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Comparative Study for Biodiesel Properties and Standards for Gas Turbine

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1. Introduction

Fuels from non-petroleum sources are becoming a necessity for the industry. However due to the high volatility of supply and the price inflation, the issue is further exacerbated. Thus, many alternatives such as bio-fuels are becoming interesting. Therefore, commitments have to be made to enhance the fundamental scientific issues that affect bio-fuel production, standards and regulations to specify their properties, applications, and performances. It is important that Canada provides funding and facilities for fundamental research on bio-fuels as well as their production, which will assure the Canadian industry the ability to compete in this rapidly changing field.

The term bio-fuel is referred to alternative fuel, which is produced from biomass. Such fuels include but not limited to: biodiesel, bioethanol, biomethanol, pyrolysis oil, biogas, synthetic gas, and synthetic fuels. Compatibility of different bio-fuels with their area of application is primarily function of their properties, which must be in accordance with established standards [1]. Thermo-physical properties which include thermodynamic and transport properties are most relevant for the design processes (e.g. production, purification and distillation), and are equally important for the finished fuel behavior. Moreover, others specifications (e.g. acidity, oxidative stability, knock index, allowable levels of trace impurities such as water, metals or sulfur, etc.) are typically applied to the finished fuel and often relate to the suitability of the fuel for a particular application (e.g. compression-ignition engines, stationary gas turbines, aircraft turbines, etc.). The selection of the alternative fuels will be based upon thermo-physical properties, atomization and spray characteristic of liquid fuels, combustion efficiency and flame, soot formation and emissions properties under various operation conditions [1][2].

In this study, we will focus on biodiesel fuels and their blends for gas turbine applications. Their properties will be discussed as well as their conformity with standards and regulations. Further, we will review the studies made by the research community to reduce pollutant emissions based on their area of application and feedstock.

2. Biodiesel Production

Biodiesel is an alternative fuel composed of Fatty Acid Alkyl Esters (FAAE). Biodiesel is made through a chemical process called trans-esterification, whereby the glycerin is separated from the fat or vegetable oil. The process renders two commercial products: (1) Fatty Acid Methyl Esters (FAME) which is the chemical name for biodiesel (if methanol is used as an alcohol during the process), (2) glycerin (a valuable co-product usually sold to be used in soaps, pharmaceuticals, and cosmetics). Among the biodiesel family (FAAE), FAME is widely produced due to the low price of methanol [3].

Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, which conform to ASTM D6751 specifications for use in diesel engines. Biodiesel refers to the pure fuel before blending with diesel fuel. Biodiesel blends are denoted as, "BXX" with "XX" representing the percentage of biodiesel contained in the blend (i.e. B20 is 20% biodiesel and 80% petroleum diesel) [4]. Biodiesel is the most diverse fuel on the planet and can be produced from agricultural co-products such as: soybean, cottonseed, rapeseed/canola, sunflower, shallower and coconut oils as well as animal fats usually tallow and recycled grease oil e.g. frying oil [5]. Next generation bio-fuels (e.g. forest residues, micro algae, etc.) produced from cellulose, hemicellulose or lignin will not be discussed in this study.

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Since biodiesel is derived from renewable lipid sources through the industrial trans-esterification process, it will be judicious to quickly review this process and cite the most influential parameters that contribute to the biodiesel quality. Trans-esterification is a chemical reaction of triglycerides with alcohol in presence of a catalyst to form esters and glycerol by modifying the molecular structure of the oil used. The triglycerides include the conversion step from di-glycerides, mono-glyceride and finally to glycerol. The presence of catalyst is to improve the reaction rate and yield. The level of Free Fatty Acids (FFAs) present in the lipid source will determine the type of catalyst to be used in the reaction. When catalysts such as NaOH or KOH are mixed with alcohol, an alkoxide group is formed. For alkali-catalyzed trans-esterification, alcohol must be substantially anhydrous because water partially changes the reaction to saponification, which produces soap. For this type of process, low level FFAs are preferred. Lipid oil with high FFAs (e.g. trap grease, yellow grease, etc.) [5] cannot be trans-esterified to biodiesel with a base catalyst; therefore acid catalysts shall be used. Thus, an esterification process in two stages should be opted for. First, an acid catalyzed esterification to convert FFAs into fatty acid methyl esters and then base trans-esterification will give the conversion a higher yield. Other variables beside the FFA level and the catalyst type that are found to influence the trans-esterification process are: reaction temperature, alcohol to oil ratio, stirring RPM, and reactants [6].

