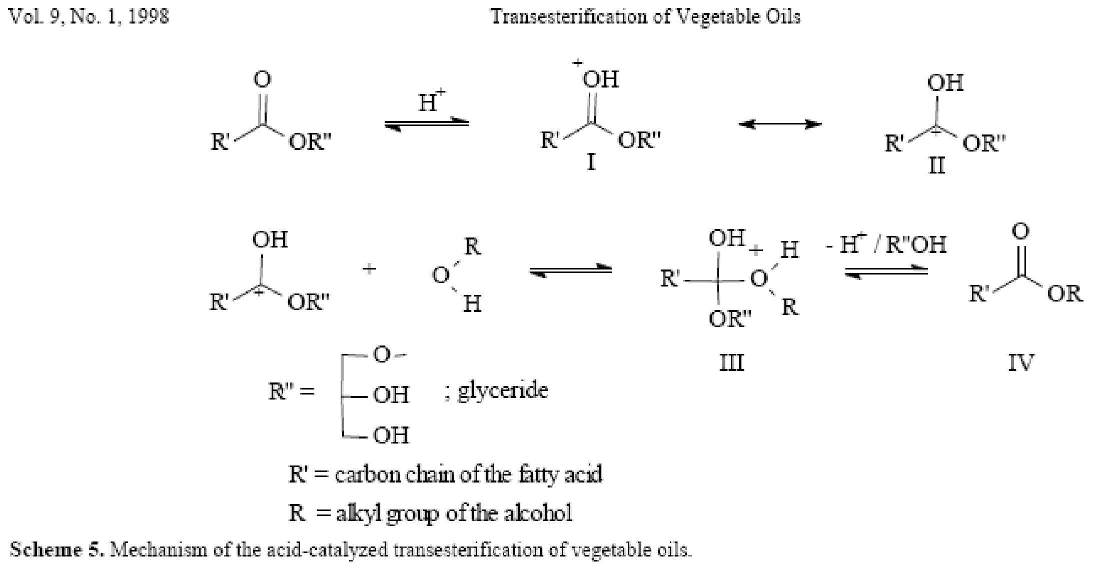
Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction26,30. Due

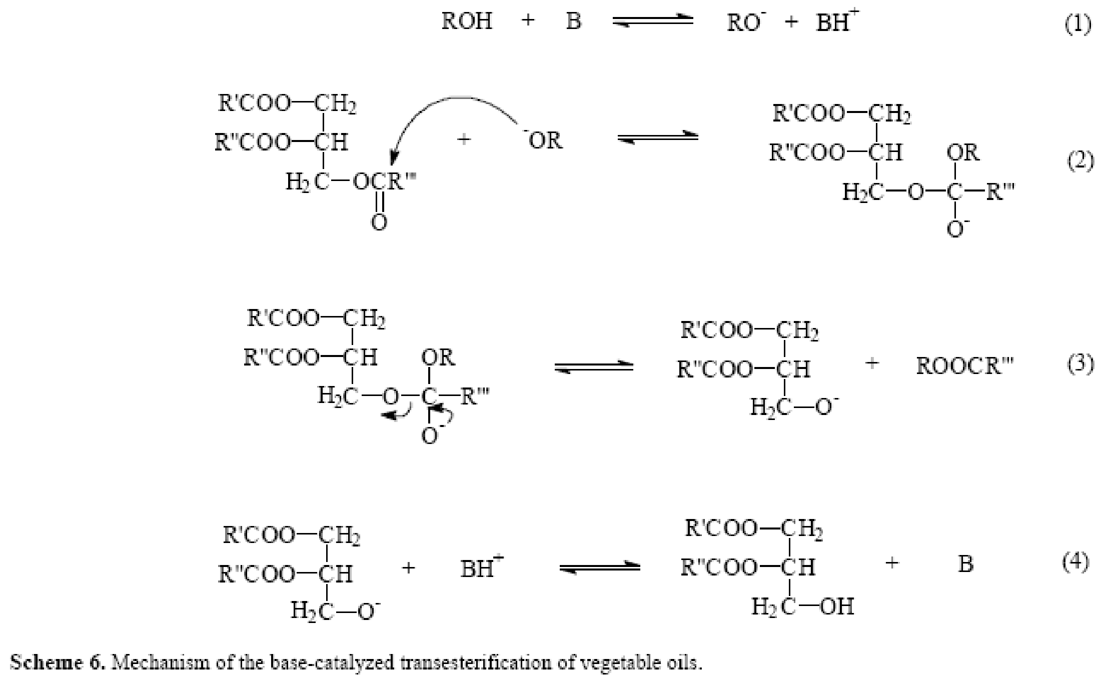


Scheme 4. Transesterification of vegetable oils.

Esters mixture of alkyl triglyceride alcohol glycerol *catalyst* to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides26,30,32 and hydroxides29,33-36 as well as sodium or potassium carbonates37-39. The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Scheme 6. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2)11,40, from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol. Alkaline metal alkoxides (as CH3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes30. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2 mol%. However, even if a water-free alcohol/oil mixture is used, some water is pro-



Scheme 5. Mechanism of the acid-catalyzed transesterification of vegetable oils.



Scheme 6. Mechanism of the base-catalyzed transesterification of vegetable oils.

duced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Scheme 7). This undesirable saponification reaction

reduces the ester yields and considerably difficults the recovery of the glycerol due to the formation of emulsions30. Potassium carbonate, used in a concentration of 2 or 3 mol% gives high yields of fatty acid alkyl esters and reduces the soap formation38. This can be explained by the formation of bicarbonate instead of water (Scheme 8), which does not hydrolyse the esters.

Lipase-Catalyzed Processes

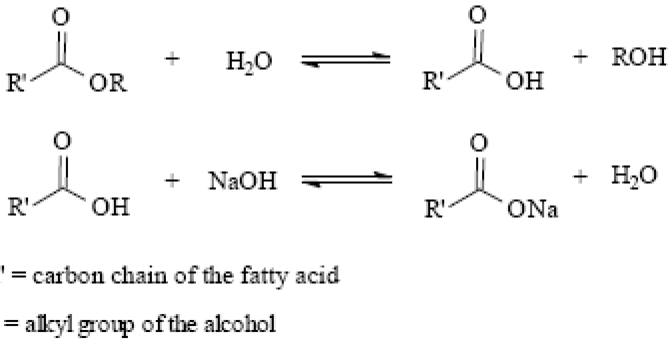
Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools41.

Although the enzyme-catalyzed transesterification processes are not yet commercially developed, new results have been reported in recent articles and patents42-48. The common aspects of these studies consist in optimizing the reaction conditions (solvent, temperature, pH, type of microorganism which generates the enzyme, etc) in order to establish suitable characteristics for an industrial application. However, the reaction yields as well as the reaction times are still unfavorable compared to the base-catalyzed reaction systems.

Non-Ionic Base-Catalyzed Processes

In order to obtain milder reaction conditions and to simplify manipulations, a great number of organic bases has been developed and used as catalyst or reactant for organic syntheses. Among these bases, amines such as triethylamine49,50, piperidine49, 1,2,2,6,6-pentamethylpiperidine49,51, pyridine49,50,51, 2,6-di-*tert*-butyl-pyridine49,51 and 4-dimethyl aminopyridine1,52 (DMAP); amidines such as 1,8-diazabicyclo- [5.4.0]undec-7-ene1,49,50,51 (DBU) and 1,5-diazabicyclo[4.3.0]non-5-ene49,51,53 (DBN); guanidines such as 1,5,7-triazabicyclo[4.4.0]dec-5-ene50,54 (TBD), 1,1,3,3-tetramethyl-guanidine 55,56,57 (TMG), 1,1,2,3,3-pentabutyl-guanidine58 (PBG), 1,3-diphenylguanidine59, 1,2,3- triphenylguanidine60,61 and amino- and nitroguanidines62; triamino (imino) phosphoranes such as *tert*-butylimino-2- diethylamino-1,3-dimethyl-perhydro-1,3,2- diazo-phosphorane51 (BEMP) and tris (dimethylamino) methylimino-phosphorane51 (Me7P), shown in Scheme 9, are frequently used in organic synthesis. The activity and efficiency of such non-ionic bases as catalysts for the transesterification of vegetable oils were studied. In a first series of studies, the catalytic activity of some guanidines was compared to that observed using other bases such as the amidines DBU and DBN, and the triamino (imino)phosphoranes BEMP and Me7P63. It was observed that TBD, even if applied at only 1 mol%, produces more than 90% of methyl esters after 1 h. Using the other bases, under the same experimental conditions, the yields were not higher than 66% (Table 1). The order of the catalytic activity is not directly related to the relative basicity of these compounds, since BEMP and Me7P should be the more efficient catalysts, followed by TBD. However, the guanidines are more active catalysts and the activity follows their relative basicity.

According to the observed results and to the mechanism of the base-catalyzed transesterification (Scheme 6), it seems that the good performance of TBD, when compared to BEMP and Me7P, is related to its kinetic activity. The catalytic site (unshared electron pair of the sp2 N) of TBD is practically unhindered (Scheme 10), allowing an easy access of the methanol for proton transfer, while the steric



Scheme 7. Saponification reaction of the produced fatty acid alkyl esters.

$K_2CO_3 + ROH \rightleftharpoons ROK + KHCO_3$

R = alkyl group of the alcohol

Scheme 8. Reaction of potassium carbonate with the alcohol.

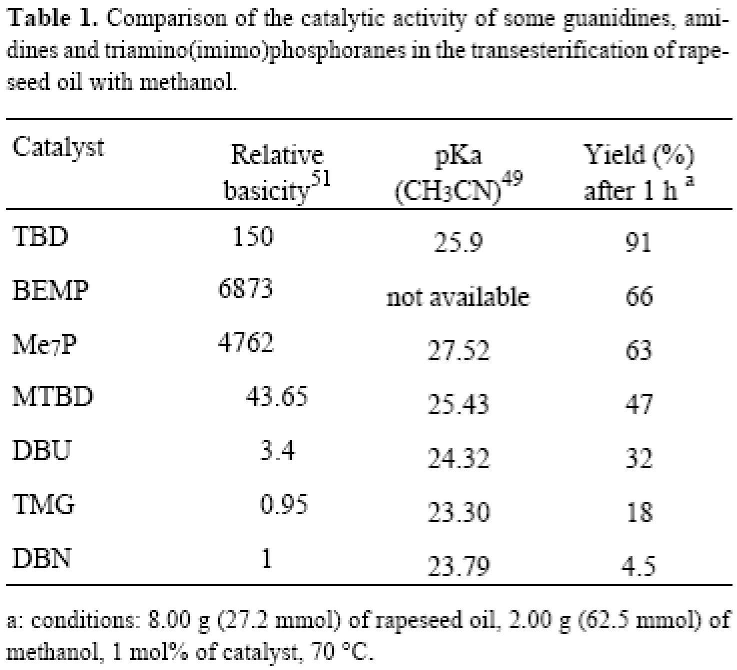


Table 1. Comparison of the catalytic activity of some guanidines, amidines and triamino(imimo)phosphoranes in the transesterification of rapeseed oil with methanol.

Catalyst	Relative basicity[51]	pKa (CH_3CN)[49]	Yield (%) after 1 h [a]
TBD	150	25.9	91
BEMP	6873	not available	66
Me_7P	4762	27.52	63
MTBD	43.65	25.43	47
DBU	3.4	24.32	32
TMG	0.95	23.30	18
DBN	1	23.79	4.5

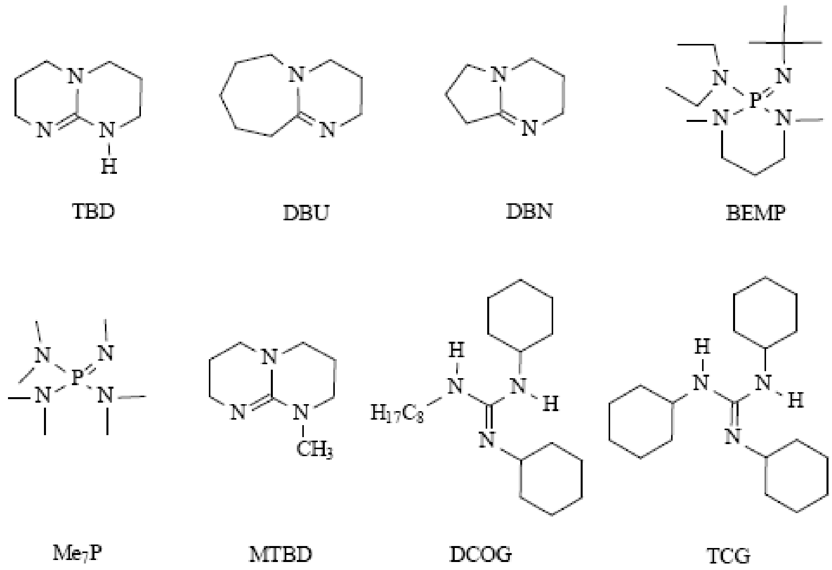
a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C.

a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C. hindrance shown by the triamino (imino) phosphoranes is so significant that they are practically inert to alkylating agents, such as isopropyl bromide, as well as extremely nresistant to react with thionyl chloride and thiophosgene51. Other bases such as DMAP, pyridine and triethylamine were also tested. However, even at 5 mol%, these amines did not give satisfactory yields. DMAP was the most active within this series, producing only 20% of methyl esters after 1 h.

In a second series of studies, the catalytic activity of TBD was compared to that observed for typical industrial catalysts (*e.g*. NaOH and K2CO3)37-39. The results of this study63 are shown in Table 2. The reaction yields obtained with TBD were close to those observed with NaOH and no undesirable by-products such as soaps (easily formed when alkaline metal hydroxides are used) were observed. When compared to potassium carbonate, TBD was always more

active, even at low molar concentrations. Although TBD is less active than sodium methoxide (at only 0.5%, CH3ONa produces more than 98% of methyl esters after 30 min), its use does not require any special condition.

Due to the excellent performance of TBD in the transesterification of vegetable oils, the catalytic activity of other alkylguanidines was also investigated, in order to establish and understand all factors that may affect their catalytic properties. In a third series of studies, the catalytic



Scheme 9. Molecular structures of some non-ionic organic bases.

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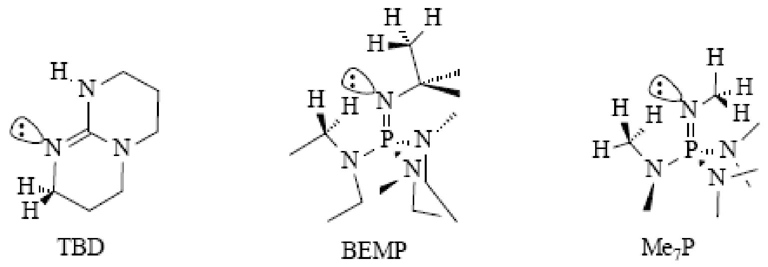


Scheme 10. Steric hindrance of TBD, BEMP and Me7P.

Scheme 10. Steric hindrance of TBD, BEMP and Me7P.

Table 2. Comparison between TBD and the conventional inorganic catalysts.

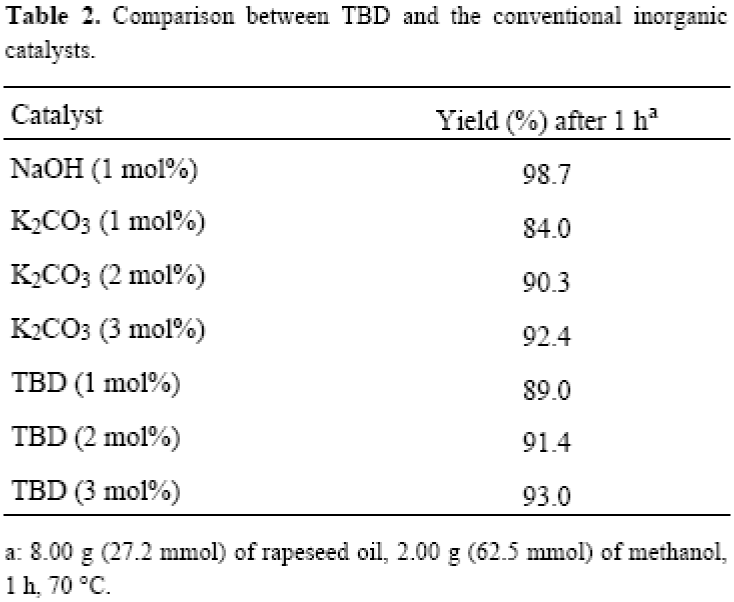


Table 2. Comparison between TBD and the conventional inorganic catalysts.

Catalyst	Yield (%) after 1 h^a
NaOH (1 mol%)	98.7
K_2CO_3 (1 mol%)	84.0
K_2CO_3 (2 mol%)	90.3
K_2CO_3 (3 mol%)	92.4
TBD (1 mol%)	89.0
TBD (2 mol%)	91.4
TBD (3 mol%)	93.0

a: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 h, 70 °C.

a: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 h, 70 °C. activity of several alkylguanidines was compared64. TBD was always the most active, however, 1,3-dicyclohexyl- 2-*n*-octylguanidine (DCOG), 1,1,2,3,3- penta-methylguanidine (PMG), 7-methyl-1,5,7-triazabicyclo[4.4.0] dec-5-ene (MTBD) and 1,2,3-tricyclohexyl-guanidine (TCG), also showed a good catalytic performance64. The activity order of the catalysts TBD > TCG > DCOG > MTBD > PMG

(Table 3) corresponds to their relative base strength, which is increased by structural factors such as number and type of substituents (cyclic or acyclic chain)51. The excellent performance of DCOG and TCG is also assigned to the high symmetry of their guanidinium cations, as observed earlier for the symmetric 1,2,3- trimethylguanidine65. Results obtained in the transesterification of soybean oil with methanol show that 1,2,3,4,5-pentacyclohexylbiguanidine

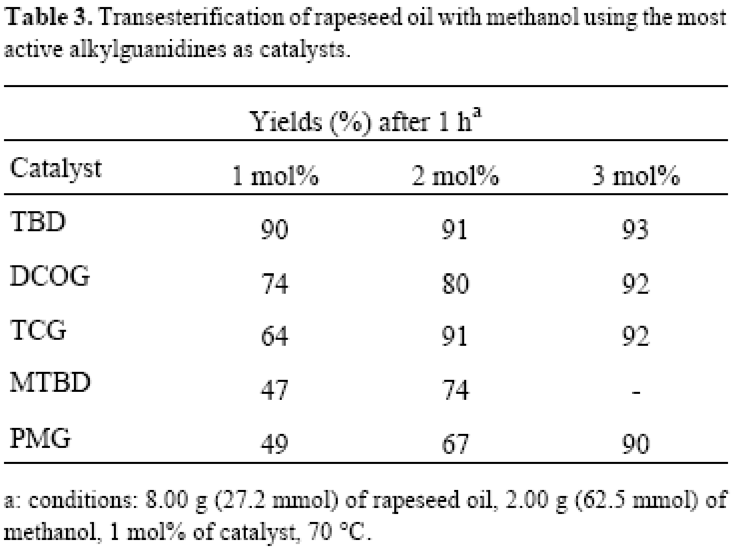


Table 3. Transesterification of rapeseed oil with methanol using the most active alkylguanidines as catalysts.

