

**FUEL PARAMETER TESTING, QUALITY ASSESSMENT AND ENGINE
EMISSIONS EVALUATION OF BIODIESEL (B100), DIESEL (D100) AND ITS
20% BLEND (B20) UNDER LONG TERM STORAGE CONDITIONS.**

by

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ABSTRACT

Diesel-powered vehicles have contributed to the emission of greenhouse gases into the atmosphere. Using biodiesel as a combustion fuel for use in diesel engines is advocated by engineers, environmentalists, industry and government for numerous reasons, including that it is derived from a renewable fuel source and can generate lower emissions than petroleum derived diesel fuel. However, biodiesel has reduced storage stability and is more prone to degradation reactions that can affect its fuel quality and cause changes in its fuel properties.

The long-term ageing under real-time conditions of two different biodiesel (B100) fuels (from soybean oil and waste vegetable oils), two petroleum derived diesel (D100) fuels and their 20% vol. or B20 fuel blend was studied by storing these blends under cool (6 °C), ambient outdoor (X °C) and warm temperature (40 °C) conditions. The aged fuel samples were monitored via characterization of several fuel properties in accordance to ASTM and EN regulation standards up to 180 days and 300 days, in some cases. The purpose to meet the standards (e.g., ASTM, EN) is to ensure safe operation, good fuel quality and industrial longevity.

The acid number (AN), kinematic viscosity (KV) and cetane number (CN) of the soy methyl ester (SME) after 300 days of ageing at 6 °C, X °C and 40 °C and waste methyl ester (WME) after 180 days of ageing at 6 °C and X °C did not change significantly. WME showed an increasing change in AN and KV after 180 days of ageing at 40 °C. Many of the fuel properties of aged SME and WME were comparable to its initial un-aged values and were within the limits of technical specifications. The correlation between oxidative stability (OS) and iodine number (IN) was poor for both biodiesels. The analysis of the fatty acid methyl ester (FAME) profiles demonstrated the ineffectiveness of employing IN as a total measure of unsaturation for biodiesel fuels. The cloud point (CP) of WME was higher than SME and like KV, CN and OS; it strongly depended on the saturation and unsaturation content of the FAME. The D100 fuels displayed a near zero change in AN, minor increases in KV and adequate stability during storage. The CN of D100 decreased slightly and the measures were within the ASTM limits pre- and post-storage. Many fuel properties of the B20 pre-mix samples differed from the B20 after-mix samples, but these differences are not significant enough to conclusively deduce which B20 blend showed better stability. CN's of

B20 were calculated from the measured cetane data of B100 and D100 and compared to the measured cetane data of B20.

Select blends of aged B100, D100 and B20 aged at 6 °C and 40 °C were tested for regulated pollutant emissions (HC, CO, NO_x, CO₂) in a 1987 Volkswagen Jetta and a 2005 Mercedes Benz Smart Car. The vehicles were driven by the same driver for all test runs at cold start conditions. The effect of certain fuel properties and fuel composition was investigated on emission production. Relative to D100, the B100 and B20 fuels tested in the 1987 VW Jetta produced significantly lower emissions, with reductions in HC and CO of at least 40% and 15%, respectively. The B100 fuels showed a 12% increase in NO_x. Storage temperature appeared to affect the produced emissions, particularly for B100 blends, but this effect is not as significant as the variations between the different fuel types (e.g., B100 versus D100). The emissions of B100 and B20 aged at 40 °C in the Smart car did not differ significantly and the results indicate the effect of fuel on emissions is small.

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LIST OF SYMBOLS

Symbols, Acronyms, Notations

ρ	Density [kg/m^3]
ν	Kinematic Viscosity [mm^2/s , cSt]
μ	Viscosity [Pa·s]
A_f	Mass percent quantity of an unsaturated fatty acid
ARC	Alberta Research Council
ASTM	American Society for Testing and Materials
B100	100 % pure biodiesel fuel
B20	20 % pure biodiesel mixed with 80 % petroleum diesel
CCR	Conradson Carbon Residue
CFPP	Cold-Filter Plugging Point
CIE	Compression Ignition Engine
CN	Cetane Number
CO	Carbon Monoxide
CO ₂	Carbon Dioxide
CP	Cloud Point
D100	100 % pure petroleum derived diesel fuel
db	Number of double bonds
EN	European Committee for Standardization
FAME	Fatty Acid Methyl Ester
FP	Fuel Property
GC	Gas Chromatography
HC	Hydrocarbons
HP	Hydroperoxides
HPLC	High Performance Liquid Chromatography
IN	Iodine Number
IR	Infrared Spectroscopy
KOH	Potassium Hydroxide
KV	Kinematic Viscosity
LTFT	Low-Temperature Flow Test
meq	Milliequivalent
MW	Molecular Weight
MW _f	Molecular Weight of an unsaturated fatty acid
NO _x	Nitrous Oxides
OS	Oxidation Stability
PAH	Polycyclic Aromatic Hydrocarbon
PM	Particulate Matter
PP	Pour Point
ppm	Parts per Million
PV	Peroxide Value
RIP	Rancimat Induction Period
RME	Rapeseed Methyl Ester
SME	Soybean Methyl Ester
T _{co}	Crystallization Onset Temperature

UBC	University of British Columbia
VW	Volkswagen
WME	Waste Vegetable Oil Methyl Esters
WVO	Waste Vegetable Oil
X °C	Local Ambient Temperature
XX	Blend Percentage
YGME	Yellow Grease Methyl Esters

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1.0 INTRODUCTION

1.1 Background

Over the last couple of decades, especially in Europe and North America, there has been an increased interest in the research, production and commercial use of biodiesel. Biodiesel is a non-toxic, biodegradable renewable fuel for use in diesel or compression ignition engines (CIE) and is also known as the mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, termed as B100 (100 % pure biodiesel) and meeting the ASTM D 6751 specifications (Dunn and Knothe 2001). Biodiesel is becoming more important as petroleum reserves are on the decline and the environmental consequences of burning fossil fuels is on the increase. Fossil fuels serve as the world's primary transport energy source and there is good potential for biodiesel to supplement the use of petroleum derived diesel (petrodiesel) fuels. References to petrodiesel or D100 in this thesis are made as No. 2 diesel. Some important benefits of using biodiesel as a substitute to petrodiesel are: 1) it is sourced from renewable materials (e.g., virgin vegetable oils, waste vegetable oils (WVO), animal fats); and 2) it yields a significant reduction in emissions (Table 1.1) when burned in diesel engines (Mushrush et al. 2005).

Table 1.1. Exhaust Emission Reduction of B100 and B20 compared to Petrodiesel Fuel (Source: Tyson, 2001)

Emission Type	B100	B20
CO (Carbon Monoxide)	- 3.2%	-12.6%
HC (Hydrocarbons)	-56.3%	-11.0%
NO _x (Nitrogen Oxides)	+5.8%	+1.2%
PM (Particulate Matter)	-55.4%	-18.0%
Air Toxics	-60 to -90%	-12 to -20%
Mutagenicity	-80 to -90%	-20%
CO ₂ (Carbon Dioxide)*	-78.3%	-15.7%

*CO₂ reductions are representative of total lifecycle emissions

Producing high quality biodiesel fuel is essential for its acceptance and longevity in the commercial marketplace (Knothe 2001). To ensure high fuel quality, technical standards are in place for biodiesel and petrodiesel, which list a specific set of quality parameters or fuel properties a fuel should meet before it is distributed and used. The standard for B100 is ASTM D 6751 in North America and EN 14214 in Europe. Biodiesel can be blended in any

ratio with petrodiesel as they have similar fuel properties (Bondioli et al. 2002). A blend of biodiesel mixed with petrodiesel is designated as BXX, with XX signifying the volume percentage of biodiesel in the blend. B20 is the most commonly used blend of biodiesel in industry, where 20 volume % biodiesel is mixed with 80 volume % petrodiesel. B20 offers the maximum benefit in terms of emissions, cold weather performance, solvency, materials compatibility and cost (Tyson 2004). However, there are no fuel standards in place yet for B20 or any other biodiesel blends (e.g., B5, B10, B50). Furthermore, blended biodiesel should not induce chemical instability in the fuel (Mushrush et al. 2004).

The storage and oxidative stability of biodiesel has been a hot topic of discussion, as biodiesel has a shorter shelf life and is more susceptible to fuel degradation reactions than petrodiesel fuels. The shelf life and initial fuel quality of biodiesel depends considerably on the production technology and the type of feedstock. Currently, biodiesel is recommended to be used within 6 months of its production; otherwise, it may degrade to such a quality in showing poor fuel performance, causing operative damage to the diesel engine, increasing repair costs and may prove unsafe (Tyson 2004). Considerations must be made on the time scheduling, distribution and supply of biodiesel from the production plants to the end users, as the methods by which biodiesel may be transported, distributed, handled and stored to and from producers, fleets and users have considerable influences on its quality (Zappi et al. 2003). For example, if users receive a biodiesel fuel 2-3 months past its production date, their storage capability is cut down to a maximum of 3-4 months and users may not be aware of this preceding fact. The stability of biodiesel is affected under long term storage conditions, where the presence of air, temperature and contact with certain metals can promote fuel oxidation reactions (Knothe 2005).

1.2 Research Objectives

The primary objective of this research is to study the storage stability of two commercially available biodiesel (B100) fuels derived from different sources, two commercially available petrodiesel (D100) fuels, and their 20 % fuel blend (B20) under real time ageing conditions. The two biodiesels in this study consist of a blend derived from soybean oils (e.g., soy methyl esters, SME) and a blend derived from waste vegetable oils (i.e., waste methyl esters, WME). Both fuels met ASTM D 6751 prior to ageing. The fuels were stored under cool (6 °C), ambient (X °C) and warm (40 °C) conditions with temperature

as the key variant. These temperatures simulate a scale of conditions that can be experienced during fuel storage. For example, storage at 6 °C evaluates the fuels response to a constant low temperature, X °C evaluates the fuels response to ambient temperatures mimicing the 'natural' environment in climatic zone 8, and 40 °C evaluates the fuel response to a constant high temperature. The quality of the fuel blends is characterized via testing of several fuel properties up to 180 days of storage and in some cases, 300 days. The testing of fuel properties is an integral part of this study, which contributes to an understanding of biodiesel fuel storage behaviour. For its commercial viability, assessing the quality of biodiesel fuel is very important and the issue of storage stability is a key concern (Zappi et al. 2003). There have been studies conducted on the storage stability and ageing of various biodiesel fuels at both accelerated and simulated natural conditions; however, there are few reports published on the combined engine emission testing of aged fuels. To the authors' knowledge, no study to date has conducted a simultaneous real-time ageing of B100, D100 and B20 blends.

The secondary objective of this work is to perform diesel engine emissions testing of select aged blends in a diesel passenger vehicle. The measured emissions include hydrocarbons (HC), carbon monoxide (CO), nitrous oxides (NO_x) and carbon dioxide (CO₂). Very few studies have been conducted combining fuel property characterization and engine emissions testing of aged fuel blends, with most specific to B100 (Bondioli et al. 2003; Canakci et al. 2006; Leung et al. 2006; Thompson et al. 1998). Particular to this study, a comparison of the storage quality of pre-mix B20 blends to after-mix B20 blends is conducted. The pre-mix B20 blend is the pre-storage blend made by mixing biodiesel at 20% by volume with diesel, while the after-mix B20 blends is the post-storage blend made by mixing the biodiesel with petrodiesel after being stored for a specific time.

This study aims to further support biodiesel usage in Canada and supplement the research activities conducted on biodiesel to date. The results could be useful to different parties concerned with biodiesel, with special consideration towards producers, consumers and engine manufacturers:

- Producers: the investigation of biodiesel storage behaviour could provide useful recommendations towards handling, distribution, scheduling and storage.

- Consumers: increasing confidence in fuel quality (e.g., meets regulation standards) that will not pose any operational problems in their diesel powered engines and equipment.
- Engine Manufacturers: need assurance that commercially produced biodiesels are of a consistent high quality to ensure optimal fuel performance, engine durability and low exhaust emissions.

Also, the results of this research are planned to be useful to local users such as UBC plant operations and UBC Utilities, who have expressed interest in acquiring information on biodiesel stability and recommendations for storage and use in the local climate.

2.0 LITERATURE REVIEW

2.1 Biodiesel: An Alternative Diesel Fuel

The first successful operation of the diesel engine took place in 1897 by Rudolph Diesel where vegetable oil was initially used as a fuel. However, from the 20th century onwards vegetable oils did not serve as the primary fuel for diesel engines, which have been mainly powered by petroleum-derived fuels. During the 1970's, experimentation into using vegetable oils in diesel engines resurfaced, but using them as a fuel in the long term caused adverse affects to the engine. Vegetable oils have a very high fluid viscosity (nearly 15-20 times that of petrodiesel fuel), poor cold flow properties and low volatility, resulting in poor fuel atomization, carbon deposits on engine parts, injector coking, piston ring sticking and possible increases in selected emissions (Chang et al. 1996; Mittelbach and Remschmidt 2004). This limitation led researchers to investigate further modifications of vegetable oils and develop fuels that could parallel the properties and performance of petrodiesel fuel. It was soon realized that a low viscosity fuel yielding properties and performance similar to standard petrodiesel fuel could be produced by the transesterification of vegetable oils and biodiesel was born. In 1980, the first patent application for using biodiesel as a diesel fuel substitute was made; and in 1991, the first industrial biodiesel production plant started operation in Austria (Mittelbach and Remschmidt 2004). Figure 2.1 displays the transesterification reaction where the triglyceride molecules of vegetable oils are reacted with a short chain alcohol (usually methanol or ethanol) over an acid or base catalyst to yield biodiesel and a glycerol by-product.

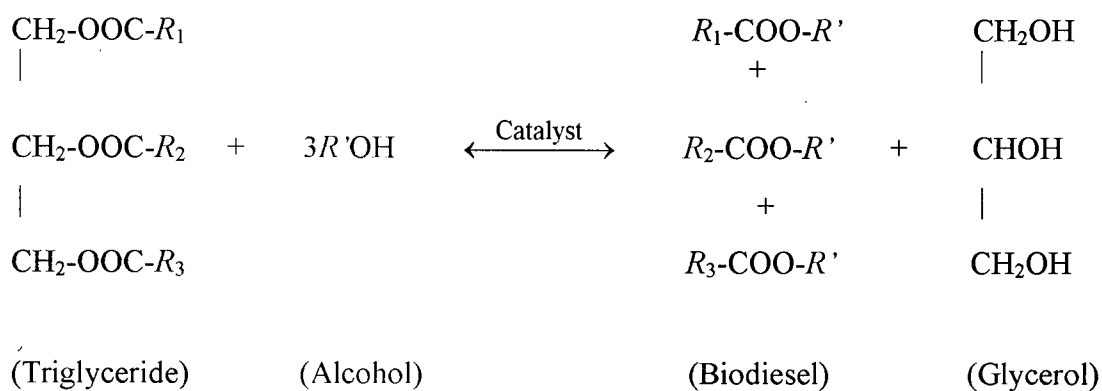


Figure 2.1. Transesterification of a Triglyceride Molecule with Alcohol

The *R* groups represent long hydrocarbon chains that can be saturated and unsaturated and *R'* represents an alkyl group. Biodiesel produced using methanol is a fatty acid methyl ester (FAME). Because methanol is cheaper than ethanol, nearly all biodiesel is produced using methanol.

Biodiesel can be produced from many types of oil seed crops (e.g., rapeseed, soybean, canola, linseed, sunflower, safflower, jatropha, etc.), waste vegetable oils (e.g., restaurant grease) and animal fats (e.g., tallow, lard, yellow grease and chicken fat). However, these resources are only viable as long as they are made available in appreciable quantities to meet production demands. Currently, the majority of biodiesel is produced from virgin vegetable oils, with soybean and rapeseed being the dominant varieties, respectively, in North America and Europe. Soybean oil is attractive for producing biodiesel because of its higher oil yield and economic production (Mushrush et al. 2005). In other regions, biodiesel is being produced from palm, coconut, sunflower and other oils, but on a smaller production scale. Waste vegetable oils are economically competitive for producing biodiesel, as edible virgin oils such as soybean and rapeseed are highly priced and limited (Falk and Meyer-Pittroff 2004). Also, using waste materials such as waste oils and animal fats promotes waste reduction and biodiesel production in this means can be sustainable.

The world production of oil from 2005-2006 averaged at 73.5 million barrels per day, which accounts for 4,263 Billion Litres per year. Table 2.1 below lists the estimated summation of the world production of biodiesel from 2004 – 2006.

Table 2.1. Estimated Yearly World Production of Biodiesel in Billion Litres (Source: Hancock, 2005)

COUNTRY	2004-2005	2005-2006
Germany	1.7	2.0
France	0.4	0.5
Italy	0.4	0.2
UK	0.0	0.2
US	0.4	0.8
Other	0.1	0.1
Total	3.0 Billion Litres	3.8 Billion Litres

The increasing demand for transportation fuel's, high prices and emission impacts of fossil fuels have motivated the growth of biodiesel production from food oil crops. However,

planting and harvesting vegetable oil food crops for the sole purpose of producing biodiesel or other biofuels has caused concerns over the social implications of this practice, especially in developing countries. For example, in some countries (e.g., palm oil in Malaysia and corn oil in Mexico), growing oil crops to produce biofuels has reduced the supply of these crops as food to the local people and also caused increases in these oil crop prices.

Biodiesel's consideration as a viable alternative to petrodiesel fuel stems on the following advantages:

- it is renewable, non-toxic, sulphur-free and biodegradable;
- it provides increased lubricity and higher cetane in terms of fuel performance;
- it can be blended with petrodiesel and used in most diesel engines;
- it reduces exhaust emissions, including unburned hydrocarbons, carbon monoxide, particulate matter and carcinogens;
- it is CO₂ neutral based on the carbon cycle;
- it reduces dependence on imported petroleum based oil and can support the enviro-agro sector.

Though biodiesel has similarities to petrodiesel in terms of fuel performance, there are distinct differences in their chemical compositions. The average chemical formula for petrodiesel fuels is C₁₂H₂₆ and it consists of hydrocarbon chains ranging from C₁₀ to C₁₆ with: (a) 65-70 % saturated hydrocarbons (mixture of paraffins); and (b) 30-35% aromatic hydrocarbons. Biodiesel has no aromatics and is mostly composed of saturated and unsaturated fatty acid esters in the C₁₆ to C₁₈ range, where the unsaturated esters can contain 1-3 double bonds per molecule (Mittelbach and Remschmidt 2004; Mushrush et al. 2001). Additionally, biodiesel has an oxygen content amounting to 11wt.%, whereas petrodiesel fuels are free of oxygen.

2.2 Quality Standards

For any fuel to be used commercially, it needs to meet specific standards. Quality standards are guidelines for: (1) maintaining proficient production fuel process; (2) ensuring top quality fuel to consumers; (3) assessing potential risks to engine or operating equipment; and (4) evaluating effects on the environment (Prankl 2002). Internal combustion engines and other fuel operating equipments are designed and manufactured around these standards. In North America, the American Society for Testing and Materials (ASTM) is the group that

mandates quality standards for all types of fuels, including petrodiesel and biodiesel. The ASTM standard for biodiesel (B100) and petrodiesel (D100) are ASTM D 6751 (Table 2.2) and ASTM D 975 (Table 2.3), respectively. EN 14214 is the European standard specification for B100 (Table 2.4).

Table 2.2. ASTM D 6751 Specification for 100% Pure Biodiesel (B100), as of June 2006

FUEL PROPERTY	ASTM METHOD	LIMITS	UNITS
Flash Point	D93	130 min	°C
Water & Sediment	D2709	0.050 max	% volume
Kinematic Viscosity (40 °C)	D445	1.9 - 6.0	mm ² /s
Sulphated Ash	D874	0.020 max	% mass
Sulphur (S 15 Grade)	D5453	0.015 max	ppm
Sulphur (S 500 Grade)	D5453	0.050 max	ppm
Copper Strip Corrosion	D130	No. 3 max	Rating
Cetane Number	D613	47 min	
Cloud Point	D2500	Report ¹	°C
Carbon Residue	D4530	0.050 max	% mass
Acid Number	D664	0.50 max	mg KOH/g
Free Glycerol	D6584	0.02 max	% mass
Total Glycerol	D6584	0.240 max	% mass
Phosphorus Content	D4951	0.001 max	% mass
Distillation Temperature	D1160	360 max	°C

Table 2.3. ASTM D 975 Specification for 100% No. 2 Diesel (D100)

FUEL PROPERTY	ASTM METHOD	LIMITS	UNITS
Flash Point	D93	52 min	°C
Water & Sediment	D2709	0.050 max	% volume
Distillation Temperature	D86	282 min 338 max	°C
Kinematic Viscosity (40 °C)	D445	1.9 - 4.1	mm ² /s
Ash	D482	0.010 max	% mass
Sulphur (Grade No.2)	D2622	0.50 max	ppm
Sulphur (Low Grade No.2)	D129	0.05 max	ppm
Copper Strip Corrosion	D130	No. 3 max	
Cetane Number	D613	40 min	
Cloud Point	D2500	Report ¹	
Carbon Residue	D524	0.035 max	% mass
Lubricity, HFRR @ 60 °C	D6079	520 max	microns

¹ The cloud point result is a reported measure as it will vary for different geographic locations.

Biodiesel producers in Canada and the US are expected to adhere to ASTM D 6751; however, certain fuel properties such as oxidation stability and iodine number are not included in ASTM D 6751, but are part of EN 14214 and have an importance in characterizing biodiesel fuel quality. Biodiesel must meet ASTM D 6751 or EN 14214 upon its production and before it is blended with any petrodiesel. For biodiesel, these standards make certain the production process resulted in a complete reaction with a low sulphur content, glycerine removal, catalyst removal, alcohol removal and a very low presence of free fatty acids.

The technical standards list the limits and ranges that the properties a fuel must meet prior to its availability in the commercial market. The standards help ensure that a fuel possesses the right fuel properties for safe operation in a compression ignition engine and poor processing has not contaminated the fuel with products which may cause damage to the engine or the fuel system. This is why engine manufacturers rely on quality standards for the release of warranties on their vehicles.

Table 2.4. EN 14214 Specifications for 100% Pure Biodiesel (B100)

FUEL PROPERTY	METHOD	LIMITS	UNITS
Density (15°C)	EN ISO 3675	0.86 - 0.90	g/cm ³
Viscosity (40°C)	EN ISO 3104	3.5 - 5.0	mm ² /s
Flash Point	ISO / CD 3679	10 min	°C
Acid Number	EN 14104	0.5 max	mg KOH/g
Oxidation stability (110°C)	EN 14112	6 min	hours
Sulfur		0.01 max	% mass
Sulfated Ash	ISO 3987	0.02 max	% mass
Water Content	EN ISO 12937	500 max	mg/kg
Carbon Residue	EN ISO 10370	0.03 max	% weight
Total Contamination	EN 12662	24 max	mg/kg
Copper Corrosion	EN ISO 2160	Class 1	Rating
Cetane Number	EN ISO 5165	51 min	
Methanol Content	EN 14110	0.20 max	% mass
Ester Content	EN 14103	96.5 min	% mass
Monoglyceride	EN 14105	0.80 max	% mass
Diglyceride	EN 14105	0.20 max	% mass
Triglyceride	EN 14105	0.40 max	% mass
Free Glycerol	EN 14105	0.02 max	% mass
Total Glycerol	EN 14105	0.25 max	% mass
Iodine Number	EN 14111	120 min	
Phosphorus	EN 14107	10 min	mg/kg
Alkaline Metals (Na, K)	EN 14108	5 max	mg/kg

Biodiesel can be used in its 100 % or pure form in most diesel engines, but many engine manufacturers caution against this as there are concerns over the effects biodiesel may have on the fuel system and on engines performance, particularly related to fuel stability and cold temperature operation (National Biodiesel Board 2006). Manufacturers such as Detroit Diesel and Cummins recommend biodiesel to be blended up to a max of 5% vol., otherwise there may be a void on engine warranty. Presently, many users are using B20 because it is the ratio that provides emissions reduction without sacrificing performance (Wain and Perez 2002). Some disadvantages and concerns of using biodiesel in diesel engines at higher blend levels than B20 are listed and summarized in Table 2.5.

Table 2.5. Disadvantages of Using Biodiesel Blends Greater than B20 in Diesel Engines (Source: National Biodiesel Board, 2005)

DISADVANTAGE	REASONING
Fuel Stability	Biodiesel is more prone to degradation reactions because it is biologically sourced, making it more unstable than No.2 diesel. Fuel oxidation can result under certain conditions and generate acid by-products, gums, sediments and polymers that reduce fuel quality.
Performance during Cold Temperatures	At low temperature conditions, particularly during winter seasons, biodiesel fuels are known to gel and thicken at higher temperatures than conventional petrodiesel fuels. This is problematic because the gelling impacts fuel flow within the engine and also causes filter plugging.
Solvency	The solvent like quality of biodiesel can degrade and wear out materials that are not compatible with biodiesel, such as elastomer and rubber compounds that are part of fuel hoses and fuel pump seals. Also, biodiesel can dissolve sediments and deposits within diesel engine systems, causing possible build-ups of these materials at the fuel filter. This can impede fuel flow and lead to plugging of the fuel filter.
Lower Energy Content	Biodiesel fuels have an energy content that is lower than No. 2 diesel fuels and this can increase fuel consumption rates, for example, more biodiesel is needed to gain the same power output as a petrodiesel fuel.

Due to the concerns discussed above, ASTM D 6751 is only recommended for biodiesel blends up to the 20 % vol. (B20) mark. Presently, there is no quality standard in place for B20, thus ASTM D 975 standard has been used in some cases as a temporary guideline.

2.3 Fuel Properties

The properties specific to biodiesel fuel include acid number, free glycerine, total glycerine, phosphorus content, alkaline metals, methanol content, ester content, monoglyceride, diglyceride, triglyceride, peroxide value, iodine value and oxidation stability, where the latter nine properties are not a part of the ASTM standard. The fuel properties applicable to petrodiesel and biodiesel are: ash, sulphur, carbon residue, copper strip corrosion, distillation temperature, flash, point, density, kinematic viscosity (40°C), cetane number, water and sediment and cloud point.

Biodiesel derived from different feedstocks can display variation in their initial fuel properties. This is attributed to the characteristic composition of the fatty acid methyl esters (FAME). For example, fuel properties such as cetane number, cloud point and oxidative stability are dependent on the type of feedstock that is used to produce the resulting biodiesel (Tyson 2004). Variability is present even within the same type of vegetable oil that is used to make biodiesel. For example, the kinematic viscosity (KV) at 40 °C of biodiesel derived from different types of soybean oils has ranged between 3.77 to 4.32 mm²/s (Yuan et al. 2003).

In the ASTM, the KV (at 40 °C) of biodiesel and petrodiesel are specified to be within 1.9 - 6.0 mm²/s and 1.9 - 4.1 mm²/s, respectively. Biodiesel fuels have characteristically higher viscosities than petrodiesel fuels. The KV (ν) of a fluid is determined by dividing its viscosity (μ) by its density (ρ).

$$\nu = \frac{\mu}{\rho} \quad (1)$$

Viscosity affects the fuel flow in an engine and its atomization; thereby influencing injection pressure, injection rate and spray characteristics (Rodrigues et al. 2006; Zappi et al. 2003). The viscosity of biodiesel is influenced by its fatty acid composition, where a higher degree of unsaturation (e.g., greater content of fatty acids with double bonds) will be of lower viscosity than a lower degree of unsaturation and vice versa (Mittelbach and Remschmidt

2004). For example, biodiesels produced from saturated oils (e.g., coconut and palm) yield higher viscosities than their unsaturated counterparts (e.g., soybean and sunflower). Additionally, the viscosity of biodiesel can correspond to the amount of un-reacted triglycerides and is a useful parameter for evaluating production quality.

Water content in biodiesel and petrodiesel is restricted to a maximum of 0.05 % by volume. Biodiesel has a higher polarity and a greater affinity towards water absorption than petrodiesel. For instance, biodiesel can absorb dissolved water up to 1500 ppm, while petrodiesel dissolves only 50 ppm (Van Gerpen et al. 1997). If the fuels surpass these limits, water can separate from the fuel and collect at the bottom of the storage vessels; thereby encouraging microbial growth, leading to sludge and slime formations that can plug fuel filters and fuel lines (Mittelbach and Remschmidt 2004). The presence of water lowers the fuel heating value and can increase corrosion. Water can promote fuel oxidation via hydrolytic reactions and cause the formation of insoluble compounds as sediments. For these reasons, it is essential not to introduce water to biodiesel during transport and storage, but is challenging since fuel tanks may gather water near its bottom from condensation (Van Gerpen 2005).

The Acid Number (AN) characterizes the amount of organic acids present in a fuel and is defined as the milligram (mg) amount of potassium hydroxide (KOH) needed to neutralize the acids in 1 gram (g) of fuel (Mittelbach and Remschmidt 2004). Depending on the concentration of the KOH solution used, the pH endpoint of titration varies and is usually between 8 and 12 (ASTM 2004). The ASTM standard for the AN of biodiesel is set to a maximum of 0.5 mg KOH/g. AN of biodiesel is influenced by the type of production process and the quality and type of feedstock. Mineral acids can result in the form of catalysts and free fatty acids from the acidic build-up of soaps (Mittelbach and Remschmidt 2004). Monitoring the changes in AN during storage is useful as it can characterize acids produced by fuel oxidation and other degradation reactions. Thermal conditions are known to cause increases in AN. Highly acidic fuels can increase the formation of deposits and cause corrosion within an engine's fuel system, which can further lead to poor fuel combustion, injector fouling and fuel pump malfunction (ASTM 2004).

The Cetane Number (CN) is a dimensionless indicator of a diesel fuel's ignition quality and is conceptually similar to the octane number in gasoline fuel. A scale of 0-100 is devised to measure cetane, where 0 refers to the α -methylnaphthalene ($C_{10}H_7CH_3$), a

naphthenic compound with poor ignition qualities and 100 signifies n-cetane ($C_{16}H_{34}$), a straight chain alkane that ignites easily when compressed (Stone 1999). The CN is a measure of the ignition delay (ID) time, defined as the time interval between the start of fuel injection into the cylinder and the start of combustion (onset of ignition) within a diesel engine (Knothe 2005). ASTM specifies biodiesel and petrodiesel fuels to have the minimum cetane ratings of 47 and 40, respectively, with higher cetane values correlating to shorter ID times. It is favourable for fuels to exhibit a high CN, as it will facilitate the fuel to run more smoothly in an engine (improved combustion) and cause less problems during cold start-up (Mittelbach and Remschmidt 2004). However, if a fuel has a CN that is either too high or too low, it can result in incomplete fuel combustion. The CN of soybean derived biodiesel has been reported with considerable differences between the reported values due to the variability in feedstock, processing and production of the fuel used in each study. The CN of biodiesel depends on the fuel volatility, molecular weight and chemical structure (e.g., straight chains, branched chains, double bonds) (Chang et al. 1996). Saturated fatty acids have a higher CN than unsaturated fatty acids; therefore, biodiesel produced from highly saturated oils or fats (e.g., palm, tallow) will demonstrate a higher CN (Kann et al. 2002). A biodiesel of this type can also display a higher viscosity and unfavourable properties related to cold flow.

The Peroxide Value (PV) measures the level of peroxide compounds contained in a fuel sample resulting from fuel oxidation and is expressed as the milliequivalents of peroxide per kilogram of sample. PV is not listed in the biodiesel specification for ASTM and EN standards, but is useful to measure as it can monitor the extent of fuel oxidation. PV is also correlated to the cetane number (CN) (Dunn 2002). The formed hydroperoxides have an increasing effect on CN as peroxide compounds (e.g., dialkylperoxide) serve as strong cetane enhancers (Van Gerpen 1996). In some cases cetane data can be compared to fuel oxidation effects if both PV and CN are reported (Mittelbach and Remschmidt 2004).

Cloud point (CP) is used to characterize the low temperature behaviour of a combustion fuel. Though not included in the ASTM standard, other fuel properties important for assessing cold flow behaviour are pour point (PP), cold-filter plugging point (CFPP), low-temperature flow test (LTFT) and crystallization onset temperature (T_{co}) (Mittelbach and Remschmidt 2004). For biodiesel, CP is the reported temperature in Celsius degrees when the liquid fatty material becomes cloudy due to solidification of saturates and crystal formations. It is the temperature at which crystals first appear as the fuel is cooled. The

formed crystals and solids can agglomerate, causing clogging of fuel filters and lines, which can negatively affect engine start-up, leading to fuel starvation and engine failure (ASTM 2004). Though there is no specified limit for CP, it is recommended to be low and the measured values will vary according to the climate conditions of the geographic area in which the fuel is used. Poor cold flow properties are a major technical hurdle for biodiesel, as it limits certain types of biodiesel to certain climatic regions (Dunn 1999). Saturated fatty compounds have higher melting points than unsaturated fatty compounds and will crystallize at higher temperatures (Knothe 2005). Because unsaturated compounds are more likely to oxidize than saturated compounds, an inverse relationship is conceived between the oxidative stability and cold flow properties of biodiesel (Kinney and Clemente 2005).