3. Biodiesel Properties

Properties for biodiesel like for any other fuels are function of the fuel structure. The type and structure of the fatty acid esters present in biodiesel both play an important role. Structural features that are found to influence biodiesel properties are: fatty acid chain length, degree of un-saturation and branching of chains. The main fuel properties that are found to be impacted most by the fatty acid profile are: viscosity, surface tension, heat of combustion, cetane number ,cold flow properties, oxidative stability, and lubricity [5][7]. The following paragraphs will review these properties in more details.

Viscosity is an important factor in the atomization process providing an adequate droplet distribution in the combustion chamber. Viscosity of biodiesel is higher than for diesel. This can be attributed to the fact that viscosity increases with the chain length and also increases with the degree of saturation, which will have a negative impact on the atomization and spray formation, thus affecting combustion efficiency and emissions. Double bond configurations are also found to lower viscosity.

Surface tension is another fuel property that affects spray atomization, droplet size, and other important properties of fuel spray. Spray properties, specifically the droplet size distribution and Sauter Mean Diameter (SMD), are influenced by fuel surface tension and viscosity. SMD has been shown to increase with the increasing of surface tension and viscosity. This effect reduces the rate of droplet evaporation, consequently the degree of mixing and penetration. Only very limited data on the surface tension of neat biodiesels and blends are available. Some studies found a value of 0.0349 N/m at 60°C for neat soya oil methyl ester and 0.0254 N/m at 100°C for rapeseed oil methyl ester whereas typical value for diesel fuel no.2 (DF2) is 0.0225 N/m at 100°C. The surface tension of biodiesels is globally higher than petroleum based diesel. Accordingly, negative influence might affect atomization performances depending on injection mode [27].

Heat of combustion is another property that proves the suitability of using fatty compounds as diesel fuel. Heat of combustion increases with the chain length. Fatty esters will contribute up to 90% of heat of combustion in diesel fuel no.2 (DF2).

Cetane number is a prime indicator of the fuel quality, the higher the cetane number the shorter the ignition time delay and vice versa. A higher cetane number is also correlated to the reduction in NOx emission for conventional diesel fuel. The cetane number is found to be decreasing by decreasing the chain length and the increment of branching, which explains the higher cetane number for biodiesel. However, some biodiesels were found to have higher NOx emission although they have a higher cetane number. This can be linked to the fact that NOx emissions increase with the higher degree of un-saturated acid present in the biodiesel structure. In general a cetane number that is too high will reduce the ignition time delay, thus combustion in compression-ignition engines as well as in gas turbines can occur before proper fuel/air mixing, leading to incomplete combustion and smoke [5][8].

Poor cold flow properties are one of the major problems with biodiesel, which is indicated by the cloud point (CP) and the pour point (PP). CP is the lowest temperature at which liquid fatty material becomes cloudy due to the formation of solids and crystals. PP is the lowest temperature at which the liquid will still flow. Saturated fatty compounds have higher melting points than the un-saturated ones, thus in a mixture (like in biodiesel) they crystallize at higher temperature than unsaturated. Consequently, biodiesel derived from fats or oils with high amounts of saturated fatty compounds will display higher CPs and PPs.

Oxidative stability is the reason behind the changes in biodiesel properties with longer storage duration. This autoxidation is due to the presence of double bonds in the chains of many fatty compounds, and thus the rate of autoxidation will be depending on the number and the position of double bonds.