	Yields (%) after 1 h[a]		
Catalyst	1 mol%	2 mol%	3 mol%
TBD	90	91	93
DCOG	74	80	92
TCG	64	91	92
MTBD	47	74	-
PMG	49	67	90

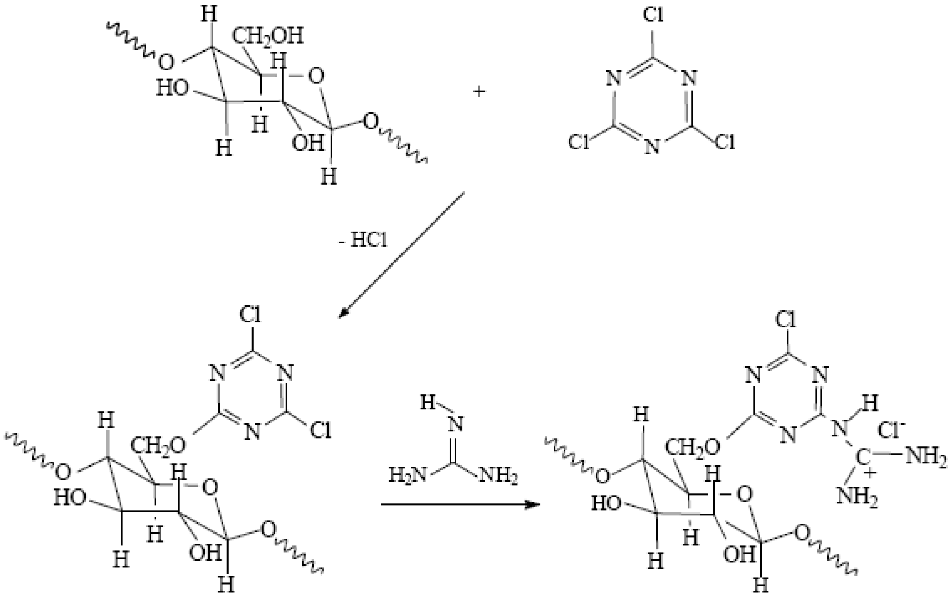
a: conditions: 8.00 g (27.2 mmol) of rapeseed oil, 2.00 g (62.5 mmol) of methanol, 1 mol% of catalyst, 70 °C.

(PCBG) is even more active than TCG, as a 82% yield of methyl esters is obtained with PCBG after 1 h, compared to 69% with TCG under the same conditions66.

Heterogeneously Catalyzed Processes

The advantage of using guanidines in the transesterification of vegetable oils is the possibility to heterogenize them on organic polymers.

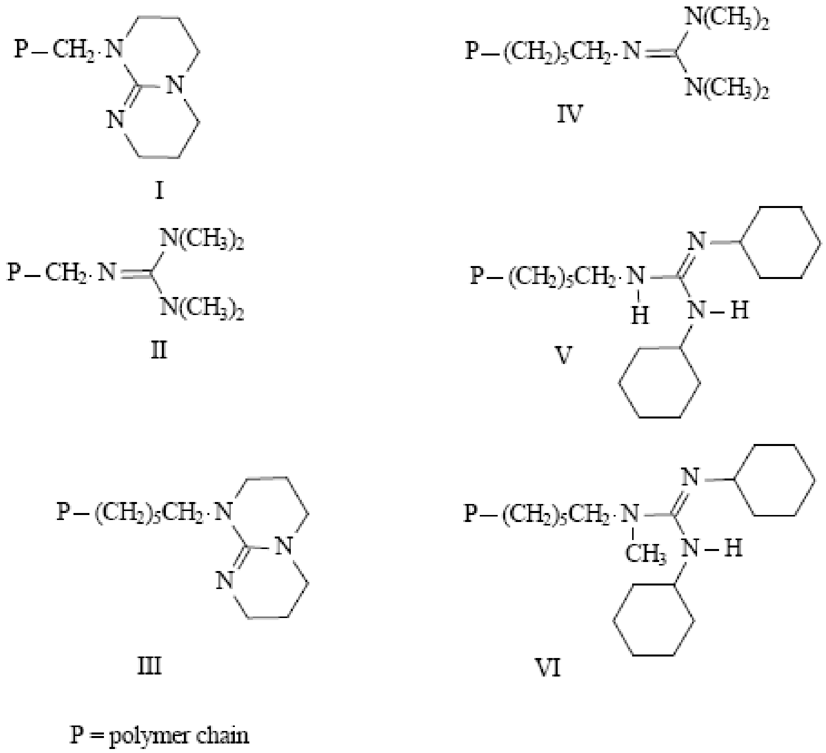
Schuchardt *et al.* tested principally cellulose and poly(styrene/divinylbenzene), but also polyuretanes and other organic polymers allow the suitable incorporation of guanidines. The heterogenization of guanidines on organic polymers and their use in the transesterification of vegetable oils were described in a patent67. The heterogenization of unsubstituted guanidines can be achieved by their reaction with microcrystalline cellulose activated by cyanuric chloride at the C-6 position (Scheme 11). After deprotonation of the guanidinium salt formed, the guanidine-containing cellulose shows a slightly reduced activity, compared to guanidine in homogeneous phase, giving a conversion of 30% after 1 h, when used at 5 mol %68. This guanidine-containing cellulose was used in a continuous reactor containing 100 g of the catalyst. An alcohol/oil mixture of 2:1 was pumped at 60°C with a rate of 0.48 L/h. In the first hour the methyl esters were obtained with high yields and the phase separation was quick69. After this, however, the reaction was incomplete and the phase separation difficult. This could be due either to leaching of the catalyst or to its irreversible protonation. As no leaching tests were performed, no definite reason can be given at this point.



Scheme 11. Heterogenization of guanidine on activated microcrystalline cellulose.

The catalytic performance of some alkylguanidines heterogenized on different substituted polystyrenes was investigated70. The guanidine-containing polymers (Scheme 12) were used in the transesterification of soybean oil with methanol in several consecutive catalytic cycles. The guanidines heterogenized on gel-type poly(styrene/ divinylbenzene) with 1 meq Cl/g (polymers I and II) showed a slightly lower activity than their homogeneous analogues but allowed the same high conversions after prolonged reaction times. However, they slowly leached from the polymers, allowing only nine catalytic cycles. The guanidines heterogenized on linear polystyrene with the use of a ‘spacer-arm’ (polymers III, IV), were less active. Polymer V, which is symmetrically substituted showed an activity as high as polymer I. When another methyl group was introduced (polymer VI) its activity was slightly reduced. Furthermore, all polymers with a ‘spacer-arm’ suffered substitution reactions during the recycling experiments to form inactive hexasubstituted guanidinium compounds. A summary of the catalytic performance of these polymers is shown in Table 4.

The lower activity of the guanidine-containing polymers I and II, when compared to their homogeneous analogues, is probably due to the hydrophobicity of the polymer chain which reduces the concentration of the methanol at the active sites. However, at prolonged reaction times, the efficiency of the anchored catalysts is practically the same. The use of a ‘spacer-arm’ (polymers III-VI) was expected to improve the performance of the heterogenized catalyst. However, polymer IV showed the same activity as



Scheme 12. Molecular structures of some guanidine-containing polystyrenes.

polymer II and polymer III was even less active than polymer I70.

Despite less active than their homogeneous analogues, all polymer-containing guanidines could be reused in several consecutive reaction cycles70. However, a loss of activity was observed, mainly due to leaching of the anchored base from the polymers, as mentioned above. Polymers I and II have the guanidine moiety bound to the benzylic CH2 group of the polystyrene. After the protonation of the base, the electrophilic character of the methylene group is in- creased, thus

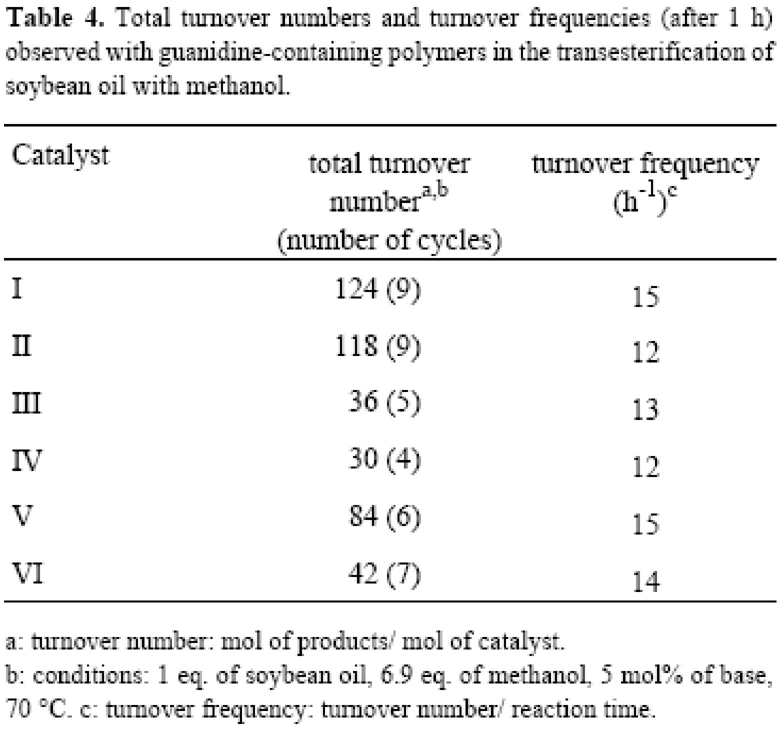


Table 4. Total turnover numbers and turnover frequencies (after 1 h) observed with guanidine-containing polymers in the transesterification of soybean oil with methanol.

Catalyst	total turnover number^{a,b} (number of cycles)	turnover frequency (h^{-1})^{c}
I	124 (9)	15
II	118 (9)	12
III	36 (5)	13
IV	30 (4)	12
V	84 (6)	15
VI	42 (7)	14

a: turnover number: mol of products/ mol of catalyst.
b: conditions: 1 eq. of soybean oil, 6.9 eq. of methanol, 5 mol% of base, 70 °C. c: turnover frequency: turnover number/ reaction time.

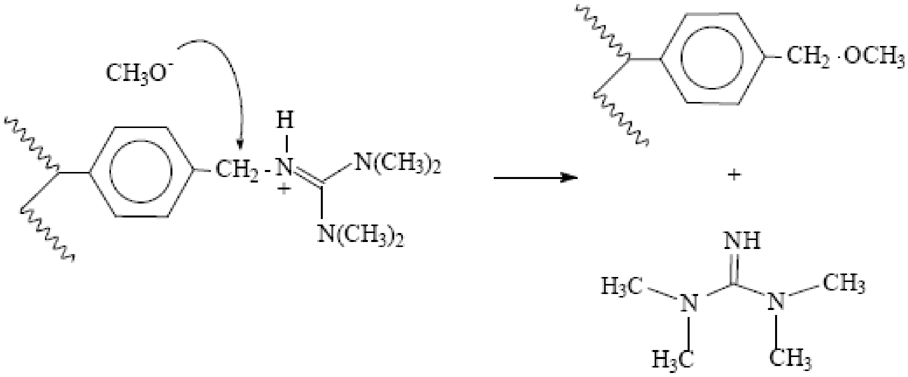
Scheme 12. Molecular structures of some guanidine-containing polystyrenes.

becoming more susceptible to nucleophilic attack by methoxide ions present in the reaction medium. This attack results in the removal of the guanidine moiety from the polymer as shown in Scheme 13. The leaching of the guanidines from the other polymers follows a similar mechanism. For the polymers containing a 'spacer-arm', there is an additional factor that accelerates the deactivation of the supported catalysts. The anchored bases can react with electrophilic functional groups which are further away on the polymer chain, producing inactive hexasubstituted guanidinium compounds64, as shown in Scheme 14. However, it is possible to deprotonate these hexasubstituted guanidinium compounds, which should give doubly anchored active guanidines whose leaching is less probable.

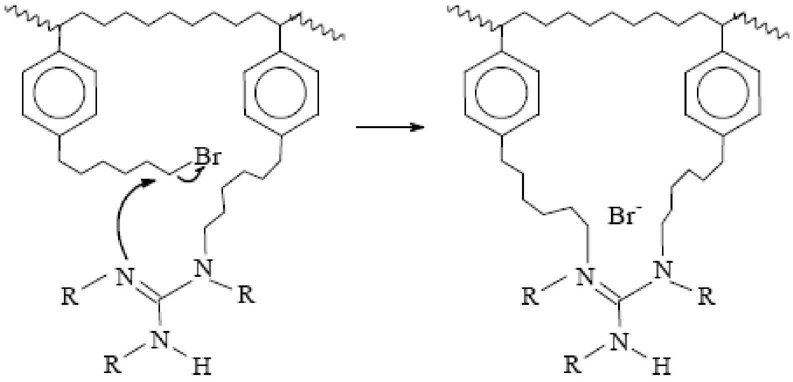
In order to circumvent the leaching of the guanidines from the polymers, Schuchardt *et al*. encapsulate TCG by the reaction of dicyclohexylcarbodiimide and cyclohexylamine in the supercages of a hydrophobic Y zeolite. The encapsulated guanidine showed a good catalytic activity in the addition reaction of benzaldehyde to acetone71. However, its activity in the transesterification of vegetable oils is low (14% conversion after 5 h72), as the diffusion of the triglycerides through the channels of the Y zeolite is slow due to steric hindrance.

Fatty Acid Alkyl Esters as Feedstocks for Industry

Fatty acid methyl esters can be transformed into a lot of useful chemicals, and raw materials for further synthesis73, as shown in Scheme 15. The alkanolamides, whose production consumes the major part of the methyl esters produced in the world, have a direct application as non-ionic surfactants, emulsifying, thickening and plastifying agents, etc73. The fatty alcohols are applied as pharmaceutical and cosmetics additives (C16-C18)73, as well as lubricants and plastifying agents (C6-C12), depending on the length of their carbon chain. The isopropyl esters are also applied as plastifying agents and emollients. However, they can not be produced in a convenient way by esterification of fatty acids, as an azeotrope formed by water and isopropanol avoids the recycling of the alcohol. The fatty acid methyl esters are further used in the manufacture of carbohydrate fatty acid esters (sucrose polyesters), which can be applied as non-ionic surfactants or edible non-calorific oils74-77, and can be used as an alternative fuel substitute for diesel engines (biodiesel)28-30, 78-80. These two applications will be discussed separately. The glycerol also has important applications, in cosmetics, toothpastes, pharmaceuticals, food, lacquers, plastics, alkyl resins, tobacco, explosives, cellulose processing, etc81.



Scheme 13. Leaching of the guanidine moiety from the polymers.

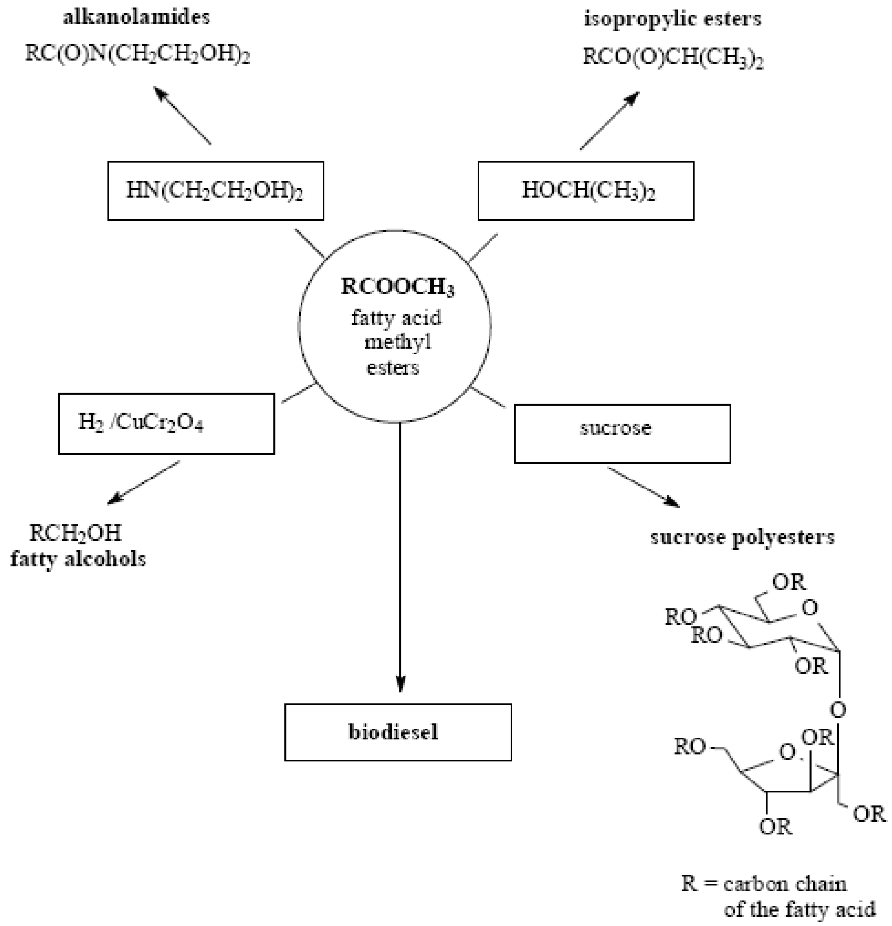


Scheme 14. Reaction of the heterogenized guanidines III-VI with unreacted 6-bromohexyl substituents.

Scheme 13. Leaching of the guanidine moiety from the polymers.

Scheme 14. Reaction of the heterogenized guanidines III-VI with unreacted 6-bromohexyl substituents.

Vol. 9, No. 1, 1998 Transesterification of Vegetable Oils



Scheme 15. Some fatty acid methyl esters applications.

Scheme 15. Some fatty acid methyl esters applications. more complicated as it requires a water-free alcohol, as well as an oil with a low water content, in order to obtain glycerol separation.

Fatty Acid Alkyl Esters as Biodiesel

With exception of hydroelectricity and nuclear energy, the major part of all energy consumed worldwide comes from petroleum, charcoal and natural gas. However, these sources are limited, and will be exhausted by the end of the next century33. Thus, looking for alternative sources of energy is of vital importance.

Vegetable oils are a renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel82. Historically, it is believed that Rudolf Diesel himself82 started research with respect to the use of vegetable oils as fuel for diesel engines. In the following decades, the studies became more systematic and, nowadays, much is known about its use as fuel. Despite energetically favorable, the direct use of vegetable oils in fuel engines is problematic. Due to their high viscosity (about 11 to 17 times higher than diesel fuel) and low volatility, they do not burn completely and form deposits in the fuel injector of diesel engines. Furthermore, acrolein (a highly toxic substance) is formed through thermal decomposition of glycerol32, 83-87. Different ways have been considered to reduce the high viscosity of vegetable oils:

- dilution of 25 parts of vegetable oil with 75 parts of diesel fuel32;
- microemulsions with short chain alcohols (*e.g.* ethanol or methanol)32;
- thermal decomposition, which produces alkanes, alkenes, carboxylic acids and aromatic compounds87;
- catalytic cracking, which produces alkanes, cycloalkanes and alkylbenzenes84, and

- transesterification with ethanol or methanol88,89. Among all these alternatives, the transesterification

seems to be the best choice, as the physical characteristics of fatty acid esters (biodiesel) are very close to those of diesel fuel32 and the process is relatively simple. Furthermore, the methyl or ethyl esters of fatty acids can be burned directly in unmodified diesel engines, with very low deposit formation37,38,79,80,82.