Oxidation stability (OS) is a biodiesel fuel property specified in the EN standard, and is tested by determining the minimum induction time by the Rancimat method, defined as the Rancimat Induction Period (RIP). The time is recorded while the fuel is aged at 110 °C under a constant air flow and degraded to a point where volatile acids are produced (Mittelbach and Remschmidt 2004). The standard is to meet a minimum RIP of 6 hours, with the length of the induction period being a measure of the fuel's resistance to oxidation. In many cases, it is difficult for biodiesel fuels to comfortably meet this limit and the addition of synthetic antioxidants is highly recommended. OS is considered to be a critical parameter for the performance of the injection pump. Accelerated stability defined by ASTM D2274 is the stability test method for petrodiesel fuels and is conceptually similar to oxidative stability, but is not included as part of the D975 property specification. It measures the fuel's tendency to form gums and sediments under accelerated oxidizing conditions, while the fuel is heated for 16 hours and placed through a filter where the formed insolubles are captured and weighed. The industry limit for the maximum accelerated stability has been defined at 1.5 mg/100 mL. Excessive levels of insolubles can cause filter plugging, combustion chamber deposit formation and gumming of injection system components with resultant sticking and wear.

Iodine number (IN) is a structure index used to specify the average unsaturation content in a mixture of fatty compounds and is stated as the number of centigrams of iodine absorbed per gram of sample (Knothe 2002). Because unsaturated bonds are more prone to oxidation than saturated bonds, a highly unsaturated biodiesel is more susceptible to effects

promoting oxidative degradation. The IN of a mixture of fatty compounds can be computed as follows,

$$IN_{\text{mixture}} = \sum 100 \times \frac{A_f \times 253.81 \times db}{MW_f} \quad (2)$$

where for each unsaturated fatty compound in the mixture, A_f is the amount present in mass percent quantity, db is the number of double bonds, MW_f is the molecular weight, and 253.81 is the combined weight of two iodine atoms added in theory for one double bond (Knothe 2002). From Equation 2, IN depends on the MW and the percent quantity of the unsaturated fatty compounds in the mixture, where the structural nature of the double bonds is not taken into account. The correlation of IN to certain fuel properties in characterizing FAME has been reported to be poor (Knothe 2002). IN has been a subject of discussion among engine manufacturers who claim that fuels which have high iodine values when heated, are likely to polymerize and form deposits on piston rings, injector nozzles and piston ring grooves (Mittelbach and Remschmidt 2004). Theoretically, highly unsaturated fatty compounds are expected to yield lower oxidation stability values; thereby, increasing the tendency to form fuel degradation products during engine operation. However, Prankl et al. (1999) concluded no significant differences in deposit formation in the cylinder liner, combustion chamber, injectors and valves from testing biodiesels with an IN of 107 – 150.

In the EN standard, the IN of biodiesel is limited to 120, thus eliminating the usage of biodiesel produced from soybean and sunflower oils. It would be difficult for economic reasons and feed availability to completely exclude the production of biodiesel from these oils and other feed materials because of their high IN (Kann et al. 2002). Table 2.6 lists the lowest and highest reported IN of the major feedstock oils that are used for producing biodiesel in the world.

Table 2.6. Iodine Number of the top 4 most important Feedstock Oils for Global Biodiesel Production (Mittelbach and Remschmidt 2004)

Feedstock Oils	Iodine Number [g Iodine / 100 g]	
	Lowest	Highest
Palm	36	58
Rapeseed	96	119
Soybean	122	143
Sunflower	128	141

Flash point is defined as the lowest temperature at which fuel vapour can ignite. It assesses the fuel flammability range which is useful for transport and storage conditions. The ASTM flash point of biodiesel at a minimum of 130 °C is much greater than that of petrodiesel at a minimum of 52 °C, making biodiesel a much safer fuel to handle. The Conradson Carbon Residue (CCR) test accounts for the content of glycerides, free fatty acids, soaps, unreacted catalyst and other impurities that may be present in a fuel (Mittelbach and Gangl 2001). Carbon residue refers to the carbonaceous matter which results after a fuel is subjected to evaporation and pyrolysis. CCR assesses the potential of a fuel to form deposits inside the combustion chamber and on fuel injectors. Because petrodiesel fuels have CCR values that are typically low, CCR is more significant for biodiesel fuels. Moreover, a high carbon residue is associated with an excessive concentration of polymers and polyunsaturated FAME (Mittelbach and Remschmidt 2004). As stated in ASTM specifications, other properties such as free glycerol, total glycerol, methanol content, phosphorus content, ash and copper strip corrosion are tested to ensure that the produced fuel is free of contaminants.

Specific to biodiesel, the amount of free and total glycerol present in the fuel is highly dependent on the production processes. Hence, the glycerol properties are an important quality measure for biodiesel, with maximum limits set at 0.02 % mass for free glycerol and 0.24 % mass for total glycerol. Total glycerol accounts for both free and bonded glycerol (in the form of mono-, di- and triglycerides) (Van Gerpen 2005). Glycerol is insoluble in biodiesel and can separate and collect near the bottom of fuel tanks, where polar bonding between the soaps and water is likely. This can lead to problems during fuel storage, leading to an increase in the fuel viscosity (Mittelbach and Remschmidt 2004). High concentrations of glycerol can lead to injector fouling, bearing metal corrosion, and deposits on pistons and valves (Kann et al. 2002; Zappi et al. 2003).

The phosphorus content is restricted to 0.001 % mass because of its effect to cause damage to catalytic converters and produce higher emissions of particulate matter. The level of phosphorus contained in biodiesel is dependent on the feedstock, and how the process of oil recovery takes place, as hot pressed oils will have more phosphorus than cold pressed oils (Mittelbach and Remschmidt 2004). The sulphated ash or ash content measures the quantity of inorganic impurities in the form of catalyst residues, soluble metals and coarse solids. If these contaminants are present in high concentrations and have not been removed from the

fuel, they can lead to injector malfunction, piston sticking, fuel pump problems, engine deposits and ring wear (Zappi et al. 2003). The copper strip corrosion property measures the degree of corrosion a fuel could cause when it comes in contact with metals in an engine or in fuel storage tanks. Petrodiesel and biodiesel fuels should also have ample lubricity for the purpose of lubricating the fuel pump and forcing the fuel through the fuel system and injectors; low lubricity can lead to engine wear and accelerate engine deterioration (Kinney and Clemente 2005; Wain and Perez 2002). Lubricity is a concern for petrodiesel fuels produced since 2007, with the mandate for low sulphur diesel fuels is in effect. The removal of sulphur from diesel causes a loss in lubricity as non-sulphur polar compounds are also removed (Knothe 2005). However, lubricity can be restored to low sulphur petrodiesels by blending biodiesel at levels of 1-2 vol. %. The sulphur content in biodiesel can depend on the type of vegetable oil used to produce it; for example, canola oil contains a higher sulphur content in comparison to other oils (Mittelbach and Gangl 2001; Zappi et al. 2003).

It is crucial to acknowledge how variation of the fatty acid profile of biodiesel weighs into the characteristics of certain fuel properties; particularly, density, viscosity, cetane number, oxidative stability, cold flow, lubricity and heat of combustion (Knothe 2005). The structural characteristics (e.g., chain length, degree of unsaturation, chain branching) and alcohol moiety of the fatty acid esters also have an impact on these fuel properties particularly for cetane number and cloud point. Table 2.7 lists the structure and chemical formula of possible fatty acids present in different types of vegetable oils.

Table 2.7. The Chemical Structure of Common Fatty Acids (Adapted from Barnwal and Sharma 2005)

FATTY ACID	CHEMICAL NAME	STRUCTURE (XX:Y)	CHEMICAL FORMULA
Lauric	Dodecanoic	12:0	$C_{12}H_{24}O_2$
Myristic	Tetradecanoic	14:0	$C_{14}H_{28}O_2$
Palmitic	Hexadecanoic	16:0	$C_{16}H_{32}O_2$
Stearic	Octadecanoic	18:0	$C_{18}H_{36}O_2$
Oleic	cis-9-Octadecenoic	18:1	$C_{18}H_{34}O_2$
Linoleic	cis-9,cis-12-Octadecadienoic	18:2	$C_{18}H_{32}O_2$
Linolenic	cis-9,cis-12,cis-15-Octadecatrienoic	18:3	$C_{18}H_{30}O_2$
Arachidic	Eicosanoic	20:0	$C_{20}H_{40}O_2$
Behenic	Docosanoic	22:0	$C_{22}H_{44}O_2$
Erucic	cis-13-Docosanoic	22:1	$C_{22}H_{42}O_2$
Lignoceric	Tetracosanoic	24:0	$C_{24}H_{48}O_2$

Furthermore, Table 2.8 highlights some of the differences between biodiesels derived from different feedstocks, as exemplified by their fuel properties.

Table 2.8. Average Fuel Properties of B100 derived from different Vegetable Oils (Adapted from Barnwal and Sharma 2005; Mittelbach and Remschmidt 2004)

Vegetable Oil Methyl Esters	Density (kg/l)	Kinematic Viscosity (mm ² /s)	Cetane Number	Cloud Point (°C)	Flash Point (°C)
Sunflower	0.86	4.6	49	1	183
Rapeseed	0.87	4.4	54	-3	170
Soybean	0.89	4.5	45	1	178
Palm	0.88	5.7	62	13	164
Peanut	0.88	4.9	54	5	176

Changes in fuel properties can potentially affect a fuels quality, composition and engine performance (Batts and Fathoni 1991). To better understand the conditions with which fuel properties change, it is necessary to discuss factors that affect fuel stability.

2.4 Fuel Stability

Fuel stability is defined as the ability of a fuel to resist change when exposed to a variety of conditions. A change in fuel stability is observed in terms of: (1) colour change; (2) development of soluble and/or insoluble gum; (3) development of sediments or deposits; (4) changes in fuel properties or fuel composition; and (5) compatibility changes with fuels/materials (Batts and Fathoni 1991). Each of these characteristics is important for evaluating fuel stability and they are often interrelated to one another. A fuel with changed characteristics is likely unstable.

A change in colour is a predecessor of sediment formation and a concern for marketing purposes. Fuels that form colour may not necessarily develop gums and sediments; however, it is rare for a fuel that develops gum and sediment to go without a colour change. The formation of soluble and/or insoluble gum can affect engine performance, with the latter having more effect. Insoluble gums should be filtered from the fuel before passing through the engine – their presence in large amounts can cause clogging of the screen and engine filters (Batts and Fathoni 1991). Insolubles can affect flow through fuel injectors and nozzles, resulting in incomplete operation and problems with engine start-up. Also, sediment deposits act as binding agents for dirt, water and rust, which promote microbial growth within the fuel distribution systems, amounting to possible contamination,

degradation and corrosion. Changes in fuel properties of a physical nature such as colour, density and viscosity give indication of reduced fuel quality, but are not as detrimental to fuel stability in comparison to changes in fuel properties of a chemical nature. However, it is expected that the fuels physical properties would change with changes in the fuels chemical properties. Extensive fuel degradation can affect engine performance by causing the engine to malfunction or fail. This leads to an increase in costs, maintenances, equipment vulnerability and less reliability.

Fuel stability is classified in terms of thermal, oxidative and storage stabilities. Thermal stability refers to the stability of a fuel when exposed to high temperatures; oxidative stability refers to the stability of a fuel has against exposure to oxygen and air; storage stability refers to the stability of a fuel under the conditions and time length of storage (Batts and Fathoni 1991; Mittelbach and Remschmidt 2004).

The thermal stability of a fuel deals with changes a fuel may undergo in a high temperature environment, specifically pertaining to conditions within the fuel injection system (e.g., 60 -100 °C) and at the tips of a fuel injector (e.g., up to 30,0 °C). As a result of thermal stress, the fuel may deteriorate and form free radicals that can lead to several oligomerization and cyclization processes. This leads to the formation of polymerized materials that may cause sticking of the injection pump or plugging of the fuel-filter (Mittelbach and Remschmidt 2004). Bondioli et al. (2002) examined the thermal stability of biodiesel fuels of differing compositions, and found that biodiesel produced from waste vegetable oils yielded a higher percentage of polymeric material. The recommendation is to distil fuels rich in polymers and to measure their polymer content as a parameter for assessing a fuel's thermal stability.

Fuel oxidation can be defined as a series of reactions that occur between certain fuel components and an oxygen molecule. Biodiesel has a greater susceptibility to oxidative degradation than petrodiesel because of its chemical composition of unsaturation (Mittelbach and Remschmidt 2004). Unlike petrodiesel consisting mainly of saturated hydrocarbons, biodiesel consists of fatty acids that are a combination of saturated and unsaturated fatty acid components. Unsaturated components, with their carbon-carbon double bonds are prone to oxidative attack. For example, an oxygen molecule can attach to the methylene (CH_2 -) groups adjacent to a double bonded carbon, resulting in hydroperoxide formation (Monyem 2000). Hydroperoxides are the initial products of oxidation and their formation follows a

peroxidation chain mechanism. There is a tendency for hydroperoxides to chemically attack elastomers in fuel systems, an ensuing concern for producers and users (Canakci et al. 1999). Hydroperoxides are a highly reactive and unstable chemical species. Due to this instability, hydroperoxides can break apart to form secondary oxidation products such as aldehydes, ketones and other shorter chain acids. Conversely, hydroperoxides induce polymerization reactions by reacting with other free radicals to form dimers and polymers: insoluble materials of higher molecular weight and higher boiling point (Van Gerpen 1996). The presence of these products results in unpleasant odours, discolouration and sediment formation within the fuel; whilst, having an altering effect on fuel properties such as AN, KV and PV.

In addition to oxygen availability, biodiesel oxidation is influenced by: (1) nature of unsaturated bonds in the original fatty acids; (2) presence of natural antioxidants; (3) presence of pro-oxidizing agents (e.g., UV light, metals); and (4) temperature (Bondioli et al. 1995; Canakci et al. 1999). The oxidation rate of unsaturated fatty acids depends on the number and position of the double bonds where an oxygen molecule could possibly attack. The oxidation rate of one double bond is 10 times slower than fatty acids with three two double bonds at temperature ranges of 20 to 100 °C (Canakci et al. 1999). For instance, linolenates (C18:3) will oxidize 98 times more and linoleates (C18:2) will oxidize 41 times more than oleates (C18:1) (Knothe 2005). This is important because many biodiesel fuels are composed of a higher proportion of esters of oleic, linoleic and linolenic acids, which are going to influence the fuels oxidative stability. Oxidative stability goes hand in hand with storage stability, since oxidative reactions are likely to occur when a fuel is in storage for a long time period.

The storage stability of a fuel is an important matter since it is concerned with the fuels shelf life or 'best before date' and as with any commodity product, it would be most favourable to have the longest life possible. Even if proper measures are taken to ensure a long shelf life, one must know the age at which a fuel deteriorates to a quality that would make it unusable in diesel engines. During long term storage, biodiesel can be subjected to fuel degradation as a result of oxidative and hydrolytic reactions (Mittelbach and Remschmidt 2004). As discussed oxidative degradation leads to hydroperoxide formation, which can result in fuel polymerization, causing an increase in fuel viscosity. During storage, the fuel oxidation rate is dependent on the availability of oxygen in the headspace of

the storage tanks/containers and the presence of oxygen in dissolved form within the fuel itself (Canakci et al. 1999). Hydrolytic degradation caused by the hydrolysis of methyl esters in the presence of water is also a problem during long term storage. This type of degradation depends on the amount of water that is present, the acidity of the fuel, the temperature, and whether the water is in a dissolved, emulsified or separated state (Bondioli et al. 1995).

Though petrodiesel is known to have better stability than biodiesel, it also can be subjected to fuel deterioration under certain conditions. Paraffins, naphthenes, olefins and aromatics are the hydrocarbons that petrodiesel fuel consists of, where the former two are saturated and the latter two are unsaturated (Bacha et al. 1998). Examples of aromatic compounds in petrodiesel are benzene and toluene, they have cyclic ring like structures and are unfavourable because they have low cetane numbers and, when released in exhaust emissions, are harmful and toxic (Van Gerpen et al. 2004). The major elements of diesel fuel are C and H, but there can be minute amounts of sulphur, nitrogen and oxygen present, otherwise referred to as heteroatoms (other atoms). The heteroatoms can be embedded as part of a molecular structure yielding a compound that is not a hydrocarbon, such as carbozole and dibenzothiophene. It is the presence of these heteroatom compounds along with organic acids and reactive olefins that can lead to diesel instability. This instability encompasses the oxidative conversion of the leading precursors to high molecular weight species (sedimentation) that have minimal solubility (Bacha et al. 1998). Reactions leading to sedimentation in petrodiesel fuel are acid/base reactions, polymerization and oxidation at points of unsaturation. Mechanisms of sediment formation usually involve chemical species that include indoles, pyrroles, aromatic thiols, heterocyclic aromatics and carbozoles (Beaver and Gilmore 1991). The absence of these species in biodiesel, clearly imply that instability reactions of petrodiesel are different from biodiesel. Figure 2.2 illustrates a conceptual map of the instability processes a petrodiesel fuel may undergo, with the marked oxidative, thermal and storage effects.

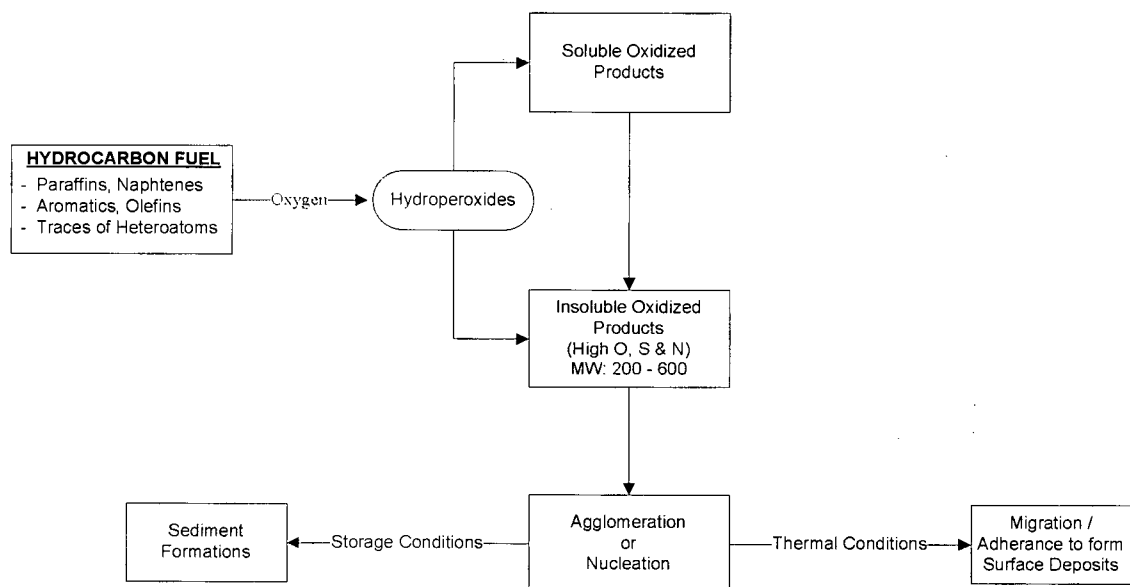


Figure 2.2. Summarized Diagram of Diesel Fuel's Stability Process (Batts and Fathoni 1991)

2.4.1 Long Term Storage

The main disadvantage in using biodiesel over petroleum diesel is its susceptibility to fuel degradation during long term storage. It is recommended that biodiesel be distributed and used within 6 months of its production (Tyson 2004). Comparatively, B20 blends are also recommended to be used within 6 months with test data suggesting 8 – 12 months. This notion also applies to petrodiesel fuels, where some suppliers recommend for it to be used within a 3-4 month time frame. It is important to know the time period for which the produced fuel can sustain its initial production quality according to the ASTM or EN standards. Although time consuming, studying the storage quality of a fuel is best under real-time conditions where it is aged naturally (Bondioli et al. 2002). To date, long term storage stability studies (6 months to 2 years) have been limited to B100 fuels (Bondioli et al. 2003; Bondioli et al. 1995; Leung et al. 2006; Mittelbach and Gangl 2001; Thompson et al. 1998).

Comparisons between published studies can be difficult due to differences in initial fuel quality, feedstock, container material, air/light contact, temperature, metal presence, testing methods and analysis (Bondioli et al. 2003). The earliest reference to a study on the storage stability of biodiesel was conducted by Du Plessis et al. (1985), where methyl and ethyl esters derived from sunflower oils were subjected to storage for 90 days. The stored biodiesel was analysed under the effects of air, temperature, light, antioxidant addition and steel contact through monitoring the AN, KV, PV and time of induction (similar to RIP).

These properties increased during storage with greater increases observed at higher temperatures.

Bondioli et al. (1995) reported on the storage stability of biodiesel derived from rapeseed oil for 180 days at controlled temperature conditions of 20 °C and 40 °C, with periodic monitoring of AN and PV at moisture levels ranging from 0.1 - 1.0 % wt. They noticed low increases in AN after 180 days of ageing, with absolute changes being no greater than 0.02 mg KOH/g at 20 °C and 0.12 mg KOH/g at 40 °C. The largest change was noticed in conditions of higher temperature (40 °C), longer contact time (180 days) and highest moisture concentration (1.0 % w/w).

Thompson et al. (1998) monitored the deterioration extent of rapeseed methyl and ethyl esters for 24 months, stored at room temperature and at local outdoor temperatures, and found that AN, KV, PV and density increased with time. They also conducted some engine performance tests of the aged fuels, where power, torque, fuel economy, injector fouling and smoke density were the tested variables. So far, this is the only study that has combined some form of engine test measure on fuels aged under real time conditions. Mittlebach and Gangl (2001) studied the storage stability of biodiesel derived from rapeseed and used frying oils (similar to WVO) up to 6 months. They monitored the AN, KV, PV and OS with air exposure and daylight being the tested factors and found significant increases in the tested parameters for increased air and light exposure.

Leung et al. (2006) conducted a storage study of biodiesel derived from rapeseed oil by periodic measuring of the AN and ester content over a 52 week time period, where temperature, water content and air exposure were the varying factors. They concluded that the combined impact of 'air + temperature + water' had a greater impact in reducing the quality of biodiesel than the effect of air or temperature by itself with water having a much lesser effect. There has been no reported effect of storage container on biodiesel ageing, unless if the container is metallic in nature or of a translucent material that can absorb light (Mittelbach and Gangl 2001; Thompson et al. 1998).

Accelerated ageing studies have examined the impact of oxygen flow rate, temperature, antioxidants, feedstock type and metals on fuel oxidation (Canakci et al. 1999; Dunn 2002). Accelerated test methods are conducted under extreme conditions involving high oxygen concentrations, high temperatures and high pressures; where the idea is to advance the chemical reactions that would occur otherwise under "non-accelerated" or "real-

time” conditions. The results of accelerated ageing can be compared to what may happen in practice, but cannot be relied upon to simulate natural ageing. As there are cases where reactions that occur during accelerated ageing may not transpire during real time ageing (Services 1997). Bondioli et al. (2004) compared results of biodiesel stored for 1 year under real time conditions and biodiesel stored for 24 weeks at 43°C with biodiesel aged at 80 °C for 24 hours and concluded differences in the rates and types of degradation reactions taking place at each case. The ageing behaviour of biodiesel is different under different conditions and there is a limit in applying accelerated ageing methods to estimate biodiesel stability and properties under real time conditions (Bondioli et al. 2004). Accelerated samples will have markedly different fuel properties when compared to samples undergoing ageing for long periods in ambient conditions.

The storage stability of blends of biodiesel with petrodiesel, particularly B20, is of interest with regards to its quality and the negative effects of fuel oxidation (Dunn 2002). The addition of biodiesel as a blending stock to petrodiesel in any percentage can pose an operation concern with respect to the blended fuels storage stability, oxidative stability, solubility and filterability (Mushrush et al. 2005). Even if two fuels, each of good quality and stability are mixed together, the resulting fuel blend may not reflect the same quality and stability of the original blends. As one fuel may contain precursors for inducing instability that may not be present in the other fuel, and once the fuels are mixed, degradation or a change could result (Bacha et al. 1998). Stemming from this, a possible discussion of interest is how well the properties of a blended fuel can reflect the fuel properties of its parental mix in terms of predicting it via volumetric mixing. Consider the following formula, where FP stands for the fuel property in question and XX stands for the blend percentage of biodiesel, ranging from 0 to 100%.

$$FP_{BXX} = \left(\frac{XX}{100} \right) * FP_{B100} + \left(\frac{100 - XX}{100} \right) * FP_{D100} \quad (3)$$

The mixing of 20% vol. biodiesel with 80% vol. petrodiesel could yield a B20 fuel with a fuel property value that is correlated to the above formula. The result can only be confirmed with experimental testing and would depend on how well the two fuels mix and blend to reflect their independent characteristics in the blend. Depending on the accuracy of

results of fuels used in blends, users and producers could better evaluate certain fuel properties of the mixed blends by using the above formula and can avoid conducting tests on the blend itself. For example, they can calculate predicted fuel properties of blends based on the fuel property information of the B100 and D100 blends. This may be useful since there is no standard in place yet for B20 or any other biodiesel blend and there have been limited comparative investigations or research into fuel property sets of biodiesel blends.

The diesel engines of today with their high temperature and pressure operating conditions require fuels of good stability (Miyata et al. 2004). Using poor quality fuel in a diesel engine may lead to plugging of fuel filters, poor atomization characteristics, formation of deposits and injector coking. Problems that arise from injector coking include engine noise, excessive smoke, power loss, poor fuel economy, poor drivability and increase of certain emissions (Batts and Fathoni 1991).

2.5 Engine Emissions of Biodiesel and Diesel fuel

The emissions of diesel engines are gaseous mixtures of pollutants that can be harmful to the environment and to human health, for example, NO_x emissions contribute to smog formation (Stone 1999). Some of these emissions are regulated via quantified limits from the diesel exhaust (e.g., HC, CO and NO_x) and the method by which they are analyzed is listed in Table 2.9. Other emissions are not regulated but are monitored for evaluating their effects on air quality (listed in Table 2.10).

Table 2.9. Regulated Exhaust Emissions and Analytical Method (Mittelbach and Remschmidt 2004)

Emitted Compound	Analytical Method
HC	Flame Ionization Detector
CO	Infrared Spectroscopy
NO _x	Chemoluminescence Detector
Particulate Matter	Gravimetry

Table 2.10. Analytical Methods of Unregulated Exhaust Emissions (Mittelbach and Remschmidt 2004)

Emitted Compound	Analytical Method
CO ₂	IR
Total Aldehydes	Photometry
Specific Aldehydes	HPLC
Sulfates	HPLC
Specific HC	GC
PAH	HPLC, GC
H ₂ S	Photometry, Mass Spectrometry
NH ₃	Photometry, Mass Spectrometry
Alcohols	GC
Particle-bound Organics	Extraction / Thermal Desorption / Chromatography

Numerous studies on the engine emissions of biodiesel blends have been reported in the literature. The quantity and quality of measured emissions is clearly dependent on the test engine, test cycle, fuel type and operating conditions. HC, CO and NO_x emissions will differ between different engines and depend on ignition timing, engine load, engine speed and fuel/air ratio (Stone 1999). Therefore, when measuring engine emissions of biodiesel and its blends, it is best to report the results as a percentage difference to results obtained from petrodiesel fuels. Table 2.11 and 2.12 summarize some reported results from engine testing B100 and B20 for regulated emissions by various researchers with D100 as the baseline comparison fuel.

Table 2.11. Regulated Emissions of B100 (Mittelbach and Remschmidt 2004)

CO (%)	HC (%)	NO _x (%)	PM (%)	
B100 (SME)				REFERENCE
-18	-43	+13	-61	(Canakci and Van Gerpen 2003)
-40	-44	+10	-72	(Haas et al. 2001)
-46	-37	+9	-68	(Sheehan et al. 1998)
-23	-35	-10	-26	(Purcell et al. 1996)
-47	-44	+11	-66	(Graboski et al. 1996)

Table 2.12. Regulated Emissions of B20 (Mittelbach and Remschmidt 2004)

CO (%)	HC (%)	NO _x (%)	PM (%)	
B20 (20 % SME / 80 % DIESEL)				REFERENCE
-8	-3	+1.5	-16	(Canakci and Van Gerpen 2003)
-11	-21	+2	-10	(EPA 2002)
-5	-3	+4	-24	(Monyem and Van Gerpen 2001)
-9	-7	+2	-14	(Sheehan et al. 1998)
-13	-22	+5	-11	(Schumacher et al. 1996)
-7	-13	+1	-14	(Graboski et al. 1996)
-7	-3	+3	-15	(Chang et al. 1996)

Canakci and Van Gerpen (2003) conducted a study comparing emissions from petrodiesel, SME and YGME (yellow grease methyl esters). The results are summarized in Table 2.13 where the change in emissions between the YGME and SME are statistically insignificant. Table 2.14 further enlists emission results from another study, where results from No. 1 diesel suggests that it may be better to use No. 1 diesel over No. 2 diesel for blends with biodiesel since it could generate lower emissions (Canakci 2005). However, No. 1 diesel has some disadvantages in that its energy content is less, by about 5 % and would yield a lower fuel economy. No. 1 diesel has lower and lubricity than No. 2 diesel fuels.

Table 2.13. Regulated Exhaust Emissions of SME and YGME (Canakci and Van Gerpen 2003)

	CO (%)	HC (%)	NO _x (%)	PM (%)
No. 2 Diesel	-	-	-	-
20 % SME	-7.5	-3.1	+1.5	-15.8
SME	-18.2	-42.5	+13.1	-61.1
20 %YGME	-7.0	-2.3	+1.1	-16.8
YGME	-17.8	-46.3	+11.6	-64.2

Table 2.14. Regulated Exhaust Emissions of No. 1 Diesel, 20 % SME and SME (Canakci 2005)

	CO (%)	HC (%)	NO _x (%)
No. 2 Diesel	-	-	-
No. 1 Diesel	-5.4	-35.4	-16
20 % SME	-7.6	-2.9	+0.6
SME	-18.3	-42.5	+11.2

The magnitude of the emission variations between different studies is not only dependent on the test engine and test conditions, but also on fuel properties. Fuel properties affecting the combustion process can influence emission characteristics. The properties of viscosity, cetane number, heat of combustion and specific gravity are known to impact combustion (Canakci et al. 2006). The requirement to conduct more research on how the properties of biodiesel effect engine emissions has been stressed. From the summarized data, biodiesel relative to petrodiesel reduces the amount of CO, HC and PM and causes increases in NO_x. Some reasons for these observations is that, compared to petrodiesel, biodiesel contains no aromatic compounds, is 10-12 % oxygen by weight, and has a higher cetane number (Canakci et al. 2006; Jeong et al. 2006).

CO emissions are formed during the intermediate combustion stages and decreases with increasing percent blends of biodiesel, reductions being significant at blends above 15 %. HC emissions depend on the engine operating conditions, fuel spray characteristics and the interaction of the fuel spray with air within the combustion chamber (Canakci et al. 2006). The main factors affecting NO_x emissions is the fuel oxygen content, combustion temperature and combustion time (Jeong et al. 2006). NO_x increases as temperature increases in the combustion chamber. NO_x is problematic due to its potential to react in the atmosphere and produce ozone, which is a component of smog.

3.0 MATERIALS AND METHODS

3.1 Test Fuels

The test fuels used in this study are commercially available biodiesel and petrodiesel fuels. Two biodiesel fuels were supplied by: (1) World Energy in the United States, derived from 100% soybean oil; and (2) Rothsay/Laurenco in Montreal, QC, derived from waste vegetable oils (WVO). The former was distributed by Yorkstone Oil Company in Bellingham, WA and the latter by West Coast Biodiesel in Vancouver, BC. The two biodiesel fuels will be referred to as SME (soy methyl esters) and WME (waste vegetable oil methyl esters). The two petrodiesel fuels were obtained from the fuel pump located inside UBC Plant Operations facility. This fuel is distributed by Imperial Oil and supplied by M.R. Smith. D100 (S) coincides with the SME blend set and D100 (W) coincides with the WME blend set. Two B20 blends were made from mixing 20 vol. % of biodiesel with 80 vol. % petrodiesel. Even though the difference between the two diesel fuels is expected to be small, it is important to characterize each of them separately and treat them as two 'different' fuels. All fuel samples were analyzed in accordance to their fuel grade ASTM standards before ageing with the fuel property results presented in Table 3.1. Of all the supplied test fuels, only the WME was provided with a detailed ASTM test specification by the supplier and this result is included in Appendix D. In observing the results of the two diesel fuels, a notable difference is observed in the fuel property set, particularly with the parameters of viscosity, cloud point, flashpoint and sulphur content, signifying the two diesel fuels to be characteristically different. D100 (S) was dispensed in August 2005 while D100 (W) in December 2005/January 2006.

Table 3.2 illustrates the initial elemental analysis of the fuel blends before storage. The measured elements are carbon (C), hydrogen (H), nitrogen (N) and oxygen (O), where the presence of N in the samples is near zero. Table 3.3 lists the pre-storage fatty acid methyl ester (FAME) profile and iodine number of SME and WME.