No significant effect was reported for the lubricity of biodiesel due to fatty acid composition. However, a study showed that castor oil esters offer better lubricity than vegetable oils [9]. Unsaturated acids exhibited better lubricity than the saturated ones. Ethyl esters showed better lubricity than methyl esters. This property can be altered by mixing biodiesel to the low sulfur petroleum-derived diesel fuels, in order to restore its lubricity. An advantage for biodiesel regarding its lubricity is that biodiesel inherently possesses fuel properties compatible with conventional diesel; and that enhancing additives usually do not possess.

4. Standards and Regulations for Biodiesel

Biodiesel must meet certain specifications in order to be certified as fuel. The American Society of Testing and Materials (ASTM) is a globally recognized leader in the development and delivery of international voluntary consensus standards [11]. Almost all the specifications available for biodiesel fuels properties are:

- *ASTM D396-10:* Specifications for petroleum based fuel oils used for home heating and boiler applications, allowed to include up to 5% vol. biodiesel content i.e. B1 to B5.
- *ASTM D975-11b*: Specifications for diesel fuel oils used for on-and off- road diesel applications, allowed to include up to 5% vol. biodiesel content i.e. B1 to B5.
- *ASTM D7467-10*: Specifications for diesel fuel oils and biodiesel blends up to 20% vol. (i.e. B6 to B20).
- *ASTM D6751-11b*: Specifications for pure biodiesels B100, i.e.100% vol. biodiesel (Grades S15 and S500).

Regarding standards that covers the use of bio-fuels in the aviation turbine section:

- *ASTM D1655-11b*: Specifications of standard aviation turbine fuels covers Jet A and Jet A1 kerosene fuels. Fatty Acid Methyl Esters (FAME) are not approved as an additive for jet fuel, except for a level up to <5mg/kg in the incidental material section, the same if found must be meeting D6751 specification [12].
- *ASTM D7566-11a*: Specification of standard aviation turbine fuels containing synthesized hydrocarbons, allowable levels of mixing non-conventional components to Jet A /Jet A1 is 50% by volume. The types of bio-fuels allowed to be used as non-conventional components: Fisher-Tropsch hydro-processed Synthesized Paraffinic Kerosene (F-T SPK) i.e. synthesis gas via F-T process using iron and cobalt catalyst to produce SPK. The second type is Synthesized Paraffinic Kerosene from Hydro-processed Esters and Fatty Acids (HEFA-SPK) i.e. Fatty Acid Methyl Esters (FAME), triglycerides are hydrogenated and deoxygenated to produce SPK [13].

Regarding fuel specifications to be used for industrial gas turbines (stationary gas turbines):

- *ASTM D2880-03*: Specifications of fuel oils to be used in industrial gas turbine.

Now we shall tabulate the properties covered in the standards addressing biodiesel for the use in on/off road diesel and industrial gas turbine applications shown in Table 1. In addition, data for soya oil methyl ester fuel properties [6], which is highly considered as a potential substitute for gas turbine, are provided.

Table 1. Specifications for biodiesel thermo-physical properties.

Analysis	ASTM-D975 DF/B1-B5 (1948-2012)	ASTM-D396 Fuel oil/ B1-B5 (1934-2010)	ASTM-D6751 B100 (1999-2011)	ASTM-D7467 B6-B20 (2008-2010)	ASTM D2880 GT fuel oil (1970-2010)	Soya oil methyl ester
Flash point	38 to 55[a] °C	38°C	130°C	>52°C	38 to 66°C	178°C
Ca+Mg+K+NA			<5 ppm		<0.5 ppm[c]	
Methanol content			<0.2% vol.			
Water and sediments	<0.05% vol.	<0.05% vol.	<0.05% vol.		<0.05% vol.	
Kinematic viscosity @40°C	1.3-4.1 mm^2/sec	1.3-5.5 mm^2/sec	1.9-6 mm^2/sec	1.9-4.1 mm^2/sec	1.3-5.5 mm^2/sec	5 mm^2/sec
Sulfated ash			<0.02% mass			