Several types of vegetable oils, with a diversified composition in fatty acids, can be used for the preparation of biodiesel. Soybean26,30,32,84, rapeseed38,78,79, sunflower28 and palm29,37 oils are the most studied. However, there are no technical restrictions to the use of other types of vegetable oils. Considering the type of the alcohol, the use of methanol is advantageous as it allows the simultaneous separation of glycerol. Normally, methanol is used as it is the cheapest alcohol in most countries. However, in Brazil it is advantageous to use anhydrous ethanol90, which is already produced in large quantities to be mixed with gasoline. The guanidines described here have been shown to be efficient catalysts for the transesterification of vegetable oils with commercial anhydrous ethanol69.

Fatty Acid Esters of Carbohydrates

The fatty acid esters of carbohydrates can be obtained by esterification of fatty acids, or by transesterification of their correspondent alkyl esters with carbohydrates (or other polyols) and constitute an important class of synthetic organic products. Their physico-chemical properties, which depend on the number and type of the esterified fatty acid, allow their application as non-ionic biodegradable surfactants74, or as substitutes of vegetable oils for noncalorific diets75-77. The mixture of hexa-, hepta- and octaesters of sucrose, known as ‘‘olestra’’, has been studied for more than 20 years75. Their physical properties are very close to those of the triglycerides with similar esterified fatty acids, and the resistance to the pancreatic lipase (which avoids the absorption by the digestive tract) allows its application as non-calorific edible oil75. Typically, the sugar polyesters (SPE) are prepared through base-catalyzed transesterification of carbohydrates with fatty acid methyl esters, using sodium methoxide as catalyst91-95. However, some of these methods require very high temperatures (above 100 °C) and toxic low-volatile solvents (*e.g.* DMF and DMSO), compromising the final product for human consumption. Alternatively, Rizzi and Taylor91, based on the studies of Feuge *et al.*96, developed a two-stage solvent-free process, in which the SPE are synthesized by transesterification, using sodium hydride, Na-K alloy and soaps as catalyst. Despite the very good reaction yields (about 90%), this process still shows some inconveniences such as the need for high temperatures (150 °C), and the difficulty to purify the final product (the soaps are not easily eliminated). Another solvent-free process was proposed by Akoh and Swanson93, in which sorbitol and trealose octaoleate are produced in excellent yields (> 90%) through trans-esterification reactions of the correspondent acetates and methyl oleate, using Na as catalyst. The temperature (110 °C) and reaction time (2.5 h) are lower when compared to the previous work.

However, the catalyst requires a water-free system in order to avoid its deactivation. New milder solvent-free catalytic systems are being developed, and consist in the use of guanidine as catalyst, which furnished good preliminary results97.

Conclusions and Perspectives

The industrial homogeneous catalysts will have to be substituted in the near future by heterogeneous catalysts due to environmental reasons. Good strong-base heterogeneous catalysts are still in development. One possibility would be the use of zeolites with strong basic sites98. Here the use of guanidines anchored on organic polymers was emphasized. To avoid leaching of the guanidine, however, it should be doubly anchored to the polymers. Another possibility would be the encapsulation of guanidines in an appropriate inorganic matrix. The Y zeolite is not appropriate for this purpose as the rather small diameter of its pore system slows down the diffusion of the fatty acid triglycerides.

III. Vegetable Oils and Their Derivatives as Alternative Diesel Fuels

Vegetable oils and their derivatives (especially methyl esters), commonly referred to as “biodiesel,” are prominent candidates as alternative diesel fuels. They have advanced from being purely experimental fuels to initial stages of commercialization. They are technically competitive with or offer technical advantages compared to conventional diesel fuel. Besides being a renewable and domestic resource, biodiesel reduces most emissions while engine performance and fuel economy are nearly identical compared to conventional fuels.


Palm oil


Coconut oil


Soy bean oil


Ground nut oil


Sunflower oil


Jatropha oil

Several problems, however, remain, which include economics, combustion, some emissions, lube oil contamination, and low-temperature properties. An overview on all aspects of biodiesel is presented. The use of vegetable oils in diesel engines is nearly as old as the diesel engine itself. The inventor of the diesel engine, Rudolf Diesel, reportedly used groundnut (peanut) oil as a fuel for demonstration purposes in 1900 (*1*). Some other work was carried out on the use of vegetable oils in diesel engines in the 1930's and 1940's. The fuel and energy crises of the late 1970's and early 1980's as well as accompanying concerns about the depletion of the world's non-renewable resources provided the incentives to seek alternatives to conventional, petroleum-based fuels. In this context, vegetable oils as fuel for diesel engines were remembered. They now occupy a prominent position in the development of alternative fuels. Hundreds of scientific articles and various other reports from around the world dealing with vegetable oil-based alternative diesel fuels ("biodiesel") have appeared in print. They have advanced from being purely experimental fuels to initial stages of commercialization. Nevertheless, various technical and economic aspects require further improvement of these fuels.

Numerous different vegetable oils have been tested as biodiesel. Often the vegetable oils investigated for their suitability as biodiesel are those which occur abundantly in the country of testing. Therefore, soybean oil is of primary interest as biodiesel source in the United States while many European countries are concerned with rapeseed oil, and countries with tropical climate prefer to utilize coconut oil or palm oil. Other vegetable oils, including sunflower, safflower, etc., have also been investigated.

Furthermore, other sources of biodiesel studied include animal fats and used or waste cooking oils. Sources of biodiesel with some emphasis on developing countries have been discussed (*2*). Several problems, however, have impaired the widespread use of biodiesel. They are related to the economics and properties of biodiesel. For example, neat vegetable oils reported to cause engine deposits. Attempting to solve these problems by using methyl esters causes operational problems at low temperatures. Furthermore, problems related to combustion and emissions remain to be solved. The problems associated with the use of biodiesel are thus very complex and no satisfactory solution has yet been achieved despite the efforts of many researchers around the world. This article will briefly discuss economics and regulatory issues as well as conventional diesel fuel (petrodiesel) and then focus on research on the use of biodiesel in a diesel engine.

Economics and Regulatory Issues

Economic reasons have been one of the major obstacles in the use of biodiesel. Diesel fuel (DF) derived from vegetable oils is more expensive than petroleum-based DF. The feedstock for biodiesel is already more expensive than conventional DF. For example, in the United States, a gallon of soybean oil costs approximately two to three times as much as a gallon of conventional DF. However, in the case of conversion of vegetable oils or fats to their esters, the resulting glycerol co-product, which has a potential market of its own, may offset some of the costs. In most European countries, however, transportation fuels are so heavily taxed that tax incentives can be applied to encourage the use of biodiesel in the form of lower or no taxes on the biofuel and higher taxes on the petroleum-based fuel (*3*,*4*). This subsidy artificially cheapens the biodiesel to make it competitive. In many developing countries, the overriding concern is to become independent of the imported commodity petroleum.

In the United States, the tax mechanism is inapplicable because of the comparatively low taxes on transportation fuels. Artificially regulating the demand for fuels from specific sources by means of taxation is currently politically not feasible. Nevertheless, biodiesel is attractive for other reasons. Besides being a renewable resource and therefore creating independence from the imported commodity petroleum and not depleting natural resources, health and environmental concerns are the driving forces overriding the economic aspects in some cases. These concerns are manifested in various regulatory mandates of pollutants, particularly CAAA (Clean Air Act Amendments of 1990) and EPACT (Energy Policy Act of 1992) in the United States, which present opportunities for alternative fuels such as biodiesel. A life-cyle analysis of biodiesel (*5*) has shown that it is competitive with other alternative fuels such as compressed natural gas (CNG) and methanol in the urban transit bus market. It is generally recognized that biodiesel has lower emissions, with the exception of nitrogen oxides (NOx), than conventional petroleum-based DF. For example, due to its lack of sulfur, biodiesel does not cause SO2 emissions. The lower emissions have caused biodiesel to be used in urban bus fleets and to make it especially suitable for other niche markets such as mining and marine engines.

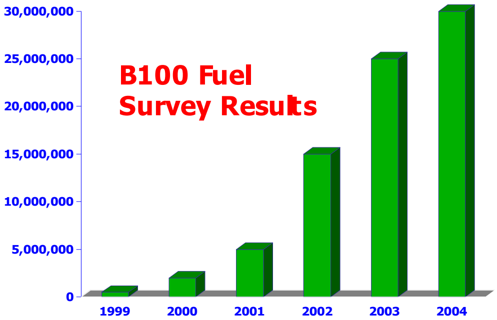
Biodiesel Production

100 lbs. of fat or oil
+
10 lbs. methanol

⇔ catalyst ⇔

100 lbs. biodiesel (B100)
+
10 lbs. of glycerin

Soybeans (90-95% of current market), Waste Greases, Edible & Inedible Tallow, Cottonseed, Sunflower, Canola/Rapeseed



Besides environmental and health reasons with accompanying Government regulations, focusing on the use of biodiesel in niche markets is rendered additionally attractive because not enough vegetable oil is produced to supply the whole diesel market with biodiesel. Numerous reports exist showing that fuel economies of certain biodiesel blends and conventional DF are virtually identical. In numerous on-the-road tests, primarily with urban bus fleets, vehicles running on blends of biodiesel with conventional DF (usually 80% conventional DF and 20% biodiesel; for a list of most biodiesel demonstration programs in the United States, see Ref. 6) required only about 2-5% more of the blended fuel than of the conventional fuel. No significant engine problems were reported as discussed later.

Diesel Engines and Conventional Diesel Fuel

In contrast to gasoline which is spark-ignited, DF after injection is ignited by the heat of compression in a diesel engine. The diesel engine is therefore also termed a compression-ignition (CI) engine. The differences in the ignition processes entail significant differences in chemical composition and physical properties of the fuels. Conventional DF is, like gasoline, obtained from cracking of petroleum. It is a fraction boiling at an initial distillation temperature of 160° (90% range of 290-360°C) (*7*), also termed middle distillates because of its boiling range in the mid-range of cracking products. The ignition quality of DF is commonly measured by ASTM D613 and reported as the cetane number (CN). Ignition quality is defined by the ignition delay time of the fuel in the engine. The shorter the ignition delay time, the higher the CN. To rank different compounds on the cetane scale, hexadecane (C16H34; also called cetane), which has a very short ignition delay, has been assigned a CN of 100. At the other end of the scale, 2,2,4,4,6,8,8-heptamethylnonane (HMN; also C16H34), which has poor ignition qualities, has been assigned a CN of 15. It should be noted that the cetane scale is arbitrary and that compounds with CN > 100 (although the cetane scale does not provide for compounds with CN > 100) or CN < 15 have been identified. The ASTM specification for conventional DF (ASTM D975) requires a minimum CN of 40. The CN scale clarifies an important aspect of the composition of, or, on a more fundamental level, the molecular structure of the compounds comprising DF. Long chain, unbranched, saturated hydrocarbons (alkanes) have high CNs and good ignition quality while branched hydrocarbons (and other materials such as aromatics) have low CNs and poor ignition quality. Since both too high and too low CN can cause operational problems (in case of too high CN, combustion can occur before the fuel and air are properly mixed, resulting in incomplete combustion and smoke; in case of too low CN, engine roughness, misfiring, higher air temperatures, slower engine warm-up and also incomplete combustion occur), most engine manufacturers designate a range of required CN for their engines. In most cases, this range is around CN 40-50. Conventional DF is classified into different grades by ASTM D 975. This classification is the following: No. 1 diesel fuel (DF1) comprises volatile fuels oils from kerosene to intermediate distillates. They are applicable for high-speed engines whose operation involves frequent and relatively wide variations in engine load and speed. Such fuel is required for use at abnormally low temperatures. No. 2 diesel fuel (DF2) includes distillate gas oils of lower volatility. This grade is suitable for use in high speed engines under relatively high loads and uniform speeds. DF2 can be used in engines not requiring fuels having the greater volatility and other properties specified for No. 1 diesel fuels. DF2 is the transportation diesel fuel to which biodiesel is usually compared. No. 4 diesel fuel (DF4) covers the more viscous distillates and their blends with residual fuel oils. It is usually satisfactory only for low-speed and medium-speed engines operated under sustained load at nearly constant speed. Besides the just discussed characteristics of conventional DF, other properties such as heat of combustion, pour point, cloud point, and viscosity are of great significance. These properties also play very important roles in the use of biodiesel. The two general types of diesel engines are the direct injection (DI) engine and the indirect injection (IDI) engine (*8*). In DI engines, the fuel is directly injected into the combustion chamber in the cylinder. In IDI engines, the fuel is injected into a prechamber which is connected with the cylinder through a narrow passage. Rapid air transfer from the main cylinder into the prechamber promotes a very high degree of air motion in the prechamber which is particularly conducive to rapid fuel air mixing (*8*). Combustion beginning in the prechamber produces high pressure and the fuels are subjected to high shear forces. The IDI engine is no longer used for heavy bus and truck engines due to somewhat lower efficiency and higher fuel consumption than the DI system (*8*). However, for special purposes, such as underground work, IDI engines are still made in the heavier class due to low exhaust emissions. For smaller vehicles such as cars and light trucks, the IDI system is used because of its ability to cover a wider speed range. The low exhaust emissions in combination with the wider speed range may lead to a continued use of IDI engines in urban areas, where the demand for low emissions can be more important than a somewhat higher fuel consumption combined with low annual mileage. The IDI engine is also less sensitive to fuel quality (*8*). Tests of biodiesel as a fuel have been performed on both DI and IDI engines.

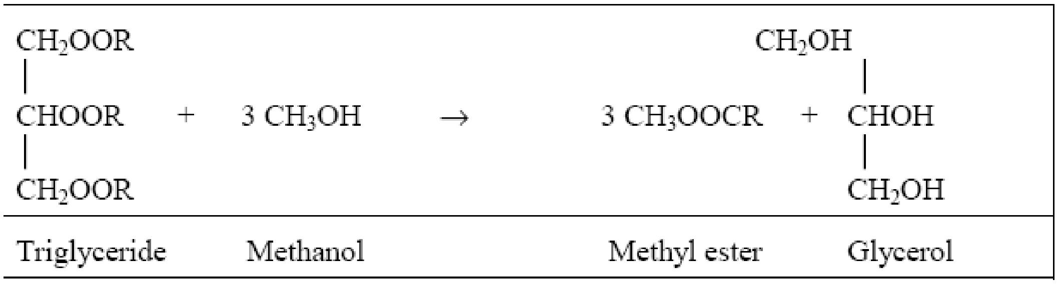
What is Biodiesel ?

The term biodiesel has no unambiguous definition. It stands for neat vegetable oils used as DF as well as neat methyl esters prepared from vegetable oils or animal fats and blends of conventional diesel fuel with vegetable oils or methyl esters. With increasing emphasis on the use of esters as DF, however, the term “biodiesel” increasingly refers to alkyl esters of vegetable oils and animal fats and not the oils or fats themselves. In an article on proposed ASTM standards, biodiesel was defined (*9*) as “the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstock, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines.” Nevertheless, clear distinction between these different vegetable oil-based or -derived alternative diesel fuels is necessary.

For use in the United States, the U.S. Department of Energy has stated (*10*), “that biodiesel is already covered in the statutory and proposed regulatory definitions of “alternative fuel” which refer to any “fuel, other than alcohol, that is derived from biological materials.” The Department, therefore, is considering amending the proposed definition of “alternative fuel” specifically to include neat biodiesel.” The definition of biodiesel was not extended to include biodiesel blends, with the Department of Energy stating that “the issue of including biodiesel mixtures or blends comprised of more than 20 percent biodiesel is currently under study. However, this subject is complex and will require significantly more data and information, and a separate, future rulemaking, before DOE can make a determination as to whether to include them in the definition of “alternative fuel.”

Vegetable oils.

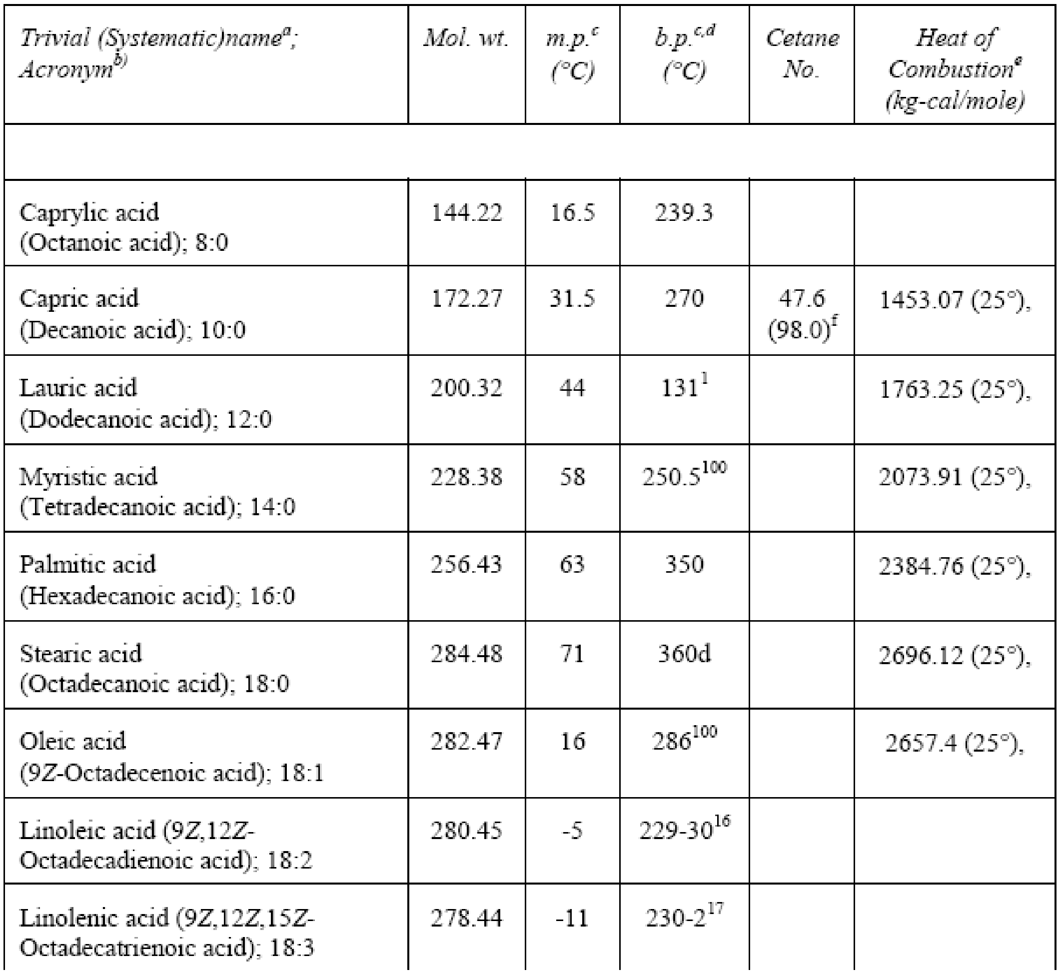
Most vegetable oils are triglycerides (TGs; triglyceride = TG). Chemically, TGs are the triacylglyceryl esters of various fatty acids with glycerol (Figure 1). Some physical properties of the most common fatty acids occurring in vegetable oils and animal fats as well as their methyl esters are listed in Table I. Besides these fatty acids, numerous other fatty acids occur in vegetable oils and animal fats, but their abundance usually is considerably lower. Table II lists the fatty acid composition of some vegetable oils and animal fats that have been studied as sources of biodiesel.