Table 3.1. Results of Analysis of Fuel Blends at 0 days of Ageing

FUEL SPECIFIC PROPERTIES	TEST METHOD	UNITS	SME Blends			WME Blends		
			B100	B20	D100 (S)	B100	B20	D100 (W)
Acid Number	ASTM D664	[mg KOH/g]	0.01	0.01	0.00	0.55	0.13	0.01
Kinematic Viscosity at 40.0 °C	ASTM D445	[mm ² /s]	3.949	3.125	2.834	4.889	1.87	1.508
Cetane Number	ASTM D613		57.5	47.9	44.6	64.2	47.8	43.7
Cloud Point	ASTM D5573	[°C]	0.6	-9.5	-10.2	5.7	-10.4	-24.2
API Gravity at 15.1 °C		[°C]	29.0	29.0	32.8	29.1	39.5	41.9
Flash Point		[°C]	158		71	173.5		54
Water Content		[% volume]	0.02	0.03	0.02	0.00	0.01	0.02
Copper Corrosion	ASTM D130		1a	1a	1a	1a	1a	1a
Sulfur	ASTM D5453	[mg/kg]	8	310	353	14	230	288
Carbon Residue	ASTM D4530	[% mass]	0.001	0.001	0	0.045	0	0
Accelerated Stability	ASTM D2274	[hour]	---	---	0.3	---	---	0
Oxidation Stability	EN 14112	[hour]	0.4	7.8	---	2.5	12.9	---
Peroxide Value	AOAC Official Method 965.33	[meq O ₂ /kg]	22.8	3.8	0.6	10	2	---
Peroxide Value	ASTM D3703		---	---	---	---	46	12
Free Glycerin	ASTM D6584	[wt-%]	<0.001	---	---	0.002	---	---
Total Glycerin	ASTM D6585	[wt-%]	0.004	---	---	0.191	---	---
Monoglycerides	ASTM D6586	[wt-%]	0.007	---	---	---	---	---
Diglycerides	ASTM D6587	[wt-%]	0.004	---	---	---	---	---
Triglycerides	ASTM D6588	[wt-%]	0.011	---	---	---	---	---
Iodine Number	EN 14111	[g I ₂ /100g]	129	---	---	90	---	---
Tocopherols	GL-ARC	[mg/kg]	< 50	---	---	< 50	---	---

Table 3.2. Elemental Composition (C, H, O) of Fuel Blends at 0 Days of Ageing

[mass %]	SME BLENDS			WME BLENDS	
	B100	B20	D100	B100	B20
C	77.19	84.7	86.63	76.86	81.37
H	11.96	11.83	12.68	12.26	12.36
N	<0.3	<0.3	<0.3	<0.3	<0.3
O	10.41	2.45	<0.3	11.16	3.42

Table 3.3. FAME Profile and Iodine Number of B100 Blends at 0 Days

Fatty Acid Methyl Ester		(% concentration by mass)	
Compound Name	Fatty Acid (Carbon Number)	SME	WME
Methyl Myristate	C14:0	0.06	0.46
Methyl Palmitate	C16:0	9.90	12.18
Methyl Palmitoleate	C16:1	0.11	0.03
Methyl Sterate	C18:0	4.30	9.91
Methyl Oleate	C18:1	25.04	48.30
Methyl Linoleate	C18:2	51.47	16.31
Methyl Linolenate	C18:3	8.32	3.05
Methyl Arachidate	C20:0	0.22	0.56
Methyl Eicosenoate	C20:1	---	0.06
Methyl Eicosadienoate	C20:2	---	0.01
Methyl Heneicosanoate	C20:5	0.03	---
Methyl Behenate	C22:0	0.02	0.02
Σ Saturated		14.51	23.13
Σ Unsaturated		84.97	67.76
Iodine Number		129	90

At the start of the studies, all of the biodiesel fuel property results met their limits and specifications of ASTM D 6751. The maximum ASTM specification of AN was changed from 0.8 mg KOH/g to 0.5 mg KOH/g in June 2006. The pre-ageing AN of the WME was 0.55 mg KOH/g and because the WME storage study was conducted before June 2006 it is considered to have met the specified standard at that time. Two fuel properties, oxidative stability (OS) and iodine number (IN), particular to the European standards (PR EN 14214), were tested at pre-storage. The OS of SME was 0.4 hour and WME was 2.5 hour; they did not meet the OS requirement as both results are below the minimum specified limit of 6 hours. This measure suggests small amounts of antioxidants in the biodiesel fuels; a

contributing factor in the low oxidation stability result. The level of antioxidants in biodiesel depends on the feedstock it is derived from and also on its process production technology (Mittelbach and Gangl 2001). The presence of natural antioxidants (also referred to as tocopherols) retards the degree of oxidative attack of the fuel and aids towards increasing its stability. Tocopherols in SME and WME were detected at levels less than 50 ppm, establishing that both biodiesels contained very low amount of natural antioxidants. Furthermore, no additional antioxidants were added to the fuel during post production. The IN of SME and WME pre-storage was 129 and 90, with WME meeting the EN standard by measuring lower than the maximum limit of 120. These results are expected for some of the commercially available biodiesel fuels in US and Canada, especially since there is no standard in place for oxidation stability and iodine number in North America.

3.2 Experimental Methods

3.2.1 Storage Conditions

B100, D100 and B20 were each stored at 3 different conditions (Table 3.4), intended to represent cold (6 °C), natural (X °C) and warm (40 °C) conditions. Table 3.5 specifies the time duration that each blend set was stored at and Figure 3.1 summarizes the temperature variations represented by the local ambient condition, X °C. The months of July 05 – June 06 are relevant for the SME study with an average temperature of 10.6 °C, while the months of December 05 – August 06 are relevant for the WME study, with an average temperature of 10.7 °C.

Table 3.4. Storage Location and Conditions of Fuel Blends

Nominal Conditions	Storage Conditions		
	Temperature Variation	Relative Humidity	Fuel Storage Locations on UBC Campus
6 °C	6.0 - 7.0 °C	~ 65 - 80 %	Cold Room: Constant Conditions (Agricultural Canada Bldg, Room 167A)
X °C	0.0 - 24.0 °C	~ 35 - 100 %	Local Ambient Outdoor: Variable Conditions (UBC Plant Operations, Fenced Area)
40 °C	36.0 - 40.0 °C	~ 30 - 50 %	Warm Room: Semi-Constant Conditions (MacMillan Bldg, Room 290)

Table 3.5. Storage Time Period of Fuel Blends

SME Blends	Storage Time Periods	
	Start	Average Time (days)
6 °C	August-05	300
X °C [10.6 °C] ²	August-05	300
40 °C	August-05	300
WME Blends		
6 °C	January-06	180
X °C [10.6 °C] ²	February-06	180
40 °C	December-06	180

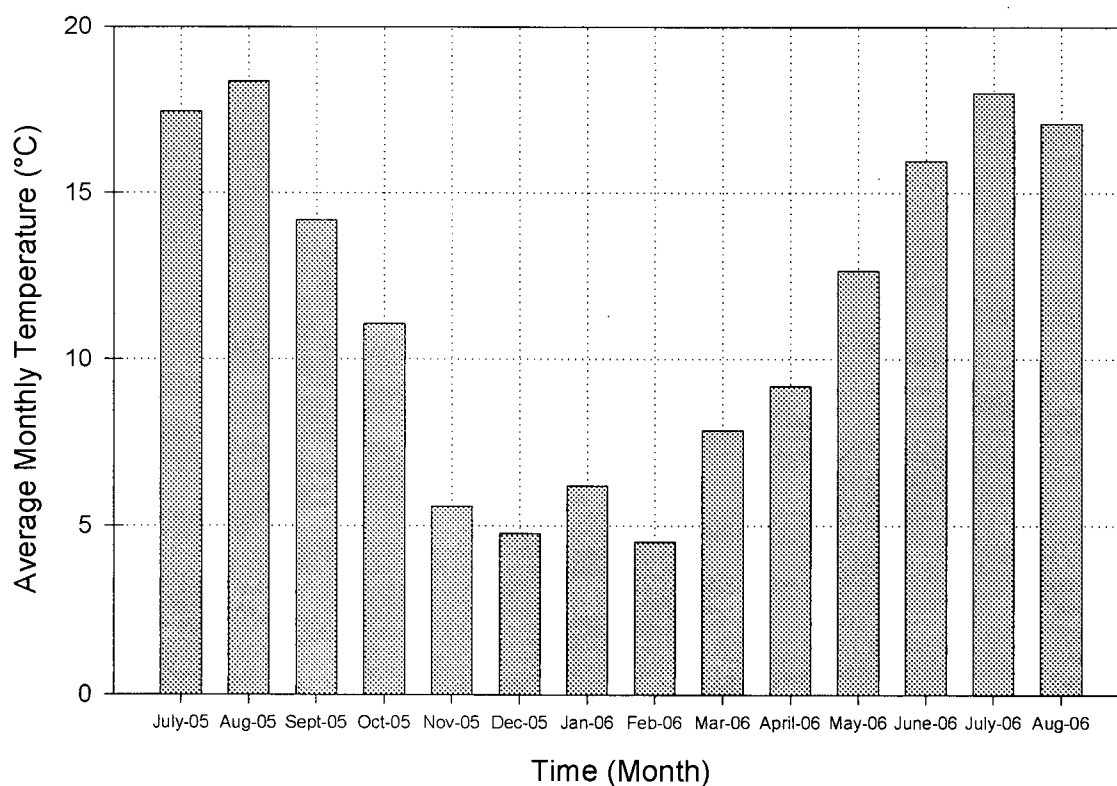


Figure 3.1. Monthly Average of Ambient Outdoor Temperatures Conditions at UBC from July 2005 - August 2006

The ageing of the SME blends were studied up to 300 days, while the WME fuel blends were studied for 180 days. B100, D100 and B20 were stored in 25 L High Density

² The monthly average temperature for SME and WME blends stored under ambient outdoor conditions were 10.6 °C and 10.7 °C, respectively.

Polyethylene (HDPE) plastic containers, designed to store petroleum based fuels such as gasoline or diesel. The solvent compatibility of biodiesel with HDPE is charted as “good”. For each of the 6 listed fuel blend sets in Table 3.6, B100 was stored in 5 containers, B20 in 4 containers and D100 in 4 containers. The fuels were stored in this number of containers for quality control purposes, where the extra storage containers can serve as backups in case of fuel contamination or container damage. 23 L was the volumetric amount of fuel stored in each container, accounting for a summed total of: 115 L of B100 fuel, 92 L of B20 fuel and 92 L of D100 fuel. The B20 blend was mixed by splash blending 4.6 L of biodiesel into 18.4 L of diesel for each container and then shaken vigorously for roughly 5 minutes. The headspace of each container was purged with N₂ gas prior to storage to minimize the effect of air exposure that would result from pumping the fuels into their containers.

3.2.2 Sampling

At pre-storage, the fuel properties listed in Table 3.1 were tested. For the SME blends, fuels were sampled and tested every 30 – 60 days for acid number, density and kinematic viscosity up to 300 days; and every 90 days for cetane number, peroxide value, iodine number, oxidation stability, FAME profile and accelerated stability up to 180 days. Similarly, the WME blends were sampled and tested every 45 days for the former properties up to 180 days. The latter properties were tested only at 180 days for the blends in storage at 6 °C and 40 °C. Sampling of each fuel blend involved pipetting the fuel in 100 mL, 50 mL or 25 mL increments from its storage container, with sample sizes varying (e.g., 100 mL – 2000 mL) with fuel blend and the properties to be tested. All fuels were collected in opaque HDPE or Nalgene bottles. The bottles were sealed tightly and filled to the top to minimize headspace. The turnover time for testing fuel properties was no more than 2 weeks for any given sample.

3.2.3 Analytical Methods

Several test methods are used to determine the pre- and post-storage characteristics of fuel blends. Samples were analyzed according to standardized methods by UBC (University of British Columbia), Alberta Research Council (ARC) and Finning Oil. Elemental analysis (C, H, N, O) of samples was completed by Canadian Microanalytical Services. The FAME profile of SME and WME was conducted by ARC via the EN 14103 method. The test

parameters and method types are listed in Table 3.1. The experimental apparatuses used to measure acid number, kinematic viscosity and density were an automatic potentiometric titrater (Metrohm), a rotary viscometer (HAAKE ROTOVISCO) and a hand held density meter (Anton Paar DMA 35N), respectively. Full details of these procedures and sample calculations are included in Appendix A and B. The data for these results are the means of at least three replicate tests to minimize uncertainty. The standard error is also calculated and shown as error bars in the graphical results.

3.2.4 Vehicle Testing

The exhaust emissions of two on-road diesel vehicles were tested with aged blends of B100, D100 and B20 from the WME blend set. The diesel vehicles used were a 2005 Mercedes Smart Car (owner: UBC Utilities) and a 1987 Volkswagen Jetta (owner: BC AirCare®), with specifications listed in Table 3.6. The fuels tested in both vehicles were from the WME blend set, with B100 and B20 blends aged up to 180 days at 40 °C tested in the Smart Car and B100, D100 and B20 blends aged up to 180 days at 6 °C and 40 °C tested in the Jetta. Also, one SME blend was tested in the Jetta, where it had been stored for 300 days at 6 °C. The tests were conducted by BC AirCare® at their Burnaby vehicle testing facility using their Dynamometer Emissions Testing Laboratory for on road vehicles. All tests on the vehicles followed the EPA 75 test cycle conducted under cold start conditions and the vehicles were operated by the same driver. Cold start testing involves leaving the vehicle in the temperature-controlled lab overnight in order to ensure the vehicle is at the correct temperature to start before each test in the morning. Details on the test procedure are listed in Appendix C.

Table 3.6. Specifications of Test Vehicles

Make and Model	2005 Smart Car (fortwo-coupe)	1987 Volkswagon Jetta
Number of Cylinders	3 (in-line)	4 (in-line)
Engine Capacity	799 cm ³	1588 cm ³
Horsepower (HP)	40.2 @ 4200 rpm	52 @ 4800 rpm
Torque	73.8 lb-ft @ 1800 - 2800 rpm	71 lb-ft @ 2000 rpm
Injection System	Common Rail Electronic	Mechanical Injection
Transmission	6 Speed Sequential	5 Speed Manual
Vehicle Weight	990 kg	---

To minimize the significance of cross contamination and ensure emission testing is being conducted on the fuel blend under test, the following steps were followed between fuel transfers: (a) for the 1987 Jetta, the old fuel was carefully drained from the vehicle and the new fuel was pumped and drained from the vehicle at least 2-3 times in 10 -15 L increments. This helped prime the vehicle for testing with the new fuel. Upon filling the vehicle with the replacement fuel, the engine was run for at least 25 minutes to purge out any of the remnants of the previous fuel from the fuel system, (b) for the Smart car, it was not possible to drain and pump the fuel in the manner indicated for the Jetta. Instead, the car was driven to a near empty volume (less than 0.5 L) and 1.5 L of the replacement fuel was pumped into the car and driven again to a near empty volume. This was repeated two times. The above steps allow for accuracy, consistency and reproducibility in the results and make certain that emission measures are specific for each fuel blend.

HC, CO, NO_x and CO₂ were measured emissions during each test resulting on a gram per mile and gram per kilometre basis for a given test cycle. Figure 3.2 illustrates a schematic of the mass emission measurement system.

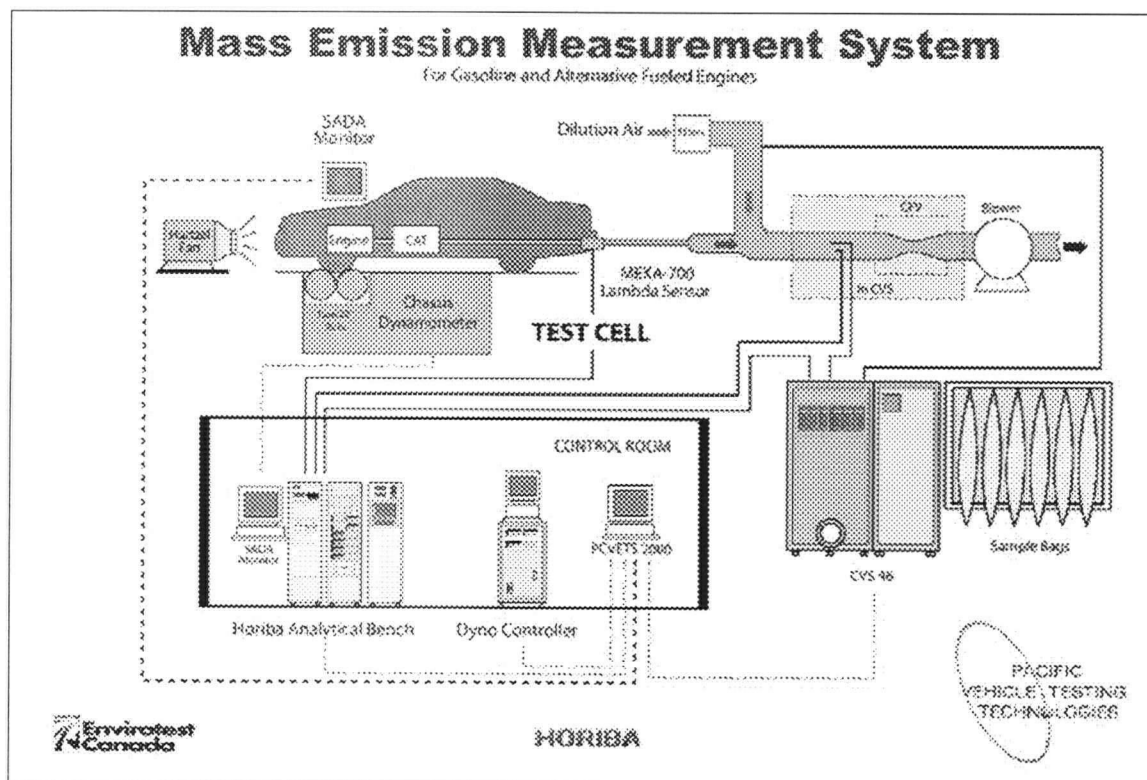


Figure 3.2. Illustration of the Mass Emission Measurement System (Source: Pacific Vehicle Testing Technologies)

The specifications of the Horiba dynamometer and analyzers used for testing emissions are listed in Table 3.7. The reported mass emission measurements for each test blend is an average mean of at least three independent cold start tests, allowing for accuracy, consistency and reproducibility in results. Details on the different components of the Horiba Vets System are listed in Appendix C.

Table 3.7. Specifications of the Horiba Dynamometer and Emission Analyzers

Horiba Dynamometer and Analyzer	Model and Type
Dynamometer	DMA-20-102-150 HP
THC Flame Ionization Detector	FMA-220
CO Analyzer	AIA-210
NO _x Generator	410 NO _x GEN
NO _x Analyzer Chemiluminescent	CLA-220
CO (L) CO ₂ Analyzer	AIA-220

4.0 RESULTS AND DISCUSSION

The ageing of two sets of B100, D100 and B20 fuel blends were studied, one pertaining to biodiesel produced from 100 % soybean oil (SME) and the other to biodiesel produced from waste vegetable oils (WME). Each 'blend set' was stored in a steady state at 6 °C, X °C and 40 °C, signified as conditions of cool, ambient outdoor and warm.

4.1 Effect of Ageing on B100 Blends

4.1.1 Acid Number

The change in AN with time of SME up to 300 days and WME up to 180 days at cool, ambient and warm conditions is displayed in Figure 4.1. The AN of SME varied with small increases and decreases throughout the 300 day ageing period. All AN's measured to be well below the 0.5 mg KOH/g ASTM and EN standards and the variations are considered to be insignificant. The AN of WME display less relative variation, where at 6 °C and X °C, slight increases are observed and at 40 °C the increases are higher. The WME showed a much greater initial AN, and a much more significant AN increase than SME.

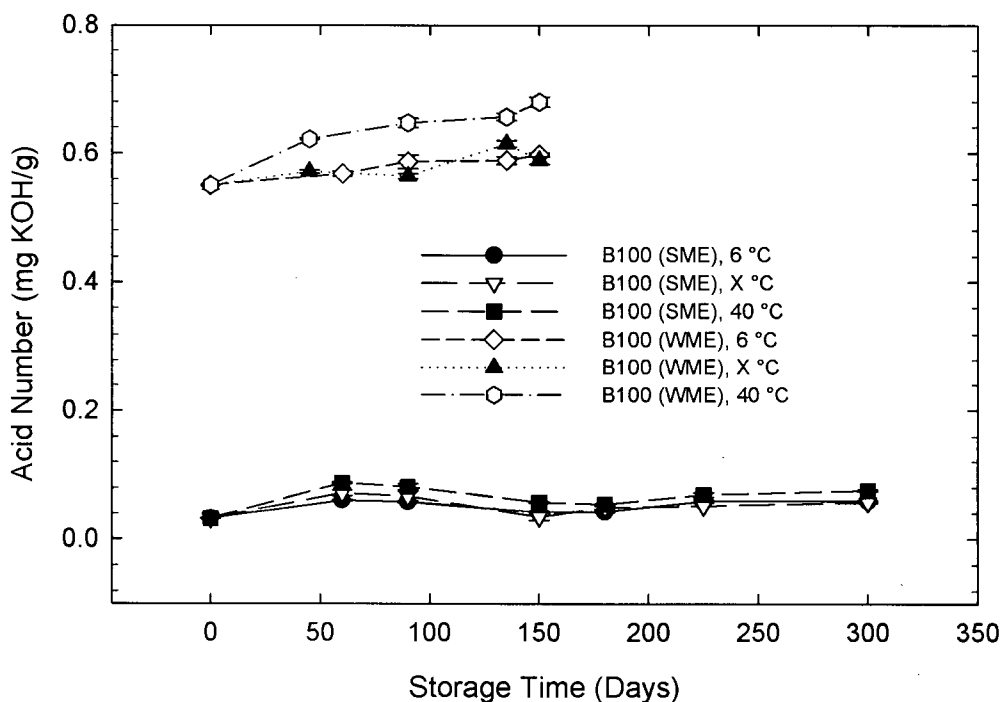


Figure 4.1. Acid Number of Aged SME and WME [Data, UBC]

Table 4.1 summarizes the AN values measured by the Alberta Research Council (ARC) for both SME and WME. The AN of SME show a near zero change for all of the storage conditions up to 180 days, relating to the results displayed in Figure 4.1. The AN results of the SME blends presented in Figure 4.1 and Table 4.1 are all below 0.10 mg KOH/g. The numerical differences between these results are not significant and the AN method is not very accurate when the acidity of fuel samples is detected below 0.10 mg KOH/g (ASTM 2004). The AN of WME aged for 180 days at 40 °C measured by ARC is 0.66 mg KOH/g and by UBC is 0.68 mg KOH/g, confirming an AN increase of at least 0.11 mg KOH/g and making it the fuel with the highest AN. The results indicate no significant change in AN for SME stored at 6 °C, X °C and 40 °C and for WME stored at 6 °C and X °C. Only the AN for WME stored at 40 °C showed significant change, as it increased by 17 %. Thus, storing WME at a low temperature could be favourable for minimizing fuel acidity.

Table 4.1. Acid Number of Aged SME and WME [Data, ARC]

Fuel Type	Acid Number (mg KOH/g)		
	t = 0	90	180
B100 (SME)			
6 °C	0.01	0.03	0.02
X °C	0.01	0.02	0.03
40 °C	0.01	0.03	0.02
B100 (WME)			
6 °C	0.55	---	0.55
40 °C	0.55	---	0.66

Leung et al. (2006) conducted a 52 week study of RME stored at 4 °C, 20 °C, and 40 °C, where the AN of biodiesel stored at 4 °C and 20 °C did not change significantly. The AN of biodiesel stored at 40 °C increased with time and was higher than at 4 °C and 20 °C. For example, the pre-storage AN in mg KOH/g at 40 °C was 0.18, which increased to 0.51 after 24 weeks (180 days), an increase of 65 % and to 0.79 after 52 weeks (360 days), an increase of 77 %. Mittelbach and Gangl (2001) found the AN of RME and WME to increase with storage time and the rate of increase was dependent on storage conditions, as samples exposed to light increased at higher rates. On the other hand, Bondioli et al. (1995) observed

no change in AN of RME aged for 180 days at storage temperatures of 20 °C and 40 °C. As the rate of increase of AN is considered proportional to the rate of oxidation, fuel samples which show minimal or no change in AN demonstrate low fuel oxidation rates (Monyem 2000). The rate of increase of a fuel's AN can depend on its initial value and if it is high to begin with, there is a greater tendency for it to increase, especially at conditions favouring fuel oxidation. For example, the initial AN value of the two biodiesels was 0.01 mg KOH/g for SME and 0.55 mg KOH/g for WME and the AN increase for WME is of a much higher degree than SME stored at the higher temperature condition of 40 °C. In practice, biodiesel produced from waste oils does contain higher levels of free fatty acids and yield higher acidity values than a biodiesel produced from pure virgin oil.

4.1.2 Kinematic Viscosity

The kinematic viscosity (KV) of both SME and WME remained within the 1.9 – 6.0 mm²/s ASTM limits and the results were nearly constant over all ageing conditions (Figures 4.2 and 4.3).

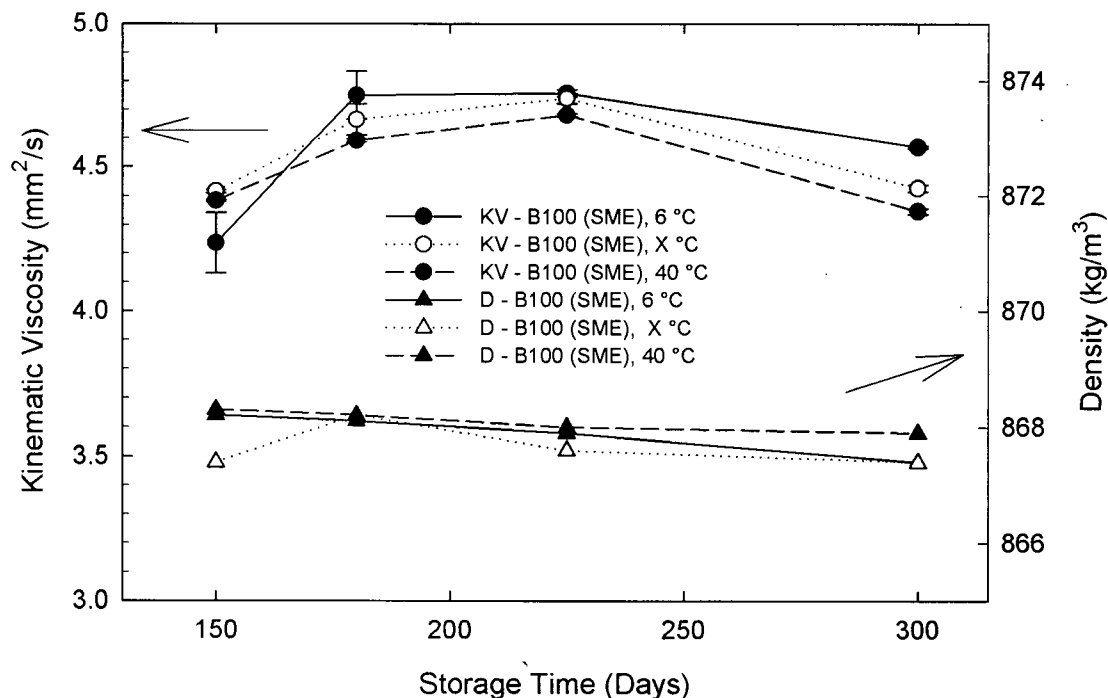


Figure 4.2. Kinematic Viscosity and Density at 40.0 °C of Aged SME [Data, UBC]

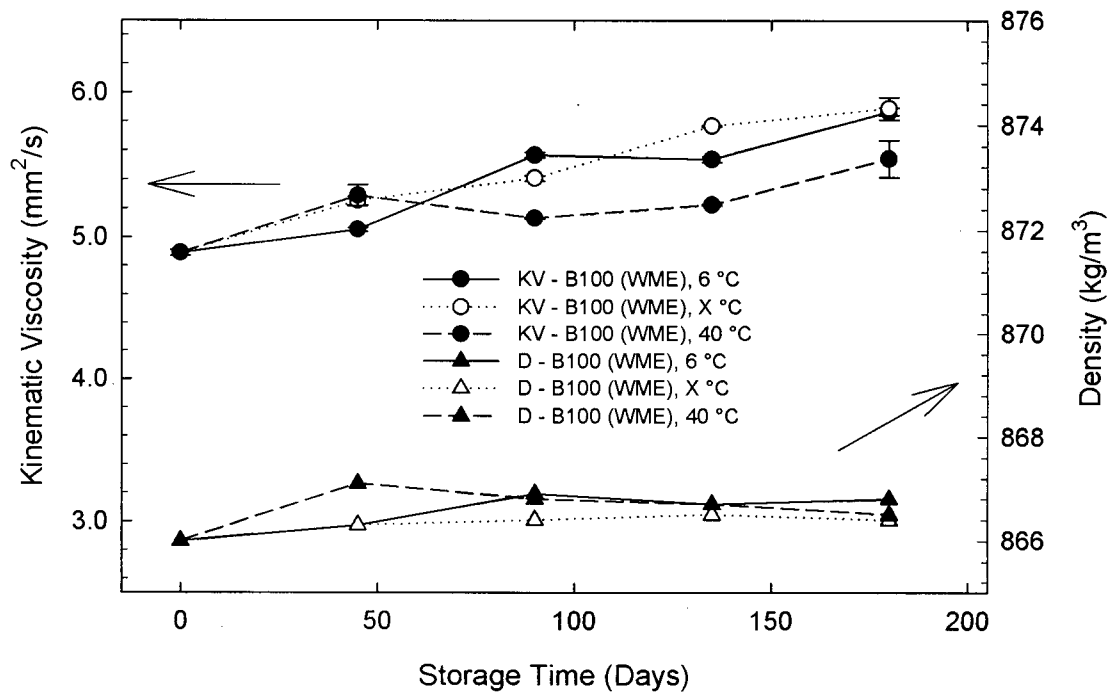


Figure 4.3. Kinematic Viscosity and Density at 40.0 °C of Aged WME [Data, UBC]

From Figure 4.2 and 4.3, the KV of WME at 180 days for 6 °C, X °C and 40 °C are higher than SME and are calculated to be greater by 19 %, 20 % and 22 %. Table 4.2 reports the KV property as measured by ARC, indicating a minimal change in KV after 180 days of storage for both SME and WME.

Table 4.2. Kinematic Viscosity of Aged B100 Blends [Data, ARC]

Fuel Type	Kinematic Viscosity (mm ² /s) at 40 °C		
	t = 0	90	180
B100 (SME)			
6 °C	3.95	3.96	3.95
X °C	3.95	3.93	3.95
40 °C	3.95	3.98	3.95
B100 (WME)			
6 °C	4.89	---	4.93
40 °C	4.89	---	4.88

The KV of WME for 6 °C and 40 °C is 20.9 % and 19.1 % higher than SME. The ARC measures were consistently low from UBC measures but both data sets show the same qualitative trend.

Bondioli et al. (1995) measured KV at 37.8 °C of RME to be 4.88 mm²/s at 0 days and 4.90 mm²/s after 180 days of storage at 40 °C; a change that is not significant. This trend is similar with the KV results of ARC listed in Table 4.2, where the change between 0 and 180 day of the SME and WME at 40 °C is not significant. Bondioli et al. (2003) studied the fuel properties of 11 different biodiesel fuels in storage for 1 year under ambient outdoor conditions; they concluded a minimal change in fuel viscosity. Similarly, RME tested by Miyata et al. (2004) stored up to 4 months under closed air conditions at 5 °C, 20 °C and 40 °C showed little change in kinematic viscosity. The slight increases in the WME seen at 6 °C in comparison to a minimal change at 40 °C can be explained as a temperature effect, where the lower temperature can temporarily contribute to a higher viscosity in the fuel, especially if the storage temperature is near the fuel cloud point (Tat and Van Gerpen 1999). As explained in Section 4.1.4, the pre-storage cloud point temperature of WME was 5.7 °C. Thus, viscosity will increase with a decrease in temperature. In summary, the measured KV values for the SME and WME are all within the specified ASTM range of 1.9 - 6.0 mm²/s, with aged WME exhibiting higher KV values than aged SME's. Biodiesel produced from waste or used frying oils are expected to have higher fuel viscosity than many vegetable oils because of their higher content of saturated fatty acids (Knothe 2006).

4.1.3 Cetane Number, Peroxide Value and Oxidation Stability

Table 4.3 reports the cetane number (CN), peroxide value (PV) and oxidation stability (OS) of SME stored at 6 °C, X °C and 40 °C, and WME stored at 6 °C and 40 °C. At all temperatures the CN of SME decreased by about 10% over 180 days. On the other hand, after 180 days of ageing the CN of WME showed a significant increase at 6 °C by 13% but not at 40 °C. PV has been reported to correlate to CN, where increases in PV has an increasing effect on CN because hydroperoxides act as cetane enhancers (Mittelbach and Remschmidt 2004; Van Gerpen 1996). However, this observation is not clear from the tabulated results of Table 4.3 for both SME and WME. For example, the increase in CN for WME at 6 °C after 180 days of storage is not connected with a PV increase. The

measurements do not indicate the positive correlation between PV and CN that has been reported previously.

The PV results of SME at 6 °C, X °C and 40 °C display a similar trend of change, where there is a measured increase at 90 days and a subsequent decrease at 180 days. This observation with a maximum increase in PV at 90 days relates qualitatively to results from other studies. For example, Monyem (2000) and Canacki et al. (1999) noted PV to increase to maximum values between 300 - 400 meq O₂/kg and then decrease, though their PV values recorded to be much greater than the results of Table 4.3 as the tests were carried out under accelerated storage conditions where oxygen was introduced during ageing. Peroxide formation is dependent on oxygen availability and will form as long as oxygen is available either in dissolved form within the fuel or from exposed air (Dunn 2002; Monyem 2000). As oxygen gets used up and it becomes unavailable, the rate of peroxide formation decreases and because peroxides are unstable species, they decompose and breakdown to form organic acids such as aldehydes and ketones, which are considered as secondary oxidation products (Canacki et al. 1999). This effect leads to a decrease in peroxide concentration, resulting in a lower measure of PV. Although peroxide formation is influenced more by the presence of oxygen than temperature, the concentration of peroxides can be lower at higher temperatures as they are not thermally stable (Canacki et al. 1999; Dunn 2002). The secondary oxidation products are acids that can be detected from measuring AN, but the PV of SME and WME did not change significantly during storage to concur any firm correlation between PV and AN in this study. Moreover, Mittelbach and Gangl (2001) observed the PV of RME and WME stored in closed containers up to 180 day to increase only slightly and PV increased more readily in conditions of greater air exposure and higher temperatures. The PV measure at 90 days for SME stored at X °C is measured to be 90 meq O₂/kg, which is higher than the results at 6 °C and 40 °C, but is not significantly higher to impart a conclusive difference in fuel oxidation rates between the SME fuels (Monyem 2000). However, a possible explanation for this difference could be that at the time of measure, the sample stored at X °C was undergoing a higher rate of peroxide formation and was exposed to more oxygen, either from within the storage container or as air introduced from sampling.