Sulfur	<0.05% mass	<0.05-0.5% mass		<0.05-0.5% mass		
S 15			<0.0015% mass (ppm)			
S 500			<0.05% mass (ppm)			
Copper strip corrosion	<no.3	<no.3	<no.3	<no.3		
Cetane no.	>40		>47	>40		
Cloud point			Report[b]			4°C
Pour point		-6 to -18°C			-6 to -18°C	0°C
Carbon residues	<0.15% mass	0.15-0.35% mass	<0.05% mass	<0.35% mass	0.15-0.35% mass	
Acid no.			<0.5mg KOH/g	<0.3mg KOH/g		0.253mg KOH/g
Free glycerin no.			<0.02% mass			
Total glycerin no.			<0.24% mass			
Distillation temperature	282-338°C	215-338°C	<360°C	343°C	282-338°C	
Density		850-876 kg/m^3	860-900 kg/m^3		850-876 kg/m^3	900 kg/m^3

[a]: Depending on diesel fuel grade.
[b]: CP of biodiesel is generally higher than petroleum based diesel fuel.
[c]: Trace fuel limits of fuel entering combustors.

Almost all the standards tests specified in the biodiesel specifications were originally developed for petroleum products, and biodiesel at that time was not in the scope of these test methods. Moreover, most of these testing methods are highly empirical, in which many correlations have been created based on years of experience.

A recent study done by R.A. Kishore [14] revealed that the Test Performance Index (TPI) for several tests used in the 2008 bio-fuel ASTM Inter-Laboratory Crosscheck Program (ILCP) was very inconsistent. It was surprising to find out that very few TPI for biodiesel were satisfactory, demonstrating the fact that most of the test methods need to be reconsidered in order to develop appropriate test methods for bio-fuels. Another study done by M. McLinden [2] in conjunction with R.A. Kishore study came to the same conclusions. Moreover, a third study by Bert H. [15] questioned the calibration standards required by ASTM that do not necessarily deliver reliable standards for biodiesel.

5. Emissions

Biodiesel is biodegradable, non-toxic and possesses relative low emission properties. Moreover, the fact that all its organic carbon is photosynthetic in origin does not contribute to a rise in the carbon dioxide levels in the atmosphere and consequently to the greenhouse effect. The use of biodiesel has a beneficial impact on the environment, since it decreases the emissions of CO, NOx, SOx, unburned hydrocarbons (UHCs), polyaromatic hydrocarbons (PAHs) and particulate matter (PM).

However, information regarding the use of biodiesel in gas turbines is limited. There exists a need to build a knowledge base relating to biodiesel, so that judicious decisions can be made by engine manufacturers and power producers. The lack of reliable data about the emissions of CO, NOx, UHCs, and soot provokes a divergent thinking regarding biodiesel emissions in gas turbines. Nevertheless, the use of biodiesel blends in gas turbines testing shows a global tendency towards the reduction of pollutant emissions.

According to experimental testing on different gas turbine applications shown in Table 2, most studies show a decrease or a modest improvement in CO emissions with respect to the fuel baseline. However, regarding the level of NOx emissions, the results are often contradictory depending on the area of application and a consensus is not well established. Most test results showed no improvement to a slight decrease of the NOx emissions, and a minority obtained results a little bit higher or much lower. Consequently, a deductive reasoning is hard to establish. Nevertheless, a majority of results indicated that B20 produced similar NOx emissions at lean combustion and significant low NOx emissions when the equivalence ratio was increased comparing to baseline. Moreover, it was found that B50 and B100 produced higher NOx than B20. Most studies that found a reduction in the NOx emissions with the combustion of B100, were mainly preheating the fuel. Thus, lower viscosity and enhancement of its atomization characters were observed, which decrease NOx emission. Concerning the UHCs and deposits, several results showed ambiguous results depending on the mixture percentage with the baseline and the type of feedstock.

