Study of the Rancimat Test Method in Measuring the Oxidation Stability of Biodiesel Ester and Blends

NRCan project # CO414 CETC-327

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Summary

The writing of Canadian standards for biodiesel ester blends by the Canadian General Standards Board (CGSB) raises questions about the possibility of including a specification for the thermo-oxidative stability – or "oxidation stability" – of biodiesel blends. To help answer those questions, OLEOTEK has been mandated by NRCan to develop a project with the following objectives:

1) To test biodiesels made from Canadian sources of oil – namely Canola oil, soybean oil, fish oil, yellow greases, and tallow – using the EN 14112 method in order to compare their oxidation stability with results obtained in USA and Europe;

2) To evaluate the influence of peroxide value (PV), acid value (AV), and feedstock source (fatty acid profile) on the oxidative stability (OSI IP) of different samples;

3) To study the possibility of developing a validated test method adapted from EN 14112 to test biodiesel blends.

Oxidative stability (OSI IP), peroxide value, and acid value were determined for 7 biodiesel samples made from different feedstock, 6 of which were of Canadian origin. Also, OSI IP measuring was attempted on biodiesel blends with petrodiesel and the effect of methanol content on OSI IP was determined.

We reached the conclusion that the EN 14112 (Rancimat) method is not suited for measuring oxidation stability of biodiesel blended with petroleum diesel. Also, no direct correlation was found between OSI IP and either PV or AV. Methanol content was shown to have no significant effect on OSI IP.

Finally, compositional data lead us to conclude that the fatty acid distribution is not the major factor causing the OSI IP differences observed between similar samples of different origin.

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OBJECTIVES

This report presents a selection of results obtained in NRCan's project # CO414 CETC-327 that can be released to the public. Of the different objectives identified in the project, this report will focus on the following:

1) To test biodiesels made from Canadian sources of oil – namely Canola oil, soybean oil, fish oil, yellow greases, and tallow – under the EN 14112 method to compare their oxidation stability with results obtained in USA and Europe;

2) To evaluate the influence of peroxide value (PV), acid value (AV), and feedstock source (fatty acid profile) on oxidative stability (OSI IP) of different samples;

3) To study the possibility to develop a validated test method adapted from EN 14112 to test biodiesel blends.

INTRODUCTION

Context

The writing of Canadian standards for biodiesel ester blends by the Canadian General Standards Board (CGSB)[1] raises questions about the possibility of including a specification for the thermo-oxidative stability – or "oxidation stability" – of biodiesel blends. While most agree that the oxidation stability of biodiesel ester blendstocks and biodiesel ester blends is an important parameter that should be monitored, additional elements are required in order to add an oxidation stability specification to the standards for blends. These are: 1) a testing method for the determination of the oxidation stability of biodiesel ester blends with petrodiesel and 2) data that could be used to determine a limiting specification.

The European Committee for Standardization (CEN) has included an oxidation stability requirement in its EN 14214 standard for pure biodiesel esters (B100) used as automotive fuel[2] and its EN 14213 standard for pure biodiesel esters used as heating fuel. Both standards comprise biodiesel esters to be used as pure fuel or as blending component to fossil fuels. The method retained to determine the oxidation stability is a modified version of the oil stability index (OSI)[3], a method first developed and broadly used to determine the oxidation stability of edible oils. This modified OSI method being used to determine the oxidation stability of fatty acid methyl esters (FAME), also known as the Rancimat method, was published by the CEN under the code EN 14112.[4] The EN 14112 method expresses the oxidation stability of the tested material in terms of an induction period (OSI IP) for the production of volatile organic acids, which are by-products of fatty acid ester oxidative degradation with heat and oxygen. The CEN set a minimum limit of 6 hours for the OSI IP. However, the rationale behind that decision is not clear, and the deliberations that the CEN committee conducted to set this limit for this method are not available.