Because the PV measures of WME were taken at the 0 and 180 day mark, it is only possible to report the absolute difference in PV, where no effective change can be reported at the storage conditions of 6 °C and 40 °C. However, if the absolute difference in PV between

0 and 180 days of the SME fuels are compared, no significant change would be noted. Further PV tests between 0 and 180 days on the WME would confirm a possibility of observing a similar trend in PV to the SME's.

Table 4.3. Cetane Number, Peroxide Value and Oxidation Stability of Aged B100 Blends [Data, ARC]

Fuel Type	Cetane Number			Peroxide Value (meq O ₂ /kg)			Oxidation Stability (RIP time in hours)		
	t = 0	90	180	t = 0	90	180	t = 0	90	180
B100 (SME)									
6 °C	57.5	54.1	51.3	22.8	31.0	23.0	0.4	0.6	0.1
X °C	57.5	54.5	51.8	22.8	90.0	23.0	0.4	0.6	0.9
40 °C	57.5	54.4	51.9	22.8	51.0	20.0	0.4	0.6	0.8
B100 (WME)									
6 °C	54.2	---	62.2	10.0	---	8.0	2.5	---	2.4
40 °C	54.2	---	55.8	10.0	---	7.0	2.5	---	2.9

From Table 4.3, the oxidation stability (OS) values of SME stored at 6 °C, X °C and 40 °C show a similar rate of change, where all samples had an induction period of 0.6 h at 90 days, a slight increase from 0.4 h at 0 days. At 180 days, the X °C and 40 °C fuels display slight increases and similar RIP (Rancimat Induction Period) values of 0.9 h and 0.8 h, while 6 °C recorded a decrease, with an RIP of 0.1 h. The pre- and post storage values of OS for WME at 6 °C and X °C did not display significant changes during storage, similar to SME. Numerous tests have shown the correlation of RIP to other fuel properties in biodiesel, especially KV, AN and PV (Mittelbach and Remschmidt 2004). Because the properties of KV, AN and PV overall showed minimal changes of nearly no significance, the reported deviations in RIP values between the different storage conditions are considered to be negligible. The RIP limit of 6 hours was not met for all the fuels, even at the start of ageing. However, there are no clear indications on whether a biodiesel not meeting the RIP limit of 6 hours would be harmful to use in a diesel engine (Mittelbach and Remschmidt 2004). OS is regulated in the EN standard but not in the ASTM standard.

A low OS can be distinctive of a biodiesel with a low concentration of natural antioxidants. Tocopherol (natural antioxidant) isomers were measured for both SME and WME at 0 days and the result was less than 50 ppm, which is quantified as a near zero

presence. Antioxidants act to only delay the oxidation process. Thus, the addition of synthetic antioxidants is highly suggested as it will increase the RIP time and improve the fuels oxidation stability. Furthermore, various researchers have questioned the use of the OS standard method as it may not quantify the real time measure of the oxidation stability in biodiesel (Canakci et al. 1999; Dunn and Knothe 2003). The OS method requires the fuel to be aged under accelerated conditions where the fuel is readily exposed to oxygen and a high temperature of 110 °C, this may generate reactions and results that would not normally occur at low storage temperatures and during real-time ageing

The OS values of WME are measured to be significantly higher than for SME. Generally speaking, biodiesel derived from waste vegetable or frying oils would show lower OS than virgin oils because of the frying process which consumes antioxidants. But, since both biodiesel samples contained a near zero concentration of antioxidants (e.g., less than 50 ppm) prior to ageing, the higher OS measure of WME is a definite result of its fatty acid composition. The unsaturation content of SME and WME at 0 days was 84.97% and 65.12%, respectively. The SME contain a higher content of unsaturated fatty acids than WME, by nearly 20% and because unsaturated fatty acids are more reactive to conditions favouring oxidation than saturated fatty acids, lower OS values will result for SME (Ferrari et al. 2005). Hence, a biodiesel fuel with a higher degree of unsaturation is expected to have a lower RIP time than a biodiesel with a lower degree of unsaturation. Another possible reasoning of a higher OS is that WME have a higher viscosity (by nearly 20 %) in comparison to SME, which could affect the mass transfer rate of the oxidation products to the air-fuel interface, the size and movement speed of the air bubbles within the fuel sample and the dissolving rate of the oxygen from the bubbles to the fuel (Knothe and Dunn 2003).

4.1.4 Iodine Number and Cloud Point

Table 4.4 lists the pre- and post-storage iodine number (IN) and cloud point (CP) results of the B100 blends. Fuel unsaturation of biodiesel can be assessed by measuring the IN, as it is supposed to quantify the total unsaturation present in a given mixture of fatty compounds.

Table 4.4. Iodine Number and Cloud Point of Aged B100 Blends [Data, ARC]

Fuel Property	Iodine Number		Cloud Point (°C)	
Fuel Type	t = 0	180	t = 0	180
B100 (SME)				
6 °C	129	152	0.6	0.8
X °C	129	144	0.6	0.3
40 °C	129	132	0.6	0.5
B100 (WME)				
6 °C	90	81	5.7	10.6
40 °C	90	96	5.7	3.0

Theoretically, higher the IN, higher is the degree of unsaturation. IN is cited to correlate with the OS of a biodiesel fuel, where high IN values relate to low OS values. This is true in the results compared directly between the two biodiesel fuels, where SME had a higher IN and a lower OS and WME had a lower IN with a higher OS. However, when comparing the blend to blend variations between the aged results of the fuel types at the different storage conditions, the IN to OS correlation is not as conclusive. This conveys uncertainty over the exact numerical ranges in which the IN and OS correlation is applicable. For example, Miyata et al. (2004) found similar IN's to represent OS's of different values, shedding some doubt over previously stated correlations between OS and IN. Also, Knothe (2002) reported poor correlations between IN and OS, where differing OS values resulted for varying IN's within narrow margins (e.g., less than 10 units). The OS measure depends on the specific type of double bonds present in each FAME, where the IN measure depends on the total number of double bonds in the FAME's, the correlations relating IN with OS and OS with IN are invalid (Knothe and Dunn 2003). The question of using IN as a measure of total unsaturation is further discussed in Section 4.1.5.

The CP of SME at 180 days is not very different from the initial starting values and storage temperature did not seriously impact CP, whereas, the same cannot be commented for WME. After 180 days, the CP of WME increased by 4.9 °C for 6 °C case and decreased by 2.7 °C for 40°C case. The CP of pre-storage WME measured at 5.7 °C; therefore WME were stored for 180 days near its cloud point for the 6 °C storage condition and this had an impact on the fuels physical structure. Figures 4.4 and 4.5 show the physical appearance of two samples of WME fuel blends prior to ageing at 20.5 °C (room temperature) and at 6.0 °C

(near CP). Hence, during storage of WME at 6 °C, the fuel was in the physical state shown in Figure 4.5. Agglomerated crystals and precipitated solids are clearly seen in Figure 4.5, illustrating the physical phase change of biodiesel at temperatures near its CP. When a fuel reaches its CP, small wax crystals start to form, and if there is enough precipitation of wax crystals with diameters greater than 0.5 μm , the fuel becomes visually cloudy due to solidification of saturates and crystal formations (Chiu et al. 2004). Based on these results, it is recommended to not store a biodiesel fuel at temperatures near its CP value, since it fixates the biodiesel in a state where the fuel does not exist as a single liquid phase.



Figure 4.4. WME at 20.5 °C



Figure 4.5. WME at 6.0 °C

A likely explanation of the differences between the IN and CP values of the WME blends at 6 °C from those at 40 °C, is that during sampling of WME at 6 °C, the fuel did not exist as a uniform liquid mixture, but rather as a multi-phase mixture, where the fuel was in a semi-separated state consisting of saturated solids, as seen in Figure 4.5. It is assumed that because of these phase separations, the fuel collected for sampling was not representative of the whole biodiesel, where a higher content of saturates were collected in the form of agglomerated solid crystals. The later point of collecting higher levels of saturates is verified by a higher CP of 10.6 °C and a lower IN of 81. Biodiesel fuels composed of a higher degree of saturates than unsaturates, as is the case for the WME, will thicken and start to gel at higher temperatures, resulting in greater CP values (Dunn 2004). To further cite fuel property specific influences of saturated and unsaturated compounds of a biodiesel fuel, an analysis of its fatty acid composition has been done.

4.1.5 Fatty Acid Methyl Ester (FAME) Profiles

The fatty acid methyl ester (FAME) profiles and iodine numbers (IN) of SME and WME at 0 and 180 days are presented in Tables 4.5 – 4.9. The percent concentration of C16:0, C18:0, C18:1, C18:2, C18:3 are highlighted since they are the main FAME that account for at least 95% of the total fatty acid composition in SME and 85% in WME. At 0 days, the SME total unsaturation was 84.97 %, showing biodiesel derived from soybean oil to be highly unsaturated. After ageing at 180 days, the unsaturated content of SME at 6 °C, X °C and 40 °C was 82.79, 82.72 and 82.63 %, respectively. In SME, the unsaturated fatty acid methyl linoleate or C18:2 amounted for nearly 50 % of this unsaturation.

The IN of SME aged for 180 days at 6 °C, X °C and 40 °C are 152, 144 and 132, correspondingly. In analyzing the IN of each of the three SME fuels against their unsaturation content, the largest difference between them in percent unsaturation is no more than 0.16 % and IN is no more than 20. Although IN is reported to be indicative of biodiesel unsaturation, this is not clear from the presented results. Moreover, Knothe (2002) discussed how different FAME compositions can give identical IN, hinting further ambiguity over using IN as a quality index for fuel unsaturation. The IN does not consider that a multiple number of fatty acid profiles and different fatty acid structures can account for the same IN.

Table 4.5. FAME Profile of SME at 6 °C [Data extracted from Appendix D, ARC]

Fatty Acid Methyl Esters (Storage at 6 °C)		(% concentration by mass)	
Compound Name	Fatty Acid (Carbon Number)	0 days	180 days
Methyl Myristate	C14:0	0.06	0.08
Methyl Palmitate	C16:0	9.90	10.31
Methyl Palmitoleate	C16:1	0.11	0.12
Methyl Sterate	C18:0	4.30	4.38
Methyl Oleate	C18:1	25.04	23.54
Methyl Linoleate	C18:2	51.47	50.95
Methyl Linolenate	C18:3	8.32	8.18
Methyl Arachidate	C20:0	0.22	0.25
Methyl Heneicosanoate	C20:5	0.03	0.00
Methyl Behenate	C22:0	0.02	0.02
Σ Saturated		14.50	15.04
Σ Unsaturated		84.97	82.79
Iodine Number		129	152

Table 4.6. FAME Profile of SME at X °C [Data extracted from Appendix D, ARC]

Fatty Acid Methyl Esters (Storage at X °C)		(% concentration by mass)	
Compound Name	Fatty Acid (Carbon Number)	0 days	180 days
Methyl Myristate	C14:0	0.06	0.08
Methyl Palmitate	C16:0	9.90	10.32
Methyl Palmitoleate	C16:1	0.11	0.12
Methyl Sterate	C18:0	4.30	4.38
Methyl Oleate	C18:1	25.04	23.54
Methyl Linoleate	C18:2	51.47	50.87
Methyl Linolenate	C18:3	8.32	8.19
Methyl Arachidate	C20:0	0.22	0.24
Methyl Heneicosanoate	C20:5	0.03	0.00
Methyl Behenate	C22:0	0.03	0.00
Σ Saturated		14.51	15.02
Σ Unsaturated		84.97	82.72
Iodine Number		129	144

Table 4.7. FAME Profile of SME at 40 °C [Data extracted from Appendix D, ARC]

Fatty Acid Methyl Esters (Storage at 40 °C)		(% concentration by mass)	
Compound Name	Fatty Acid (Carbon Number)	0 days	180 days
Methyl Myristate	C14:0	0.06	0.07
Methyl Palmitate	C16:0	9.90	10.26
Methyl Palmitoleate	C16:1	0.11	0.12
Methyl Sterate	C18:0	4.30	4.37
Methyl Oleate	C18:1	25.04	23.53
Methyl Linoleate	C18:2	51.47	50.80
Methyl Linolenate	C18:3	8.32	8.18
Methyl Arachidate	C20:0	0.22	0.25
Methyl Heneicosanoate	C20:5	0.03	0.00
Methyl Behenate	C22:0	0.03	0.00
Σ Saturated		14.51	14.95
Σ Unsaturated		84.97	82.63
Iodine Number		129	132

Tables 4.8 and 4.9 list the FAME composition of WME at 6 °C and 40 °C, where the quantity of saturated and unsaturated fatty acids is numerically different from SME results. Overall, WME are characterized to have a higher content of saturated fatty acids and a lower

content of unsaturated fatty acids than SME. The unsaturation content of the WME at 0 days was 65.12%, nearly 20% lower than the SME, which had an unsaturation content of 84.97%. These differences were observed in some of the fuel property results explained in Sections 4.13 and 4.14, particularly for OS and CP. The varied results of OS and CP between SME and WME were due to differences in the composition of the fuels saturated and unsaturated fatty acids. Fuels of higher saturation, like the WME, have a higher OS and because saturated fatty acids are more resistant to oxidation than unsaturated fatty acids.

Unsaturated fatty acids are more susceptible to oxidation reactions and these reactions are accelerated when exposed to oxygen and high temperatures, causing the formation of high density polymeric compounds (Ferrari et al. 2005). But, the higher saturation content of WME yields a fuel with poor cold flow properties and a higher CP. Also, after 180 days of ageing, the saturated content at 6 °C was 27.96 %, an increase from the 0 day result of 23.19 %. As explained in Section 4.1.4, the higher measure of saturates at 6 °C reflects a higher CP than at 40 °C. A fuel stored near or at its cloud point temperature would cause an increase in viscosity as it encourages the growth and agglomeration of crystals and this increases the number of crystals per unit volume and a subsequent rise in viscosity results due to fuel thickening from crystal formations (Dunn 1996).

Table 4.8. FAME Profile of WME at 6 °C [Data extracted from Appendix D, ARC]

Fatty Acid Methyl Esters (Storage at 6°C)		(% concentration by mass)	
Compound Name	Fatty Acid (Carbon Number)	0 days	180 days
Methyl Myristate	C14:0	0.46	0.67
Methyl Palmitate	C16:0	12.18	14.31
Methyl Palmitoleate	C16:1	0.03	0.06
Methyl Sterate	C18:0	9.91	12.34
Methyl Oleate	C18:1	48.30	46.31
Methyl Linoleate	C18:2	16.31	15.29
Methyl Linolenate	C18:3	3.05	0.27
Methyl Arachidate	C20:0	0.56	0.62
Methyl Eicosenoate	C20:1	0.06	0.04
Methyl Eicosadienoate	C20:2	0.01	0.14
Methyl Behenate	C22:0	0.02	0.02
Σ Saturated		23.13	27.96
Σ Unsaturated		67.76	62.08
Iodine Number		90	81

Table 4.9. FAME Profile of WME at 40 °C [Data extracted from Appendix D, ARC]

Fatty Acid Methyl Esters (Storage at 40°C)		(% concentration by mass)	
Compound Name	Fatty Acid (Carbon Number)	0 days	180 days
Methyl Myristate	C14:0	0.46	0.59
Methyl Palmitate	C16:0	12.18	11.54
Methyl Palmitoleate	C16:1	0.03	0.03
Methyl Sterate	C18:0	9.91	8.35
Methyl Oleate	C18:1	48.30	43.74
Methyl Linoleate	C18:2	16.31	14.14
Methyl Linolenate	C18:3	3.05	2.68
Methyl Arachidate	C20:0	0.56	0.31
Methyl Eicosenoate	C20:1	0.06	0.01
Methyl Eicosadienoate	C20:2	0.01	0.00
Methyl Behenate	C22:0	0.02	0.02
Σ Saturated		23.13	17.57
Σ Unsaturated		67.76	60.61
Iodine Number		90	96

After 180 days of ageing at 40 °C, the concentration of the following fatty acids in WME decreased: methyl sterate (C16:0), methyl oleate (C18:1) and methyl linoleate (C18:2). The AN of this fuel changed significantly, where it increased from 0.55 to 0.66 after 180 days of storage (see Section 4.1.1), supporting the generation of acid by-products during storage via a possible degradation of the aforementioned fatty acids. Like SME, the WME show similar discrepancies between IN and the unsaturation content, where the unsaturated fatty acid content and IN after 180 days of ageing at 6 °C and 40 °C is 62.08 % and 60.61 % and 81 and 96, respectively. The percent differences in unsaturation compared to the differences in IN show poor correlation between these characteristics. From the above results and previous research findings, using IN as a measure of total unsaturation is not recommended as different FAME compositions can give the same IN and similar FAME compositions can give different IN. The drawback of using IN is that it does not account for the type of double bonds present and only quantifies the total number of double bonds assuming them to be equally reactive (Knothe 2002; Mittelbach and Remschmidt 2004).

4.2 Effect of Ageing on D100 Blends

4.2.1 Acid Number

Table 4.10 and Figure 4.6 summarize the AN results of the aged petrodiesel fuels for 180 days. The AN of petrodiesel fuels is not standardized in the ASTM specifications as the build up of acidity is not considered to be an issue for hydrocarbon based fuels.

Table 4.10. Acid Number of Aged D100 Blends [Data, ARC]

Fuel Type	Acid Number (mg KOH/g)		
	t = 0	90	180
D100 (S)			
6 °C	0.00	0.01	0.01
X °C	0.00	0.01	0.00
40 °C	0.00	0.00	0.00
D100 (W)			
6 °C	0.01	---	0.01
40 °C	0.01	---	0.01

The results show a near zero change in acidity of the D100 (S) and D100 (W) blends with measures being very low and below 0.04 mg KOH/g. Because the method for measuring AN loses precision when sample acidity is detected below 0.10 mg KOH/g, the UBC and ARC results are insignificant and negligible (ASTM 2004). The production of acidic constituents up to 180 days for D100 (S) and D100 (W) is not a concern for the aged conditions of the petrodiesel fuels in this study.

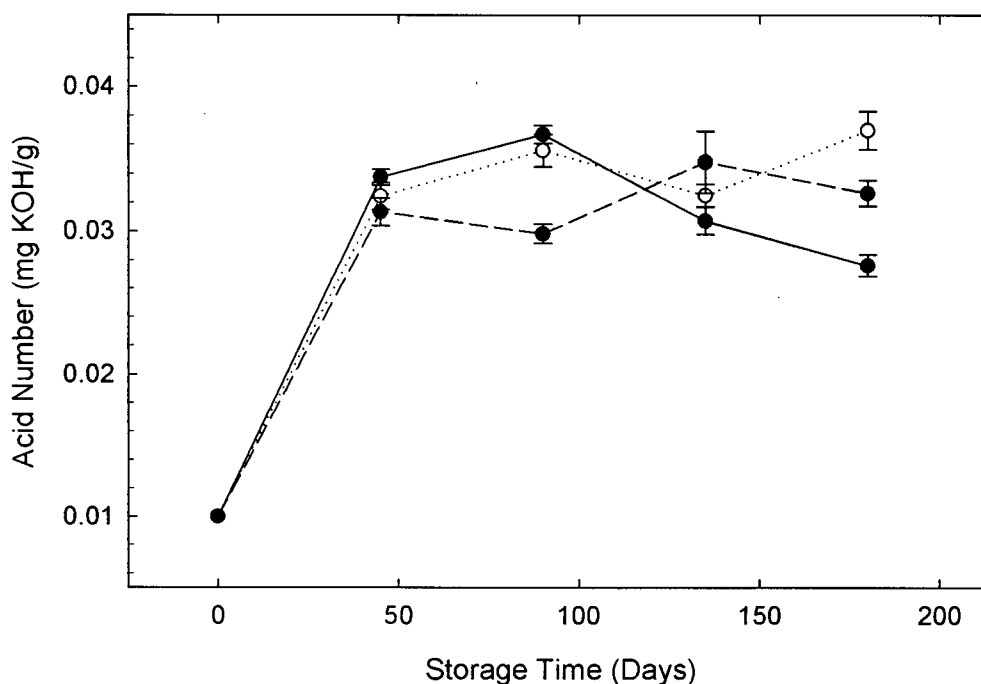


Figure 4.6. Acid Number of Aged D100 (W) Blends [Data, UBC]

4.2.2 Kinematic Viscosity

The ASTM standard for the kinematic viscosity (KV) measured at 40 °C of No.2 diesel fuel is specified to be in the range of 1.9 – 4.1 mm²/s. Figures 4.7 and 4.8 shows the KV of D100 (S) and D100 (W) display slight increases and minor variations, which are not significant enough to consider as an effect of storage temperatures. The KV results are within ASTM's specified limits and no real changes in density are observed for both petrodiesel fuels. D100 (W) is lower in KV than the D100 (S), by at least 37 %. The two petrodiesel fuels had different density measures, where density of D100 (S) ranged between 840.0 – 840.8 kg/m³ and D100 (W) between 800.0 – 810.0 kg/m³. Table 4.11 lists the KV results obtained from ARC. Slight increases are observed in KV for D100 (S) and D100 (W) stored at 6 °C. This data also shows the KV of D100 (W) to be significantly lower than the KV of D100 (S), by nearly 46 %. These observations highlight variations that can be present between petrodiesel fuels.

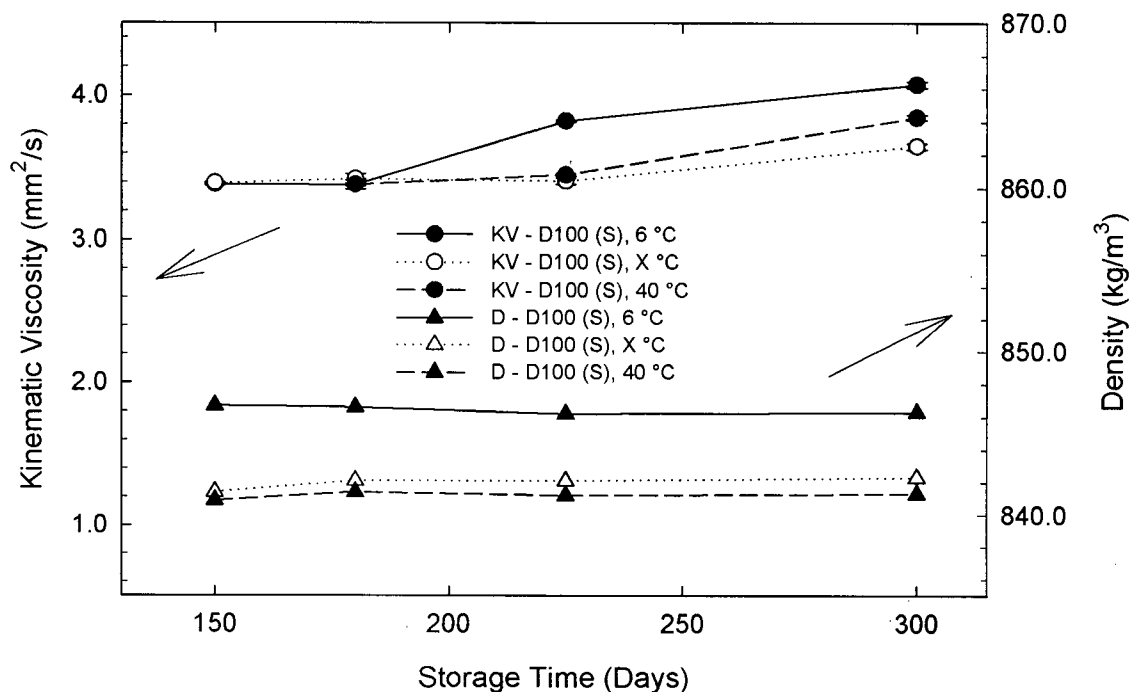


Figure 4.7. Kinematic Viscosity and Density of Aged D100 (S) Blends [Data, UBC]

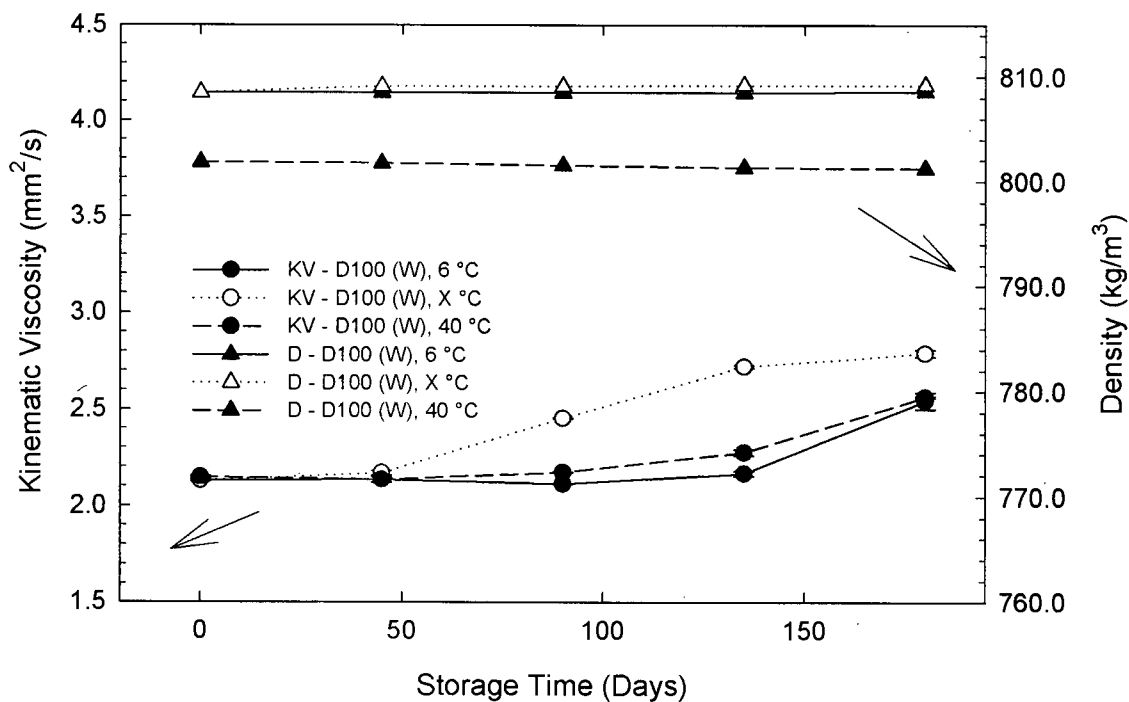


Figure 4.8. Kinematic Viscosity and Density of Aged D100 (W) Blends [Data, UBC]

Table 4.11. Kinematic Viscosity of Aged D100 Blends [Data, ARC]

Kinematic Viscosity (mm ² /s) at 40 °C			
Fuel Type	t = 0	90	180
D100 (S)			
6 °C	2.83	3.05	3.03
X °C	2.83	2.89	2.85
40 °C	2.83	2.86	2.85
D100 (W)			
6 °C	1.51	---	1.62
40 °C	1.51	---	1.52

4.2.3 Cetane Number, Accelerated Stability and Cloud Point

Table 4.12 shows results of cetane number (CN), accelerated stability and cloud point (CP) of the two petrodiesel fuels. In the ASTM standard, the CN of petrodiesel is specified to have a minimum cetane rating of 40 and the results show that this specification is met for all storage conditions up to 180 days. The rate of change in CN of the D100(S) and D100 (W) fuels is not considered to be significant stored as the numerical differences are minimal. Also, the degree of change in CN of the D100 fuels is less than the B100 fuels (reported in Section 4.1.3).

Table 4.12. Cetane Number, Accelerated Stability and Cloud Point of Aged D100 [Data, ARC]

Fuel Type	Cetane Number			Accelerated Stability (mg/100 mL)			Cloud Point (°C)		
	t = 0	90	180	t = 0	90	180	t = 0	90	180
D100 (S)									
6 °C	44.6	42.3	41.6	0.3	0.4	---	-10.2	---	---
X °C	44.6	45.9	45.2	0.3	0.3	---	-10.2	---	---
40 °C	44.6	45.3	44.6	0.3	0.4	0.0	-10.2	---	-10.1
D100 (W)									
6 °C	43.7	---	40.3	0.0	---	0.1	-24.2	---	-28.0
40 °C	43.7	---	43.6	0.0	---	0.2	-24.2	---	-22.6

The accelerated stability method is used for determining the oxidation stability of diesel fuels under accelerated oxidizing conditions. For the diesel fuel to be of good stability,

it must not exceed the maximum limit of 1.5 mg/100 mL. D100 (S) and D100 (W) illustrate good fuel stability up to 180 days as the results demonstrate a low production of insolubles, maximum being 0.4 mg of solids. Comparatively, Mushrush et al. (2005) reported an accelerated stability result of 0.6 mg/100 mL for a stable petrodiesel fuel. The CP of the D100 fuels are much lower than the CP of B100 fuels, signifying D100 fuels to have better cold flow properties than B100 fuels. Biodiesel fuels gels at temperatures near freezing or 0 °C in comparison to temperatures of -15 °C to -17 °C for petrodiesel (Dunn and Knothe 2001). D100 (W) has better cold flow operability than D100(S) as its initial CP measured very low at -24.2 °C. The cloud point of biodiesel fuels are on average up to 15 °C higher than petrodiesel fuels (Srivastava and Prasad 2000).

4.3 Effect of Ageing on B20 Blends

Limited information is available on the natural storage fuel quality of B20 blends; researchers have approximated the quality of B20 to mirror D100, but without actual experimentation this assumption is not fully valid. Currently, there is no quality standard specified for B20 blends but analogous fuel property results are compared to ASTM D975 and D6751 where applicable.

4.3.1 Acid Number

The change in acid number (AN) with time of B20 (SME pre-mix and WME pre-mix) and B20 (WME pre-mix) blends are presented in Figures 4.9 - 4.10, with comparisons made between the pre-mix and after-mix cases. From Figure 4.9, it is evident that the AN of the B20 fuels stored at 6 °C and X °C do not change significantly and are nearly similar up to 300 days of storage. The B20 fuel stored at 40 °C displays an increasing change after 200 days of storage, where AN increased very significantly. This increase can be considered a real effect of the higher storage temperature, but the AN of the B100 and D100 fuels this B20 was made from did not change significantly and was lower than the B20 result, presenting some speculation over this trend. The results of the pre-mix and after-mix B20 blends in Figure 4.9 to 4.10 are comparable and show AN to marginally increase with time. Overall, the AN of WME B20 is higher than the AN of SME B20 because the AN of the WME used to make WME B20 was higher than the SME used to make SME B20.

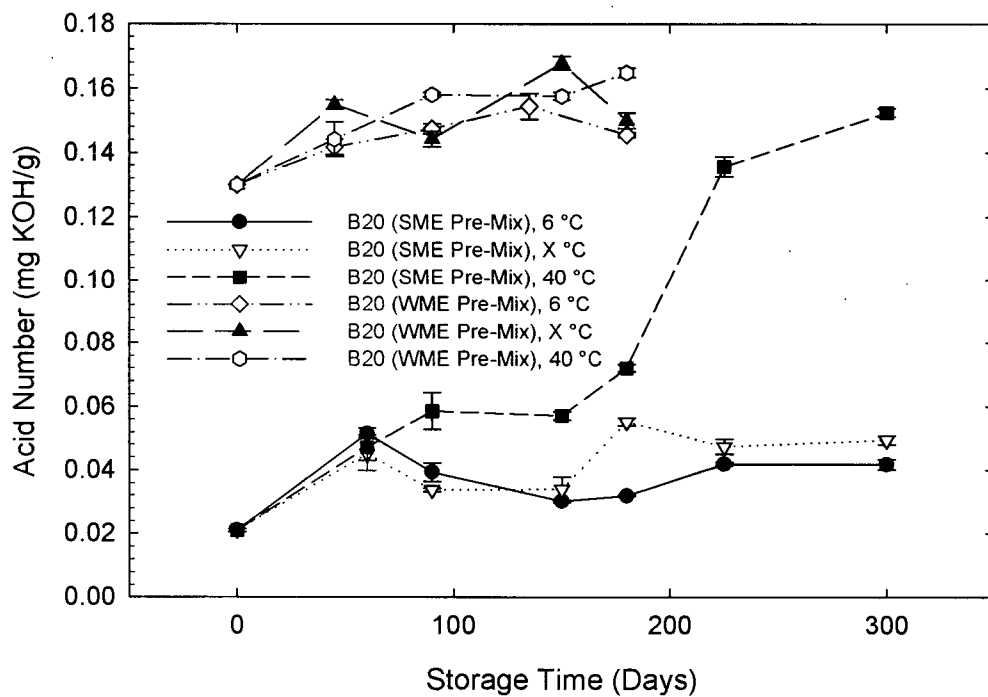


Figure 4.9. Acid Number of Aged B20 (SME Pre-Mix and WME Pre-Mix) Blends [Data, UBC]

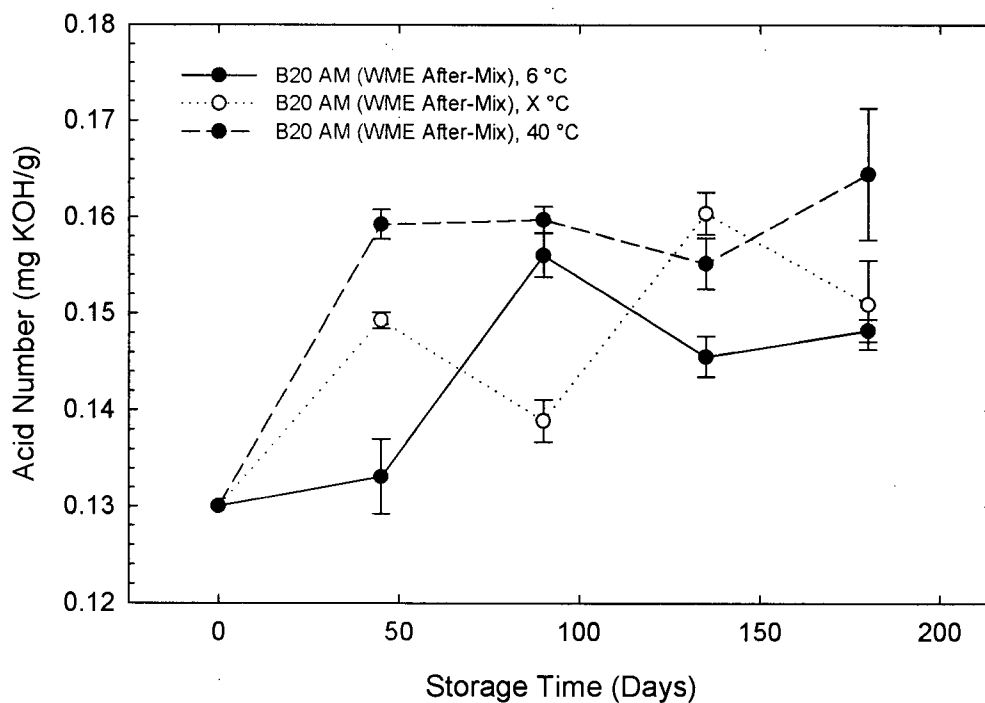


Figure 4.10. Acid Number of Aged B20 (WME After-Mix) Blends [Data, UBC]

The AN results from ARC for the B20 (pre-mix) and B20 (after-mix) blends are presented in Tables 4.13 and 4.14. After 180 days of storage, the AN of all B20 blends is relatively unaffected for the tested conditions. Furthermore, there are no significant differences in AN between the pre-mix and after-mix cases as the results are nearly identical.