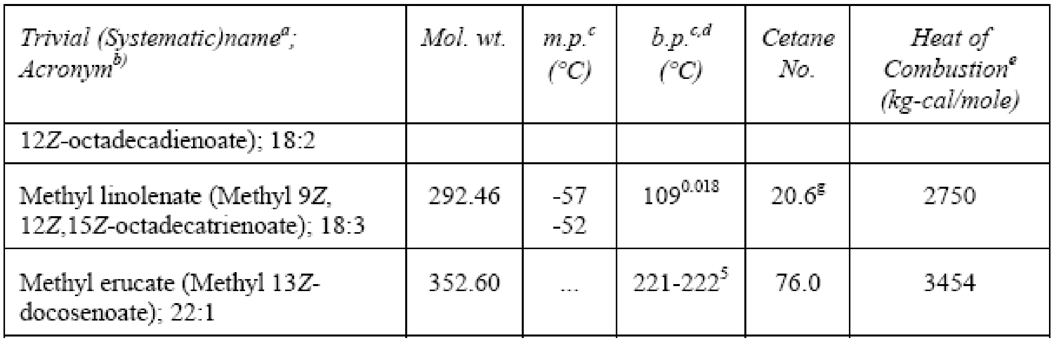
$$\begin{array}{lccccl} CH_2OOR & & & & & CH_2OH \\ | & & & & & | \\ CHOOR & + & 3\ CH_3OH & \rightarrow & 3\ CH_3OOCR\ + & CHOH \\ | & & & & & | \\ CH_2OOR & & & & & CH_2OH \end{array}$$

Figure 1. Structure of triglycerides and principle of the transesterification reaction (shown for methyl esters; R = (CH2)xCH3 or unsaturated rests according to the fatty acids listed in Table I).

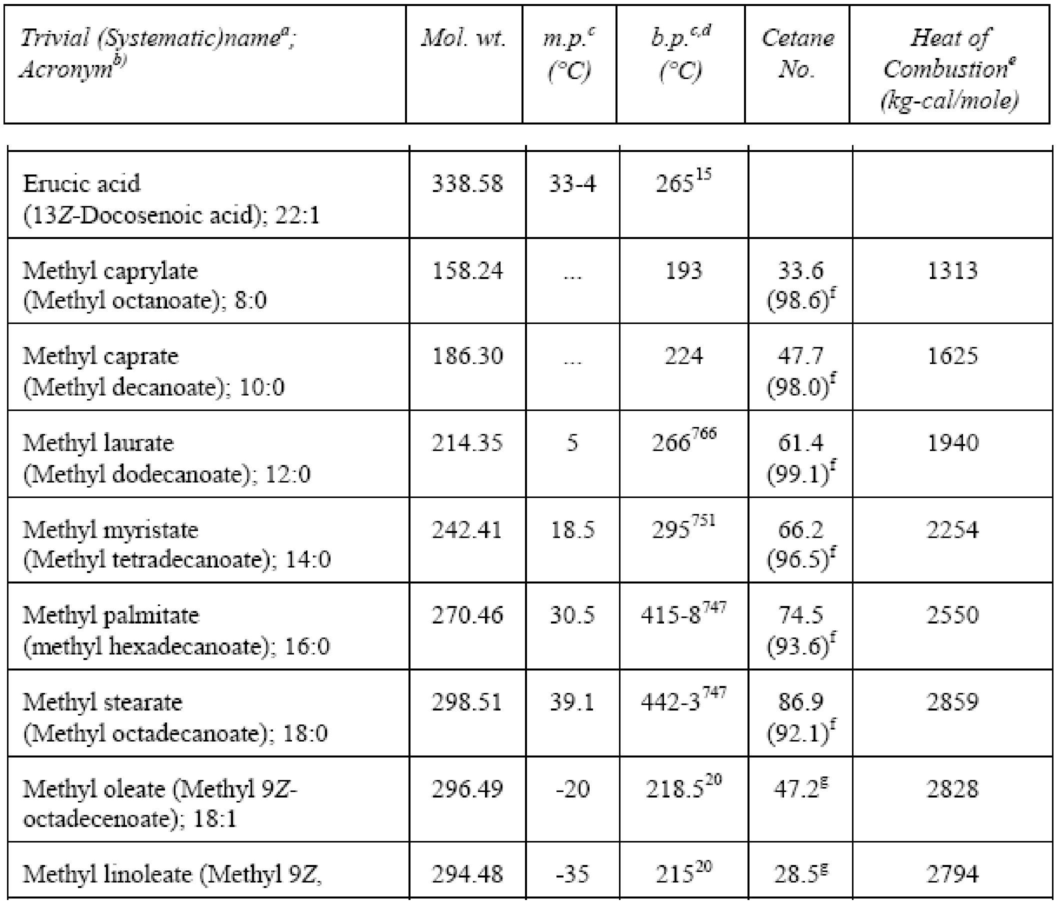
Table I. Selected properties of some common fatty acids and esters.



Trivial (Systematic)name[a]; *Acronym*[b)]	*Mol. wt.*	*m.p.*[c] *(°C)*	*b.p.*[c,d] *(°C)*	*Cetane No.*	*Heat of Combustion*[e] *(kg-cal/mole)*
Caprylic acid (Octanoic acid); 8:0	144.22	16.5	239.3		
Capric acid (Decanoic acid); 10:0	172.27	31.5	270	47.6 (98.0)[f]	1453.07 (25°),
Lauric acid (Dodecanoic acid); 12:0	200.32	44	131^{1}		1763.25 (25°),
Myristic acid (Tetradecanoic acid); 14:0	228.38	58	250.5^{100}		2073.91 (25°),
Palmitic acid (Hexadecanoic acid); 16:0	256.43	63	350		2384.76 (25°),
Stearic acid (Octadecanoic acid); 18:0	284.48	71	360d		2696.12 (25°),
Oleic acid (9*Z*-Octadecenoic acid); 18:1	282.47	16	286^{100}		2657.4 (25°),
Linoleic acid (9*Z*,12*Z*-Octadecadienoic acid); 18:2	280.45	-5	$229\text{-}30^{16}$		
Linolenic acid (9*Z*,12*Z*,15*Z*-Octadecatrienoic acid); 18:3	278.44	-11	$230\text{-}2^{17}$		



Trivial (Systematic)name[a]; *Acronym*[b)]	*Mol. wt.*	*m.p.*[c] *(°C)*	*b.p.*[c,d] *(°C)*	*Cetane No.*	*Heat of Combustion*[e] *(kg-cal/mole)*
12*Z*-octadecadienoate); 18:2					
Methyl linolenate (Methyl 9*Z*, 12*Z*,15*Z*-octadecatrienoate); 18:3	292.46	-57 -52	$109^{0.018}$	20.6[g]	2750
Methyl erucate (Methyl 13*Z*-docosenoate); 22:1	352.60	...	$221\text{-}222^{5}$	76.0	3454



Trivial (Systematic)name[a]*; Acronym*[b)]	*Mol. wt.*	*m.p.*[c] *(°C)*	*b.p.*[c,d] *(°C)*	*Cetane No.*	*Heat of Combustion*[e] *(kg-cal/mole)*
Erucic acid (13*Z*-Docosenoic acid); 22:1	338.58	33-4	265^{15}		
Methyl caprylate (Methyl octanoate); 8:0	158.24	...	193	33.6 (98.6)[f]	1313
Methyl caprate (Methyl decanoate); 10:0	186.30	...	224	47.7 (98.0)[f]	1625
Methyl laurate (Methyl dodecanoate); 12:0	214.35	5	266^{766}	61.4 (99.1)[f]	1940
Methyl myristate (Methyl tetradecanoate); 14:0	242.41	18.5	295^{751}	66.2 (96.5)[f]	2254
Methyl palmitate (methyl hexadecanoate); 16:0	270.46	30.5	$415\text{-}8^{747}$	74.5 (93.6)[f]	2550
Methyl stearate (Methyl octadecanoate); 18:0	298.51	39.1	$442\text{-}3^{747}$	86.9 (92.1)[f]	2859
Methyl oleate (Methyl 9*Z*-octadecenoate); 18:1	296.49	-20	218.5^{20}	47.2[g]	2828
Methyl linoleate (Methyl 9*Z*,	294.48	-35	215^{20}	28.5[g]	2794

a) *Z* denotes *cis* configuration.

b) The numbers denote the number of carbons and double bonds. For example, in oleic acid, 18:1 stands for eighteen carbons and one double bond.

c) Melting points and boiling points given in Ref. 28, pp. C-42 to C-553. Melting points and boiling points of 12:0 - 18:0 and 18:3 esters given in Ref. 181.

d) Superscripts in boiling point column denote pressure (mm Hg) at which the boiling point was determined.

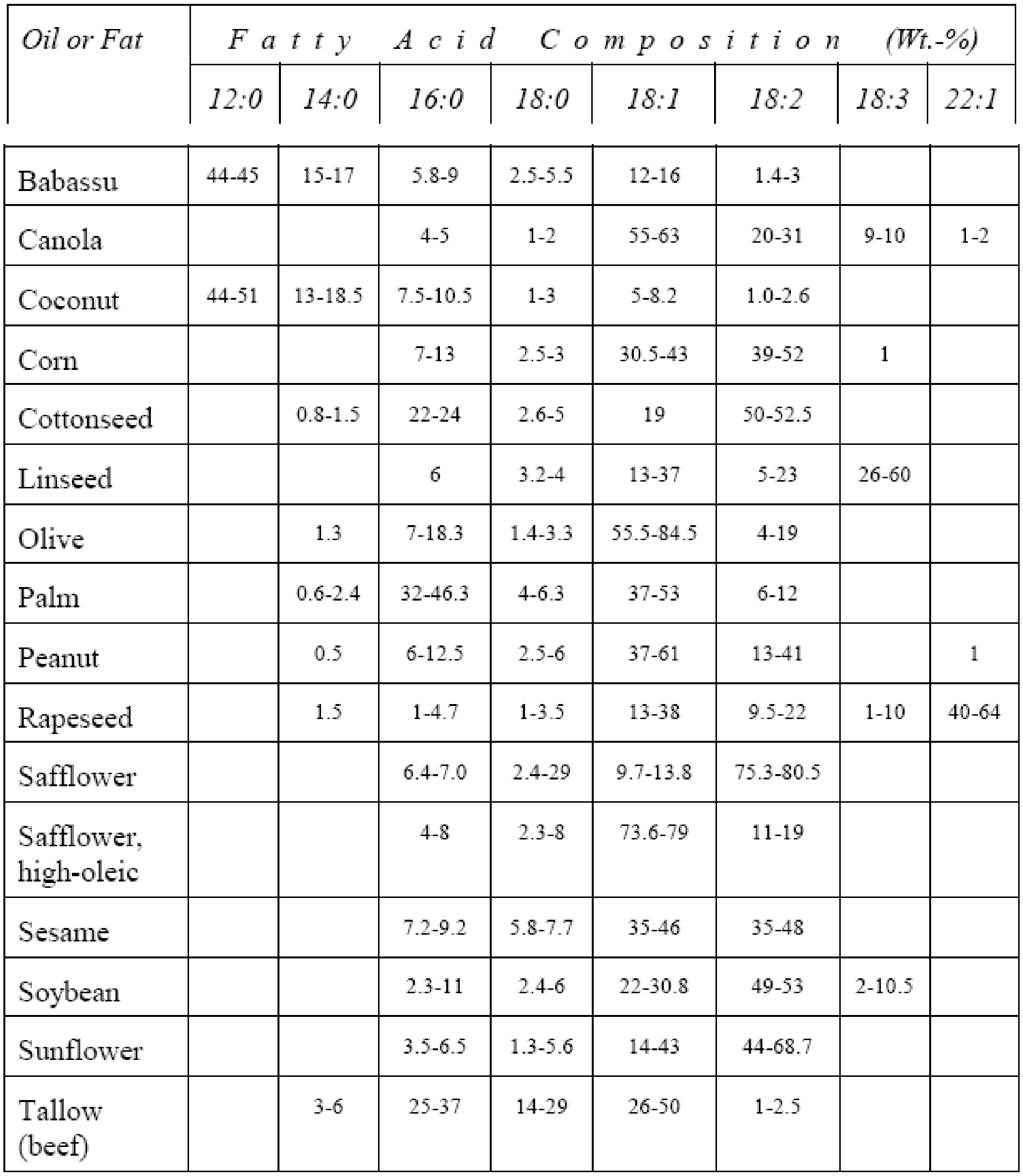
e) See Ref. 27.

f) Cetane number from Ref. 21. Number in parentheses indicates purity (%) of the material used for CN determinations as given by the author. Other CNs given in Ref. 21 not tabulated here (purities in parentheses): ethyl caprate (10:0) 51.2 (99.4); ethylmyristate (14:0) 66.9 (99.3); propyl caprate (10:0) 52.9 (98.0); isopropyl caprate (10:0) 46.6 (97.7); butyl caprylate (8:0) 39.6 (98.7); butyl caprate (10:0) 54.6 (98.6); butyl myristate (14:0) 69.4 (99.0).

g) CN from Ref. 17. CNs (lipid combustion quality numbers) deviating from Ref. 21 as given in Ref. 17: Methyl laurate 54, methyl myristate 72, methyl palmitate 91, methyl stearate 159. contents of various vegetable oils (Table III) are also nearly 90% that of DF2 (*11-13*). The heats of combustion of fatty esters and triglycerides (*14*) as well as fatty alcohols (*15*) have been determined and shown to be within the same range. The suitability of fats and oils as DF results from their molecular structure and high energy content. Long-chain, saturated, unbranched hydrocarbons are especially suitable for conventional DF as shown by the CN scale. The long, unbranched hydrocarbon chains in fatty acids meet this requirement. Saturated fatty compounds have higher CNs. Other observations (*16*) are (i) that (a) double bond(s) decrease(s) quality (therefore, the number of double bonds should be small rather than large, (ii) that a double bond, if present, should be positioned near the end of the molecule, and (iii) no aromatic compounds should be present. A correlation to the statement on double bond position is the comparison of the CNs of methyl oleate (Table I), methyl petroselinate (methyl 6(*Z*)- octadecenoate and methyl *cis*-vaccenate (methyl 11(*Z*)-octadecenoate). The CN of methyl petroselinate (petroselinic acid occurs in less common oils such as parsley and celery seed oils) is 55.4 and that of methyl *cis*-vaccenate (vaccenic acid occurs in fats such as butter and tallow) is 49.5 (*17*).

The most common derivatives of TGs (or fatty acids) for fuels are methyl esters. These are formed by transesterification of the TG with methanol in presence of usually a basic catalyst to give the methyl ester and glycerol (see Figure 1). Other alcohols have been used to generate esters, for example, the ethyl, propyl, and butyl esters. Selected physical properties of vegetable oils and fats as they relate to their use as DF are listed in Table III. For esters these properties are given in Table IV. Also listed in Table III are the ranges of iodine values (centigrams iodine absorbed per gram of sample) of these oils and fats. The higher the iodine value, the more unsaturation is present in the fat or oil. That vegetable oils and their derivatives are suited as DF is shown by their CNs (Table III) which generally are in the range suitable for or close to that of DF.

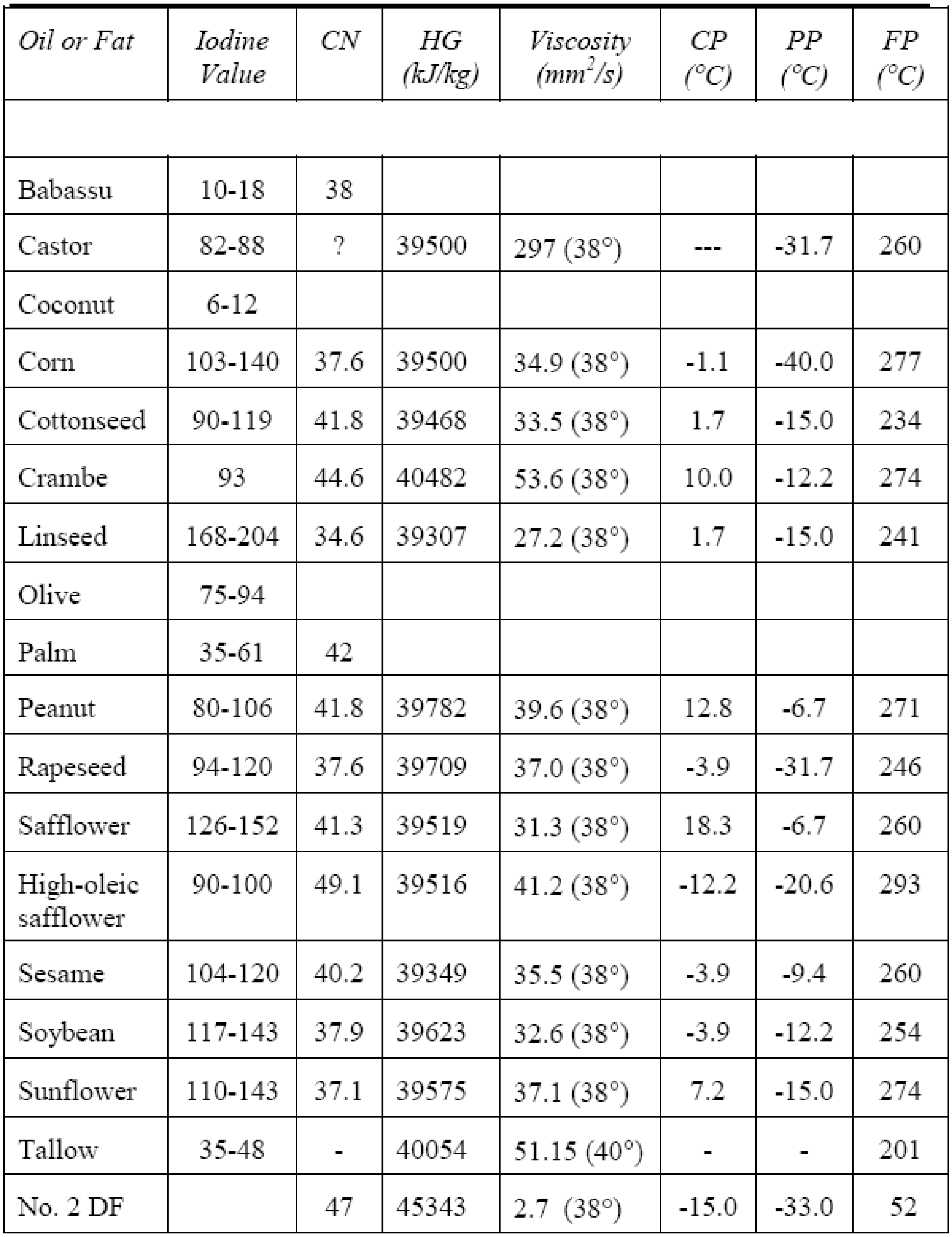
Table II. Major fatty acids (in wt.-%) of some oils and fats used or tested as alternative diesel fuels.a All values combined from Refs. 176 and 181.