The European Union had funded a group of nine European industrial and research laboratories, called BIOSTAB,[5] in order to conduct an extensive investigation of different test methods amenable to measuring the thermo-oxidative stability of fatty acid methyl

esters. BIOSTAB reported that the EN 14112 method provides consistent measurements of oxidation stability for fatty esters displaying a range of stability levels. They also have observed that the evolution of a wide variety of quality parameters (acid value, peroxide value, polymer content, and others) was correlated with the variation of the OSI IP during oxidation with the EN 14112 method.[6] The tested biodiesel esters were made from four different kinds of European feedstock: rapeseed, sunflower, tallow, and used frying oil ("yellow grease"). OSI IP obtained for those different sources of undistilled biodiesel esters are listed in Table 1.

Table 1 – OSI IP for undistilled biodiesel produced from different European sources using the EN 14112 method

Feedstock	Tallow	Sunflower oil	Used frying oil (yellow grease)	Rapeseed oil
OSI IP (h)	1.2	2.0	7.1	8.6

Source: BIOSTAB

Also, BIOSTAB conducted a series of engine tests with biodiesel esters of different stability levels[7] (low, medium, high) as well as vehicle road tests[8] with pure biodiesel esters and a 5 % blend of used frying oil esters in order to assess the effects of low stability levels and of "ageing" (fuel degradation) resulting from exposing the fuel to air and high temperature in the vehicle fuel system (the tank-engine loop).

Later, the National Renewable Energy Laboratory (NREL) of the US Department of Energy presented some oxidation stability results with American biodiesel samples (B100) measured by the Southwest Research Institute (SwRI).[9] They tested the EN 14112 and ASTM D 2274 methods with 27 samples obtained from blenders. While NREL did not explicitly disclose the feedstock of the 27 samples that were tested, biodiesels produced in the USA generally are made from soybean oil, tallow, and yellow greases. The OSI IP obtained for those biodiesels are presented in Figure 1. NREL concluded that "Considerable work remains to be done in order to determine an appropriate test and limit for biodiesel oxidation stability".

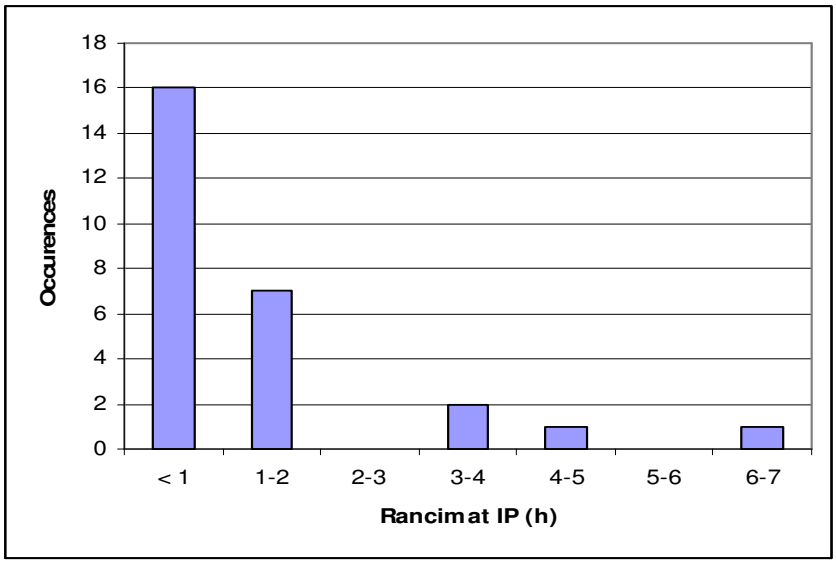

Figure 1 – Distribution of OSI IP for biodiesel obtained from different American sources in NREL's study

NREL is now involved in an important project exploring the validity of using different oxidation stability testing methods (OSI, D525, D2274, D6468, and D4625) on a large variety of biodiesel samples obtained in the USA and Canada, ranging from B100 to B5 and B20 blends with LSD and ULSD diesel fuel. The objective of that project is to define which test method and what limits are appropriate to determine the oxidative stability for B100 to be used as a blend component up to B20, and for B5 and B20 fuels themselves.