Table 4.13. Acid Number of Aged B20 (Pre-Mix) Blends [Data, ARC]

Acid Number (mg KOH/g)			
Fuel Type	t = 0	90	180
B20 (SME Pre-Mix)			
6 °C	0.01	0.01	0.01
X °C	0.01	0.01	0.02
40 °C	0.01	0.01	0.01
B20 (WME Pre-Mix)			
6 °C	0.13	---	0.13
40 °C	0.13	---	0.14

Table 4.14. Acid Number of Aged B20 (After-Mix) Blends [Data, ARC]

Acid Number (mg KOH/g)			
Fuel Type	t = 0	90	180
B20 (SME After-Mix)			
6 °C	0.01	0.01	0.01
X °C	0.01	0.01	0.01
40 °C	0.01	0.01	0.02
B20 (WME After-Mix)			
6 °C	0.13	---	0.13
40 °C	0.13	---	0.14

The AN of the SME B20 blends measured below 0.10 mg KOH/g, where AN results below this value are indicated to have low precision and mediocre reproducibility as is indicated within the ASTM D664 methodology (Knothe 2006).

4.3.2 Kinematic Viscosity

The change in kinematic viscosity (KV) and density with time for the B20 (SME/WME pre-mix and SME/WME after-mix) blends are presented in Figures 4.11 - 4.14. The density of all B20 blends remained adequately stable throughout the indicated storage periods. Figure 4.11 and 4.12 illustrate the KV of the SME B20 blends, where ageing at 40 °C had an increasing effect on both pre-mixed and after-mixed samples. The KV changes in ageing the SME B20 blends at 6 °C and X °C was similar for the pre-mix and after-mix cases, suggesting a comparable effect of these blends in storage at low and ambient temperature ranges.

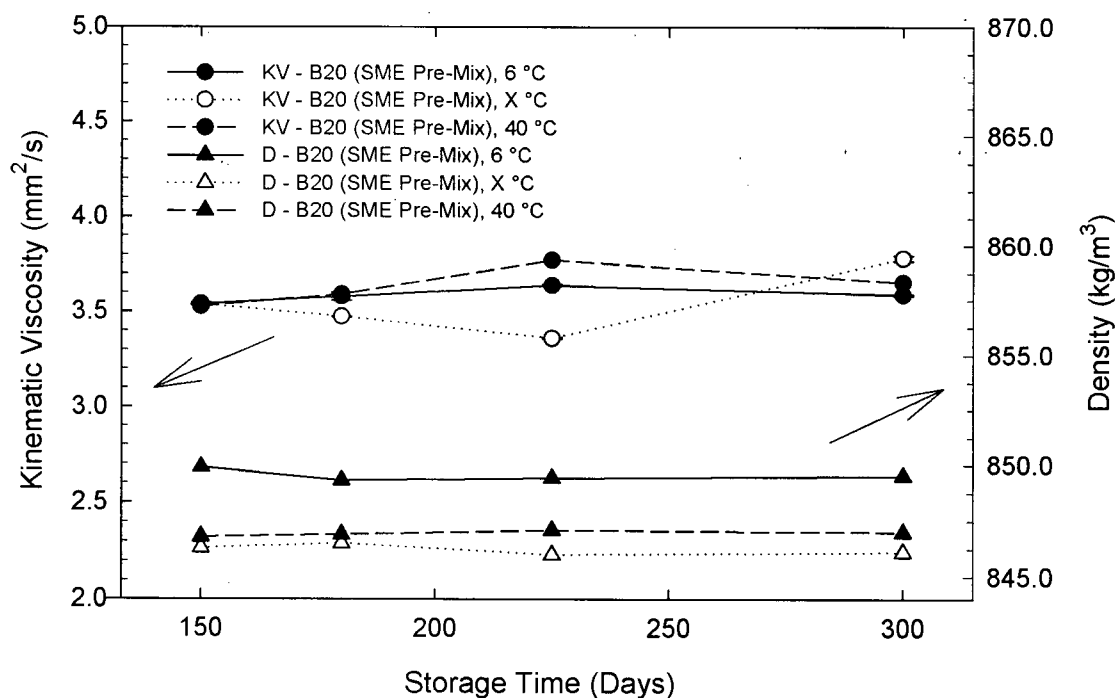


Figure 4.11. Kinematic Viscosity and Density measured at 40.0 °C of Aged B20 (SME Pre-Mix) Blends [Data, UBC]

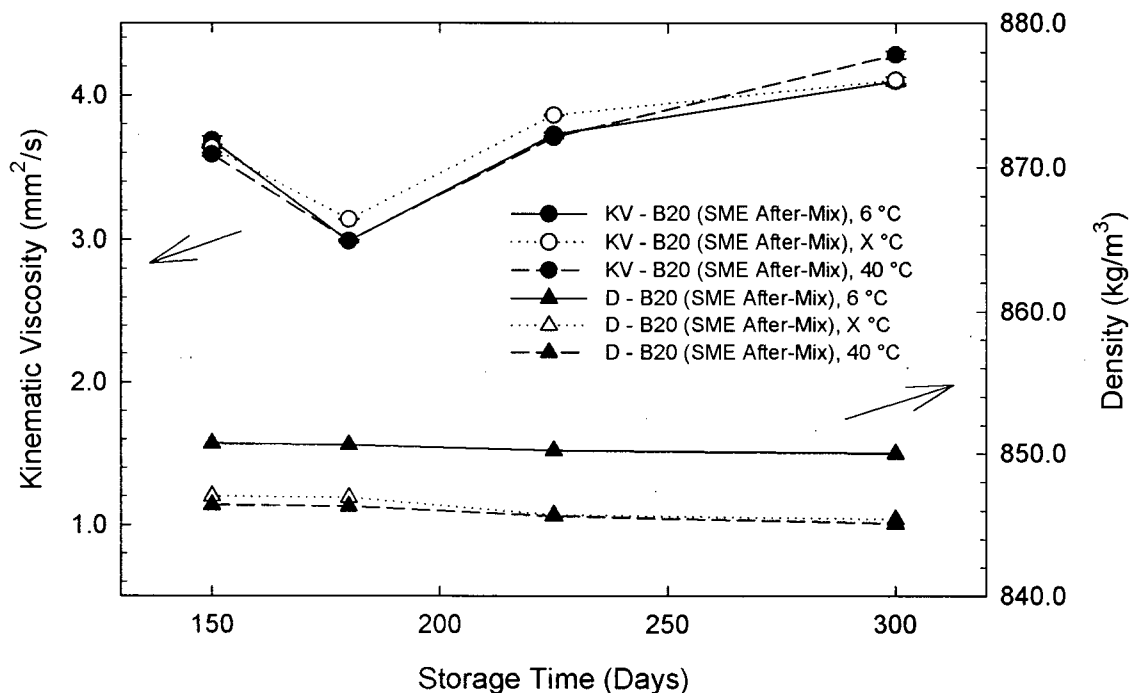


Figure 4.12. Kinematic Viscosity and Density measured at 40.0 °C of Aged B20 (SME After-Mix) Blends [Data, UBC]

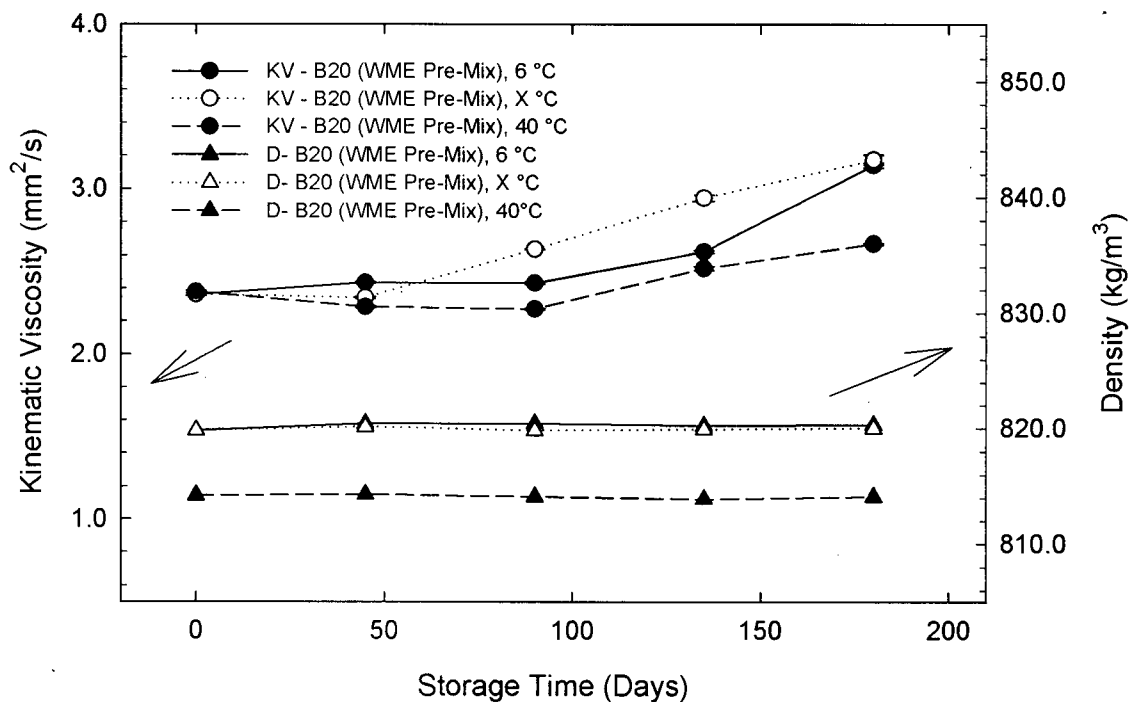


Figure 4.13. Kinematic Viscosity and Density measured at 40.0 °C of Aged B20 (WME Pre-Mix) Blends [Data, UBC]

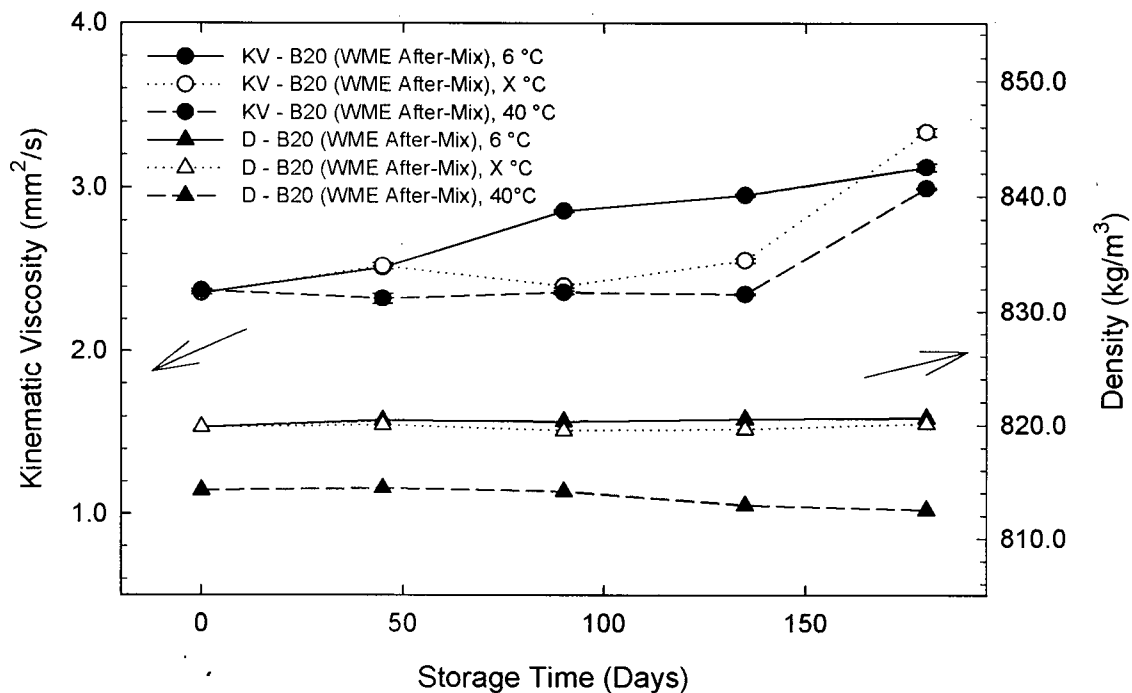


Figure 4.14. Kinematic Viscosity and Density measured at 40.0 °C of Aged B20 (WME After-Mix) Blends [Data, UBC]

Figures 4.13 and 4.14 illustrate the KV of the WME B20 blends, where storage at 40 °C in the pre-mix case increased by 11 % and the after-mix case increased by 21%. The KV of B20 blends stored at 6 °C showed some change over time with no real differences between the pre-mix and after-mix fuels. The KV results for the after-mix case increased on average by about 5 % at X °C and by about 11 % at 40 °C, hinting that storage of the WME B20 blends in a pre-mixed state is favourable at temperatures above ambient. On the whole, KV of the SME B20 blends are reported to be higher than the WME B20 blends because the D100 (W) used to blend the WME B20 was of a much lower viscosity than the D100 (S) to blend the SME B20. Tables 4.15 and 4.16 lists the KV measures conducted by the ARC lab, which underline no significant differences between pre-mix and after-mix for all conditions in the SME and WME blend sets.

Table 4.15. Kinematic Viscosity of Aged B20 (Pre-Mix) Blends [Data, ARC]

Kinematic Viscosity (mm ² /s) at 40 °C			
Fuel Type	t = 0	90	180
B20 (SME Pre-Mix)			
6 °C	3.13	3.13	3.13
X °C	3.13	3.02	3.04
40 °C	3.13	3.01	3.05
B20 (WME Pre-Mix)			
6 °C	1.87	---	2.01
40 °C	1.87	---	1.90

Table 4.16. Kinematic Viscosity of Aged B20 (After-Mix) Blends [Data, ARC]

Kinematic Viscosity (mm ² /s) at 40 °C			
Fuel Type	t = 0	90	180
B20 (SME After-Mix)			
6 °C	3.13	3.17	3.14
X °C	3.13	3.03	3.02
40 °C	3.13	3.01	3.03
B20 (WME After-Mix)			
6 °C	1.87	---	1.99
40 °C	1.87	---	1.90

The numerical data is different than the previous KV results, but the trend between the SME and WME set is comparable, where KV of the SME blends are higher than the WME blends. As seen for KV of B100 and D100, the absolute value differences between the ARC and UBC data is a direct result of the different apparatuses used to measure KV.

4.3.3 Cetane Number, Peroxide Value, Oxidation Stability and Cloud Point

Tables 4.17 and 4.18 give the results of cetane number (CN), peroxide value (PV) and oxidation stability (OS) of aged B20 blends of both pre- and after- mixed biodiesel blend sets. The CN results for the SME B20 blends fluctuated slightly with time, with the 6 °C storage condition denoting a decrease by 11 % for pre-mix and 7.5 % for after-mix. CN for

the WME B20 blends decreased after 180 days of storage by at least 4 % with minimal variation between the pre-mix and after-mix results. Although, the CN of B20 (SME pre-mix) did not change much after 180 days of storage and showed less fluctuation than B20 (SME after-mix), the changes are not significant enough to conclude any effect between the blends at their storage conditions.

The PV measure of SME pre-mix at 40 °C increased to 26.0 meqO₂/kg after 180 days of storage, while after-mix increased to 6.0 meqO₂/kg. Although, the pre-mix result had a higher concentrative presence of peroxides than the after-mix case the difference is not significant. The measured PV of WME B20 blends at 6 °C and 40 °C at 180 days showed no net change when compared to the result at 0 days.

Table 4.17. Cetane Number, Peroxide Value, Oxidation Stability of Aged B20 (Pre-Mix) Blends [Data, ARC]

Fuel Type	Cetane Number			Peroxide Value (meqO ₂ /kg)			Oxidation Stability (RIP time in hours)		
	t = 0	90	180	t = 0	90	180	t = 0	90	180
B20 (SME Pre-Mix)									
6 °C	47.9	47.9	43.6	3.8	11.0	---	7.8	4.8	---
X °C	47.9	48.8	47.7	3.8	7.0	---	7.8	4.9	---
40 °C	47.9	48.7	47.7	3.8	12.0	26.0	7.8	3.6	1.8
B20 (WME Pre-Mix)									
6 °C	47.8	---	45.3	2	---	1	12.9	---	11.9
40 °C	47.8	---	46.1	2	---	1	12.9	---	16.8

Table 4.18. Cetane Number, Peroxide Value, Oxidation Stability of Aged B20 (After-Mix) Blends [Data, ARC]

Fuel Type	Cetane Number			Peroxide Value (meqO ₂ /kg)			Oxidation Stability (RIP time in hours)		
	t = 0	90	180	t = 0	90	180	t = 0	90	180
B20 (SME After-Mix)									
6 °C	47.9	47.2	44.3	3.8	5.0	---	7.8	4.4	---
X °C	47.9	48.2	45.7	3.8	8.0	---	7.8	4.7	---
40 °C	47.9	48.2	47.6	3.8	10.0	6.0	7.8	4.4	3.9
B20 (WME After-Mix)									
6 °C	47.8	---	45.6	2	---	2	12.9	---	10.6
40 °C	47.8	---	45.4	2	---	1	12.9	---	14.4

From the OS measures, the results suggest the SME after-mix blend at 40 °C to have greater stability than the SME pre-mix blend. The B20 WME blends displayed much better stability than the B20 SME blends, a function of the individual stabilities of the parent biodiesel and petrodiesel fuels used for preparing the B20 fuels. Hence, the B20 blend serves to meet the minimum RIP time of 6 hours as a biodiesel blend. This result is inferred from the fatty acid composition of WME used to blend the B20 fuel as WME showed greater OS than SME. Table 4.19 lists the pre- and post-storage cloud point (CP) of the B20 fuel blends.

Table 4.19. Cloud Point of Aged B20 Blends [Data, ARC]

Fuel Type	Cloud Point (°C)	
	t = 0	180
B20 (SME)		
Pre-Mix - 40 °C	-9.5	-10.3
After-Mix - 40 °C	-9.5	-10.7
B20 (WME)		
Pre-Mix - 6 °C	-18.4	-17.3
After-Mix - 6 °C	-18.4	-17.8
Pre-Mix - 40 °C	-18.4	-16.7
After-Mix - 40 °C	-18.4	-17.0

The SME blends displayed lower CP values than WME blends and this is a direct function of the original CP of the petrodiesel used to make the B20 blends. However, the results indicate that B20 fuel blends have better cold flow properties than the B100 blends and the fuels will not gel or cloud until they reach temperatures of -10 °C. No significant effect of the pre- and post-mixing has been observed for CP. In the above results for the B20 fuel blends, it is difficult to state any firm conclusion about which B20 blend is the preferred fuel and the presented results have to be considered as an indication for further studies to explore this fact.

4.4 Cetane Number Calculation of B20 Blends

Measured cetane numbers (using ASTM D613 method) of the pre- and after-mix B20 fuel blends were compared to its calculated set by linear addition by volume % via Equation (3). The CN of biodiesel fuels have very rarely been determined via the ASTM D613 engine test as many cetane data have been computed from an ignition delay apparatus (McCormick

et al. 2006; Murphy et al. 2004). Murphy et. al. (2004) remarked that it is possible to compute the CN of a blend fuel from knowing the CN of the pure components used to blend it but there is some uncertainty on whether the CN of a blend can be a linear combination of the CN of its components. Table 4.20 and 4.21 evaluates the measured cetane data of B20 against the calculated cetane data of B20 from linear addition of B100 and D100. The percent error results show a good possibility of computing the CN's of blends as a linear addition of the blends pure components.

Table 4.20. Measured and Calculated Cetane Numbers of B20 (Pre-Mix) Blends

CETANE NUMBER		Measured			Calculated			% Error		
Fuel Type		t = 0	90	180	t = 0	90	180	t = 0	90	180
B20 (SME Pre-Mix)										
6 °C		47.9	47.9	43.6	47.2	44.7	43.5	-1.50	-6.76	-0.14
X °C		47.9	48.8	47.7	47.2	47.6	46.5	-1.50	-2.42	-2.47
40 °C		47.9	48.7	47.7	47.2	47.1	46.1	-1.50	-3.24	-3.44
B20 (WME Pre-Mix)										
6 °C		47.8	---	45.3	47.8	---	44.7	0.00	---	-1.37
40 °C		47.8	---	46.1	47.8	---	46.0	0.00	---	-0.13

Table 4.21. Measured and Calculated Cetane Numbers of B20 (After-Mix) Blends

CETANE NUMBER		Measured			Calculated			% Error		
Fuel Type		t = 0	90	180	t = 0	90	180	t = 0	90	180
B20 (SME After-Mix)										
6 °C		47.9	47.2	44.3	47.2	44.7	43.5	-1.50	-5.38	-1.72
X °C		47.9	48.2	45.7	47.2	47.6	46.5	-1.50	-1.20	1.79
40 °C		47.9	48.2	47.6	47.2	47.1	46.1	-1.50	-2.24	-3.24
B20 (WME After-Mix)										
6 °C		47.8	---	45.6	47.8	---	44.7	0.00	---	-2.02
40 °C		47.8	---	45.4	47.8	---	46.0	0.00	---	1.41

For example, the maximum difference between the predicted cetane numbers and the measured data is less than 6.8 % of the measured values for the pre-mix B20 fuels and 5.4 % of the measured values for the after-mix B20 fuels. Out of the 17 calculated results and with

the exception of two fuel blends, the SME pre-mix and SME after-mix at 90 days, the maximum difference between the calculated and measured B20 fuels is less than 3.5 %. Murphy et al. (2004) calculated the CN of a blend fuel as a linear combination of the pure components and indicated that higher errors may result if the CN of the pure components also measured to have high errors.

In summary, the above results are promising in verifying the existence of a linear relationship between the CN of biodiesel and petrodiesel fuels, where linear addition can be used to estimate the CN of B20 and other volumetric ratios of biodiesel blends. This result is valuable as the CN is a function of a fuels composition and can effect engine start-up, noise level and exhaust emissions (Van Gerpen 1996).

4.5 Diesel Vehicle Emissions of Aged Fuel Blends

Vehicle emission testing of 7 different aged fuel blends (6 WME /1 SME) were conducted at the AirCare[®] research facility in Burnaby, BC, where regulated pollutants HC, CO, NO_x and CO₂ were measured from the tailpipes of a 1987 Volkswagen Jetta and a 2005 Mercedes Benz Smart Car. Testing in the Smart Car was limited to two fuel blends due to restrictions on vehicle availability. The reported emission results are an average mean of at least three independent cold start tests.

4.5.1 1987 Volkswagen Jetta Emission Test Results

Figures 4.15 – 4.18 summarize the average results of HC, CO, NO_x and CO₂ emissions from 7 different aged fuels tested in a 1987 VW Jetta. Table 4.22 further lists these results in numerical form with results of some fuel properties and characteristics of the aged fuels. Fuel property differences between biodiesel and petrodiesel will affect the fuels ignition and combustion characteristics via injection pressure, injection rate and spray formation, thus affecting the level and type of emissions produced (Yamane et al. 2001).

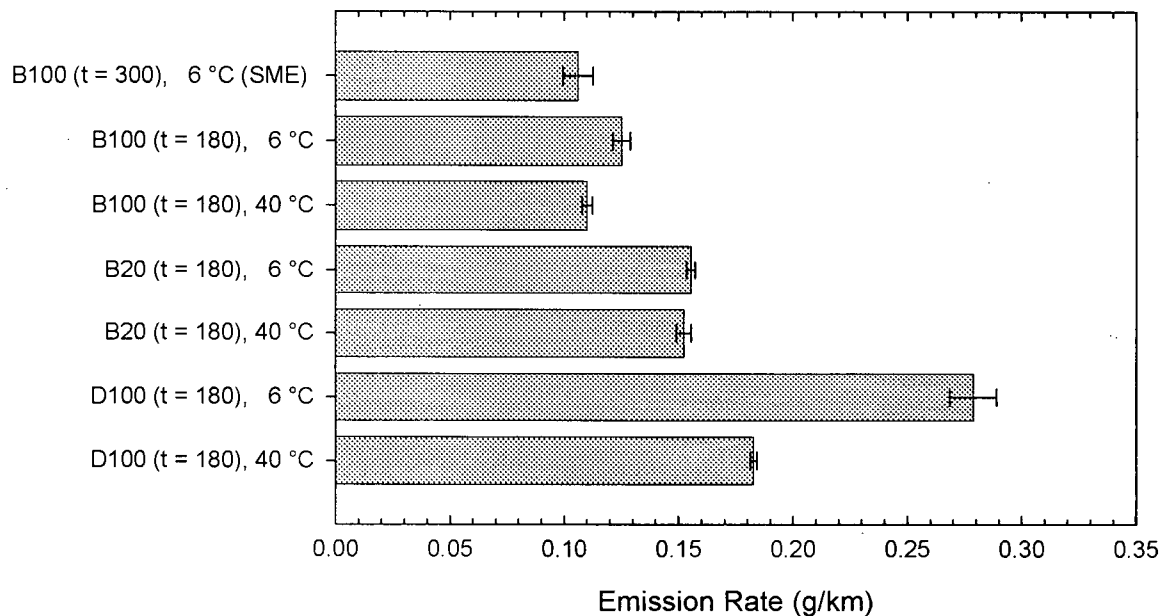


Figure 4.15. Specific HC Emission Rates of Aged Blends in VW Jetta

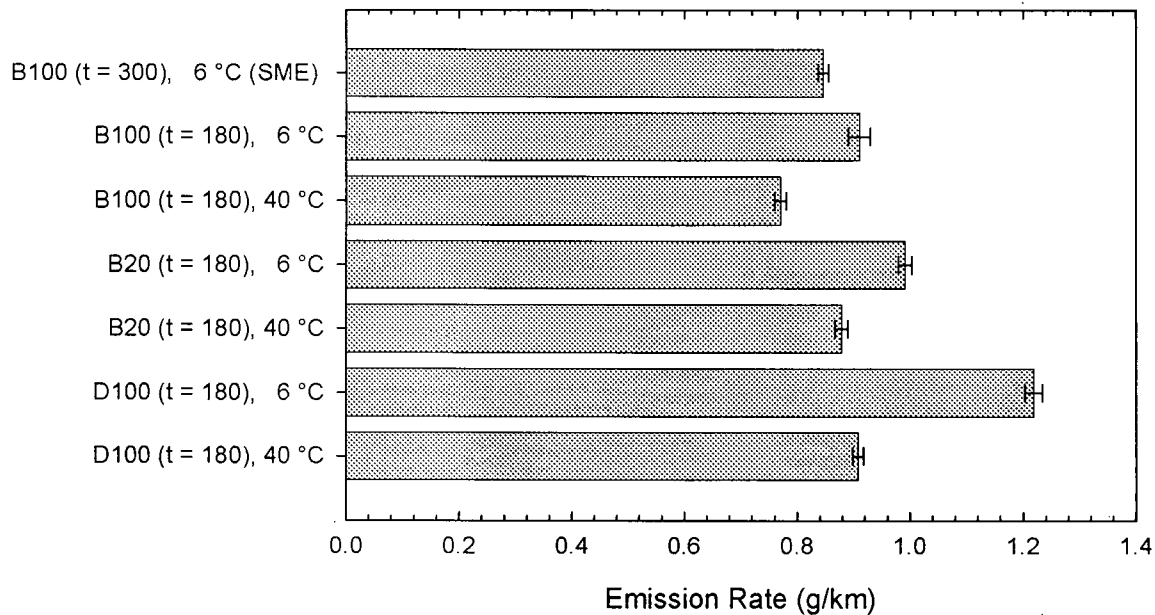


Figure 4.16. Specific CO Emission Rates for Aged Blends in VW Jetta

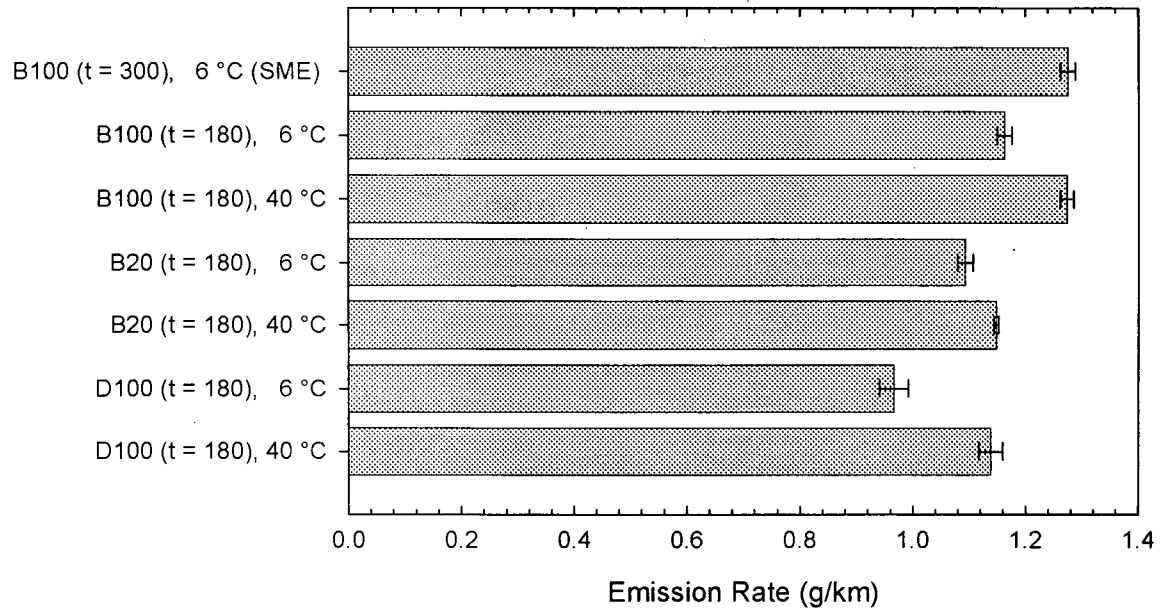


Figure 4.17. Specific NO_x Emission Rates for Aged Blends in VW Jetta

Table 4.22. Select Fuel Properties and Emission Results of Test Blends

	SELECT FUEL PROPERTIES			EMISSION RATES (g/km)			
	Kinematic Viscosity at 40 °C (mm ² /s)	Cetane Number	Oxygen Content (%)	HC	CO	NO _x	CO ₂
1987 VW Jetta							
*B100 (t=300), 6 °C (SME)	3.95	51.3	10.41	0.11	0.85	1.28	173.15
B100 (t=180), 6 °C	4.93	62.2	11.5	0.13	0.91	1.16	170.72
B100 (t=180), 40 °C	4.88	55.8	12.2	0.11	0.77	1.27	168.34
B20 (t=180), 6 °C	2.01	45.3	3.6	0.16	0.99	1.09	163.75
B20 (t=180), 40 °C	1.90	46.1	2.9	0.15	0.88	1.15	162.16
D100 (t=180), 6 °C	1.62	40.3	0.0	0.28	1.22	0.97	162.17
D100 (t=180), 40 °C	1.52	43.6	0.0	0.18	0.91	1.14	163.48
Average Standard Error (±)				0.0038	0.0119	0.0167	0.8013
2005 SMART Car							
B100 (t=180), 40 °C	4.88	55.8	12.2	0.01	0.07	0.41	137.90
B20 (t=180), 40 °C	1.90	46.1	2.9	0.02	0.08	0.42	136.68
Average Standard Error (±)				0.0008	0.0033	0.0154	0.4986

*The fuel properties of this blend are reported at the 180 day mark

The fuel labelled as 'B100 (t=300), 6 °C (SME)' is representative of SME aged for 300 days at 6 °C. The other six fuel blends are part of the WME blend set and aged for at least 180 days. During testing of the D100 (t = 180), 6 °C fuel, the test vehicle encountered operational problems during engine start-up and there was some difficulty in keeping the vehicle running during the testing phase. The vehicle did not operate in a similar manner for each of its test cycles and the broader error bar (shown on figures) models this observation. Because of this, it is likely that 'D100 (t=180), 6 °C' emitted significantly higher HC and CO and lower NO_x emissions than 'D100 (t=180), 40 °C'. The fuel property results of the two diesel fuels further supports this speculation as the differences between the fuel properties is not large enough to solely account for the higher emission variations.

