Lecture-18.

Biodiesel Production Processes

Bio-Diesel

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. Several problems, however, remain, which include economics, combustion, some emissions, lube oil contamination, and low-temperature properties.

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. 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.

Conventional Diesel Fuel Diesel Engines

In contrast to gasoline, which is spark-ignited, the heat of compression in a diesel engine ignites DF after injection. 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 ($C_{16}H_{34}$; 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 $C_{16}H_{34}$), 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. 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. 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.

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. Tests of biodiesel as a fuel have been performed on both DI and IDI engines.

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.

Vegetable oils.

Most vegetable oils are triglycerides (TGs; triglyceride = TG). Chemically, TGs are the triacylglyceryl esters of various fatty acids with glycerol.

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.

CH_2OOR CH_2OH

II

$CHOOR$ $+$ $3\ CH_3OH$ $\rightarrow$ $3\ CH_3OOCR$ $+$ $CHOH$

II

CH_2OOR CH_2OH

Triglyceride   Methanol   Methyl ester   Glycerol

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. 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

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	-3.9	-12.2	254

				(38°)			
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

Where,

CN = cetane number; CP = cloud point, PP = pour point, FP = flash point.

Combustion Chemistry, Emissions, Engine problems and deposits.

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 exists 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 (CO_2) and water according to the equation (shown for alkanes (saturated hydrocarbons)

$$C_nH_{2n}+2 + (1.5n + 0.5)O_2 \rightarrow nCO_2 + (n + 1)H_2O$$

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 CO_2 (decarboxylation), as indicated above, from the ester moiety of the triglyceride or methyl ester occurs besides combustion formation of CO_2 from the hydrocarbon portions of biodiesel. The formation of CO_2, 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 CO_2 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.

The composition of particulate matter has been studied for conventional diesel fuels. Particulates from conventional DF have a high carbon to hydrogen ratio of approximately 10:1. 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.

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. NOx emissions are difficult to control because such techniques may increase other emissions or fuel consumption.

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. Besides higher NOx levels, aldehydes are reported to present problems with neat vegetable oils. Total aldehydes increased dramatically with vegetable oils. 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 (CH_2=CH-CHO) from the glycerol moiety. Another author observed significantly lower emissions of C3 aldehydes (for example, acrolein) for methyl esters of rapeseed oil than for the oil itself. Another study 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. These problems were confirmed and studied by other authors. A test for external detection of coking tendencies of vegetable oils was reported. 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. Fumigation with propane was studied as a means to reduce injector coking. 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.

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, 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. 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. The study on PAH emissions, 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. The general trend on reduced emissions except NOx was confirmed by later studies, although some studies report little changes in NOx. In a DI engine, sunflower methyl ester produced equal hydrocarbon emissions but less smoke than a 75:25 blend of sunflower oil with DF. Using a diesel oxidation catalyst (DOC) in conjunction with soy methyl ester was reported to be a possible emissions reduction technology for underground mines. Soy methyl esters were reported to be more sensitive towards changes in engine parameters than conventional DF.

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, the unsaturated TGs triolein, trilinolein, and trilinolenin were studied at temperatures up to 400°C in air or N_2 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, tristearin and tripalmitin were studied besides the three unsaturated TGs at temperatures of 450°C in air and N_2. 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 N_2) had considerable influence on product formation. The number of components was less for samples of tripalmitin, tristearin and triolein for reactions under N_2 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. Few studies on such compounds in biodiesel exist. One paper reports that in a turbulence combustion chamber and at an intake air temperature of 105°C, 8% hexyl-nitrate in vegetable oils (cottonseed, rape, and 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.

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.

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. 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 or blends of ≤ 15% rapeseed oil with DF2 , and an 80:20 DF2 / safflower oil blend with reduced CO and hydrocarbon emissions. 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. In early studies on sunflower oil, 80:20 DF / sunflower oil blends 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 .

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.

Transesterification.

The conversion of component TGs to simple alkyl esters (transesterification) with various alcohols reduces the high viscosity of oils and fats. Base catalysis of the transesterification with reagents such as sodium hydroxide is preferred over acid catalysis because the former is more rapid. 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.

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. 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. 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. Another early study used H_2SO_4 as the transesterification catalyst. 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. 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. 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. In a study, similar to previous work on the transesterification of soybean oil, it was concluded that KOH is preferable to NaOH in the transesterification of safflower oil of Turkish origin. 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.