Also, B. Terry (Octel) produced a study in 2005 for the Coordinating Research Council and the US National Renewable Energy Laboratory dealing with the impact of highly oxidized biodiesel, B5, and B20 blends on the durability of fuel system components (fuel injectors, pumps, seals) – which provides data of relevance[10].

Oxidation stability

Differences in oxidation stability between various biodiesel esters may be caused by multiple factors. That topic has been very well covered and reviewed by Andrew Waynick of the SwRI, and we recommend referring to his report on the characterization of biodiesel oxidation and oxidation products.[11] Herein, we will summarize the most important factors.

1) Molecular structure of the fatty esters

Biodiesel is a blend of fatty acid esters having different molecular structures with varying chain lengths, levels of unsaturations, and conformations. It is generally recognized that the following chemical aspects can have an impact on the overall oxidation stability of fatty acid derivatives:

- The presence and number of unsaturated bonds which are prone to oxidation by oxygen from air.
- The presence of bis-allylic configurations (i.e., -CH=CH-CH2-CH=CH-) where the central methylene group is activated by two double bonds. This kind of moiety is very prone to oxidation by air and leads to polymerisation reactions.
- The occurrence of molecular isomerization induced by high temperatures:
    - Positional isomerization of unsaturated bonds can lead to the creation of reactive conjugated and bis-allylic configurations.
    - Conformational *cis* / *trans* isomerization can also affect oxidative stability. It is important to note that while a single *trans* unsaturation is more stable than a *cis* unsaturation, conjugated *trans* unsaturations are more sensitive to oxidation than neighbouring *cis* unsaturations.

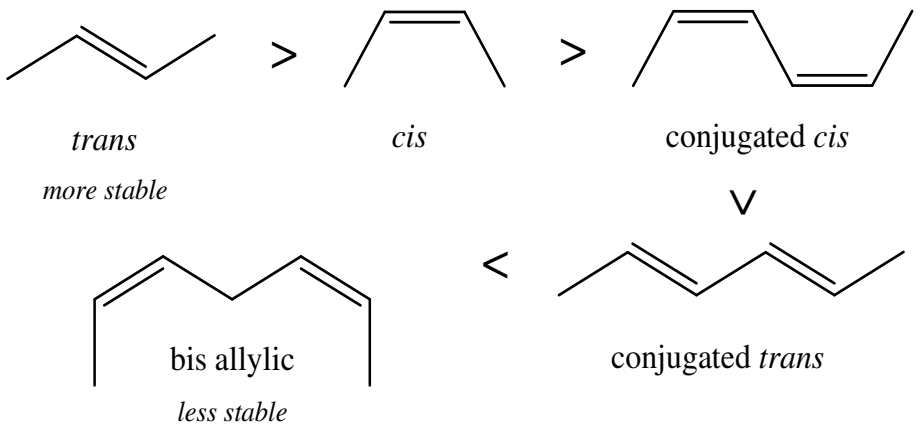

Figure 2 – Order of stability for different alkene isomers

2) Presence of antioxidants

Antioxidants can be naturally present in the feedstock or can be added during or after processing. These compounds usually prevent radicals formed in oils by oxygen or light to propagate further and cause degradation. Usually, the natural antioxidants are mainly tocopherols (4 types). Antioxidants added after (or sometimes before or during) processing can be of natural source or synthetic.

3) Presence of impurities and degradation products

Some impurities can catalyze the formation of radicals in oils, while other impurities can catalyze the degradation pathways of oils once radicals are formed. Degradation products may also be more susceptible to further degradation and produce compounds that can act as degradation catalysts. Examples of these impurities and degradation products: residual free fatty acids, residual process acidic catalyst, metals, metallic ions, peroxides, hydroperoxides, short chain organic acids, etc. Very often, the presence of these impurities in the final product is linked to the quality of the process or degradation of the sample due to ageing.