Emission results of the WME biodiesels relative to the petrodiesels are a 40 – 55 % reduction in HC, a 15 – 25% reduction in CO; a 12 – 20 % increase in NO_x and a 3-5 % increase in CO₂. Similarly, if the emissions of B100 (t=300), 6 °C (SME) are compared relative to D100 (t=180), 40 °C, the results indicate a 42 % reduction in HC, a 7% reduction in CO; a 12% increase in NO_x and a 6 % increase in CO₂. D100 (t=180), 40 °C is chosen over D100 (t = 180), 6 °C as testing of the former petrodiesel fuel was not affected by any operational problems in the vehicle and produced more reliable results. The average emission results of B20 fuels relative to D100 are a 30 % reduction in HC, a 10 % reduction in CO; a 6 % increase in NO_x and no real change in CO₂. The results indicate blending of B100 with D100 is advantageous in reducing HC and CO emissions from a diesel engine vehicle. McCormick et al. (2006) tested eight heavy duty diesel vehicles (e.g., three transit buses, two school buses, two trucks, 1 motor coach) and their results for B20 relative to D100 showed an average reduction of 12% for HC emissions and 17 % reduction for CO emissions. The NO_x emissions of B20 in these vehicles varied between -5.8 to 5.2% with the disparity of the results being a definite function of engine design, vehicle technology and test cycle. Thus, the HC and CO emissions for B100 and B20 are significantly lower relative to D100.

HC emissions stem from crevices (e.g., piston ring grooves) and the flame quench layer, where a narrow quench zone near the cool cylinder walls puts the flame out and this results in unburned hydrocarbons or fuel (Stone 1999). HC emissions also result from unburned fuel ensuing from the burning of fuel/air mixtures that are too rich for auto-ignition (Wang et al. 2000). CO emissions from internal combustion engines are determined by the

fuel/air equivalence ratio and greater levels of CO can be formed under fuel-rich conditions, a sign of incomplete combustion. The reduction of HC and CO emissions can be attributed to the fuel oxygen content of biodiesel (Chang et al. 1996; Mittelbach and Remschmidt 2004). In engine testing a 1992 Cummins L10E (electronic control) engine under transient conditions, Schumacher et al. (2001) reported a 16- 26 % reduction in CO emissions with biodiesel and its blends. Previous studies have reported reductions in HC and CO to be as high as 50% (Peterson et al. 2000). It has been well researched from various engine and vehicle emissions testing studies that the presence of oxygen in biodiesel is what accounts for reductions in HC and CO emissions (McCormick et al. 2006). Reductions in HC can be attributed to fuels with higher cetane numbers, as the ignition delay time is less and this promotes a complete combustion. Because high cetane fuels have shorter ignition periods, there is less burn time available for the combustible fuel/air mixture, which decreases the combustion temperature and pressure, resulting in lower HC (Chang et al. 1996). However, advances in injection timing can encourage the formation of NO_x emissions. NO_x emissions are dependent on the combustion temperature, combustion time and oxygen concentration of combustion products (Chang et al. 1996; Stone 1999).

NO_x emissions for B100 were higher by at least 12 % and for B20 by at least 1 % relative to D100. In agreement with previous research findings, B100 emitted significantly higher NO_x levels than D100. For example, Knothe et al. (2006) tested B100 to have a 12% NO_x increase relative to D100. McCormick et al. (2006) reviewed an on slate of recent studies for B20 emissions and reported the average change in NO_x from D100 to be -0.6 ± 2.0 % and concluded the difference in results between studies to be highly dependent on engine technology. Fuels with higher cetane have a shorter ignition delay time and this advances the combustion timing, which causes increases in peak temperature and pressure, resulting in higher NO_x levels (Wang et al. 2000).

Though higher cetane is a proposed cause for high NO_x emissions in biodiesel, so is the presence of double bonds in the fuels molecular structure as that may contribute in some pre-combustion chemistry to increase NO_x (McCormick et al. 2001). McCormick et al. (2001) observed NO_x emissions to increase in biodiesel fuels of increasing unsaturation, or decreasing cetane numbers, asserting the presence of double bonds as an influential factor for producing NO_x. Among the three B100 fuels, B100 (t=180), 6 °C showed the lowest NO_x

rate and its saturation content is higher than the other biodiesels, where % saturation for B100 (t=180), 6 °C was 27 % and for B100 (t=180), 40 °C was 18%.

The effect of storage temperature on emissions was marginal for the B20 fuel blends, but an effect was seen between B100 (t=180), 6 °C and B100 (t=180), 40 °C, where the biodiesel stored at the colder condition generated higher CO and lower NO_x. As discussed above, the lower NO_x can be explained by analyzing the saturation content of the two fuels. From their findings, McCormick et al. (2006) and Knothe et al. (2006) have found biodiesel fuels with a higher degree of saturation to display lower NO_x. However this may contradict the effect of a higher cetane producing more NO_x as high cetane biodiesels have a higher degree of saturation. Although the biodiesel stored at the colder temperature had a higher cetane number, it still produced more CO than the warmer temperature biodiesel, as fuels with higher cetane numbers can be expected to produce lower CO levels. This indicates that the cetane number effect alone is not enough to generate lower CO emissions in a biodiesel fuel and multiple effects will combine to affect emission levels. Peterson et al. (2000) reported that a reduction in NO_x is strongly connected to an increase in the fuels cetane number; however, there may be differences depending on the type of test engine, fuel and operating conditions.

It can be noted that there is an anti-correlation effect between CO and NO_x, where lower CO results in higher NO_x and vice versa. This is obvious for some of the blends, particularly B100 (t=180), 6 °C, B100 (t=180), 40 °C, B20 (t=180), 40 °C and D100 (t=180), 40 °C. With cetane number being an indicator of ignition quality, it does influence fuel combustion, which in turn impacts emissions, but to assume a singular correlation between cetane and diesel exhaust emissions is premature as other factors besides cetane can and will affect the fuel combustion process, engine technology being one key factor. From the presented results, the effect of kinematic viscosity did not appear to be well correlated between fuel type and emissions. Further research might be necessary to confirm if the poor operating conditions of the 1987 VW Jetta observed during the testing of D100 (t=180), 6 °C are fully responsible for the distinctive emission (HC, CO, NO_x) differences shown between the two petrodiesel fuels; given the difference in their fuel properties is not significant enough to impart such a difference in the tested emissions.

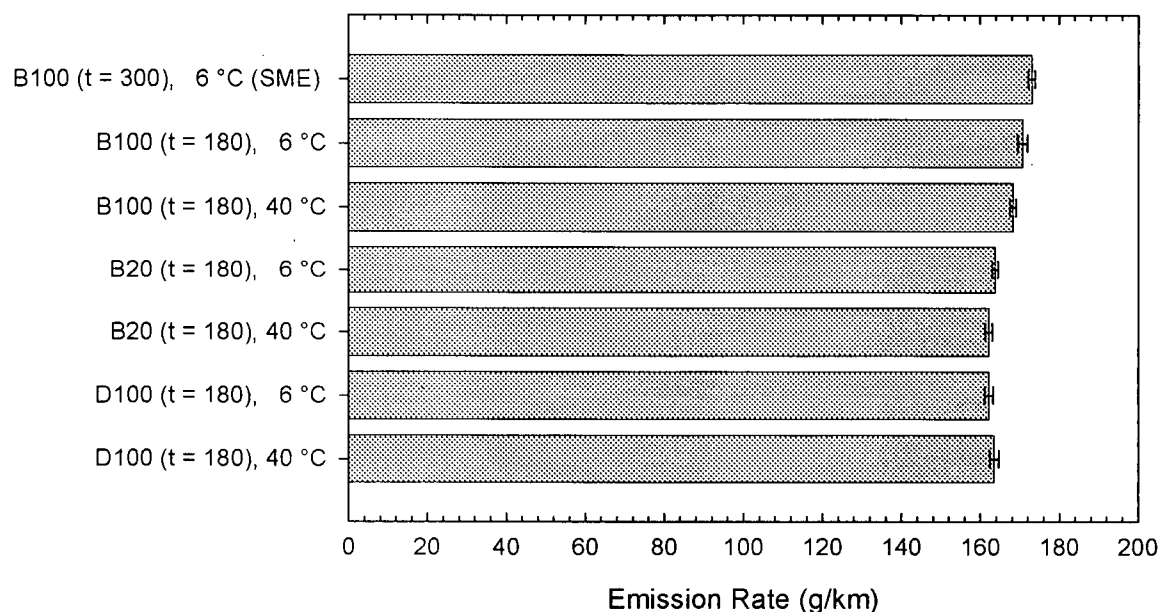


Figure 4.18. Specific CO₂ Emission Rates for Aged Blends in VW Jetta

The CO₂ emission results depicted in Figure 4.18 show the extent of fuel consumption and the concentrated levels at which it is being produced. The CO₂ emission rates of the 7 test fuels range between 162.2 – 173.2 g/km; with the three B100 fuels emitting relatively higher rates than the B20 and D100 fuels. This result is attributed to the lower energy content of biodiesel. Biodiesel fuels will have higher fuel consumption rates than diesel fuels because their energy content is lower, in some cases by at least 12% (Chang et al. 1996). In their study, Jeong et al. (2006) observed B100 blends to emit a greater quantity of CO₂ than D100 blends. Also, Knothe et al. (2006) reported the fuel consumption of petrodiesel to be lower than biodiesel.

4.5.2 Emissions Comparison of 1987 VW Jetta and 2004 Smart Car

The HC, CO, NO_x and CO₂ emission results of the B100 and B20 fuel blends tested in the Smart Car and the VW Jetta are plotted on Figures 4.19-4.22. The results clearly highlight a strong contrast in emission levels between the two diesel vehicles, where emissions from the Smart car are significantly lower by multiple degrees than from the Volkswagen Jetta. For example, the emissions generated from burning the same B100 fuel in

both vehicles resulted in the following reductions: 87 % in HC, 92% in CO, 68% in NO_x and 18 % in CO₂. Similarly the emission reductions for B20 are 88 % in HC, 91% in CO, 64% in NO_x and 16 % in CO₂.

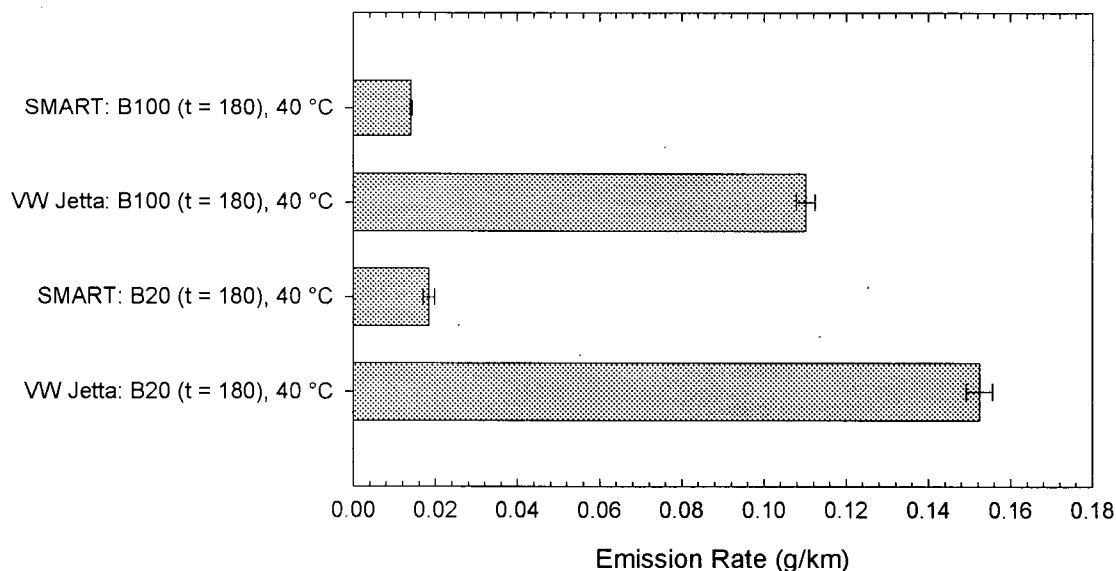


Figure 4.19. VW versus SMART: Specific HC Emission Rates for Aged Blends

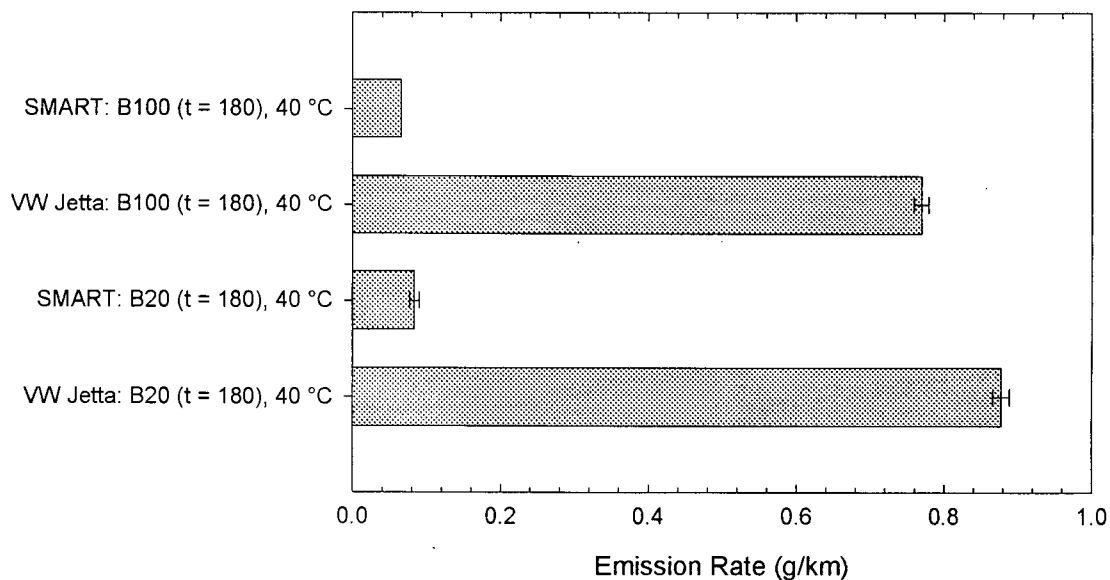


Figure 4.20. VW versus SMART: Specific CO Emission Rates for Aged Blends

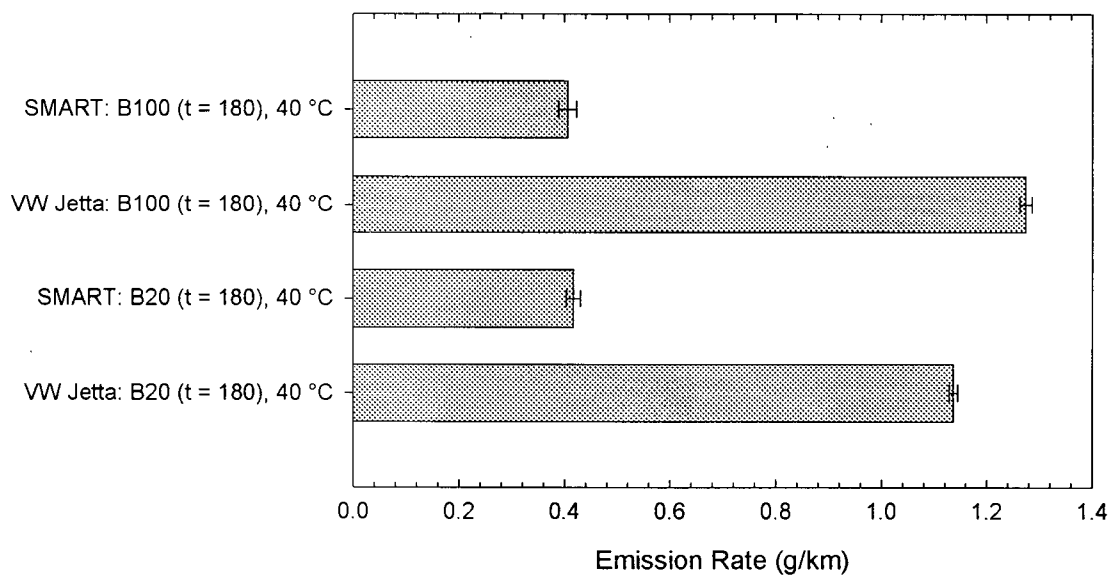


Figure 4.21. VW versus SMART: Specific NO_x Emission Rates for Aged Blends

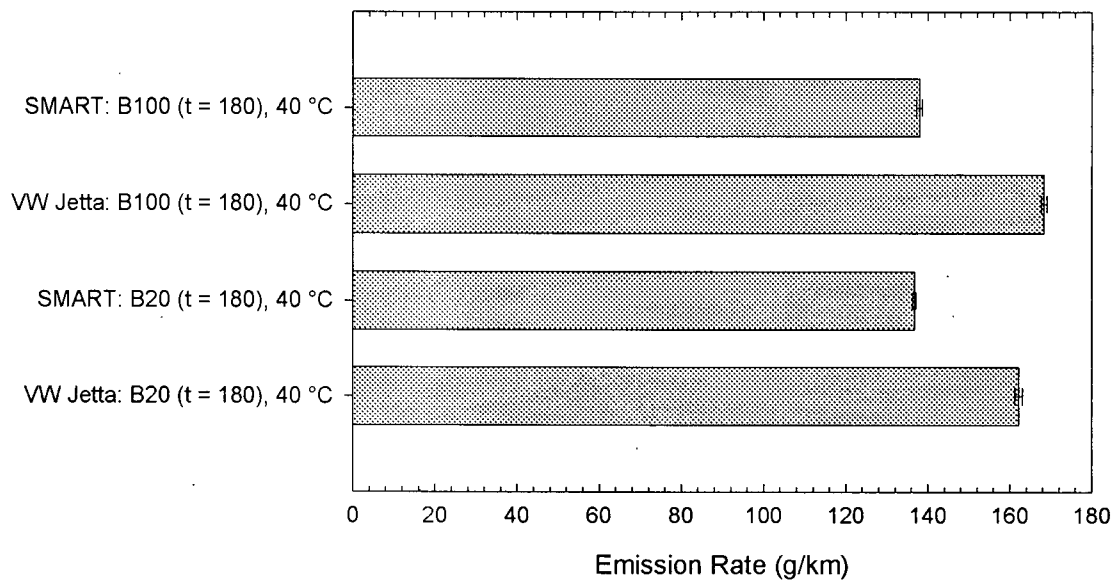


Figure 4.22. VW versus SMART: Specific CO₂ Emission Rates for Aged Blends

The above results indicate no significant differences between the emission measures of B100 and B20 in the Smart car, demonstrating the fuel effect to be negligible. This also cancels any discussion of fuel property influences on the resulting emissions. For the same fuel blends, HC, CO and NO_x emitted at much higher rates in the 1987 VW Jetta than the 2005 Smart car, highlighting the fuel effect to be more sensitive in the Jetta and it is a clear result of modern engine and/or vehicle technology. Older diesel engines are less efficient than modern engines and usually operate at lower injection pressures and temperatures, where they have an increased sensitivity to fuel properties like cetane and result in producing higher emissions. The modern diesel engines operate with electronically controlled injection systems and do not display a great sensitivity to certain combustion or fuel properties as their older counterparts (Knothe 2005). Fuel combustion is a very complex process depending on a variety of factors and the resulting emissions not only depend on the nature of the combustion process and effect of fuel properties, but very much on engine technology.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

Commercially available biodiesel and petrodiesel fuels were stored for at least 180 days under the conditions prescribed as cool, ambient and warm. The fuel blends were: (i) two biodiesel fuels (B100), one derived from 100 % pure soybean oil (SME) and the other from waste vegetable oils (WME) (ii) two petroleum derived diesel fuels (D100) and (iii) two B20 fuels, made from blending 80% biodiesel with 20% diesel. Fuels were characterized by most of the properties specified in the fuel standards. Regulated gaseous emissions (HC, CO, NO_x) and CO₂ were measured from burning seven fuel blends in a 1987 VW Jetta and two fuel blends in a 2005 Mercedes Benz Smart Car, both of which are diesel operated passenger vehicles. The following conclusions are drawn from the experimental results of the fuel ageing and vehicle emissions testing of the stored B100, B20 and D100 fuel blends:

Real Time Fuel Ageing

- A key conclusion of this thesis is that fuel chemistry impacts the fuel properties of biodiesel. The initial properties of SME and WME were different and the two biodiesel fuels aged differently.
- There were no significant changes in acid number and kinematic viscosity of SME stored at 6 °C, X °C and 40 °C. The acid number of the WME showed an increasing effect with time only at 40 °C and kinematic viscosity increased slightly at 6 °C and X °C.
- The cetane number of SME decreased at all conditions and for WME increased at 6 °C.
- The oxidation stability of SME and WME were below the minimum RIP of 6 hours, but WME displayed higher oxidation stabilities because it contained a lesser quantity of unsaturated fatty acids. Hence, the fatty acid composition or chemical structure of biodiesel has a greater impact than temperature on how fuel properties change during storage.
- The iodine number measurements were variable and did not correlate with the oxidation stability and unsaturation content of SME and WME.
- The fuel properties of B20 blends did not change significantly and further ageing studies are recommended to be conducted on B20 fuels.

- The petrodiesel fuels were not affected by ageing in the way the biodiesel fuels were and displayed a near zero acid number, slight changes in kinematic viscosity and maintained good accelerated stability during ageing.
- The actual cetane numbers of the stored B20 blends via the ASTM D613 method were compared to predicted values that were calculated linearly from cetane data of B100 and D100. This comparison yielded sufficient results suggesting that linear interpolation of B100 and D100 cetane data for biodiesel blend fuels is reasonable.
- Cetane numbers of the B20 blends were well predicted by linear interpolation between B100 and D100 cetane numbers.

Diesel Engine Emissions

- Relative to D100, the B100 and B20 fuels tested in the 1987 VW Jetta showed significant reductions in HC and CO emissions. The B100 fuels emitted higher NO_x emissions than B20 or D100.
- Reductions in HC and CO are likely due to the fuel oxygen content. High NO_x emissions from B100 is likely due to high cetane numbers.
- The emissions from the 2005 Smart car were essentially unaffected by the fuel type.

5.2 Recommendations for Future Work

In future work, studying the effect of air or oxygen and adding water at differing concentrations is suggested for the B100, D100 and B20 fuels during long term storage. Studying these combined effects will allow for a more complete assessment of biodiesel fuel behaviour at factors that affect its stability.

The accelerated ageing of fresh B100, B20 and D100 samples could have been performed for each sample interval in conjunction with steady-state sampling. This analysis may have been useful in comparing accelerated ageing to real time ageing and seeing if any correlations could be drawn. It would be recommended to measure fuel properties such as CN, IN, PV and OS at increased intervals and past the original 180 day measures. This may have aided in identifying trends or correlations that were not obvious from the current data set. The extra measures may have provided useful information on whether these properties varied any differently after longer ageing.

Using biodiesel as a fuel in place of petrodiesel achieved significant reductions in HC and CO from the vehicle exhaust of the 1987 VW Jetta, but not from the 2005 Smart car. This suggests that older (much cited) studies on the effect of biodiesel on emissions must be updated.

6.0 REFERENCES

- ASTM. (2004). "D 6751-02: Standard specification for biodiesel fuel (B100) blend stock for distillate fuels." ASTM, West Conshohocken, PA.
- Bacha, J., Blondis, L., Freel, J., Hemighaus, G., Hoekman, K., Hogue, N., Horn, J., Lesnini, D., McDonald, C., Nikanjam, M., Olsen, E., Scott, B., and Sztenderowicz, M. (1998). "Diesel fuels technical review (FTR-2)." Chevron Products Company.
- Barnwal, B. K., and Sharma, M. P. (2005). "Prospects of biodiesel production from vegetable oils in india." *Renewable and Sustainable Energy Reviews*, (9), 363-378.
- Batts, B. D., and Fathoni, A. Z. (1991). "A literature review on fuel stability studies with particular emphasis on diesel oil." *Energy & Fuels*, 5(1), 2-21.
- Beaver, B. D., and Gilmore, C. (1991). "Oxidative degradation of petroleum products via a non-peroxyl radical chain pathway. Electron transfer initiated oxidation (ETIO) revisited." *Fuel Science & Technology International*, 9(7), 811-23.
- Bondioli, P., Gasparoli, A., Lanzani, A., Fedeli, E., Veronese, S., and Sala, M. (1995). "Storage stability of biodiesel." *Journal of the American Oil Chemists' Society*, 72(6), 699-702.
- Bondioli, P., Gasparoli, A., Della Bella, L., and Tagliabue, S. (2002). "Evaluation of biodiesel storage stability using reference methods." *European Journal of Lipid Science and Technology*, 104(12), 777-784.
- Bondioli, P., Gasparoli, A., della Bella, L., Tagliabue, S., Lacoste, F., and Lagardere, L. (2004). "The prediction of biodiesel storage stability. Proposal for a quick test." *European Journal of Lipid Science and Technology*, 106(12), 822-830.
- Bondioli, P., Gasparoli, A., Della Bella, L., Tagliabue, S., and Toso, G. (2003). "Biodiesel stability under commercial storage conditions over one year." *European Journal of Lipid Science and Technology*, 105(12), 735-741.
- Bondioli, P., Gasparoli, A., Lanzani, A., Fedeli, E., Veronese, S., and Sala, M. (1995). "Storage stability of biodiesel." *Journal of the American Oil Chemists' Society*, 72(6), 699-702.
- Canakci, M. (2005). "Performance and emissions characteristics of biodiesel from soybean oil." *Journal of Automobile Engineering*, 219, 915-922.

- Canakci, M., Erdil, A., and Arcaklioglu, E. (2006). "Performance and exhaust emissions of a biodiesel engine." *Applied Energy*, 83, 594-605.
- Canakci, M., Monyem, A., and Van Gerpen, J. (1999). "Accelerated oxidation processes in biodiesel." *Transactions of the ASAE*, 42(6), 1565-1572.
- Canakci, M., and Van Gerpen, J. H. (2003). "Comparison of engine performance and emissions for petroleum diesel fuel, yellow grease biodiesel, and soybean oil biodiesel." *Transactions of the ASAE*, 46(4), 937-944.
- Chang, D. Y., Van Gerpen, J., Lee, I., Johnson, L. A., Hammond, E. G., and Marley, S. J. (1996). "Fuel properties and emissions of soybean oil esters as diesel fuel." *Journal of the American Oil Chemists' Society*, 73(11), 1549-1555.
- Chiu, C.-W., Schumacher, L. G., and Suppes, G. J. (2004). "Impact of cold flow improvers on soybean biodiesel blend." *Biomass and Bioenergy*, 27(5), 485-491.
- Dunn R.O., Shockley, M.W., Bagby, M.O. (1996). "Improving the low-temperature properties of alternative diesel fuels: vegetable oil-derived methyl esters." *Journal of the American Oil Chemists' Society*, 73(12), 1719-1728.
- Dunn, R. O. (1999). "Thermal analysis of alternative diesel fuels from vegetable oils." *Journal of the American Oil Chemists' Society*, 76(1), 109-115.
- Dunn, R. O. (2002). "Effect of oxidation under accelerated conditions on fuel properties of methyl soyate (biodiesel)." *Journal of the American Oil Chemists' Society*, 79(9), 915-920.
- Dunn, R. O. (2004). "Cold flow properties of biodiesel: things you should know." *Abstracts, 36th Great Lakes Regional Meeting of the American Chemical Society, Peoria, IL, United States, October 17-20, LAKES04-328*.
- Dunn, R. O., and Knothe, G. (2001). "Alternative diesel fuels from vegetable oils and animal fats." *Journal of Oleo Science*, 50(5), 415-426.
- Dunn, R. O., and Knothe, G. (2003). "Oxidative stability of biodiesel in blends with jet fuel by analysis of oil stability index." *Journal of the American Oil Chemists' Society*, 80(10), 1047-1048.
- Du Plessis, L. M., De Villiers, J.B.M., Van Der Walt, W.H. (1985). "Stability Studies on Methyl and Ethyl Fatty Acid Esters of Sunflower Oil." *Journal of Americal Oil Chemists Society*, 62, 748-752.

Environmental Protection Agency (EPA), (2002). "Code of federal regulations." 40 CFR Ch. I (7-1-03 Edition) 86.1310-2007.

Falk, O., and Meyer-Pittroff, R. (2004). "The effect of fatty acid composition on biodiesel oxidative stability." *European Journal of Lipid Science and Technology*, 106(12), 837-843.

Ferrari, R. A., Da Silva Oliveira, V., and Scabio, A. (2005). "Oxidative stability of biodiesel from soybean oil fatty acid ethyl esters." *Sci. Agric. (Piracicaba, Braz)*, 62(3), 291-295.

Graboski, M.S., Ross, J.D., and McCormick, R.L., (1996). "Transient emissions from no.2 diesel and biodiesel blends in a DDC series 60 engine." *Society of Automotive Engineers. Special Publications* SP-1179 (Diesel engine combustion and emissions characteristics), 55-62.

Haas, M.J., Scott, K.M., Alleman, T.L., and McCormick, R.L. (2001). "Engine performance of biodiesel fuel prepared from soybean soapstock: A high quality renewable fuel produced from a waste feedstock. *Energy & Fuels*, 15(5), 1207-1212.

Hancock, N., (2005). Global biodiesel market, Oilseeds WA, Agribusiness Opportunities. http://www.australianoilseeds.com/data/assets/pdf_file/728/Global_Biodiesel_Market_Overview_Nathan_Hancock_Dept_Ag_Read-Only.pdf, accessed in October 2006.

Jeong, G.-T., Oh, Y.-T., and Park, D.-H. (2006). "Emission profile of rapeseed methyl ester and its blend in a diesel engine." *Applied Biochemistry and Biotechnology*, 129, 165-178.

Kann, J., Rang, H., and Kriis, J. (2002). "Advances in biodiesel fuel research." *Proceedings of the Estonian Academy of Sciences, Chemistry*, 51(2), 75-117.

Kinney, A. J., and Clemente, T. E. (2005). "Modifying soybean oil for enhanced performance in biodiesel blends." *Fuel Processing Technology*, (86), 1137-1147.

Knothe, G. (2001). "Analytical methods used in the production and fuel quality assessment of biodiesel." *Transactions of the ASAE*, 44(2), 193-200.

Knothe, G. (2002). "Structure indices in FA chemistry. How relevant is the iodine value?" *Journal of the American Oil Chemists' Society*, 79(9), 847-854.

Knothe, G. (2005). "Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters." *Fuel Processing Technology*, 86(10), 1059-1070.

- Knothe, G. (2006). "Analyzing biodiesel: standards and other methods." *Journal of the American Oil Chemists' Society*, 83(10), 823-833.
- Knothe, G., and Dunn, R. O. (2003). "Dependence of oil stability index of fatty compounds on their structure and concentration and presence of metals." *Journal of the American Oil Chemists' Society*, 80(10), 1021-1026.
- Knothe, G., Sharp, C. A., and Ryan, T. W. (2006). "Exhaust emissions of biodiesel, petrodiesel, neat methyl esters, and alkanes in a new technology engine." *Energy & Fuels*, 20, 403-408.
- Leung, D. Y. C., Koo, B. C. P., and Guo, Y. (2006). "Degradation of biodiesel under different storage conditions." *Bioresource Technology*, 97(2), 250-256.
- McCormick, R. L., Graboski, M. S., Alleman, T. L., and Herring, A. M. (2001). "Impact of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy-duty engine." *Environmental Science and Technology*, 35, 1742-1747.
- McCormick, R. L., Williams, A., Ireland, J., Brimhall, M., and Hayes, R. R. (2006). "Effects of biodiesel blends on vehicle emissions, fiscal year 2006 annual operating plan milestone 10.4." Technical Report, NREL/MP-540-40554, National Renewable Energy Laboratory, Golden, CO.
- Mittelbach, M., and Gangl, S. (2001). "Long storage stability of biodiesel made from rapeseed and used frying oil." *Journal of the American Oil Chemists' Society*, 78(6), 573-577.
- Mittelbach, M., and Remschmidt, C. (2004). *Biodiesel: The Comprehensive Handbook*, Martin Mittelbach, Vienna.
- Miyata, I., Takei, Y., Tsurutani, K., and Okada, M. (2004). "Effects of bio-fuels on vehicle performance: degradation mechanism analysis of bio-fuels." *Society of Automotive Engineers, [Special Publication] SP*, SP-1897(Alternative and Oxygenated Fuels), 107-115.
- Monyem, A. (2000). "Investigation of biodiesel thermal stability under simulated in-use conditions." *American Society of Agricultural Engineers*, 16(4), 373-378.
- Monyem, A., and Van Gerpen, J. H. (2001). "The effect of biodiesel oxidation on engine performance and emissions." *Biomass and Bioenergy*, 20(4), 317-325.