Oil or Fat	*Fatty Acid Composition (Wt.-%)*							
	12:0	*14:0*	*16:0*	*18:0*	*18:1*	*18:2*	*18:3*	*22:1*
Babassu	44-45	15-17	5.8-9	2.5-5.5	12-16	1.4-3		
Canola			4-5	1-2	55-63	20-31	9-10	1-2
Coconut	44-51	13-18.5	7.5-10.5	1-3	5-8.2	1.0-2.6		
Corn			7-13	2.5-3	30.5-43	39-52	1	
Cottonseed		0.8-1.5	22-24	2.6-5	19	50-52.5		
Linseed			6	3.2-4	13-37	5-23	26-60	
Olive		1.3	7-18.3	1.4-3.3	55.5-84.5	4-19		
Palm		0.6-2.4	32-46.3	4-6.3	37-53	6-12		
Peanut		0.5	6-12.5	2.5-6	37-61	13-41		1
Rapeseed		1.5	1-4.7	1-3.5	13-38	9.5-22	1-10	40-64
Safflower			6.4-7.0	2.4-29	9.7-13.8	75.3-80.5		
Safflower, high-oleic			4-8	2.3-8	73.6-79	11-19		
Sesame			7.2-9.2	5.8-7.7	35-46	35-48		
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		

a) These oils and fats may contain small amounts of other fatty acids not listed here. For example, peanut oil contains 1.2% 20:0, 2.5 22:0, and 1.3% 24:0 fatty acids (*181*). oleate was 47.2, the lowest of these 18:1 methyl esters. The double bond of methyl petroselinate is closer to one end of the molecule. It also has the longest uninterrupted alkyl chain of these compounds, which may play a role because alkanes have higher CNs as discussed above. This complements the observations in Ref. 16. Another possibility is benzene formation by a disproportionation reaction from cyclohexane, which in turn would arise from cleavage of methyl oleate (*17*). The low CN of benzene would account for the lower CN of methyl oleate. The other 18:1 compounds would not form cyclohexane due to the different positions of the double bond.

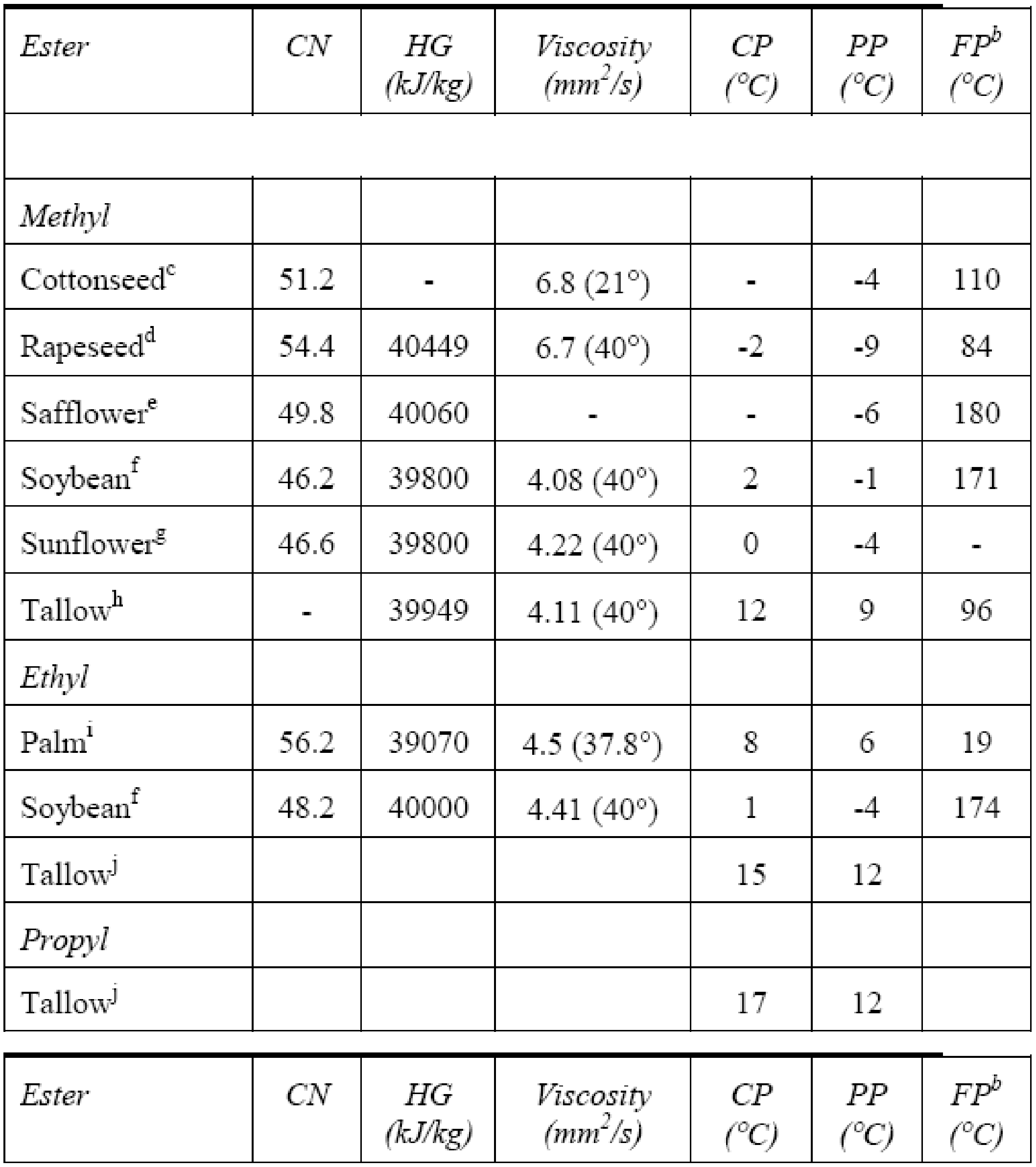
Table III. Fuel-related properties and iodine values of various fats and oils.



Oil or Fat	*Iodine Value*	*CN*	*HG (kJ/kg)*	*Viscosity (mm^2/s)*	*CP (°C)*	*PP (°C)*	*FP (°C)*
Babassu	10-18	38					
Castor	82-88	?	39500	297 (38°)	---	-31.7	260
Coconut	6-12						
Corn	103-140	37.6	39500	34.9 (38°)	-1.1	-40.0	277
Cottonseed	90-119	41.8	39468	33.5 (38°)	1.7	-15.0	234
Crambe	93	44.6	40482	53.6 (38°)	10.0	-12.2	274
Linseed	168-204	34.6	39307	27.2 (38°)	1.7	-15.0	241
Olive	75-94						
Palm	35-61	42					
Peanut	80-106	41.8	39782	39.6 (38°)	12.8	-6.7	271
Rapeseed	94-120	37.6	39709	37.0 (38°)	-3.9	-31.7	246
Safflower	126-152	41.3	39519	31.3 (38°)	18.3	-6.7	260
High-oleic safflower	90-100	49.1	39516	41.2 (38°)	-12.2	-20.6	293
Sesame	104-120	40.2	39349	35.5 (38°)	-3.9	-9.4	260
Soybean	117-143	37.9	39623	32.6 (38°)	-3.9	-12.2	254
Sunflower	110-143	37.1	39575	37.1 (38°)	7.2	-15.0	274
Tallow	35-48	-	40054	51.15 (40°)	-	-	201
No. 2 DF		47	45343	2.7 (38°)	-15.0	-33.0	52

a) Iodine values combined from Refs. 176 and 181. Fuel properties from Ref. 11. All tallow values from Ref. 177 (No CN given in Ref. 177, calcd. cetane index 40.15). The combustion of the glyceryl moiety of the TGs could lead to formation of acrolein and this in turn to the formation of aromatics (*16*), although no acrolein was found in precombustion of TGs (*18*). This may be one reason why fatty esters of vegetable oils perform better in a diesel engine than the oils containing the TGs (*16*). On the other hand, as discussed above, benzene may arise from the oleic moiety also.

Table IV. Fuel-related physical properties of esters of oils and fats.



Ester	*CN*	*HG (kJ/kg)*	*Viscosity (mm^2/s)*	*CP (°C)*	*PP (°C)*	*FP[b] (°C)*
Methyl						
Cottonseed[c]	51.2	-	6.8 (21°)	-	-4	110
Rapeseed[d]	54.4	40449	6.7 (40°)	-2	-9	84
Safflower[e]	49.8	40060	-	-	-6	180
Soybean[f]	46.2	39800	4.08 (40°)	2	-1	171
Sunflower[g]	46.6	39800	4.22 (40°)	0	-4	-
Tallow[h]	-	39949	4.11 (40°)	12	9	96
Ethyl						
Palm[i]	56.2	39070	4.5 (37.8°)	8	6	19
Soybean[f]	48.2	40000	4.41 (40°)	1	-4	174
Tallow[j]				15	12	
Propyl						
Tallow[j]				17	12	

Ester	*CN*	*HG (kJ/kg)*	*Viscosity (mm^2/s)*	*CP (°C)*	*PP (°C)*	*FP[b] (°C)*

Isopropyl						
Soybean	52.6[k]			-9[l]	-12[l]	
Tallow[j]				8	0	
n-Butyl						
Soybean[f]	51.7	40700	5.24 (40°)	-3	-7	185
Tallow[j]				13	9	
2-Butyl						
Soybean[l]				-12	-15	
Tallow[j]				9	0	

a) CN = cetane number; CP = cloud point, PP = pour point, FP = flash point. b) Some flash points are very low. These may be typographical errors in the references or the materials may have contained residual alcohols. c) Ref. 42. d) Ref. 55. e) Ref. 178. f) Ref. 17. g) Ref. 179. h) Ref. 177. i) Ref. 180. j) Ref. 95. k) Ref. 127. l) Ref. 123. However, the high viscosity of the TGs is a major contributing factor to the onset and severity of durability problems when using vegetable oils (*19-20*). The above statements on CNs correlate with the values given in Tables I, III and IV. For example, corresponding to components of conventional DF, saturated fatty compounds show higher CNs than the unsaturated compounds. CNs generally increase with increasing chain length (*21*). The CNs of mixtures are influenced by the nature of their components. Correlation of data from Tables II, III and IV shows that major high- CN components lead to relatively high CNs of vegetable oils or their esters.

In some literature it is emphasized that biodiesel is an oxygenated fuel, thus implying that their oxygen content plays a role in making fatty compounds suitable as DF by “cleaner” burning. However, the responsibility for this suitability rests mainly with the hydrocarbon portion which is similar to conventional DF. Furthermore, the oxygen in fatty compounds may be removed from the combustion process by decarboxylation, which yields incombustible CO2, as precombustion (*18*), pyrolysis and thermal decomposition studies discussed below imply. Also, pure unoxygenated hydrocarbons, like cetane, have CNs higher than biodiesel. Fatty alcohols, whose oxygen content is lower than that of the corresponding esters, also have CNs higher than the corresponding methyl esters as determined with ASTM D613. For example, the CN of 1-tetradecanol is 80.8 (*22*). The CNs of fatty alcohols also increase with chain length with 1-pentanol having a CN of 18.2 (*22*). The CNs of 1-hexadecanol and 1- octadecanol were not determined in this work due to their high melting points (*22*), but ignition delay with the constant volume combustion apparatus (CVCA) vessel discussed below was measured. The CNs of some fatty alcohols were lower when employing the CVCA. Fatty ethers (*23*) were also shown to have CNs higher than the corresponding fatty esters and were suggested as DF extenders. Their main disadvantage compared to esters is their less straightforward synthesis. The CNs of esters correlate well with boiling points (*21*). Quantitative correlations and comparison to numerous other physical properties of fatty esters confirmed that the boiling point gives the best approximation of CN (*22*). ASTM D613 is used in determining CNs. For vegetable oil-derived materials, an alternative utilizes a CVCA (*24*). The amount of material needed for CN determination was reduced significantly with this bomb and it also allows studying materials with high melting points that cannot be measured by ASTM D613. Estimated cetane numbers (ECN) were determined on a revised scale permitting values greater than 100. In this case, the ECN of methyl stearate is 159 and that of methyl arachidate (20:0) is 196 (*24*). The ECNs of other esters were methyl laurate 54, methyl myristate 72, methyl palmitate 91, and methyl oleate 80. ECNs of fatty alcohols were 1-tetradecanol 51, 1-hexadecanol 68, 1-octadecanol 81, oleyl alcohol 51, linoleyl alcohol 44, linolenyl alcohol 41, and palmitoleyl alcohol 46. The ECNs of the TGs trilaurin and trimyristin exceeded 100, while the ECN of tripalmitin was 89, tristearin 95, triolein 45, trilinolein 32, and trilinolenin 23. The term “Lipid Combustion Quality Number” with an accompanying scale was suggested instead of CN to provide for values in excess of CN 100. Often the “cetane index” of a fuel is published and should not be confused with CN. This is an ASTM-approved alternative method for a “non -engine” predictive equation of CN for petroleum distillates (*25* and references therein). Equations for predicting CNs are usually not applicable to non-conventional DFs such as biodiesel or other lipid materials (*26*) . Cetane indices are not given here. A method for estimating the cetane indices of vegetable oil methyl esters has been presented (*27*). Besides CN, heat of combustion (HG) is another property of fatty compounds that is essential in proving the suitability of these materials as DF (*14*). Heats of combustion of fatty compounds, oils and fats as well as their methyl esters are listed in Tables I, III,

and IV. For purposes of comparison, the literature values (*28*) for the heat of combustion of hexadecane (cetane), the high CN standard for conventional DF, is

2559.1 kg-cal (at 20°C). The data in Table I show that the heats of combustion of fatty compounds are similar to those of the compounds of similar CH content (long-chain, unbranched alkanes such as hexadecane) ideally comprising conventional DF. For example, the heat of combustion of methyl palmitate is 2550 kg-cal, that of methyl stearate is 2859 kg-cal, and that of unsaturated methyl oleate is 2828 kg-cal. Even the combined CN and heat data do not suffice to determine the suitability of a material as DF. This is shown by the data in Tables III, which list the viscosities as well as cloud and pour points of numerous vegetable oils and fats. The viscosity of vegetable oils is approximately one order of magnitude greater than that of conventional DF. The high viscosity with resulting poor atomization in the combustion chamber was identified early as a major cause of engine problems such as nozzle coking, deposits, etc. (*14, 29- 31*). Therefore, neat oils have been largely abandoned as alternative DFs. Four possible solutions to the viscosity problem have been evaluated (*32*). The most common applied solution to this problem is the preparation of the methyl esters by transesterification. The three other solutions to the problem of high vegetable oil viscosity are dilution (blending) with conventional DF or other suitable hydrocarbons, microemulsification or (co-solvency), and pyrolysis.

These processes are also discussed below. As shown in Table IV, the methyl esters of oils and fats have viscosities approaching that of DF2.

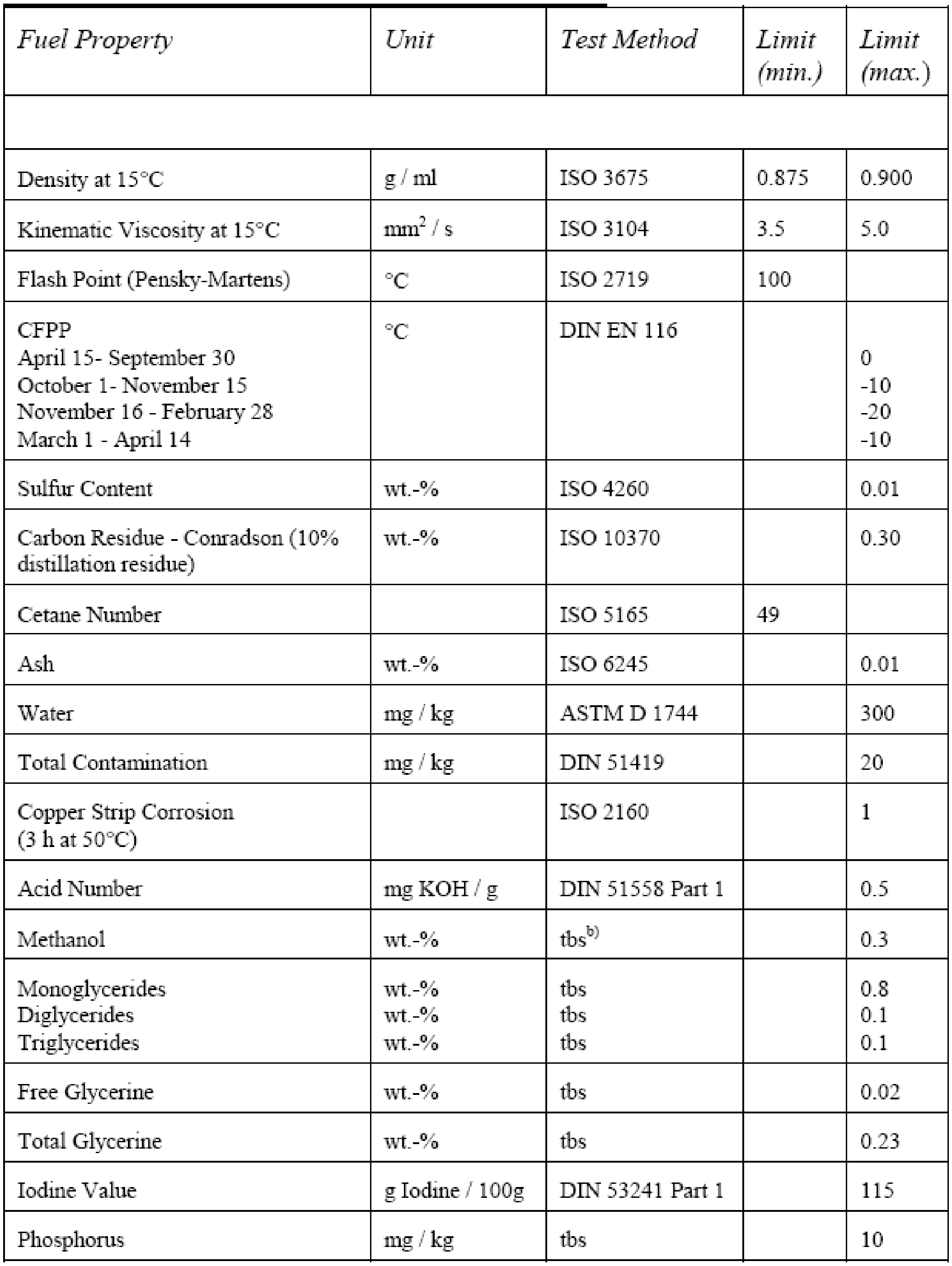
The methyl esters, however, have higher cloud and pour points than their parent oils and fats and conventional DF (Tables III and IV). This is important for engine operation in cold or cooler environments. The cloud point is defined as the temperature at which the fuel becomes cloudy due to formation of crystals which can clog fuel filters and supply lines. The pour point is the lowest temperature at which the fuel will flow. It is recommended by engine manufacturers that the cloud point be below the temperature of use and not more than 6°C above the pour point.