EXPERIMENTAL SECTION

Methods

OSI IP were obtained in accordance with the EN 14112 method “Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of oxidation stability (accelerated oxidation test)”[4] using a Metrohm Rancimat model 743. As specified in the method, the samples were heated to 110 °C with an air flow of 10 L/h.

Acid values were determined with the ASTM D 664 method “Neutralization Number by Potentiometric Titration”[12] using a Metrohm Titrando model 835 with a Metrohm Solvotrode combined electrode #6.0229.100 (glass/LiCl).

Peroxide values were determined with the AOCS Cd 8b 90 method “Peroxide value: acetic acid-isooctane method”[13] using a Metrohm Titrando model 835 with a Metrohm Pt Titrode combined electrode #6.0431.100 (Pt/pH).

Fatty acid methyl ester compositions were determined with the ISO 5508 method “Animal and vegetable fats and oils – Analysis by gas chromatography of methyl esters of fatty acids”[14] using a HP 5890 Series II gas chromatograph equipped with a Supelco wax capillary column (l=30m, d=0.25mm, f=0.25µm).

Materials

The biodiesel esters tested in this project and their identification codes used further in this report are presented in Table 2.

Table 2 – Description of the biodiesel esters samples tested

Type	Sample	ID
Biodiesel esters (B100)	Rapeseed oil methyl ester (European origin)	RAP-EU
	Canola oil methyl ester	CAN
	Fish oil ethyl ester	FIS
	Yellow grease methyl ester	YG1
	Yellow grease methyl ester	YG2
	Tallow methyl ester	TAL
	Soybean oil methyl ester	SOY
Petrodiesel	Ultralow sulfur diesel (around 15 ppm S)	ULSD

A European rapeseed methyl ester biodiesel (RAP-EU) was obtained from ADM (Oelmühle Hamburg, Germany). All other biodiesel samples were obtained from Canadian biodiesel producers. Since some producers requested to be anonymity, we decided not to disclose the exact origin of any Canadian samples.

Ultra low sulphur diesel (ULSD) was provided courtesy of Shell Canada Ltd. HPLC grade methanol used to determine the effect of methanol content on OSI was purchased from Laboratoire Mat.

The biodiesel blends (B5 and B20) were prepared by mixing measured volumes of a specific B100 sample and ULSD.

RESULTS

Characterization of biodiesel samples

We characterized the biodiesel samples by testing for peroxide value, acid value, oxidation stability, and fatty acid composition. For reference, you will find the certificate of analysis of some samples annexed to the end of this report.

The peroxide value (PV) determination measures the presence of oxidative moieties (i.e. portion of a molecule bearing characteristic oxidative properties) in a sample. The oxidative moieties usually found in biodiesel are hydroperoxides formed when oxygen from the air reacts with fatty esters. This usually is the first step in the oxidative degradation pathway of biodiesel.[15] We observed that peroxide values varied significantly from sample to sample, ranging from 3 to 62 meq O_2/kg. Complete peroxide value results are presented in Table 3. Some people consider that a PV over 10 meq O_2/kg is a sign of an ongoing oxidation process.

Another parameter we checked was the presence of acidity in the sample before the OSI test. The acid value (AV) determination is used to quantify the presence of acid moieties in a sample. The acidic compounds that could possibly be found in biodiesel are: 1) residual mineral acids from the production process, 2) residual free fatty acid from the process or the post-process hydrolysis of the esters, and 3) oxidation by-products in the form of other organic acids. By measuring the acid value of the samples, we wanted to determine whether or not the presence of such acidic compounds in biodiesel would affect its OSI IP. We observed that acid values ranged from 0.03 to 0.43 mg KOH/g with an exception at 2.23 mg KOH/g for the FIS sample. The results obtained are also presented in Table 3. For reference, the maximum value accepted in B100 standards (EN 14214 or ASTM D 6751) is 0.5 mg KOH/g.