The amount of soot emissions is less controversial with measurements based on the well-established standard procedure (SAE ARP 1179) for turbine engine smoke measurement, which provides relevant information about the quantity and size of soot produced. Thus, the results from the different studies show that biodiesel has a small effect on the measured smoke number. The smoke emissions seem to decrease depending of the type of feedstock and the equivalent ratio with respect to the baseline.

The burning of biodiesel has so far indicated that less exhaust emissions are produced when these fuels are used. There are many factors that could be contributing to this, including more oxygen in the fuel, the absence of aromatics, and the absence of sulfur dioxide.

Table 2. Comparative emission study.

Study	Baseline	Biodiesel comparison	CO	NOx	UHC	Smoke emission
RR T56-A-15 combustion system[a]	Neat Jet A-1	Blend Jet A-1+(B2 & B20)	Modest improvement	Same	Higher	Globally the same
RR T63-A-700 turboshaft engine[b]	JP-8	B2, B10, B20	Reduced except at idle	Reduced except at idle	Reduced except at idle	Same
GE LM6000PA gas turbine[c]	Diesel	B99.9 (ASTM D6751 & GE Spec.)	Lower	5 ppm lower		Significantly less
Radial low NOx premix gas turbine combustor[d]	Kerosene	Blend Kerosene+(B20 & B50)	Lower (low φ)	B20:Low φ = same High φ = low B50 & B100: higher	Lower in the lean combustion range	
Preheated combustion chamber with air-blast atomizer	No. 2 Diesel	CME (Canola) B100	Same	Slight reduction of NO		Reduction of soot
Preheated combustion chamber with high swirl injector	No. 2 Diesel	PME (Palm) B100		Reduction		Lower soot tendency
High speed turbines locomotive	No. 2 Diesel	REE (Rapeseed), SME (Soy), HySEE (Waste french-fry oil)	Lower except for REE	Much Lower	Same for B20. Lower for B100	

[a]: Allison/Rolls Royce T56-A-15 combustion system [24].
[b]: T63-A-700 turbo shaft engine [25].
[c]: General Electric LM6000PA gas turbine [26].
[d]: Radial low NOx Premix gas turbine combustor [22].
[e]: Preheated large combustion chamber with air-blast atomizer 300μm injector [18].
[f]: Preheated combustion chamber with high swirl injector [21].
[g]: TF40 dual shaft gas turbine at 80% power [23].

6. Conclusions and suggestions

Biodiesel has certainly many advantages such as reduction of greenhouse gas emissions, non-toxicity, and safer handling due to its high flash point. It has high level of biodegradability, which helps in reducing the toxic environmental impact that might occur in case of accidental spillage [16]. However, some of its disadvantages are: the high viscosity, high cetane number, lower cold-temperature characteristics, and lower energy content. The above studies show that fuel properties for biodiesel are strongly influenced by the properties of the individual fatty esters in biodiesel. Several studies in genetic engineering made by many parent oil companies are currently working on improving these parameters in order to enable its growth in the fuel chain. Standards and regulations should reconsider the testing methods for future improvements and allow for the use of higher blends level of biodiesel such as B30, B40, etc. One draw-back in the use of biodiesel fuels seems to be the increase in NOx levels by 1-14%; this has been reported from biodiesel fuelled compression-ignition engines. A variety of reasons was cited for this increase in NOx emission: (1) Increasing iodine number (degree of unsaturation of FA), (2) the presence of double bonds in biodiesels [17]. The same tendency was not observed in gas turbines; this discrepancy can be attributed to the difference in combustion mode between CI engines (non-continuous combustion) and GT engines (continuous combustion).

Large differences in pressure, temperature, droplet residence time, equivalence ratio, and mode of combustion between the CI and GT engines certainly affect the in-flame temperature profile and spray characteristic, hence the NOx emission. Concerning the soot formation reduction for biodiesels, this parameter was directly related to the presence of fuel bound oxygen in the ester function group of the fuel molecule, which aids the oxidation process and suppress soot precursors [18]. Another study related it to the absence of aromatic ring molecules, which found to be a strong parameter affecting the soot formation [19][20][21].

7. References

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