- Murphy, M. J., Taylor, J. D., and McCormick, R. L. (2004). "Compendium of experimental cetane number data." *NREL/SR-540-36805*, National Renewable Energy Laboratory, Golden, Colorado.
- Mushrush, G. W., Mose, D. G., Wray, C. L., and Sullivan, K. T. (2001). "Biofuels as means of improving the quality of petroleum middle distillate fuels." *Energy Sources*, 23(7), 649-655.
- Mushrush, G. W., Wynne, J. H., Lloyd, C. T., Willauer, H. D., and Hughes, J. M. (2005). "Recycled soybean derived cooking oils as blending stocks for middle distillate transportation fuels." *Energy Sources*, 27(9), 781-786.
- Mushrush, G. W., Wynne, J. H., Willauer, H. D., Lloyd, C. T., Hughes, J. M., and Beal, E. J. (2004). "Recycled soybean cooking oils as blending stocks for diesel fuels." *Industrial & Engineering Chemistry Research*, 43(16), 4944-4946.
- National Biodiesel Board, (2005). National Biodiesel Board Guidance, Issued November 30, 2005, Use of biodiesel blends above 20% biodiesel.
http://www.mnsoy.com/documents/Biodiesel_Blends_above_20.pdf; accessed in December 2006.
- National Biodiesel Board, (2006). Standards and Warranties.
http://www.biodiesel.org/resources/fuelsheets/standards_and_warranties.shtm; accessed in December 2006
- Pacific Vehicle Testing Technologies, (2007), Copyright Image: Mass Emission Measurement System. Permission Granted.
- Peterson, C. L., Taberski, J. S., Thompson, J. C., and Chase, C. L. (2000). "The effect of biodiesel feedstock on regulated emissions in chassis dynamometer tests of a pickup truck." *American Society of Agricultural Engineers*, 43(6), 1371-1381.
- Prankl, H., Worgetter, M., and Rathbauer, J. (1999). "Technical performance of vegetable oil methyl esters with a high iodine number." *Biomass: A Growth Opportunity in Green Energy and Value-Added Products, Proceedings of the Biomass Conference of the Americas, 4th, Oakland, Calif., Aug. 29-Sept. 2, 1999*, 1, 805-810.
- Prankl, H. (2002). "High biodiesel quality required by European standards." *European Journal of Lipid Science and Technology*, 104(6), 371-375.
- Purcell, D.L., McClure, B.T., McDonald, J., Basu, H.N., (1996). "Transient testing of soy methyl ester fuels in an indirect injection, compression ignition engine." *Journal of the American Oil Chemists' Society*, 73(3), 381-388.

- Rodrigues, J. D. A., Jr., Cardoso, F. D. P., Lachter, E., R., Estevao, L. R. M., Lima, E., and Nascimento, R. S. V. (2006). "Correlating chemical structure and physical properties of vegetable oil esters." *Journal of the American Oil Chemists' Society*, 83(4), 353-357.
- Schumacher, L.G., Borgelt, S.C., Fossen, D., Goetz, W., and Hires, W.G., (1996). "Heavy-duty engine exhaust emission tests using methyl ester soybean oil/diesel fuel blends." *Bioresource Technology*, 57, 31-36.
- Schumacher, L.G., Clark, N.N., Lyon, D.W., Marshall, W., (2001). "Diesel engine exhaust emissions evaluation of biodiesel blends using a Cummins L10E engine." *American Society of Agricultural Engineers*, 44(6), 1461-1464.
- Services, S. L. (1997). "Determination of biodiesel oxidation and thermal stability." National Biodiesel Board. Technical Report.
http://www.biodiesel.org/resources/reportsdatabase/reports/gen/19970212_gen-230.pdf, accessed in March 2006.
- Sheehan, J., Camobreco, Duffiedl, J., Graboski, M., and Shapouri, H., (1998). "An overview of biodiesel and petroleum diesel life cycles." A joint study sponsored by the U.S Department of Agriculture and the U.S. Department of Energy.
- Srivastava, A., and Prasad, R. (2000). "Triglycerides-based diesel fuels." *Renewable and Sustainable Energy Reviews*, (4), 111-133.
- Stone, R. (1999). Introduction to Internal Combustion Engines, *Society of Automotive Engineers, Inc.*, Warrendale, PA.
- Tat, M. E., and Van Gerpen, J. H. (1999). "The kinematic viscosity of biodiesel and its blends with diesel fuel." *Journal of the American Oil Chemists' Society*, 76(12), 1511-1513.
- Thompson, J. C., Peterson, C. L., Reece, D. L., and Beck, S. M. (1998). "Two year storage study with methyl and ethyl esters of rapeseed." *Transactions of the ASAE*, 41(4), 931-939.
- Tyson, K. S. (2001). "Biodiesel handling and use guidelines." *NREL/TP-580-30004*, National Renewable Energy Laboratory, U.S. Department of Energy, Golden, Colorado.
- Tyson, K. S. (2004). "Biodiesel handling and use guidelines." *DOE/GO-102004-1999*, U.S. Department of Energy, Energy Efficiency and Renewable Energy.

- Van Gerpen, J. (1996). "Cetane number testing of biodiesel." *Liquid Fuel and Industrial Products from Renewable Resources, Proceedings of the Liquid Fuel Conference, 3rd, Nashville, Sept. 15 -17, 1996*, 197-206.
- Van Gerpen, J. H., Hammond, E. G., Yu, L., and Monyem, A. (1997). "Determining the influence of contaminants on biodiesel properties." *Society of Automotive Engineers, [Special Publication] SP*, SP-1274(State of Alternative Fuel Technologies), 173-190.
- Van Gerpen, J., Shanks, B., Pruszko, R., Clements, D., and Knothe, G. (2004). "Biodiesel production technology." National Renewable Energy Laboratory, Golden, Colorado.
- Van Gerpen, J. H. (2005). "Biodiesel production and fuel quality." Technical Report. University of Idaho, Moscow, ID.
- Wain, S. K., and Perez, J. M. (2002). "Oxidation of biodiesel fuels for improved lubricity." *ICE (American Society of Mechanical Engineers)*, 38, 27-34.
- Wang, W. G., Lyons, D. W., Clark, N. N., and Gautam, M. (2000). "Emissions from nine heavy trucks fueled by diesel and biodiesel blend without engine modification." *Environmental Science and Technology*, 34(6), 933-939.
- Yamane, K., Ueta, A., and Shimamoto, Y. (2001). "Influence of physical and chemical properties of biodiesel fuels on injection, combustion and exhaust emission characteristics in a direct injection compression ignition engine." *International Journal of Engine Research*, 2(4), 249-261.
- Yuan, W., Hansen, A. C., and Zhang, Q. (2003). "Predicting the physical properties of biodiesel for combustion modeling." *American Society of Agricultural Engineers*, 46(6), 1487-1493.
- Zappi, M., Hernandez, R., Sparks, D., Horne, J., Brough, M., Arora, S. M., and Motsenbocker, W. D. (2003). "A review of the engineering aspects of the biodiesel industry." *ET-03-003*, Mississippi Biomass Council, Jackson, MS.

Appendix A: Acid Number Method

The acid number of B100, D100 and B20 samples were determined using an automatic titrator (Carl Fischer) and followed testing procedures according to ASTM D664.

For a given fuel sample, the methods are as follows:

- a clean and dry 250 mL beaker with a magnetic stir pill is used for each independent acid test.
- 25 - 30 mL of sample is accurately measured and weighed using an electronic balance (sample weight is recorded).
- the measured fuel sample is added to the 250 mL beaker.
- 100 mL of isopropanol and 5 mL of distilled water is added to the 250 mL beaker
- the beaker containing the fuel + isopropanol + water mixture is placed on the magnetic stir plate of the automatic titrator.
- the electrode and KOH dispensing tube is immersed into the beaker and the machine is set in DET mode and begins the titration process and automatically detects for the end points (EP).
- a titration curve representing the titration process is printed out and it illustrates the possible EP points.
- this procedure is repeated at least three times to ensure accuracy.

The acid number in mg KOH/g is calculated via the following formula:

$$\text{Acid Number} = \frac{EP \times M \times 56.1}{W} \quad (\text{A.1})$$

where	EP	=	end point (mL)
	M	=	concentration of KOH titrant (mol/L)
	56.1	=	molecular weight of KOH (g /mol)
	W	=	sample weight (g)

The acid number reported in the results is an average of at least three independent trials and the standard error is calculated by taking the standard deviation and dividing by the square root of $n - 1$, where n is the number of trials.

Appendix B: Kinematic Viscosity Method

The kinematic viscosity of liquid fuel samples at any temperature is calculated by measuring the viscosity and density at those temperatures. The viscosity of all fuels was measured using a rotation viscometer (the HAAKE ROTOVISCO) and the density using a hand held density meter. The HAAKE ROTOVISCO consisted of a rotary viscometer, a temperature control bath, computer logging system and three types of sensors. The NV sensor was used as it is the sensor primarily used to measure low viscosity liquids, such as oils and fuels. The NV sensor consists of a cup and a bell shaped rotor and is classified as a coaxial cylinder system with two gaps for shearing the samples on the inside and on the outside of the rotor. The measuring range of the NV sensor is given in a log-log graph of viscosity versus shear rate, where the shear rate was selected to be 2000 s⁻¹ for all samples as it covers viscosities between 1 – 20 mPa·s.

All viscosity results measured by the HAAKE ROTOVISCO were corrected by a factor of 1.15. This was undertaken based on an average of several measurements at different temperatures of a CANNON standard solution. The viscosities of these results were taken from 4 – 6 test runs to ensure consistency and repeatability. The differences between the actual theoretical viscosity measures of the standard versus the experimental result proved that correction was necessary (results listed in Table B.1).

Table B.1. Viscosity Measure of CANNON Standard at Varying Temperatures

Temperature (°C)	V _{Experimental} (mPa·s)	V _{Actual} (mPa·s)	V _{Experimental} /V _{Actual}
20	10.896	9.640	1.130
25	8.845	8.011	1.104
37.8	6.104	5.304	1.151
40	5.741	4.972	1.155
50	4.511	3.805	1.186
80	2.385	2.019	1.181
Average			1.151
Standard Deviation			0.0281
Standard Error			0.0126

The procedure for testing the viscosity of a given sample is as follows:

- the correct sensor is selected based on the expected viscosity range of the liquid sample (in this case, the NV sensor).
- it is essential to ensure the sensor is clean, dry and free of any residue as this can affect results. Therefore, between each given test run, the sensor was thoroughly washed with a detergent, rinsed with distilled water, air dried and rinsed with acetone.
- the rotor of the sensor is connected to the VT500 (part of viscometer attached to the computer for digital data recording).
- the temperature bath is turned on and set to measure the viscosity at the a specified temperature in °C.
- the sample is measured in a graduated cylinder at 12 mL and poured into the outer cup of the NV sensor.
- the outer cup is attached to the rotor and securely fit.
- the computer is turned on and details are entered to record the results, such as, sensor type, shear rate, time and temperature. The time for each run was 3 minutes.
- after the completion of each run, the file would be saved on a floppy disk and the data analysed to calculate the experimental viscosity values. The shear stress is divided by the shear rate to compute the average viscosity result.

The viscosity reported in the results is an average of at least three independent trials and the standard error is calculated by taking the standard deviation and dividing by the square root of $n - 1$, where n is the number of trials.

Appendix C: Vehicle Test Cycle and Emission Collection Information

The emissions test cycle is transient and followed the EPA 75 standard for all vehicles. The final result is obtained by a constant volume sampling (CVS) technique via electronic integration of a fast response, continuous emission measurement system. The test cycle is a three phase transient cycle test with a cold start, with phases specified as:

Phase 1: Crank (10 sec max) + 505 sec

Phase 2: 869 seconds

Hot Soak: 600 seconds \pm 60 seconds

Phase 3: 505 seconds

The test distance covered is 11.09 miles (17.84 km) and test duration is 41 minutes. The CVS system fills and analyzes three pairs of bags. Upon completion of Phase 2, the computer lights the pendant stop button, indicating for the driver to turn off the engine and press stop. The bag sampling and continuous sampling carries on for 5 seconds after the stop button is pressed. Nine minutes into the soak, the computer lights the pendant start button and a buzzer goes off to signal the end of the soak. The driver has two minutes to start the test vehicle and proceed with Phase 3. About ten to eleven minutes into the soak, if the driver has not begun with Phase 3 the buzzer will sound again.

The mechanical specifications of the dynamometer are: (1) 150 HP Absorber (2) 102" overall roll length, four 20" diameter x 36" length rolls with 30" spacing opening between rolls and (3) 1500-8000 lbs inertia range. The detailed specifications of the various components of the HORIBA VETS SYSTEM are provided by BC AirCare® and listed as follows:

A. Test Computer: AT compatible personal computer, Hard disk, 1.2 MB 5 1/4" floppy disk, Printer, VGA monitor, LAN interface to driver's aid, Process input/output to control and/or collect data from the CVS, bench, weather station, and up to 6 auxiliary analog signals.

B. Driver's Aid: AT compatible personal computer, Hard disk, 1.2 MB 5 1/4" floppy disk, VGA monitor, LAN interface to the test computer, Driver's pendant with START, STOP, HOLD, CONTINUE buttons and a buzzer, Process input/output to control and/or collect data from the pendant, dynamometer rolls, (frequency), cooling fan, and chart recorder.

C. Other Hardware: Power supplies, Cabinet for computer and process I/O, Cables

D. Software for Emissions Testing: EPA, ECE and Japanese emission test schedules, User-defined test schedules and shift points, Bag and continuous dilute analysis capabilities, Analyzer, CVS and signal calibration programs, NO_x efficiency check, propane injection check, analyzer zero/span

E. 350 SCFM Turbocompressor: with 7.5 horsepower motor, 230/460V AC, 3 ph, 60 Hz, floor mount

F. Remote control panel : mounted in analyzer bench bay with readout of flows and elapsed time

The CVS Ductwork from tailpipe to sample, sampler to blower, and blower to facility consisted of:

- SAO Calibration Venturi with Manometers, 40-400 SCFM SAO Venturi @ 10" WC, aluminum, 4" outlet.
- Traceable to NBS; accuracy: $\pm 2\%$ of reading, Meriam model 40HE35WM inclined manometer, dual range, 0-10" WC.
- Graduations 0.01"; supplied with green fluid (SG = 1.0), Meriam model 30EB25 vertical manometer, dual range, 0-40" WC.
- Graduations 0.1", supplied with green fluid (SG=1.0), Horiba CFO-201B Critical Flow Orifice. The CFO-201B is a CVS calibration instrument, calibrated with propane gas for 325 SCFM nominal CVS flow rate, 80 ppm at 40 psig.
- Hartzel Engine Cooling Fan: Hartzel fan #23-24 NDD, 5245 CFM. Used for general air circulation during dynamometer operation.

Because emissions are sensitive to environmental conditions, the ambient air temperature, pressure and relative humidity were carefully controlled and kept at the same levels during each test. The PC-VETS took analog signals from the weather station instruments, such as:

- Barometric Pressure: Setra Model 270 pressure transducer with analog output for computer and Newport Model 2002A digital display.
- Dewpoint Temperature: General Eastern Model Hygro M1 Hygrometer with digital display and analog output for the computer
- Ambient Temperature: Omega RTD probe with analog output and digital display.



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-3677	B100 Biodiesel; 28-Sep-2005				
		ASTM D664	Acid Number, mg KOH/g	0.01	
		ASTM D613	Cetane Number	57.5	
		ASTM D5773	Cloud Point, °C	0.6	
		ASTM D130	Copper Corrosion	1a	
		Modified EN14103	Ester Profile		1,2
		ASTM D6584	Test Method for Determination of Free and Total Glycerine in B-100 Biodiesel Methyl Ester by Gas Chromatography		
			Free Glycerin, mass %	<0.001	
			Total Glycerin, mass %	0.004	
			Monoglycerides, mass%	0.007	
			Diglycerides, mass %	0.004	
			Triglycerides, mass %	0.011	
		EN 14111	Fat and Oil Derivatives-Fatty Acid Methyl Esters(FAME)-Determination of Iodine Value, g/100g	129	3,4
		ASTM D4530	Carbon Residue, Mass %	0.001	5
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	0.4	6
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	22.8	7



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-3677	B100 Biodiesel; 28-Sep-2005	ASTM D5453	Total Sulfur by Ultraviolet Fluorescence, ppm (mg/kg)	8	
		GL-ARC	Quantitation of Tocopherol Isomers in Biodiesel, ppm(wt)		
			Alpha	<50	
			Gamma	<50	
			Delta	<50	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	3.949	



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-3678	D100 Diesel Fuel; 28-Sep-2005	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.3	8
		ASTM D664	Acid Number, mg KOH/g	0.00	
		ASTM D613	Cetane Number	44.6	
		ASTM D5773	Cloud Point, °C	-10.2	
		ASTM D130	Copper Corrosion	1a	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	0.6	7
		CAN/CGSB-3.0 No. 16.0	Sulfur, Mass%	0.040	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	2.834	



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-3679	B20 Biodiesel; 28-Sep-2005				
		ASTM D664	Acid Number, mg KOH/g	0.01	
		ASTM D613	Cetane Number	47.9	
		ASTM D5773	Cloud Point, °C	-9.5	
		ASTM D130	Copper Corrosion	1a	
		ASTM D4530	Carbon Residue, Mass %	0.001	5
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	7.8	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	3.8	7
		CAN/CGSB-3.0 No. 16.0	Sulfur, Mass%	0.032	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.125	

Remarks and Notes

- 1 Please find attached the chromatogram and analytical results.
- 2 This test was repeated in duplicate as a error was made in the original test data.
- 3 Oleic acid methyl ester has an iodine value of approximately 86 g/100g, and it was run as a check sample. The iodine value obtained for oleic acid methyl ester was 85g/100g.
- 4 The iodine value obtained is greater than the 120 g/100g maximum requirement of EN 14214 specification "Requirements and Test Methods for Automotive Fuels - Fatty Acid Methyl Esters (FAME) for Diesel Engines." The analysis was performed in duplicate and the result reported is an average of the two determinations.
- 5 ASTM D6751 Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels states that for the carbon residue (ASTM D4530) a 100% sample is used to replace the 10% residual sample, with the calculation executed as if it were the 10% residual. Parameter E (final weight of the flask charge/original weight of the flask charge) in 8.1.2 of



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
	ASTM D4530-93 is a constant 20/200. The carbon residue was performed on the original sample and the result obtained was calculated as if it were performed on the 10% residual.				
6	The oxidation stability result is below the acceptable limit of 6.0 hours set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."				
7	The analysis was performed in duplicate and the result reported is an average of the two determinations.				
8	The Accelerated Stability measures a fuel's tendency to form gums and sediments under accelerated oxidizing conditions. Excessive levels of these gums and sediments can cause filter plugging, combustion chamber deposit formation, and gumming or lacquering of injection system components with resultant sticking and wear. The Accelerated Stability is not applicable to fuels containing residual oil, or any significant component derived from a nonpetroleum source. The correlation of accelerated stability to operability and fuel suitability is tenuous. An industry limit for maximum accelerated stability has been proposed at 1.5 mg/100mL.				

Please find attached the biodiesel ester profile and chromatogram for laboratory sample GO-2005-3677.

97

Signature: _____

Business Unit Manager

Phone: (780) 450-5108 email: wispinski@arc.ab.ca

Date: _____

Biodiesel Ester Profile

Sample

GO-2005-3877

Compound name	Carbon #	% (mass of ester/ total sample mass)
methyl caproate	8:0	<0.01
methyl caprylate	8:0	<0.01
methyl capric acid	10:0	<0.01
methyl undecanoate	11:0	89.01
methyl laurate	12:0	<0.01
Unknown		
methyl tridecanoate	13:0	<0.01
methyl myristate	14:0	0.06
	14:1 cis	<0.01
Unknown		
methyl pentadecanoate	15:0	0.01
Unknown		
Unknown		<0.01
	15:1 cis	<0.01
methyl palmitate	16:0	0.06
methyl palmitoleate	16:1	0.11
Unknown		0.01
Internal std		
	17:1 cis	<0.01
Unknown		0.04
methyl stearate	18:0	4.30
methyl oleate	18:1 cis trans 9	25.03
methyl linoleate	18:2 cis trans 9,12	51.47
methyl linolenate	18:3 all cis 9,12,15	0.06
methyl linolenate	18:3 all cis 9,12,15	0.15
methyl linolenate		0.12
Unknown		0.06
Unknown		
Unknown		0.25
methyl arachidate	20:0	0.02
methyl eicosanoate	20:1 ps 4,1	<0.01
Unknown		0.03
methyl aricosanoate	20:2 all cis 11,14	<0.01
	20:3 all cis	<0.01
	20:4 all cis	<0.01
methyl heneicosanoate	21:0	<0.01
	21:5 all cis	0.03
methyl behenate	22:0	0.02
methyl erucate	22:1	<0.01
methyl docosadienoate	22:3	<0.01
	23:0	<0.01
Unknown		0.02
methyl lignocerate	24:0	<0.01
methyl nervonate	24:1 cis 15	<0.01
Total ester content		98.92



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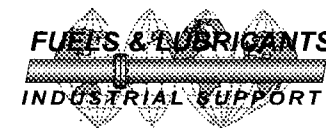
Report GO-2005-4967 to 4978

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-4967	D100_6°C Diesel Fuel; 15-Dec-2005	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.4	1
		ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	42.3	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	9	3
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.051	
GO-2005-4968	D100_40°C Diesel Fuel; 15-Dec-2005	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.4	1
		ASTM D664	Acid Number, mg KOH/g	0.00	2
		ASTM D613	Cetane Number	45.3	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	13	3
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	2.859	



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-4969	D100_X°C Diesel Fuel; 15-Dec-2005	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.3	1
		ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	45.9	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	125	3
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	2.888	
GO-2005-4970	B100_6°C B100 Biodiesel; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.03	2
		ASTM D613	Cetane Number	54.1	
		EN14103 (Modified)	Ester Profile		4
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	0.6	5
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	31	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.957	



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-4971	B100_40°C B100 Biodiesel; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.03	2
		ASTM D613	Cetane Number	54.4	
		EN14103 (Modified)	Ester Profile		4
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	0.6	5
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	51	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.983	
GO-2005-4972	B100_X°C B100 Biodiesel; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.02	2
		ASTM D613	Cetane Number	54.5	
		EN14103 (Modified)	Ester Profile		4
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	0.6	5
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	90	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.929	



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-4973	B20_6°C (Before) Biodiesel Blend; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	47.9	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	4.4	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	11	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.131	
GO-2005-4974	B20_40°C (Before) Biodiesel Blend; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	48.7	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	3.6	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	12	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.010	



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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-4975	B20_X°C (Before) Biodiesel Blend; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	48.8	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	4.9	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	7	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.023	
GO-2005-4976	B20_6°C (After) Biodiesel Blend; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	47.2	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	4.4	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	5	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.169	



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306-2216 Main Mall
Vancouver, BC, V6T 1Z4

Attention: Kruti Patel

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Report GO-2005-4967 to 4978

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-4977	B20_40°C (After) Biodiesel Blend; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	48.2	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	4.4	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	10	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.008	
GO-2005-4978	B20_X°C (After) Biodiesel Blend; 15-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.01	2
		ASTM D613	Cetane Number	48.2	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	4.7	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	8	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	3.034	

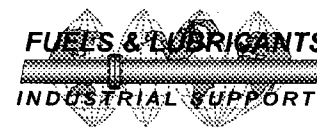
Remarks and Notes

- 1 The Accelerated Stability measures a fuel's tendency to form gums and sediments under accelerated oxidizing conditions. Excessive levels of these gums and sediments can cause filter plugging, combustion chamber deposit formation, and gumming or lacquering of injection system components with resultant sticking and wear. The Accelerated Stability is not applicable to fuels containing residual oil, or any significant component derived from a nonpetroleum source. The correlation of accelerated stability to operability



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Report GO-2005-4967 to 4978

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
			and fuel suitability is tenuous. An industry limit for maximum accelerated stability has been proposed at 1.5 mg/100mL.		
2			The scope of ASTM D664 states that the range of acid numbers included in the precision statement is 0.1 mg/g KOH to 150 mg/g KOH. The value obtained for the sample is outside the scope of the test method therefore the precision statement may not apply.		
3			ASTM D3703 states: "A quantity of sample dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane is contacted with aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide. An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution." The solvent 1,1,2-trichloro-1,2,2-trifluoroethane cannot be imported or sold in Canada, therefore it was replaced with iso-octane.		
4			EN 14103 states that the test method is suitable for FAME which contain methyl esters between C14 and C24. The test methods sums the esters between C14 and C24. The ester profile was obtained by running standards to expand the range to include esters from C4 to C24:1 and calculating the individual ester concentrations. Please find attached a table of the "Biodiesel Ester Profile."		
5			The oxidation stability is below the minimum acceptable limit of 6 hours set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."		

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Signature: _____

Date: _____

Business Unit Manager

Phone: (780) 450-5108 email: wispinski@arc.ab.ca

SAMPLE

GO-2005-4970

Name	Designation	Area Percent
methyl caproate	6:0	<0.01
methyl caprylate	8:0	0.01
Unknown		<0.01
Unknown		<0.01
methyl caprate	10:0	<0.01
methyl undecanoate	11:0	<0.01
Unknown		<0.01
methyl laurate	12:0	<0.01
Unknown		<0.01
Unknown		0.01
methyl tridecanoate	13:0	<0.01
Unknown		<0.01
Unknown		<0.01
methyl myristate	14:0	0.05
Unknown		<0.01
	14:1 cis 4	<0.01
Unknown		<0.01
methyl pentadecanoate	15:0	0.01
Unknown		0.01
Unknown		<0.01
	15:1 cis 10	<0.01
methyl palmitate	16:0	8.89
Unknown		0.01
Unknown		0.09
methyl palmitoleate	16:1	0.01
Unknown		<0.01
Unknown		<0.01
Unknown		0.07
methyl	17:1 cis 10	<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		0.04
methyl stearate	18:0	4.40
methyl oleate	18:1 cis/trans 9	25.25
Unknown		0.08
methyl linoleate	18:2 all cis/trans 9,12	52.00
methyl linolenate	18:3 all cis 9,12,15	0.09
Unknown		0.03
Unknown		0.15
methyl linolenate	18:3 all cis 8,11,14	8.10
Unknown		0.12
Unknown		0.02
Unknown		0.04

Unknown		0.02
methyl arachidate	20:0	<0.01
Unknown		0.23
methyl eicosanoate	20:1 cis 11	<0.01
Unknown		0.04
methyl eicosadienoate	20:2 all cis 11,14	0.03
	20:3 all cis 8,11,14,17	0.01
	20:4 all cis 5,8,11,14	<0.01
methyl heneicosanoate	21:0	<0.01
	20:5 all cis 5,8,11,14,17	0.04
methyl behenate	22:0	0.01
Unknown		<0.01
methyl erucate	22:1	<0.01
methyl docosadienoate	22:3	<0.01
Unknown		<0.01
Unknown		<0.01
	23:0	<0.01
methyl lignocerate	24:0	<0.01
methyl nervonate	24:1 cis 15	<0.01

SAMPLE

GO-2005-4971

Name	Designation	Area Percent
methyl caproate	6:0	<0.01
methyl caprylate	8:0	0.01
Unknown		<0.01
Unknown		<0.01
methyl caprate	10:0	<0.01
Unknown		<0.01
methyl undecanoate	11:0	<0.01
Unknown		<0.01
Unknown		<0.01
methyl laurate	12:0	<0.01
Unknown		<0.01
Unknown		0.01
Unknown		<0.01
methyl tridecanoate	13:0	<0.01
Unknown		<0.01
Unknown		<0.01
methyl myristate	14:0	0.05
Unknown		<0.01
	14:1 cis 4	<0.01
Unknown		<0.01
methyl pentadecanoate	15:0	0.01
Unknown		0.01
Unknown		<0.01
	15:1 cis 10	<0.01
Unknown		<0.01
methyl palmitate	16:0	9.02
Unknown		0.02
Unknown		0.09
methyl palmitoleate	16:1	0.01
Unknown		<0.01
Unknown		<0.01
Unknown		0.07
methyl	17:1 cis 10	<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		0.04
methyl stearate	18:0	4.37
methyl oleate	18:1 cis/trans 9	23.90
Unknown		1.28
Unknown		0.07
methyl linoleate	18:2 all cis/trans 9,12	51.82
Unknown		0.03
methyl linolenate	18:3 all cis 9,12,15	0.05

Unknown		0.01
Unknown		0.13
methyl linolenate	18:3 all cis 8,11,14	8.05
Unknown		0.12
Unknown		0.02
Unknown		0.04
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
methyl arachidate	20:0	0.26
Unknown		0.21
methyl eicosenoate	20:1 cis 11	<0.01
Unknown		<0.01
Unknown		0.04
methyl eicosadienoate	20:2 all cis 11,14	0.03
Unknown		<0.01
	20:3 all cis 8,11,14,17	0.01
	20:4 all cis 5,8,11,14	<0.01
methyl heneicosanoate	21:0	<0.01
Unknown		<0.01
	20:5 all cis 5,8,11,14,17	0.04
methyl behenate	22:0	0.01
Unknown		<0.01
methyl erucate	22:1	<0.01
methyl docosadienoate	22:3	<0.01
Unknown		<0.01
Unknown		0.02
	23:0	<0.01
methyl lignocerate	24:0	<0.01
methyl nervonate	24:1 cis 15	<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01

SAMPLE

GO-2005-4972

Name	Designation	Area Percent
methyl caproate	6:0	<0.01
methyl caprylate	8:0	<0.01
methyl caprate	10:0	<0.01
methyl undecanoate	11:0	<0.01
Unknown		<0.01
methyl laurate	12:0	<0.01
Unknown		<0.01
Unknown		0.01
methyl tridecanoate	13:0	<0.01
Unknown		<0.01
Unknown		<0.01
methyl myristate	14:0	0.05
Unknown		<0.01
	14:1 cis 4	<0.01
Unknown		<0.01
methyl pentadecanoate	15:0	0.01
Unknown		0.01
Unknown		<0.01
	15:1 cis 10	<0.01
methyl palmitate	16:0	9.01
Unknown		0.10
methyl palmitoleate	16:1	0.01
Unknown		<0.01
Unknown		0.07
methyl	17:1 cis 10	<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		0.04
methyl stearate	18:0	4.38
methyl oleate	18:1 cis/trans 9	23.93
Unknown		1.26
Unknown		0.06
methyl linoleate	18:2 all cis/trans 9,12	51.83
Unknown		0.02
methyl linolenate	18:3 all cis 9,12,15	0.04
Unknown		0.01
Unknown		0.14
methyl linolenate	18:3 all cis 8,11,14	8.07
Unknown		0.11
Unknown		0.02
Unknown		0.04
Unknown		0.01
Unknown		<0.01

methyl arachidate	20:0	0.26
Unknown		0.21
methyl eicosenoate	20:1 cis 11	<0.01
Unknown		0.04
methyl eicosadienoate	20:2 all cis 11,14	0.03
	20:3 all cis 8,11,14,17	0.01
	20:4 all cis 5,8,11,14	<0.01
methyl heneicosanoate	21:0	<0.01
Unknown		<0.01
Unknown		<0.01
	20:5 all cis 5,8,11,14,17	<0.01
Unknown		0.04
methyl behenate	22:0	0.01
Unknown		0.01
methyl erucate	22:1	<0.01
methyl docosadienoate	22:3	<0.01
Unknown		<0.01
	23:0	<0.01
methyl lignocerate	24:0	<0.01
methyl nervonate	24:1 cis 15	<0.01



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306-2216 Main Mall
Vancouver, BC, V6T 1Z4

Attention: Kruti Patel

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Report GO-2006-2744 to 2749

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-2744	B100-6°C-180days B100 Biodiesel; 28-Mar-2006	ASTM D664	Acid Number, mg KOH/g	0.02	
		ASTM D613	Cetane Number	51.3	
		ASTM D5773	Cloud Point, °C	0.8	
		EN 14103	Determination of Ester and Linolenic Acid Methyl Ester Content in Biodiesel		1
			Ester Content, % (m/m)	99.5	
			Linolenic Acid Methyl Ester, % (m/m)	8.0	
			Polyunsaturated (>= 4 double bonds) Methyl Ester % (m/m)	<0.5	
		EN 14111	Iodine Value, gr iodine/100gr	152	2
		EN 14112	Oxidation Stability, 110°C, hours	0.1	3
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	23	
GO-2006-2744	B100 Biodiesel; 28-Mar-2006	ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	3.948	

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Report GO-2006-2744 to 2749

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-2745	B100-40°C-180days B100 Biodiesel; 28-Mar-2006	ASTM D664	Acid Number, mg KOH/g	0.03	
		ASTM D613	Cetane Number	51.8	
		ASTM D5773	Cloud Point, °C	0.3	
		EN 14103	Determination of Ester and Linolenic Acid Methyl Ester Content in Biodiesel		1
			Ester Content, % (m/m)	>99.5	
			Linolenic Acid Methyl Ester, % (m/m)	8.0	
			Polyunsaturated (>= 4 double bonds) Methyl Ester %(m/m)	<0.5	
		EN 14111	Iodine Value, gr iodine/100gr	144	2
		EN 14112	Oxidation Stability, 110°C, hours	0.9	3
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	23	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	3.948	



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Report GO-2006-2744 to 2749

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-2746	B100-X°C-180days B100 Biodiesel; 28-Mar-2006	ASTM D664	Acid Number, mg KOH/g	0.02	
		ASTM D613	Cetane Number	51.9	
		ASTM D5773	Cloud Point, °C	0.5	
		EN 14103	Determination of Ester and Linolenic Acid Methyl Ester Content in Biodiesel		1
			Ester Content, % (m/m)	96.7	
			Linolenic Acid Methyl Ester, % (m/m)	8.6	
			Polyunsaturated (>= 4 double bonds) Methyl Ester %(m/m)	<0.5	
		EN 14111	Iodine Value, gr iodine/100gr	132	2
		EN 14112	Oxidation Stability, 110°C, hours	0.8	3
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	20	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	3.950	



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Report GO-2006-2744 to 2749

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-2747	D100-6°C-180days Diesel Fuel; 28-Mar-2006	ASTM D664	Acid Number, mg KOH/g	0.01	
		ASTM D613	Cetane Number	41.6	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	3.032	
GO-2006-2748	D100-40°C-180days Diesel Fuel; 28-Mar-2006	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.0	4
		ASTM D664	Acid Number, mg KOH/g	0.01	
		ASTM D613	Cetane Number	44.6	
		ASTM D5773	Cloud Point, °C	-10.1	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	0	5
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
GO-2006-2749	D100-X°C-180days B100 Biodiesel; 28-Mar-2006		Clear, at 40 °C	2.846	
		ASTM D664	Acid Number, mg KOH/g	0.00	
		ASTM D613	Cetane Number	45.2	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	2.854	



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Report GO-2006-2744 to 2749

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
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Remarks and Notes

- 1 EN 14214 states that the Polyunsaturated (≥ 4 double bonds) Methyl Ester content official method is under development and unavailable at this time. The value reported is an estimate from the ester content analysis.
- 2 The iodine value obtained is greater than the 120 g/100g maximum requirement of EN 14214 specification "Requirements and Test Methods for Automotive Fuels - Fatty Acid Methyl Esters (FAME) for Diesel Engines."
- 3 The oxidation stability is below the minimum acceptable limit of 6 hours set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines- Requirements and Test Methods."
- 4 The Accelerated Stability measures a fuel's tendency to form gums and sediments under accelerated oxidizing conditions. Excessive levels of these gums and sediments can cause filter plugging, combustion chamber deposit formation, and gumming or lacquering of injection system components with resultant sticking and wear. The Accelerated Stability is not applicable to fuels containing residual oil, or any significant component derived from a nonpetroleum source. The correlation of accelerated stability to operability and fuel suitability is tenuous. An industry limit for maximum accelerated stability has been proposed at 1.5 mg/100mL.
- 5 ASTM D3703 states: "A quantity of sample dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane is contacted with aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide. An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution." The solvent 1,1,2-trichloro-1,2,2-trifluoroethane cannot be imported or sold in Canada, therefore it was replaced with iso-octane.