Biodiesel Standards.

Besides favorable economics and environmental and health benefits, the development of reliable standards, which will instill confidence in biodiesel users,

engine manufacturers, and other parties, is a milestone in facilitating commercialization (*6*). Austria (ÖNORM C 1190) and Germany (DIN V 51606) have established similar standards for neat biodiesel. In the United States, an ASTM standard was suggested (*9*). Table V gives the German standard and Table VI lists the proposed ASTM standard. The standards contain specifications particular to biodiesel (for example, glycerol quantitation) which are not given for conventional DF.

Table V. German biodiesel standard DIN V 51606.



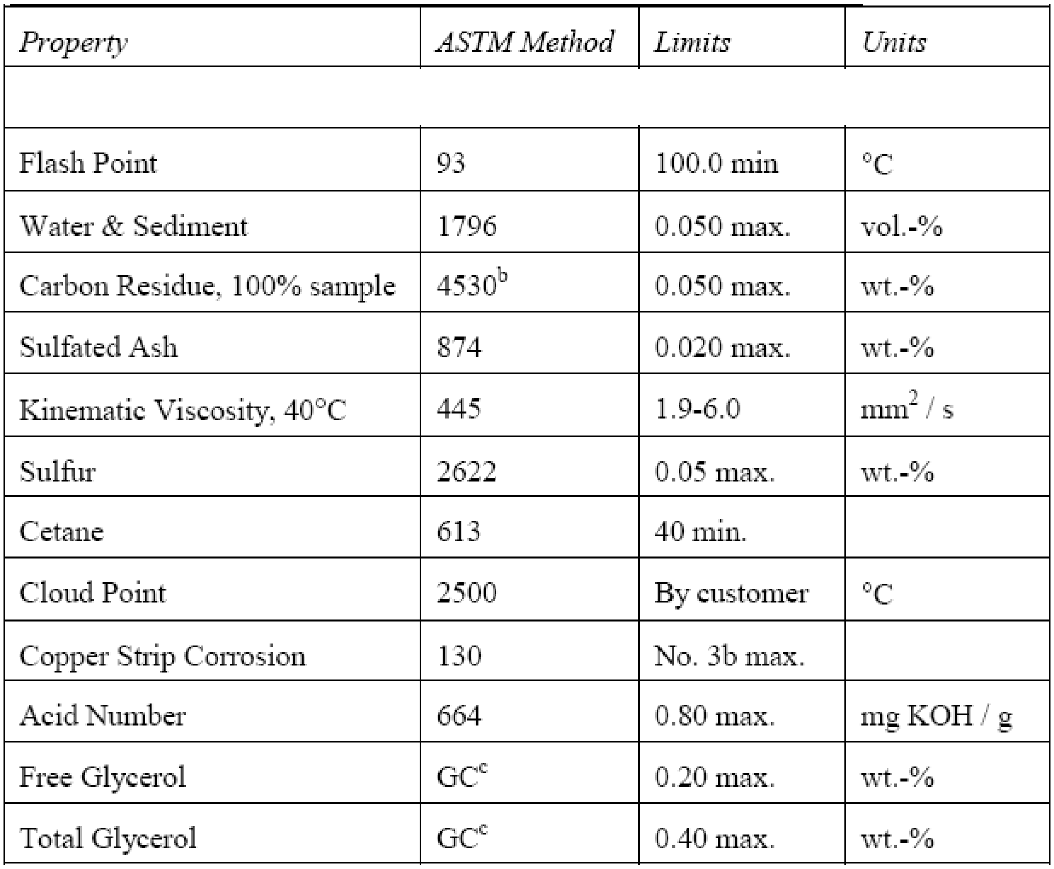
Fuel Property	*Unit*	*Test Method*	*Limit (min.)*	*Limit (max.)*
Density at 15°C	g / ml	ISO 3675	0.875	0.900
Kinematic Viscosity at 15°C	mm^2 / s	ISO 3104	3.5	5.0
Flash Point (Pensky-Martens)	°C	ISO 2719	100	
CFPP April 15- September 30 October 1- November 15 November 16 - February 28 March 1 - April 14	°C	DIN EN 116		 0 -10 -20 -10
Sulfur Content	wt.-%	ISO 4260		0.01
Carbon Residue - Conradson (10% distillation residue)	wt.-%	ISO 10370		0.30
Cetane Number		ISO 5165	49	
Ash	wt.-%	ISO 6245		0.01
Water	mg / kg	ASTM D 1744		300
Total Contamination	mg / kg	DIN 51419		20
Copper Strip Corrosion (3 h at 50°C)		ISO 2160		1
Acid Number	mg KOH / g	DIN 51558 Part 1		0.5
Methanol	wt.-%	tbs[b)]		0.3
Monoglycerides Diglycerides Triglycerides	wt.-% wt.-% wt.-%	tbs tbs tbs		0.8 0.1 0.1
Free Glycerine	wt.-%	tbs		0.02
Total Glycerine	wt.-%	tbs		0.23
Iodine Value	g Iodine / 100g	DIN 53241 Part 1		115
Phosphorus	mg / kg	tbs		10

a) CFPP = Cold-filter plugging point. b) tbs = to be standardized.

The iodine value (IV; see Table III) has been included in the European standards and is based on rapeseed oil as biodiesel feedstock. It is set at

IV = 115, which would exclude soybean oil (neat vegetable oils and their methyl esters have nearly identical IVs) as biodiesel feedstock. The discussion in the previous section, however, shows that

Table VI. Suggested ASTM standard for pure (100%) biodiesel[a].



Property	*ASTM Method*	*Limits*	*Units*
Flash Point	93	100.0 min	°C
Water & Sediment	1796	0.050 max.	vol.-%
Carbon Residue, 100% sample	4530[b]	0.050 max.	wt.-%
Sulfated Ash	874	0.020 max.	wt.-%
Kinematic Viscosity, 40°C	445	1.9-6.0	mm^2 / s
Sulfur	2622	0.05 max.	wt.-%
Cetane	613	40 min.	
Cloud Point	2500	By customer	°C
Copper Strip Corrosion	130	No. 3b max.	
Acid Number	664	0.80 max.	mg KOH / g
Free Glycerol	GC[c]	0.20 max.	wt.-%
Total Glycerol	GC[c]	0.40 max.	wt.-%

a) This specification is the process of being evaluated by ASTM. A considerable

amount of experience exists in the U.S. with a 20 percent blend of biodiesel with 80 percent petroleum-based diesel. Although biodiesel can be used in the pure form, use of blends of over 20 percent biodiesel should be evaluated on a case-by-case basis until further experience is available.

b) Or equivalent ASTM testing method.

c) Austrian (Christina Plank) update of USDA test method (author's note: refers to Refs. 97 and 104). this is not without problems (*33*). Biodiesel from vegetable oils with high amounts of saturates (low IVs) will have a higher CN while the low-temperature properties are poor. Biodiesel from vegetable oils with high amounts of unsaturates (high IVs) will have low CN while the low-temperature properties are better. Thus, CN and low-temperature properties run counter to each other and this must affect IVs for biodiesel standards.

Another argument against inclusion of the IV in biodiesel standards is the observation that different fatty acid compositions give identical IVs (e.g., neat methyl oleate has the same IV as a 1:1 mixture of methyl stearate and methyl linoleate). The IV also does not take into consideration structural factors of fatty compounds as discussed above where the CNs depend on double bond position, etc. Furthermore, once in place, the IV will hinder further research and development. It is possible that plants with desirable highcetane fatty acid profile can be genetically engineered and bred (for example,

improving additives are developed which are highly effective even for high degrees of unsaturation. It was suggested that it appears better to limit the amount of higher unsaturated fatty acids (e.g. linolenic acid) than to limit the degree of unsaturation by means of the IV (*34*). Note that soybean oil, rapeseed oil, and canola oil (low-erucic rapeseed oil) have very similar 18:3 fatty acid content (Table II), which is the most problematic in the formation of engine deposits through polymerization. However, linseed oil methyl ester (high 18:3 content and IV) satisfactorily completed 1000 hours of testing in a DI engine while neat linseed oil caused the engine to fail (*35* and references therein). These observations make the IV even more debatable. Since most esters have higher CNs than neat vegetable oils and conventional DF, the esters could accommodate higher CNs than the minimum of 40 given in the ASTM standard for conventional DF. For example, the lowest reported CN for methyl soyate is 46.2 (see Table IV). The German biodiesel standard includes the so-called Cold-Filter Plugging Point (CFPP) that pertains to the low-temperature flow properties of biodiesel. This low temperature property test is used in Europe, South America, and the Pacific rim. In North America, a more stringent test, the Low-Temperature Flow Test (LTFT), is used and specified by ASTM D4539. Although the LTFT is more useful in evaluating low temperature flow properties, ASTM requires only specification of cloud point for certification.

IV. Combustion Chemistry.

(Emissions, Engine problems and deposits)

Besides the properties discussed above and accompanying operational problems, the question of combustion, emissions, and engine deposits of biodiesel fuels is of extreme significance and will be discussed here. Generally, similar types of compounds are observed in the exhaust emissions of conventional DF and vegetable oil-derived fuels. This is additional proof of the suitability of fatty compounds as DF because there presumably exist similarities in their combustion behavior. Emissions from any kind of engine are the result of the preceding combustion within in the engine. The combustion process, in relation to the properties of the fuel, and its completeness are responsible for any problems associated with the use of biodiesel, such as formation of deposits, etc. To understand the formation of emissions and deposits, and possibly direct the combustion to suppress undesirable emissions and deposits, it is essential to study the combustion of the fuel. Ideally, the products of complete combustion of hydrocarbons are carbon dioxide (CO2) and water according to the equation (shown for alkanes (saturated hydrocarbons)):

$$CnH_2n+2 + (1.5n + 0.5)O_2 \text{ ® } nCO_2 + (n + 1)H_2O$$

Combustion in a diesel engine occurs mainly through a diffusion flame and is therefore incomplete. This causes the formation of partially oxidized materials such as carbon monoxide (CO), other oxygenated species (aldehydes, etc.), and hydrocarbons. In the case of biodiesel, liberation of CO2 (decarboxylation), as indicated above, from the ester moiety of the triglyceride or methyl ester occurs besides combustion formation of CO2 from the hydrocarbon portions of biodiesel. The formation of CO2, an incombustible compound despite its high oxygen content (although mistakenly assumed by some that it can serve as a combustion enhancer because of its high oxygen content), shows that one has to be judicious in choosing oxygenated compounds as combustion enhancers because the combustion-enhancing properties will depend on the nature of the oxygen (bonding, etc.) in those compounds. Therefore, the higher oxygen content of biodiesel does not necessarily imply improved combustion compared to conventional DF because of removal of this oxygen from the combustion process by decarboxylation, but CO2 may contribute to combustion in other ways.

Exhaust emissions observed in the combustion of conventional DF and biodiesel are smoke, particulates (particulate matter), polyaromatic hydrocarbons (PAHs), hydrocarbons, CO, and oxides of nitrogen (NOx; also referred to as nitrous oxides, or nitrogen oxides). An important difference are sulfur-containing emissions which are not formed from biodiesel due to its lack of sulfur. Note that rapeseed contains low amounts of sulfur but variations such as canola have not only lower erucic acid content but also reduced sulfur (*36*). The composition of particulate matter has been studied for conventional diesel fuels (*37*). Particulates from conventional DF have a high carbon to hydrogen ratio of approximately 10:1 (*38*). Thus, particulates are mainly carbon in forms of crystallites. As temperatures decrease below 500°C, the particles are coated with adsorbed and condensed species, which include unburned hydrocarbons, various oxygenated hydrocarbons, PAHs and nitrogen dioxide (in case of conventional DF, also sulfur containing species). With rapeseed methyl ester as fuel in DI engines, particulate matter showed large amounts of volatile and extractable compounds adsorbed on the soot, which caused the particulate emissions to be higher than with conventional DF (*39*). PAHs are compounds composed of fused aromatic rings that may carry alkyl substituents such as a methyl group. They are of concern because many of them are known carcinogens. Hydrocarbons represent a broad category of compounds including hydrocarbons and oxygenated species such as aldehydes, ketones, ethers, etc. Nitrogen oxides (NOx) arise by the reaction of nitrogen and oxygen from air at an early stage in the combustion process (*40*). NOx emissions are difficult to control because such techniques may increase other emissions or fuel consumption (*8*).

Emissions of Neat Vegetable Oil Fuel

While neat vegetable oils are competitive with conventional DF in some emission categories, problems were identified for other kinds of emissions. For example, it was shown that PAH emissions were lower for neat vegetable oils, especially very little amounts of alkylated PAHs, which are common in the emissions of conventional DF (*41*). Besides higher NOx levels (*42*), aldehydes are reported to present problems with neat vegetable oils. Total aldehydes increased dramatically with vegetable oils (*42*). Formaldehyde formation was also consistently higher than with DF2. It was reported that component TGs in vegetable oils can lead to formation of aromatics via acrolein (CH2=CH-CHO) from the glycerol moiety (*16*). Another author observed significantly lower emissions of C3 aldehydes (for example, acrolein) for methyl esters of rapeseed oil than for the oil itself (*43*). Another study (*44*) attributes increased emissions of aldehydes and ketones when using vegetable oils as fuels to the formation of acidic water during decomposition of the oils. This acidic water could be an indication for the formation of short-chain oxygenates which likely ignite poorly compared to the long-chain carbon-rich fatty compounds.

Engine Problems with Neat Vegetable Oil Fuel

Most references in this section report that, at least in short-term trials, neat oils gave satisfactory engine performance and power output, often equal to or even slightly better than conventional DF. However, vegetable oils cause engine problems. This was recognized in the early stages of renewed interest in vegetable oil-based alternative DFs. Studies on sunflower oil as fuel noted coking of injector nozzles, sticking piston rings, crankcase oil dilution, lubricating oil contamination, and other problems (*29-31*). These problems were confirmed and studied by other authors (*45-52*). A test for external detection of coking tendencies of vegetable oils was reported (*53*). The causes of these problems were attributed to the polymerization of TGs via their double bonds which leads to formation of engine deposits as well as the low volatility and high viscosity with resulting poor atomization patterns. An oxidative free-radical mechanism was suggested as governing TG polymerization in lubricating oil contamination when using sunflower oil as fuel (*54*). Fumigation with propane was studied as a means to reduce injector coking (*55*). The engine problems have caused neat vegetable oils to be largely abandoned as alternative DF and lead to the research on the aforementioned four solutions (*32*).

Emissions of esters

Generally, most emissions observed for conventional DF are reduced when using esters. NOx emissions are the exception. In an early paper reporting emissions with methyl and ethyl soyate as fuel (*20*), it was found that CO and hydrocarbons were reduced but NOx were produced consistently at a higher level than with the conventional reference DF. The differences in exhaust gas temperatures corresponded with the differences in NOx levels. Similar results were obtained from a study on the emissions of rapeseed oil methyl ester (*43*). NOx emissions were slightly increased, while hydrocarbon, CO, particulate and PAH emissions were in ranges similar to the DF reference. As mentioned above, the esters emitted less aldehydes than the corresponding neat rapeseed oil. Unrefined rapeseed methyl ester emitted slightly more aldehydes than the refined ester, while the opposite case held for PAH emissions. A 31% increase in aldehyde and ketone emissions was reported when using rapeseed methyl ester as fuel, mainly due to increased acrolein and formaldehyde, while hydrocarbons and PAHs were significantly reduced, NOx increased slightly, and CO was nearly unchanged (*56*). The study on PAH emissions (*41*), where also the influence of various engine parameters was explored, found that the PAH emissions of sunflower ethyl ester were situated between DF and the corresponding neat vegetable oil. Reduced PAH emissions may correlate with the reduced carcinogenity of particulates when using rapeseed methyl ester as fuel (*57*). The general trend on reduced emissions except NOx was confirmed by later studies (*58*), although some studies report little changes in NOx (*59*-*60*). In a DI engine, sunflower methyl ester produced equal hydrocarbon emissions but less smoke than a 75:25 blend of sunflower oil with DF (*61*). Using a diesel oxidation catalyst (DOC) in conjunction with soy methyl ester was reported to be a possible emissions reduction technology for underground mines (*62*). Soy methyl esters were reported to be more sensitive towards changes in engine parameters than conventional DF (*63*).

Precombustion of Triglycerides

As discussed, every DF, conventional or vegetable oil-based, experiences an ignition delay, which is the basis of CN measurements. The fuel passes through a temperature and pressure gradient directly after injection but before combustion begins. Chemical reactions already occur in this precombustion phase. In an initial study (*64*), the unsaturated TGs triolein, trilinolein, and trilinolenin were studied at temperatures up to 400°C in air or N2 in a reactor simulating conditions in a diesel engine. The compounds arising in this phase were fatty acids of different chain lengths (some even longer than those in the parent fatty acids), various aliphatic hydrocarbons, and smaller amounts of other compounds such as aldehydes. The parent acids were the most prominent compounds in the precombustion mixture. Component patterns were largely independent of the starting material and reaction conditions. In a second study (*65*), tristearin and tripalmitin were studied besides the three unsaturated TGs at temperatures of 450°C in air and N2. Presumably due to the higher temperature, different component patterns were observed. Besides mainly unsaturated aliphatic hydrocarbons and unsaturated aldehydes, various aromatics, including benzene, toluene, compounds with unsaturated side chains, and polyaromatic hydrocarbons were detected. The atmosphere (air or N2) had considerable influence on product formation. The number of components was less for samples of tripalmitin, tristearin and triolein for reactions under N2 than under air while this finding was reversed for trilinolein and trilinolenin. No fatty acids, glycerol or acrolein (as decomposition product of glycerol) were detected. Extensive decarboxylation occurred, showing that the oxygen in biodiesel does not necessarily contribute to its combustion as an oxidizer. The compounds identified are also found in the exhaust emissions of engines running on conventional DF. It is therefore necessary to influence not only combustion but also precombustion to improve the combustion properties and emissions of biodiesel.

Cetane Improvers.

Various compounds such as alkyl nitrates are used as cetane enhancing additives in conventional DF (*66*). Few studies on such compounds in biodiesel exist. One paper reports (*67*) that in a turbulence combustion chamber and at an intake air temperature of 105°C, 8% hexyl nitrate in vegetable oils (cottonseed, rape, palm) was necessary to exhibit the same ignition delay as conventional DF. The use of nitrate esters of fatty acids as cetane improvers in DF was reported in a patent (*68*).

Dilution of vegetable oils with conventional diesel fuel

Dilution is an additional possible solution to the viscosity problem of vegetable oils as discussed above. Results with this technology have been mixed and engine problems similar to those found with neat vegetable oils as fuels were observed here also. A model on vegetable oil atomization showed that blends of DF2 with vegetable oil should contain from 0 to 34% vegetable oil if proper atomization was to be achieved (*69*). A 75:25(vol-%) petrodiesel / sunflower oil blend had a viscosity of 4.88 mm2/s at 40°C, exceeding the ASTM maximum value of 4.0. The blend was not recommended for long-term use in the DI diesel engine (*64*). A 75:25 (vol-%) petrodiesel / high-oleic safflower oil blend with a viscosity of 4.92 mm2/s passed the 200 hr EMA (Engine Manufacturers

Association) test. The different results were attributed to the degree of unsaturation of the respective vegetable oil (*32*). The more unsaturated oil (sunflower) that accumulates in the crankcase and hot engine parts tends to oxidize and polymerize due to its reactivity. Accumulation of such products in the lube oil could lead to lubricant thickening. A lube oil change is called for by the EMA test after 100 hr and at that time the viscosity of the lube oils had not varied greatly in either test. Other reports include successfully using a 70:30 winter rapeseed oil / DF1 mixture (*47*) or blends of £ 15% rapeseed oil with DF2 (*71*), and an 80:20 DF2 / safflower oil blend with reduced CO and hydrocarbon emissions (*72*). A 75:25 DF / crude sunflower oil blend produced greatest solids contamination in the lubricating oil (*49*) similar to the results mentioned above, while another report mentions satisfactory performance of a 75:25 DF / sunflower oil blend (*61*). In early studies on sunflower oil, 80:20 DF / sunflower oil blends (*31*) were run for prolonged periods of time before exhaust smoke increased due to carbon build-up or power loss ensued. Another engine, due to inadequate atomization, showed more of the engine problems associated with neat vegetable oils.

The CP of a 50:50 DF2/ high-oleic safflower oil was -13°C and the PP was -15°C, and similar blends with high-linoleic safflower oil had CP -13°C and PP -15°C or winter rapeseed oil had CP -11°C and PP -18°C (*55*). A 50:50 blend of Stoddard solvent (a dry-cleaning fluid, viscosity 0.95 mm2/s, estimated CN 50, heat of combustion 46,800 kJ/kg, CP < -16°C, PP < -35°C, flash point 42.2°C) with soybean oil gave low CP (-

18.9°C) and PP (-31.7°C) but performed less well in a diesel engine than DF2 (*73*).

Transesterification.

The conversion of component TGs to simple alkyl esters (transesterification) with various alcohols reduces the high viscosity of oils and fats (see also Figure 1). Base catalysis of the transesterification with reagents such as sodium hydroxide is preferred over acid catalysis because the former is more rapid (*74*). Transesterification is a reversible reaction. The transesterification of soybean oil with methanol or 1-butanol proceeded with pseudo-first order or second order kinetics, depending on the molar ratio of alcohol to soybean oil (30:1 pseudo-first order, 6:1 second order; NaOBu catalyst) while the reverse reaction was second order (*75*). Methyl esters are the most "popular" esters for several reasons. One reason is the low price of methanol compared to other alcohols. Generally, esters have significantly lower viscosities than the parent oils and fats (Tables III and IV). Accordingly, they improve the injection process and ensure better atomization of the fuel in the combustion chamber. The effect of the possible polymerization reaction is also decreased. The advantages of alkyl esters were noted early in studies on the use of sunflower oil and its esters as DF (*29-31*). Another advantage of the esters is possibly more benign emissions, for example, with the removal of glycerol (which is separated from the esters) the formation of undesirable acrolein may be avoided, as discussed above. These reasons as well as ease and rapidity of the process are responsible for the popularity of the transesterification method for reducing the viscosity-related problems of vegetable oils. The popularity of methyl esters has contributed to the term “biodiesel” now usually referring to vegetable oil esters and not neat vegetable oils. In the early studies on sunflower esters, no transesterification method was reported (*29-31*). Another early study used H_2SO_4 as the transesterification catalyst (*76*). It was then shown, however, that in homogeneous catalysis, alkali catalysis is a much more rapid process than acid catalysis in the transesterification reaction (*74*, *77*). At 32°C, transesterification was 99% complete in 4 h when using an alkaline catalyst (NaOH or NaOMe). At 60°C and a molar ratio alcohol:oil of at least 6:1 and with fully refined oils, the reaction was complete in 1 h to give methyl, ethyl, or butyl esters. The reaction parameters investigated were molar ratio of alcohol to vegetable oil, type of catalyst (alkaline vs. acidic), temperature, reaction time, degree of refinement of the vegetable oil, and effect of the presence of moisture and free fatty acid. Although the crude oils could be transesterified, ester yields were reduced because of gums and extraneous material present in the crude oils. Besides sodium hydroxide and sodium methoxide, potassium hydroxide is another common transesterification catalyst. Both NaOH and KOH were used in early work on the transesterification of rapeseed oil (*78*). Recent work on producing biodiesel (suitable for waste frying oils) employed KOH. With the reaction conducted at ambient pressure and temperature, conversion rates of 80 to 90% were achieved within 5 minutes, even when stoichiometric amounts of methanol were employed (*79*). In two steps, the ester yields are 99%. It was concluded that even a free fatty acid content of up to 3% in the feedstock did not affect the process negatively and phosphatides up to 300 ppm phosphorus were acceptable. The resulting methyl ester met the quality requirements for Austrian and European biodiesel without further treatment. In a study similar to previous work on the transesterification of soybean oil (*74, 77*), it was concluded that KOH is preferable to NaOH in the transesterification of safflower oil of Turkish origin (*80*). The optimal conditions were given as 1 wt-% KOH at 69±1°C with a 7:1 alcohol : vegetable oil molar ratio to give 97.7% methyl ester yield in 18 minutes.

Patents.

Most patents dealing with transesterification emphasize the engineering improvement of the process. Using patented procedures, a transesterification process permitting the recovery of all byproducts such as glycerol and fatty acids has been described (*81*). The use of alkaline catalysts is also preferred on the technical scale, as is documented by patents using sodium hydroxide, sodium methoxide, and potassium hydroxide (*82*-*85*). Different esters of C9-24 fatty acids were prepared with Al2O3- or Fe2O3- containing catalysts (*86*). A sulfonated ion exchange catalyst was preferred as catalyst in the esterification of free fatty acids (*87*).

Other procedures.

Besides the methods discussed here, other catalysts have been applied in transesterification reactions (*88*). Some recently studied variations of the above methods as applied to biodiesel preparation are briefly discussed here. Methyl and ethyl esters of palm and coconut oils were produced by alcoholysis of raw or refined oils using boiler ashes, H2SO4 and KOH as catalysts (*89*). Fuel yields >

90% were obtained using alcohols with low moisture content and EtOH-H2O azeotrope. Instead of using the extracted oil as starting material for transesterification, sunflower seed oils were transesterified in situ using macerated seeds with methanol in the presence of H2SO4 (*90*). Higher yields were obtained than from transesterification of the extracted oils. Moisture in the seeds reduced the yield of methyl esters. The cloud points of the *in situ* prepared esters appear slightly lower than those prepared by conventional methods.

Another study (*91*) reported the synthesis of methyl or ethyl esters with 90% yield

by reacting palm and coconut oil from the press cake and oil mill and refinery waste with MeOH or EtOH in the presence of easily available catalysts such as ashes of the waste of these two oilseeds (fibers, shell, husk), lime, zeolites, etc. Similarly, it was reported that the methanolysis of vegetable oils is catalyzed by ashes from the combustion of plant wastes such as coconut shells or fibers of a palm tree that contain K2CO3 or Na2CO3 as catalyst (*92*). Thus the methanolysis of palm oil by refluxing 2 h with MeOH in the presence of coconut shell ash gave

96-98% methyl esters containing only 0.8-1.0% soap. The ethanolysis of vegetable oils over the readily accessible ash catalysts gave lower yields and less pure esters than the methanolysis.

Several catalysts (CaO, K2CO3, Na2CO3, Fe2O3, MeONa, NaAlO2, Zn, Cu, Sn, Pb, ZnO, and *Dowex 2X8* (anion exchange resin)) were tested (mainly at 60-63°C) for catalytic activity in the transesterification of low-erucic rapeseed oil with MeOH (*93*). The best catalyst was CaO on MgO. At 200°C and 68 atm, the anion exchange resin produced substantial amounts of fatty methyl esters and straight-chain hydrocarbons. An enzymatic transesterification method utilizing lipases and methanol, ethanol, 2- propanol, and 2-methyl-1-propanol as alcohols gave alkyl esters of fatty acids (*94*, *95*). This method eliminates product isolation and waste disposal problems.

Analysis of Transesterification Products.

Hardly any chemical reaction, including transesterification, ever proceeds to completion. Therefore, the transesterified product, biodiesel, contains other materials. There are unreacted TGs and residual alcohol present as well as partially reacted mono- and diglycerides and glycerol co-product. Glyceride mixtures were analyzed by TLC / FID (thin-layer chromatography / flame ionization detection) (*96*), which was also used in the studies on the variables affecting the yields of fatty esters from transesterified vegetable oils (*74*). Analysis of reaction mixtures by capillary GC determined esters, triglycerides, diglycerides and mono glycerides in one run (*97*). Free glycerol was determined in transesterified vegetable oils (*98*) Besides analyzing esters for sterols (*99-101*), which are often minor components in vegetable oils, and different glycerides (*102-103*), recently the previous GC method (*97*) was extended to include analysis of glycerol in one GC run (*104*). In both papers (*97, 104*), the hydroxy groups of the glycerides and glycerol were derivatized by silylation with *N*-methyl-*N*-trimethylsilyltrifluoroacetamide. A simultaneous analysis of methanol and glycerol was recently reported (*105*). Other authors, using GC to determine the conversion of TGs to methyl esters, gave a correlation between the bound glycerol content determined by TLC/FID and the acyl conversion determined by GC (*106*). Glycerol has also been detected by high performance liquid chromatography (HPLC) using pulsed amperometric detection, which offers the advantage of being more sensitive than refractometry and also suitable for detection of small amounts of glycerol for which GC may not be suitable (*107*).

Recently, an alternative method for determining the methyl ester content based on viscosity measurements, which agreed well with GC determinations, was reported (*108*). The method is reportedly more rapid than GC and therefore especially suitable for process control.

Properties of Vegetable Oil Esters.

Early 100 hr tests on transesterified sunflower oil initially showed the improved properties of esters for use in a diesel engine by reducing the viscosity of vegetable oils and solving engine problems (*29-31*).

Table IV compares the essential fuel properties of some esters. In all cases the viscosity decreases dramatically and is only about twice that of DF2. The CNs are also improved, now being higher than that of DF2. The methyl and ethyl esters of soybean oil generally compared well with DF2 with the exception of gum formation which leads to problems with fuel filter plugging (*20*). Another study reports that methyl esters of rapeseed and high-linoleic safflower oils formed equal and lesser amounts of deposits than a DF standard while the methyl ester of high-oleic safflower oil formed more deposits (*55*). Methyl and ethyl esters of soybean oil were evaluated by 200 hr EMA (Engine Manufacturers Association) engine tests and compared to DF2. Engine performance with soybean esters differed little from that with DF. In that work, also a slight power loss was observed, together with an increase in fuel consumption due to the lower heating values of the esters. The emissions for the two fuels were similar, with the exception of NOx which are higher for the esters as discussed above. Engine wear and fuel-injection system tests showed no abnormal characteristics for any of the fuels. Deposit amounts in the engine were comparable, however, the methyl ester showed greater varnish and carbon deposits on the pistons. Operating DI engines with neat soybean oil esters under certain conditions produced lubricating oil dilution which was not observed with an IDI engine (*109*). Lubricating oil dilution was estimated by Fourier-

Transform infrared spectroscopy combined with a fiber optic probe when using rapeseed methyl ester as a fuel (*110*). The carbonyl absorption was used for quantitation.

Low-temperature Properties.

As discussed above, one of the major problems associated with the use of biodiesel, including methyl esters, is its poor low-temperature properties, documented by relatively high cloud point (CP) and pour point (PP) (Tables III and IV) . CPs and PPs of vegetable oils and their esters are a result of these materials being mixtures of various compounds. For example, as seen in Table I, saturated fatty compounds have significantly higher melting points than unsaturated fatty compounds and in a mixture they therefore crystallize at higher temperature than the unsaturates. The CP, which occurs at a higher temperature than the PP, is the temperature at which a fatty material becomes cloudy due to formation of crystals and saturates solidifying. These solids can clog fuel lines. With decreasing temperature, more material solidifies and the compound approaches the pour point, at which it will no longer flow. Besides CP (ASTM D2500) and PP (ASTM D97), two test methods exist for examining the low-temperature properties of diesel fuel (as discussed briefly in the section on "Biodiesel Standards"), the Low-Temperature Flow Test (LTFT; used in North America; ASTM D4539) and the Cold-Filter Plugging Point (CFPP; used in Europe). These methods have also been used to evaluate biodiesel. Low-temperature filterability tests are necessary because they correlate better with operability tests than CP or PP (*111*). Recent results showed that for fuel formulations containing at least 10% methyl esters, both LTFT and CFPP are linear functions of the CP (*112*). Additional statistical analysis showed a strong 1:1 correlation between LTFT and CP (*112*). Five possible solutions to the low-temperature problems of esters have been investigated: blending with conventional DF, additives, branched-chain esters, bulky substituents in the chain, and winterization. Blending of esters is currently the preferred method for improving low-temperature properties and is discussed in the next section.

Numerous additives have been synthesized and reported mainly in the patent literature, which allegedly have the effect of lowering CP and PP. These additives are usually a variety of viscosity-modifying polymers such as carboxy-containing interpolymers (*113*), styrene-maleic anhydride copolymer (*114*), polymethacrylates (*114-115*), polyacrylates (*113-115*), nitrogen-containing polyacrylates (*113*), poly[alkyl (meth)acrylates] (*116*), ethylene-vinyl ester (acetate) copolymers (*117-120*), fumarate or itaconate polymers and copolymers (comb polymers) (*117-118*), polyoxyalkylene compounds (*113*). Polar nitrogen compounds (*117*) have also been reported as additives. Similar additives have also been tested for conventional diesel fuel (*7*). The beneficial effect of some additives appears to be limited, however, because they more strongly affect the PP than the CP, and the CP is more important than the PP for improving low-temperature flow properties (*121*). Another route is the synthesis of fatty compound-derived materials with bulky substituents in the chain (*122*). The idea associated with these materials is that the bulky substituents would destroy the harmony of the solids which are usually oriented in one direction. However, these materials had only slight influence on the CP and PP. The use of secondary alcohols in the transesterification reaction provides branched chain esters such as isopropyl and 2-butyl instead of the methyl esters (*95, 123)* . These esters showed a lower crystallization onset temperature (TCO) as determined by differential scanning calorimetry (DSC) for the isopropyl esters of SBO by 7-11°C and for the 2-butyl esters of SBO by 12-14°C (*123*). The CPs and PPs were also lowered by the branched-chain esters. However, economics would only permit the isopropyl soyate appear attractive as branched-chain ester, raising the price of a biodiesel blend containing 30% isopropyl soyate by $0.02/L while lowering the TCO by 15°C. In the winterization method (*121, 124*), solids formed during cooling of the vegetable oil are removed by filtration, thus leaving a mixture of more unsaturated fatty compounds with lower CP and PP. This procedure can be repeated to achieve the desired CPs and PPs. Saturated fatty compounds, which have higher CNs, are among the major compounds removed by winterization. Thus the CN of the biodiesel decreases. The TCO of typical methyl soyate was lowered from 3.7°C to -7.1°C by winterization (*124*), but the yield was low (26%). Winterization of low-palmitate methyl soyate, however, gave a TCO of -6.5°C with a yield of 86%. Winterization of typical methyl soyate diluted in hexane gave a TCO of -5.8°C with 77% yield. In the latter method, crystal formation was greatly affected by the nature of the solvent, with acetone and chloroform being unsuitable for winterization. In a paper on fatty acid derivatives for improving ignition and low-temperature properties (*125*), it was reported that tertiary fatty amines and amides were effective in enhancing the ignition quality of biodiesel without negatively affecting the low temperature properties. In that paper, saturated fatty alcohols of chain lengths C12 and greater increased the PP substantially. Ethyl laurate was weakly decreased the PP.

Blending of Esters.

Blending conventional DF with esters (usually methyl esters) of vegetable oils is

presently the most common form of biodiesel. The most common ratio is 80% conventional diesel fuel and 20% vegetable oil ester (also termed “B20,” indicating the 20% level of biodiesel; see also list of biodiesel demonstration programs in Ref. 6). There have been numerous reports that significant emission reductions are achieved with these blends. No engine problems were reported in larger-scale tests with, for example, urban bus fleets running on B20. Fuel economy was comparable to DF2, with the consumption of biodiesel blend being only 2-5% higher than that of conventional DF. Another advantage of biodiesel blends is the simplicity of fuel preparation which only requires mixing of the components. Ester blends have been reported to be stable, for example, a blend of 20% peanut oil with 80% DF did not separate at room temperature over a period of 3 months (*126*). Stability was also found for 50:50 blends of peanut oil with DF (*43*). A few examples from the literature may illustrate the suitability of blends of esters with conventional DF in terms of fuel properties. In transient emission tests on an IDI engine for mining applications (*62*), the soybean methyl ester used had a CN of 54.7, viscosity 3.05 mm2/s at 40°, and a CP of -2°C. The DF2 used had CN 43.2, viscosity 2.37 mm2/s at 40° and a CP of -21°C. A 70:30 DF2 : soybean methyl ester blend had CN 49.1, viscosity 2.84 mm2/s at 40°C, and a CP of -17°C. The blend had 4% less power and 4% higher fuel consumption than the DF2, while the neat esters had 9% less power and 13% higher fuel consumption than DF2. Emissions of CO and hydrocarbons as well as other materials were reduced. NOx emissions were not increased here,

although higher NOx emissions have been reported for blends (DI engines) (*43, 59*). Irregularities compared to other ester blends were observed when using blends of the isopropyl ester of soybean oil with conventional DF (*127*). Deposits were formed on the injector tips. This was attributed to the isopropyl ester containing 5.2 mole-% monoglyceride which was difficult to separate form the isopropyl ester.

Microemulsification.