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Signature: _____

Business Unit Manager

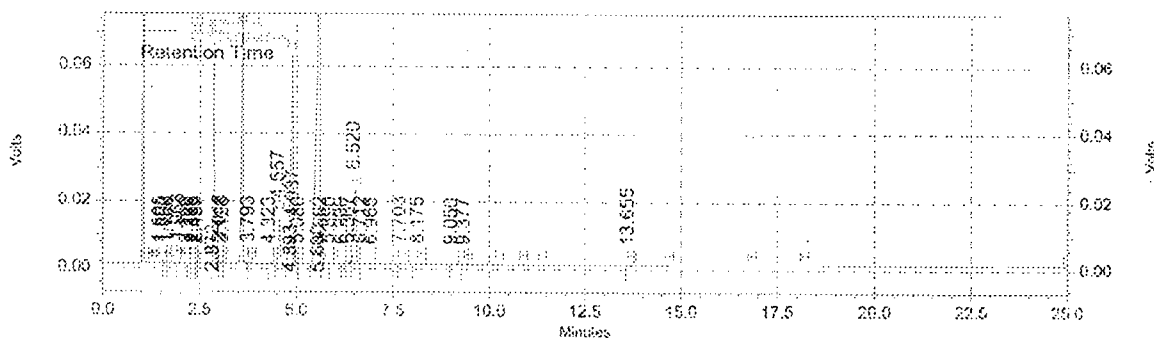
Phone: (780) 450-5108 email: wispinski@arc.ab.ca

Date: _____

Area % Report

Sample Name: GO-2006-2744

Data File: CAEZChrom Elite\Public\ester3\2744_1.ezc
 Method: CAEZChrom Elite\Projects\Default\Methods\en14103.met
 Acquired: 05/05/2006 12:12:45 PM
 Printed: 09/05/2006 11:43:50 AM
 Description: (Data Description)



Detector 1 Results

Name	Retention Time	Area	Area Percent
C8:0			
C9:0			
C10:0			
C11:0			
C12:0	1.505	116	0.010
	1.592	161	0.014
C13:0	1.700	77	0.007
C14:0	1.968	904	0.079
C14:1	2.200	101	0.009
C15:0	2.338	204	0.018
	2.425	190	0.017
	2.457	106	0.009
C15:1			
C16:0	2.872	118191	10.305
C16:1	3.048	1360	0.119
	3.128	144	0.013
ISTD C17:0			
C17:1	3.793	724	0.063
	4.323	481	0.042
C18:0	4.557	50202	4.377
C18:1	4.893	269979	23.540
	4.937	15553	1.356
	5.080	469	0.041

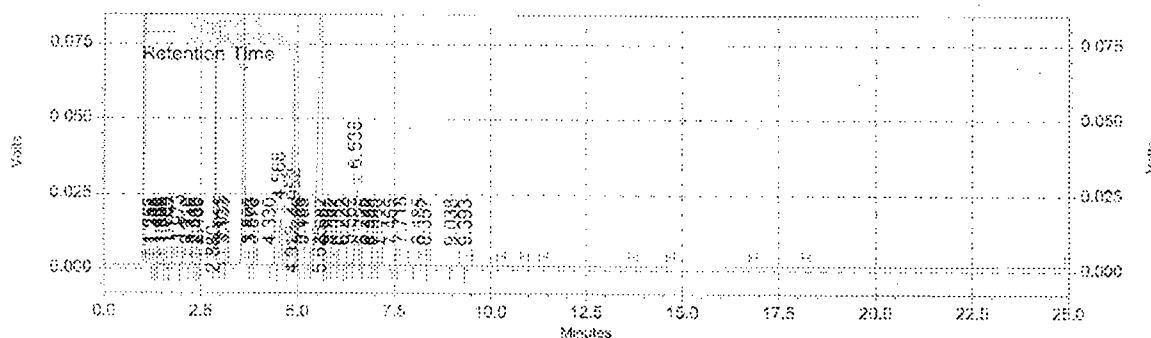
C18:2	5.600	584378	50.953
	5.662	498	0.043
C18:3(6,9,12)	5.890	282	0.025
	6.200	149	0.013
	6.367	1371	0.120
C18:3(9,12,15)	6.520	93519	8.154
	6.712	1210	0.106
	6.965	470	0.041
C20:0	7.703	2856	0.249
C20:1	8.175	2350	0.205
	9.050	324	0.028
C20:2	9.377	309	0.027
C20:3/C21:0			
C20:4			
C20:5			
C22:0	13.655	215	0.019
C22:1			
C22:2			
C23:0			
C24:0			
C34:1			

Totals		1146893	100.000
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Area % Report

Sample Name: GO-2006-2745

Data File: C:\EZChrom Elite\Public\ester3\2745_1.ezc
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 Description: {Data Description}



Detector 1 Results

Name	Retention Time	Area	Area Percent
C8:0			
C9:0			
C10:0	1.253	60	0.004
C11:0	1.345	87	0.006
	1.430	126	0.009
C12:0	1.508	284	0.021
	1.598	270	0.020
C13:0	1.705	89	0.007
C14:0	1.973	1027	0.076
C14:1	2.210	128	0.010
C15:0	2.345	219	0.016
	2.430	221	0.016
C15:1	2.465	145	0.011
C16:0	2.880	138138	10.262
C16:1	3.055	1601	0.119
	3.133	165	0.012
ISTD C17:0			
C17:1	3.803	875	0.065
	3.878	85	0.006
	4.330	567	0.042
C18:0	4.568	58792	4.368
C18:1	4.912	316730	23.530
	4.952	17915	1.331

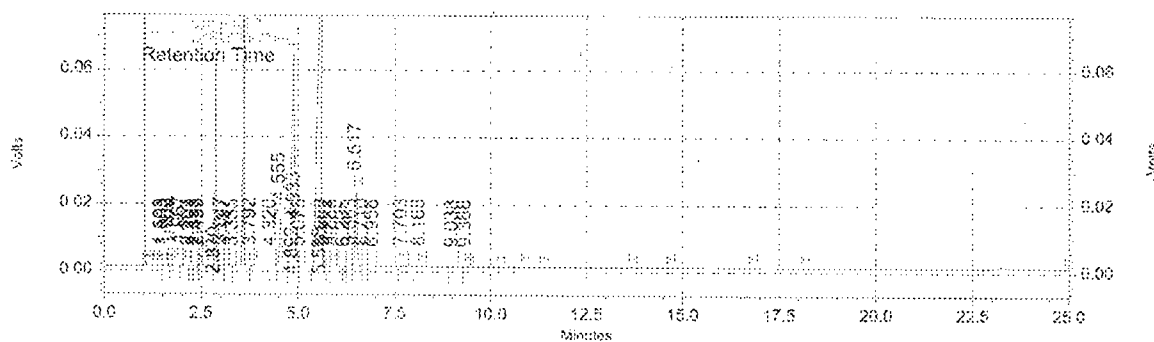
	3.088	878	0.065
	5.183	398	0.030
C18:2	5.625	683826	50.802
	5.687	896	0.067
	5.795	742	0.055
C18:3(6,9,12)	5.902	948	0.070
	6.033	62	0.005
	6.222	172	0.013
	6.382	1711	0.127
C18:3(9,12,15)	6.538	109225	8.114
	6.725	1610	0.120
	6.883	278	0.021
	6.968	619	0.046
	7.080	155	0.012
	7.465	61	0.005
C20:0	7.718	3301	0.245
C20:1	8.185	2817	0.209
	8.357	60	0.004
	9.038	494	0.037
C20:2	9.393	275	0.020
C20:3/C21:0			
C20:4			
C20:5			
C22:0			
C22:1			
C22:2			
C23:0			
C24:0			
C24:1			

Totals		1346052	100.000
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Area % Report

Sample Name: GO-2006-2746

Data File: CAEZChrom Elite/Public/ester3\2746_1.eze
 Method: CAEZChrom Elite/Projects/Default/Methods/Ven14103.met
 Acquired: 05/05/2006 1:07:07 PM
 Printed: 09/05/2006 11:45:06 AM
 Description: {Data Description}



Detector 1 Results

Name	Retention Time	Area	Area Percent
C8:0			
C9:0			
C10:0			
C11:0			
C12:0	1.503	129	0.011
	1.592	200	0.017
C13:0	1.700	56	0.005
C14:0	1.967	891	0.076
C14:1	2.203	151	0.013
C15:0	2.338	216	0.018
	2.423	199	0.017
	2.457	150	0.013
C15:1			
C16:0	2.870	120867	10.318
C16:1	3.047	1370	0.117
	3.127	161	0.014
	3.335	52	0.004
ISTD C17:0			
C17:1	3.792	752	0.064
	4.320	533	0.046
C18:0	4.555	51342	4.383
C18:1	4.892	275687	23.535
	4.933	15831	1.351

	5.075	527	0.045
C18:2	5.598	595844	50.867
	5.662	717	0.061
	5.772	537	0.046
C18:3(6,9,12)	5.885	883	0.075
	6.205	151	0.013
	6.363	1411	0.120
C18:3(9,12,15)	6.517	95043	8.114
	6.710	1229	0.105
	6.958	494	0.042
C20:0	7.703	2857	0.244
C20:1	8.168	2331	0.199
	9.038	444	0.038
C20:2	9.368	315	0.027
C20:3/C21:0			
C20:4			
C20:5			
C22:0			
C22:1			
C22:2			
C23:0			
C24:0			
C24:1			

Totals	1171370	100.000
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Attention: Kruti Patel

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Report GO-2005-5105 to 5107

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-5105	B100 KP-WVO-B100 B100 Biodiesel; 29-Dec-2005	ASTM D664	Acid Number, mg KOH/g	0.55	
		ASTM D5773	Cloud Point, °C	5.7	
		EN14103 (Modified)	Ester Profile		1
		EN 14111	Fat and Oil Derivatives-Fatty Acid Methyl Esters(FAME)-Determination of Iodine Value, g/100g	90	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	2.5	2
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	64	3
		GL-ARC	Quantitation of Tocopherol Isomers in Biodiesel, ppm(wt)		
			Alpha	<50	
			Gamma	<50	
			Delta	<50	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	4.889	
		ASTM D2709	Water and Sediment in Middle Distillate Fuels by Centrifuge, Volume %	0	



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Report GO-2005-5105 to 5107

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-5106	KPD100-Dec 05 Diesel Fuel; 29-Dec-2005	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.0	4
		ASTM D664	Acid Number, mg KOH/g	0.01	5
		ASTM D613	Cetane Number	43.7	
		ASTM D5773	Cloud Point, °C	-24.2	
		ASTM D130	Copper Corrosion	1a	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	12	3
		ASTM D5453	Total Sulfur by Ultraviolet Fluorescence, ppm (mg/kg)	288	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.508	



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Report GO-2005-5105 to 5107

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2005-5107	KP-WVO-B20 B100 Biodiesel; 29-Dec-2005				
		ASTM D664	Acid Number, mg KOH/g	0.13	
		ASTM D613	Cetane Number	47.8	
		ASTM D5773	Cloud Point, °C	-10.4	
		ASTM D130	Copper Corrosion	1a	
		ASTM D4530 & D86	Carbon Residue, 10% Bottoms, Mass %	0.000	
		EN 14112	Determination of Oxidation Stability, Fatty Acid Methyl Esters (FAME), hours	12.9	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	46	3
		ASTM D5453	Total Sulfur by Ultraviolet Fluorescence, ppm (mg/kg)	230	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.870	

Remarks and Notes

- 1 EN 14103 states that the test method is suitable for FAME which contain methyl esters between C14 and C24. The test methods sums the esters between C14 and C24. The ester profile was obtained by running standards to expand the range to include esters from C4 to C24:1 and calculating the individual ester concentrations. Please find attached a table of the "Biodiesel Ester Profile."
- 2 The oxidation stability is below the minimum acceptable limit of 6 hours set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."
- 3 ASTM D3703 states: "A quantity of sample dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane is contacted with aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide. An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution." The solvent 1,1,2-trichloro-1,2,2-trifluoroethane cannot be imported or sold in Canada, therefore it was replaced with iso-octane.

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Report GO-2005-5105 to 5107

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
4	The Accelerated Stability measures a fuel's tendency to form gums and sediments under accelerated oxidizing conditions. Excessive levels of these gums and sediments can cause filter plugging, combustion chamber deposit formation, and gumming or lacquering of injection system components with resultant sticking and wear. The Accelerated Stability is not applicable to fuels containing residual oil, or any significant component derived from a nonpetroleum source. The correlation of accelerated stability to operability and fuel suitability is tenuous. An industry limit for maximum accelerated stability has been proposed at 1.5 mg/100mL.				
5	The scope of ASTM D664 states that the range of acid numbers included in the precision statement is 0.1 mg/g KOH to 150 mg/g KOH. The value obtained for the sample is outside the scope of the test method therefore the precision statement may not apply.				

Signature: _____

Business Unit Manager

Phone: (780) 450-5108 email: wispinski@arc.ab.ca

Date: _____

SAMPLE

GO-2005-5105

Name	Designation	Area Percent
methyl caproate	6:0	<0.01
Unknown		<0.01
methyl caprylate	8:0	0.02
Unknown		<0.01
Unknown		<0.01
methyl caprate	10:0	0.01
Unknown		<0.01
methyl undecanoate	11:0	<0.01
Unknown		<0.01
methyl laurate	12:0	0.04
Unknown		<0.01
Unknown		<0.01
methyl tridecanoate	13:0	<0.01
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
methyl myristate	14:0	0.46
Unknown		<0.01
Unknown		<0.01
Unknown		0.05
	14:1 cis 4	0.01
Unknown		0.02
Unknown		<0.01
methyl pentadecanoate	15:0	0.06
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
	15:1 cis 10	0.02
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
methyl palmitate	16:0	12.10
Unknown		1.17
methyl palmitoleate	16:1	0.03
Unknown		0.05
Unknown		0.10
Unknown		0.20
methyl	17:0 cis 10	0.03
Unknown		0.03
Unknown		<0.01
Unknown		<0.01
Unknown		<0.01
methyl stearate	18:0	2.91

methyl oleate	18:1 cis/trans 9	45.50
Unknown		1.00
Unknown		0.33
Unknown		0.12
Unknown		0.59
methyl linoleate	18:2 all cis/trans 9,12	15.31
Unknown		0.78
Unknown		0.07
Unknown		0.06
methyl linolenate	18:3 all cis 9,12,15	0.01
Unknown		0.08
Unknown		0.36
Unknown		0.03
methyl linolenate	18:3 all cis 8,11,14	0.27
Unknown		0.13
Unknown		0.04
Unknown		<0.01
Unknown		0.02
methyl arachidate	20:0	0.55
Unknown		0.13
Unknown		0.95
methyl eicosanoate	20:1 cis 11	0.05
Unknown		0.03
Unknown		<0.01
Unknown		0.02
Unknown		0.17
methyl eicosatrienoate	20:3 all cis 11,14	0.01
Unknown		<0.01
Unknown		<0.01
Unknown		0.03
	20:3 all cis 8,11,14,17	0.01
Unknown		0.07
	20:4 all cis 5,8,11,14	0.03
methyl heneicosanoate	21:0	<0.01
Unknown		0.03
	20:5 all cis 5,8,11,14,17	0.36
methyl behenate	22:0	0.02
Unknown		0.08
methyl erucate	22:1	<0.01
Unknown		0.03
methyl docosatrienoate	22:3	0.06
	23:0	0.04
Unknown		0.03
Unknown		0.17
Unknown		0.15
methyl lignocerate	24:0	0.04

methy nenonate	24:1 cis 15	0.13
Unknown		0.02
Unknown		0.06
Unknown		0.10
Unknown		0.04



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Vancouver, BC, V6T 1Z4

Attention: Kruti Patel

Page 1 of 4

Report GO-2006-4240 to 4243

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-4240	B100, 40°C, WVO Study B100 Biodiesel; 06-Jul-2006	ASTM D664	Acid Number, mg KOH/g	0.66	1
		ASTM D613	Cetane Number	55.8	
		ASTM D2500	Cloud Point, °C	3	
		EN 14103	Determination of Ester and Linolenic Acid Methyl Ester Content in Biodiesel		2,3
			Ester Content, % (m/m)	93.5	
			Linolenic Acid Methyl Ester, % (m/m)	4.5	
			Polyunsaturated (>= 4 double bonds) Methyl Ester %(m/m)	<0.5	
		EN 14111	Iodine Value, gr iodine/100gr	96	4
		EN 14112	Oxidation Stability, 110°C, hours	2.9	5
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	7	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt)		
			Clear, at 40 °C	4.878	



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Report GO-2006-4240 to 4243

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-4241	D100, 180 days, WVO Study Diesel Fuel; 06-Jul-2006	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.2	6
		ASTM D664	Acid Number, mg KOH/g	0.01	
		ASTM D613	Cetane Number	43.6	
		ASTM D5773	Cloud Point, °C	-22.6	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	14	7
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.521	
GO-2006-4242	B20, Before Mix, WVO Study Biodiesel Blend; 06-Jul-2006	ASTM D664	Acid Number, mg KOH/g	0.14	
		ASTM D613	Cetane Number	46.1	
		ASTM D5773	Cloud Point, °C	-16.7	
		EN 14112	Oxidation Stability, 110°C, hours	16.8	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	1	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.896	



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Report GO-2006-4240 to 4243

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-4243	B20, After Mix, 180 days, WVO Study Biodiesel Blend; 06-Jul-2006				
		ASTM D664	Acid Number, mg KOH/g	0.14	
		ASTM D613	Cetane Number	45.4	
		ASTM D5773	Cloud Point, °C	-17.0	
		EN 14112	Oxidation Stability, 110°C, hours	14.4	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	1	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.902	

Remarks and Notes

- 1 ASTM D6751 "Standard Specification for Biodiesel Fuel (B 100) Blend Stock for Distillate Fuels" states that the maximum acid number shall be 0.50 mg KOH/g.
- 2 EN 14214 states that the Polyunsaturated (≥ 4 double bonds) Methyl Ester content official method is under development and unavailable at this time. The value reported is an estimate from the ester content analysis.
- 3 The ester content is below the minimum acceptable limit of 96.5 mass % set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."
- 4 The iodine value obtained is greater than the 120 g/100g maximum requirement of EN 14214 specification "Requirements and Test Methods for Automotive Fuels - Fatty Acid Methyl Esters (FAME) for Diesel Engines." The analysis was performed in duplicate and the result reported is an average of the two determinations.
- 5 The oxidation stability is below the minimum acceptable limit of 6 hours set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."
- 6 The Accelerated Stability measures a fuel's tendency to form gums and sediments under accelerated oxidizing conditions. Excessive levels of these gums and sediments can cause filter plugging, combustion chamber deposit formation, and gumming or lacquering of injection system components with resultant sticking and wear. The Accelerated Stability is not applicable to fuels containing residual oil, or any significant component derived from a nonpetroleum source. The correlation of accelerated stability to operability



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Report GO-2006-4240 to 4243

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
			and fuel suitability is tenuous. An industry limit for maximum accelerated stability has been proposed at 1.5 mg/100mL.		
7			ASTM D3703 states: "A quantity of sample dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane is contacted with aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide. An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution." The solvent 1,1,2-trichloro-1,2,2-trifluoroethane cannot be imported or sold in Canada, therefore it was replaced with iso-octane.		

133

Signature: _____

Date: _____

Business Unit Manager

Phone: (780) 450-5108 email: wispinski@arc.ab.ca

Area % Report

Sample Name: GO-2006-4240

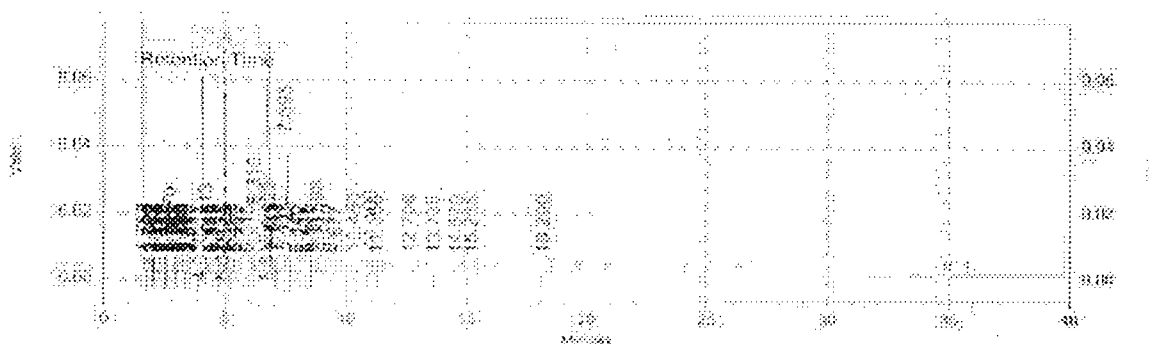
Data File: C:\EZChem\Elite\Projects\Default\Methoden\14162a.m31

Method: C:\EZChem\Elite\Projects\Default\Methoden\14162a.m31

Acquired: 27/07/2006 5:58:20 PM

Printed: 31/07/2006 11:02:35 AM

Description: (Data Description)



Detector 1 Results:

Name	Retention Time	Area	Area Percent
C8.0			
C9.0	1.008	506	0.037
C10.0			
C11.0	1.935	429	0.031
	2.007	52	0.004
	2.053	32	0.004
C12.0	2.152	52	0.004
	2.255	850	0.064
C13.0	2.377	202	0.015
	2.517	79	0.006
	2.570	103	0.007
	2.682	113	0.008
	2.760	61	0.004
C14.0	2.870	8144	0.591
	2.902	80	0.006
C15.0	3.013	111	0.008
	3.067	1214	0.088
	3.186	182	0.0128
C15.0	3.360	1126	0.082
	3.478	121	0.009
	3.527	135	0.010
C15.0	3.613	198	0.008
	3.680	242	0.018
C16.0	4.000	111938	10.306
	4.313	16971	1.233
C16.0	4.418	444	0.032

	4.485	513	0.037
	4.448	235	0.016
	4.018	939	0.069
	4.000	331	0.025
ISTD C17.0			
	5.173	68	0.005
	5.292	2363	0.186
C17.1	5.439	239	0.033
	5.567	278	0.020
	6.012	100	0.008
	6.510	20304	0.105
C18.0			
	6.812	370505	0.124
C18.1	6.928	19458	0.027
	7.018	3717	0.020
	7.342	1288	0.010
	7.647	6119	0.037
	7.695	100788	0.143
	7.743	9283	0.061
C18.2	8.040	303	0.010
	8.140	545	0.012
C18.3(6.9,1.0)	8.473	208	0.021
	8.595	445	0.012
	8.713	3158	0.029
C18.3(9.12,15)	8.998	36919	0.061
	9.178	2109	0.020
	9.390	1439	0.010
	9.677	387	0.008
	10.440	3326	0.014
C20.0			
	11.100	11690	0.049
	11.388	473	0.013
C20.1			
	12.208	1606	0.020
C20.2			
	13.718	460	0.033
C20.3,C21.0	14.670	756	0.059
C20.4			
	15.288	268	0.010
C20.5			
	16.290	3100	0.023
C22.0			
C22.1			
C22.2			
C23.0			
C24.0			
C24.1			
Totals			
		877347	100.000



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Attention: Kruti Patel

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Report GO-2006-5642 to 5645

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-5642	D100-6°C-WVO Study- 200 days Diesel Fuel; 25-Sep-2006	ASTM D2274	Accelerated Stability (16 hrs.), mg/100 mL	0.1	1
		ASTM D664	Acid Number, mg KOH/g	0.01	
		ASTM D613	Cetane Number	40.3	
		ASTM D5773	Cloud Point, °C	-28.0	
		ASTM D3703 (Modified)	Peroxide Number of Aviation Turbine Fuels	12	2
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.615	
GO-2006-5643	B100-6°C-WVO derived- 200 days B100 Biodiesel; 25-Sep-2006	ASTM D664	Acid Number, mg KOH/g	0.55	3,4
		ASTM D613	Cetane Number	62.2	
		ASTM D5773	Cloud Point, °C	10.6	
		Modified EN14103	Ester Profile		5
		EN 14111	Iodine Value, gr iodine/100gr	81	
		EN 14112	Oxidation Stability, 110°C, hours	2.4	6
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	8	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	4.932	



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Report GO-2006-5642 to 5645

Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
GO-2006-5644	B20- 6°C- Before Mix- 200 days Biodiesel Blend; 31-Mar-2006	ASTM D664	Acid Number, mg KOH/g	0.13	
		ASTM D613	Cetane Number	45.3	
		ASTM D5773	Cloud Point, °C	-17.3	
		EN 14112	Oxidation Stability, 110°C, hours	11.9	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	1	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	2.019	
GO-2006-5645	B20- 6°C- After Mix- 200 days Biodiesel Blend; 31-Mar-2006	ASTM D664	Acid Number, mg KOH/g	0.13	
		ASTM D613	Cetane Number	45.6	
		ASTM D5773	Cloud Point, °C	-7.8	
		EN 14112	Oxidation Stability, 110°C, hours	10.6	
		AOAC Official Method 965.33	Peroxide Value of Oils and Fats	2	
		ASTM D445	Kinematic Viscosity, mm ² /s(cSt) Clear, at 40 °C	1.988	

Remarks and Notes

- 1 The Accelerated Stability measures a fuel's tendency to form gums and sediments under accelerated oxidizing conditions. Excessive levels of these gums and sediments can cause filter plugging, combustion chamber deposit formation, and gumming or lacquering of injection system components with resultant sticking and wear. The Accelerated Stability is not applicable to fuels containing residual oil, or any significant component derived from a nonpetroleum source. The correlation of accelerated stability to operability and fuel suitability is tenuous. An industry limit for maximum accelerated stability has been proposed at 1.5 mg/100mL.



Industrial Support ~ Fuels & Lubricants Group

250 Karl Clark Road, Edmonton, Alberta Canada T6N 1E4

Certified by the Standards Council of Canada as an Accredited Testing Organization complying with the requirements of ISO/IEC 17025 for specific tests registered with the Council



Report of Analysis

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Client: University of British Columbia - Chemical and Bio. Engineering
306-2216 Main Mall
Vancouver, BC, V6T 1Z4

Attention: Kruti Patel

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Lab Sample Number	Client's Reference Sample Type; Date Received	Method	Analysis	Result	Notes
2	ASTM D3703 states: "A quantity of sample dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane is contacted with aqueous potassium iodide solution. The peroxides present are reduced by the potassium iodide. An equivalent amount of iodine is liberated, which is titrated with sodium thiosulfate solution." The solvent 1,1,2-trichloro-1,2,2-trifluoroethane cannot be imported or sold in Canada, therefore it was replaced with iso-octane.				
3	ASTM D6751 "Standard Specification for Biodiesel Fuel (B 100) Blend Stock for Distillate Fuels" states that the maximum acid number shall be 0.50 mg KOH/g.				
4	The acid number is above the maximum acceptable limit of 0.50 mg KOH/g set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."				
5	Please find attached the chromatogram and analytical results.				
6	The oxidation stability is below the minimum acceptable limit of 6 hours set out in Table 1 of EN 14214 "Automotive Fuels-Fatty Acid Methyl Esters (FAME) for Diesel Engines-Requirements and Test Methods."				

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Signature: _____

Date: _____

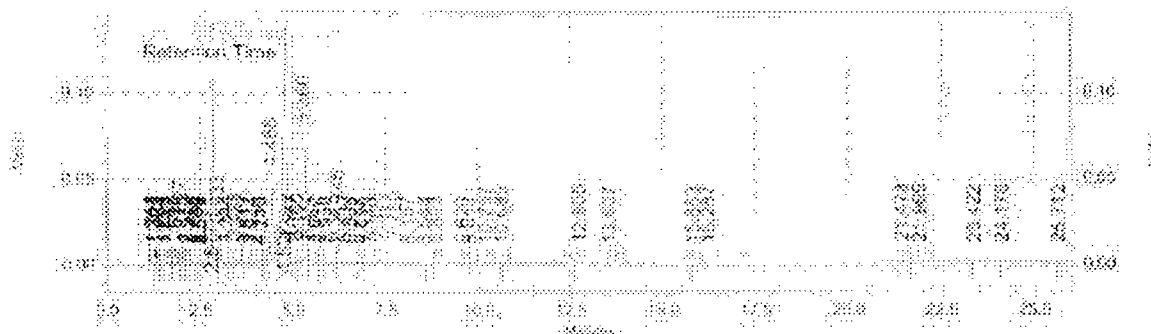
Business Unit Manager

Phone: (780) 450-5108 email: wispinski@arc.ab.ca

Area % Report

Sample Name: GO-2006-5643 no 1STD

Data File: L:\EZChrom Data\800\client\17563\ps.gvs
 Method: C:\EZChrom\EN6\Project\Default Methods\en14101.met
 Acquired: 27/09/2006 12:46:30 PM
 Printed: 27/09/2006 10:52:56 PM
 Description: [Data Description]



Detector 1 Results

Name	Retention Time	Area	Area Percent
C8:0	1.258	813	0.007
C9:0	1.307	72	0.000
C10:0	1.385	683	0.031
	1.423	63	0.003
C11:0	1.463	58	0.002
C12:0	1.598	977	0.072
	1.682	219	0.010
C13:0	1.812	230	0.010
	1.895	116	0.005
C14:0	2.027	1566	0.068
C15:0	2.163	2231	0.102
	2.248	888	0.031
C15:0	2.368	1997	0.091
	2.442	161	0.009
	2.480	281	0.011
C15:1	2.540	281	0.009
	2.592	543	0.023
C16:0	2.877	318482	14.314
C16:1	3.032	30482	1.388
	3.152	1008	0.059
	3.265	3174	0.099
C17:0	3.498	7378	0.336
C17:0	3.717	4149	0.189

	3.812	891	0.031
	3.923	902	0.018
	4.150	87	0.003
	4.219	181	0.008
C18.0	4.468	271011	12.336
C18.1	4.887	1017472	48.313
	4.947	8742	0.309
	5.027	2414	0.110
	5.100	11553	0.426
C18.2	5.360	335850	15.287
	5.450	10095	0.760
	5.607	278	0.044
C18.3(6,9,12)	5.710	1136	0.052
	5.950	1410	0.064
	6.114	6108	0.278
C18.5(9,12,15)	6.245	64274	2.926
	6.432	8788	0.263
	6.588	2521	0.120
	6.777	743	0.036
	6.898	101	0.005
	7.143	404	0.018
C20.0	7.323	13582	0.618
C20.1	7.780	22097	1.006
	8.157	914	0.042
	8.588	134	0.006
C20.2	8.893	3055	0.139
C20.3	9.820	1024	0.047
	9.813	303	0.010
C20.4	10.257	1204	0.058
C21.0	10.683	423	0.019
C20.5			
C22.0	12.603	8243	0.378
C22.1	13.607	1026	0.047
C22.2			
	15.563	227	0.010
	16.287	553	0.025
C23.0			
C24.0	21.478	6136	0.279
C24.1	21.063	2982	0.135
	23.422	249	0.011
	24.178	8029	0.158
	25.712	544	0.025

Totals		2196963	100.000
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