The formation of microemulsions (co-solvency) is one of the four potential solutions for solving the problem of vegetable oil viscosity. Microemulsions are defined as transparent, thermodynamically stable colloidal dispersions in which the diameter of the dispersed-phase particles is less than one-fourth the wavelength of visible light. Microemulsion-based fuels are sometimes also termed “hybrid fuels,” although blends of conventional diesel fuel with vegetable oils have also been called hybrid fuels (*128*). Some of these fuels were tested in engines including the 200 hr EMA test. A microemulsion fuel containing soybean oil, methanol, 2-octanol, and a cetane enhancer was the cheapest vegetable oil-based alternative diesel fuel ever to pass the EMA test. The components of microemulsions can be conventional DF, vegetable oil, an alcohol, a surfactant, and a cetane improver. Water (from aqueous ethanol) may also be present in order to use lower-proof ethanol (*129*), thus increasing water tolerance of the microemulsions is important.

Microemulsions are classified as non-ionic or ionic, depending on the surfactant present. Microemulsions containing, for example, a basic nitrogen compound are termed ionic while those consisting, for example, only of a vegetable oil, aqueous ethanol, and another alcohol, such as 1-butanol, are termed non-ionic. Non-ionic microemulsions are often referred to as detergentless microemulsions, indicating the absence of a surfactant. Viscosity-lowering additives were usually with C1-3alcohols length while longerchain alcohols and alkylamines served as surfactants. *n*-Butanol (CN 42) was claimed to be the alcohol most suitable for microemulsions, giving microemulsions more stable and lower in viscosity than those made with methanol or ethanol (*130*). Microemulsions with hexanol and an ionic surfactant had no major effect on gaseous emissions or efficiency. Emulsions were reported to be suitable as diesel fuels with viscosities close to that of neat DF. No additional engine tests were reported here (*130*). Physical property studies of mixtures of TGs with aqueous ethanol and 1-butanol (*131*) showed that they form detergentless microemulsions. Mixtures of hexadecane, 1- butanol, and 95% ethanol were shown to be detergentless microemulsions. Evidence was presented in that paper that 1-butanol in combination with ethanol associates and interacts with water to form systems exhibiting microemulsion features.

Solubilization and microemulsification studies on TGs, especially triolein, with methanol in the presence of several even-numbered *n*-alcohols as surfactants showed that 1-octanol produced the microemulsions with the best water tolerance. Among the octanols, 1- and 4-octanol were superior to the 2- and 3- isomers. 1-Butanol and 1-tetradecanol gave microemulsions with the least water tolerance. The formation of molecular dispersions seemed more likely than the formation of nonaqueous microemulsions, but the addition of water produced systems that exhibited microemulsion properties (*132*). Studies on micellar solubilization of methanol with TGs and 2-octanol as co-surfactant gave the following sequence for water tolerance of three surfactant systems: tetradecyldimethylammonium linoleate > bis(2-ethylhexyl) sodium sulfosuccinate > triethylammonium linoleate. A nonaqueous microemulsion system formed from triolein / oleyl alcohol (9(*Z*)octadecen-1-ol) / methanol (*133*). When studying different unsaturated fatty alcohols, it was reported that the viscosity is nearly independent of the configuration of the double bonds in the tailgroup structure. However, with increasing unsaturation in the tailgroup, viscosity decreased at constant methanol concentration. Generally, adding long-chain fatty alcohols substantially increased methanol solubility in non-aqueous triolein / unsaturated long-chain fatty alcohol / methanol solutions under most conditions. Physical property data were consistent with those for systems exhibiting co-solvent phenomena. However, for solutions with methanol concentration exceeding 0.444 vol frac, the results showed that solubilization of methanol within large aggregates was feasible (*134*). Mixed amphiphile systems investigating four unsaturated C18 fatty alcohols and five C4-C12 alkanols showed that large methanol-in-amphiphile aggregates resembling a microemulsion were feasible under limited conditions (*135*). These binary systems strongly affect miscibility between methanol and TG. Critical micelle concentration (CMC) studies showed that degree of unsaturation and double bond configuration significantly affected aggregation when using six unsaturated C18 fatty alcohols as amphiphiles (*136*). These compounds form large and polydisperse aggregates in methanol. The effect of solubilized soybean oil was studied. Viscosity results were consistent with those for microemulsions. Presumably soybean oil is solubilized by incorporation into large soybean oil-in-fatty alcohol aggregates in methanol solvent, resembling a nonaqueous detergentless microemulsion.

Microemulsions containing conventional diesel fuel.

Fuel formulations containing conventional DF in emulsion with soybean oil have been subjected to engine testing. In an emulsion with ethanol (*137*), such a fuel burned faster with higher levels of premixed burning due to longer ignition delays and lower levels of diffusion flame burning than DF, resulting in higher brake thermal efficiencies, cylinder pressures, and rates of pressure rise. NOx and CO emissions increased with these fuels, while smoke and unburned hydrocarbons decreased. A microemulsion consisting of 50 vol-% DF, 25 vol- % degummed, alkali-refined soybean oil, 5 vol-% 95% aqueous ethanol and 20 vol-% 1-butanol was studied by the 200 hr EMA (Engine Manufacturers Association) test (*138*).

The engine running on this fuel completed the EMA test without difficulty. The microemulsion fuel caused less engine wear than conventional DF but produced greater amounts of carbon and lacquer on the injector tips, intake valves and tops of the cylinder liners besides the observation that engine performance degraded 5% at the end of the test. Another report on blends of alcohols with vegetable oils and conventional DF (the 40:40:20 and 30:40:30 DF/ degummed, dewaxed soybean oil / ethanol blends used in this study were not fully miscible and no surfactant system was used) confirmed that the performance of such fuels was comparable to conventional DF but the tests were too short-term to determine potential problems of carbon buildup, etc. (*139*). Microemulsions for blending alcohols with diesel fuel employed unsaturated fatty acids. Saturated fatty acids were unsatisfactory because crystalline phases separated upon refrigeration (*129*). Addition of *N*,*N*-dimethylamino ethanol (DMAE) gave microemulsions with satisfactory viscosity. Two fuels were tested: (1) 66.7% DF2, 16.7% 95% ethanol, 12.5% soybean acids, and 4.1% DMAE (ionic); (2) 66.7% DF2, 11.1% 95% EtOH, and 22.2% 1-butanol (non-ionic). Both hybrid fuels gave acceptable performance, for example improved brake thermal efficiency and lower exhaust temperatures. Smoke and CO levels were reduced but the unburned hydrocarbons level increased. The detergentless microemulsion was superior to the ionic one in those SAE properties relevant to good engine performance. On the other hand, fundamental studies on properties of microemulsions such as rheology, density, water tolerance, and critical solution temperatures showed that the water tolerance of ionic systems was greater than that of the 1-butanol system (*138*). The relative viscosities of the detergentless microemulsion varied directly with the volume percent of the dispersed water phase while for the ionic system the relative viscosities varied with increasing volume percent of dispersed water by values greater than those predicted by theory (*140*). Variations of the microemulsion technology have been reported in the patent literature not using vegetable oils but conventional DFs and the fatty ingredient being present only as part of a surfactant system in such emulsions. These microemulsions usually consisted of DF, water, an alcohol (or, combining the latter two components, an aqueous solution of an alcohol), and a system of surfactants. Several such microemulsions with a surfactant system comprising DMAE and a long-chain fatty substance (C9-C22) were patented (*141*). This microemulsion, which contains a fatty compound only in small amounts, showed a high tolerance for water, which enabled hybridizing diesel fuel with relatively high levels of aqueous alcohol and also showed low-temperature stability. Other systems were a cosurfactant combination of methanol and a fatty acid partially neutralized by a nitrogeneous base such as ammonia, ethanolamine, or *iso*-propanolamine (*142*) and, in a similar system, the use of ammonium salts of fatty acids as cosurfactants was patented (*143*).

Microemulsions with vegetable oils and without conventional DF are the most widely studied. A microemulsion comprising a vegetable oil, a lower (C1-C3) alcohol, water, and a surfactant system consisting of a trialkylamine or the reaction product of a trialkylamine with a long-chain fatty compound was reported (*144*). Addition of 1- butanol to the surfactant system was optional. In another patent (*145*), a microemulsion consisted of a vegetable oil, a C1-C3 alcohol, water, and 1-butanol as nonionic surfactant. These fuels had acceptable viscosity and compared favorably to DF2 in terms of engine performance. Another fuel composition consisted of a vegetable oil, methanol or ethanol, a straight-chain isomer of octanol, and optionally water (*146*), which again had properties such as high water tolerance, acceptable viscosity and performance properties comparable to DF2. Another patent (*147*) reported the formation of microemulsions from vegetable oil (preferably degummed; mainly rapeseed oil), water, and a surfactant such as an alkaline soap or a potassium salt of fatty acids. Another microemulsion composition was fatty esters, aqueous alcohol, and small amount of alkali metal soap with subsequent separation of the aqueous layer from the microemulsion (*148*). Engine tests were performed on several microemulsions. A non-ionic microemulsion comprising of alkali-refined, winterized sunflower oil (53.3 vol-%), 95% aqueous ethanol (13.3 vol-%) and 1-butanol (33.4 vol-%) encountered incomplete combustion at low-load engine operation as major problem (*149*). Lubricating oil dilution was observed, followed by an abnormal increase in viscosity. Heavier carbon residues on the piston lands, in the piston ring grooves and in the intake ports were noted. Furthermore, premature injection-nozzle deterioration (needle sticking) was experienced. The tested microemulsion was not recommended for long-term use in a DI engine, but further modifications in formulation might produce acceptable microemulsions.

Two other hybrid fuels were tested. One was non-ionic consisting of 53.3 vol-%

soybean oil, 13.3 vol-% 95% aqueous ethanol and 33.4 vol-% 1-butanol (*150*), and the other was ionic composed of 52.3 vol-% soybean oil, 17.4 vol-% 95% aqueous ethanol, 20.5 vol-% 1-butanol, 6.54 vol-% linoleic acid, and 3.27 vol-% triethylamine. Generally, these fuels performed nearly as well as DF2 despite their lower CNs and less energy content, producing nearly as much engine power (non-ionic emulsion). The increased viscosity of the hybrid fuels produced a 16% increase in the mass of each fuel injection at maximum power, but the injections contained 6% less energy than those of DF2. There was a 6% gain in thermal efficiency. Another paper reports using methyl *tert.*-butyl ether (MTBE), which is normally used as octane enhancer in gasoline, to homogenize mixtures of soybean or rape oil with ethanol (*151*). No engine tests were performed. In two papers (*152-153*), emulsions of palm oil with diesel fuel and 5-10% water were tested to determine engine performance and wear characteristics on an IDI diesel engine under steady-state conditions and 20 h endurance tests. Engine performance and fuel consumption were comparable to conventional DF. Wear metal debris accumulation in the crankcase oil was lower than with conventional DF.

Pyrolysis.

Soybean oil pyrolyzed distillate, which consisted mainly of alkanes, alkenes, and

carboxylic acids had a CN of 43, exceeding that of soybean oil (37.9) and the ASTM minimum value of 40 (*154*). The viscosity of the distillate was 10.2 cSt at 38°C, which is higher than the ASTM specification for DF2 (1.9-4.1 cSt) but considerably below that of soybean oil (32.6 cSt). Short-term engine tests were carried out on this fuel (*155*). Used cottonseed oil from the frying process was decomposed with Na2CO3 as catalyst at 450° to give a pyrolyzate containing mainly C8-20 alkanes (70%) besides alkenes and aromatics (*156*). The pyrolyzate had lower viscosity, flash point, and PP than DF and equivalent calorific values. The CN of the pyrolyzate was lower.

Rapeseed oil methyl esters were pyrolyzed at 550 to 850°C and in nitrogen dilution (*157*). The major products were linear 1-alkenes, straight-chain alkenes, and unsaturated methyl esters. CO, CO2, and H2 were contained in the gas fraction. The C10-14 alkenes and short-chain unsaturated esters were optimally produced at 700°. Catalytic conversion of vegetable oils using a medium severity refinery hydroprocess yielded a product in the diesel boiling range with a CN of 75-100 (*158*). The main liquid product was a straight-chain alkane. Other products of the process included propane, water, and CO2. Soybean, babassu and some less common vegetable oils were hydrocracked with a 1L0R_ _-Al2O3 catalyst sulfided *in situ* with elemental sulfur under hydrogen pressure (*159*). Various alkanes, alkylcycloalkanes, and alkylbenzenes were observed. Oxygen in the oil feed was liberated as CO2, H 2O, and CO. Decarboxylation was indicated by water and CO2. C 1-4 formation indicated acrolein decomposition. Differences between γ-Al_2O_3, an $NiSiO_2$ catalyst was studied (*160*) in the hydrocracking of vegetable oils at 10-200 bars hydrogen pressure and 623-673 K. The resulting product was a mixture of hydrocarbons, mainly alkanes, in the diesel fraction. Hydrogenolysis of palm oil over Ni/SiO_2 or over Co at 300° and 50 bar gave a nearly colorless oil, mainly $C_{15\text{-}17}$ alkane (*161*). The same process gave soft solid with 80.4% C_{17} alkanes when applied to rapeseed oil. An octadecane model compound gave 50% conversion over Co/oil catalyst to C_{17} alkane as the main product.

Catalytic hydrocracking (Rh-Al_2O_3 catalyst) of soybean oil at 693 K and 40 bar hydrogen pressure gave liquid products which were distilled to gasoline and gas oil boiling-range hydrocarbons (*162*). Decarboxylation / decarbonylation was again noted. Crude and partially hydrogenated soybean oil were decomposed by passage over solid acidic Al_2O_3 or basic MgO (*163*). The degree of unsaturation of the oil influenced product formation. Partially hydrogenated soybean oil yielded more hydrocarbons while crude soybean oil yielded a mixture of oxygenated products and hydrocarbons of lower mean molecular weight. The products derived from MgO cracking showed more unsaturates and aromatics than those from Al_2O_3 decomposition. Kolbe electrolysis of the potassium salts of coconut fatty acids and acetic acid reportedly gave a liquid with good DF properties (*164*) and the products resembled those from pyrolytic procedures. This product contained 83% alkanes, mainly even-numbered compounds from C_{10-24}, with C_{12-18} being the most abundant.

Storage stability

While most aspects of biodiesel discussed above have received considerable attention, relatively few papers (*165-167*) deal with the aspect of (storage) stability of biodiesel or fatty alkyl esters. The use of biodiesel is advantageous compared to conventional diesel fuel from the aspect of handling and storage safety because of the higher flash point of both vegetable oils and their methyl esters. Generally, the stability of fatty compounds is influenced by factors such as presence of air, heat, traces of metal, peroxides, light, or structural features of the compounds themselves, mainly the presence of double bonds. The more conjugated or methylene-interrupted double bonds in a fatty molecule, the more susceptible the material is to oxidation and degradation. Early storage tests gave the following decreasing order of stability for different refinement grades of various vegetable oils (*165*): soybean oil >> degummed soybean oil > refined soybean oil = refined sunflower oil > degummed sunflower oil = crude sunflower oil. The stability of the crude and degummed oils was significantly improved by the addition of diesel fuel (in 1:1 mixtures) but this did not improve the stability of refined oils. The storage stability of 1:1 mixtures were in the decreasing order of crude soybean oil ³ crude sunflower oil > degummed soybean oil > degummed sunflower oil >> refined soybean oil > refined sunflower oil. A degummed oil / diesel blend with better stability characteristics than that of a refined oil / diesel blend could be prepared. Additionally, the purity of the degummed oils was sufficiently improved by the addition of diesel fuel to meet the required fuel specification. A study on the stability of the methyl and ethyl esters of sunflower oil reports that ester fuels (biodiesel) should be stored in airtight containers, the storage temperature should be < 30°C, that mild steel (rust-free) containers could be used, and that *tert.*-butyl hydroquinone (TBHQ), an oxidation inhibitor, has a beneficial effect on oxidation stability (*166*). Methyl esters were slightly more stable than ethyl esters. Light caused only a small increase in the oxidation parameters of esters stored at the high temperature level. The changes in the samples were reflected by increasing acid and peroxide values in storage at 50°C and increases in ultraviolet (UV) absorption. Two parameters, namely temperature and the nature of the storage container, were claimed to have the greatest influence on the storage stability (*167*). Samples stored in the presence of iron behaved differently than those stored in glass. Higher temperature favored degradation of the hydroperoxide at a faster rate than when it was stored at room temperature. Secondary oxidation products were formed in greater amounts in the presence of iron (from the primary peroxides) while in glass the concentration of primary oxidation products is higher. Acidity values were also monitored in this work. Even for samples stored at 40°C, the increase in free acids was within the limits of technical specifications. The free acids need to be controlled because they are mainly responsible for corrosion.

Other Sources of Biodiesel

Animal fats. The most prominent animal fat to be studied for potential biodiesel use is tallow. Tallow contains a high amount of saturated fatty acids (Table II), and it has therefore a melting point above ambient temperature. Blends of tallow esters (methyl, ethyl, and butyl) with conventional DF were studied for this reason (*168*). Smoke emissions were reduced with the esters, particularly the butyl ester. Other features such as torque, power, and thermal efficiency did not deviate from conventional DF by more than 3% in any case. Specific fuel consumption was higher for the neat esters but only 1.8% higher for a 50:50 blend of butyl tallowate with conventional DF. A study on beef tallow and an inedible yellow grease both neat and a 1:1 (weight ratio) blend of tallow with DF in short-term engine tests with DI and IDI engines was carried out (*169*). The deposits were softer than those formed with reference cottonseed oil but still excessive.

In a 200 h EMA test the deposits caused ring sticking and cylinder wear. Thus animal fats, like vegetable oils, were not suitable for long-term use unless modified. Other researchers blended methyl tallowate with 35 vol-% ethanol to achieve the viscosity of petrodiesel and the fuel properties were closely related to that of No. 2 diesel fuel (*170*). In an investigation of blends of DF2 with methyl tallowate and ethanol (*171*), an 80:13:7 blend of DF2:methyl tallowate:ethanol reduced emissions the most without a significant drop in engine power output. The same authors determined numerous physical properties of blends of DF with methyl tallowate, methyl soyate and ethanol and found them to be similar to the pertinent properties of DF2.

Waste vegetable oils

Vegetable oils have many other applications, notably as food ingredients and cooking oils. Especially the latter use produces significant amounts of waste vegetable oils. These vegetable oils contain some degradation products of vegetable oils and foreign material. However, analyses of used vegetable oils claimed (*172*) that the differences between used and unused fats are not very great and in most cases simple heating and removal by filtration of solid particles suffices for subsequent transesterification. The cetane number of a used frying oil methyl ester was given as 49 (*173*), thus comparing well with other materials, but little demand could be covered by this source. Biodiesel in form of esters from waste cooking oils was tested and it was reported that emissions were favorable (*174*). Used canola oil (only purified by filtration) was blended with DF2 (*175*). Fuel property tests, engine performance tests and exhaust emission values gave promising results. Filtered frying oil was transesterified under both acidic and basic conditions with different alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-ethoxyethanol) (*175*). The formation of methyl esters with base catalysis (KOH) gave the best yields. The methyl, ethyl, and 1-butyl esters obtained here performed well in short-term engine tests on a laboratory high-speed diesel engine.

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III. Vegetable Oils and Their Derivatives as Alternative Diesel Fuels

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