The next parameter that was studied was the oxidative stability of the biodiesel samples. We observed generally low OSI IPs throughout the samples, ranging from 0.2 h to 1.3 h with the exception of the RAP sample which displayed an OSI IP of 6.1 h. The complete OSI IP results are presented in Table 3. For the sake of comparison, we also included

the results reported by BIOSTAB for undistilled rapeseed (RU), used frying oils (UU), and tallow-derived (TU) biodiesel esters.

Table 3 – Peroxide value, acid value, and OSI IP of tested biodiesel samples and comparison with data obtained by BIOSTAB[16]

	Sample	PV (meq O_2/kg)	AV (mg KOH/g)	OSI IP (h)
OLEOTEK (present work)	Canola methyl ester (CAN)	62	0.25	1.3
	Soybean methyl ester (SOY)	32	0.03	0.8
	Tallow methyl ester (TAL)	54	0.30	0.8
	Yellow grease methyl ester (YG1)	39	0.42	0.5
	Yellow grease methyl ester (YG2)	28	0.43	0.4
	Fish oil ethyl ester (FIS)	3	2.23	0.2
	Rapeseed methyl ester (RAP-EU)	5	0.13	6.1
BIO-STAB	*Rapeseed methyl ester (RU)*	3.4	0.37	9.2
	Yellow grease methyl ester (UU)	9.3	0.36	8.0
	Tallow methyl ester (TU)	-	0.26	0.7

Finally, the fatty acid composition of the samples was determined. This last element was expected to be very helpful in understanding the differences between the oxidation stability of various biodiesel esters from different feedstock. The fatty acid compositions of the fatty acid methyl esters were determined and are reported in Table 4. For the sake of comparison, we also included the results reported by BIOSTAB for rapeseed, used frying oils, and tallow-derived biodiesel esters. One should note that we have extrapolated the fish oil-derived biodiesel composition in ethyl esters from a methyl ester reference sample. This extrapolation and the very large variety of positional and conformational isomers possible with highly unsaturated compounds explain the higher amount of “not identified” compounds in the fish oil composition compared to other samples.

There are different methods that attempt to predict the stability of fatty acids and their derivatives based on structural information. Typically, those methods rely on the number of double bonds. On a structural basis, it is not the double bond but the adjacent position on the molecule (allylic) that is most sensitive to oxidation, especially when such a

position is surrounded by two double bonds (bis-allylic). Hence, new structural indices were developed by Knothe[17] to try and account for this reality. These indices, Allylic Position Equivalent (APE) and Bis-Allylic Position Equivalent (BAPE), are based on the number of the more reactive positions on the molecule. BAPE has been correlated with OSI IP somewhat successfully[18] in the past, but this work was done at a lower temperature (90 ℃) than 110 ℃. This difference in temperature can significantly affect the oxidation mechanisms in play, thus a correlation might not be found for the conditions of EN 14112. We have calculated the bis-allylic position equivalents (BAPE) from the compositional data presented in Table 4, but because of the aforementioned limitation, great care should be exercised in interpreting that data.

Table 4 – Fatty acid (FA) distribution, PV, AV, BAPE and OSI IP of tested biodiesel samples and comparison with data obtained by BIOSTAB

	OLEOTEK (present work)							BIOSTAB [16]		
Test	**YG1**	**YG2**	**TAL**	**CAN**	**RAP-EU**	**SOY**	**FIS**	**RU**	**UU**	**TU**
FA (%w/w)										
C8:0	0.1	-	-	-	-	-	-	nd	nd	nd
C10:0	-	-	0.1	-	-	-	-	nd	nd	nd
C12:0	0.1	0.1	0.1	-	-	-	-	nd	nd	nd
C14:0	0.8	0.7	1.5	-	0.1	0.1	1.5	0.09	0.41	2.20
C14:1	0.1	0.1	-	-	-	-	-	nd	nd	nd
C15:0	0.1	0.1	0.1	-	-	-	-	nd	nd	nd
C16:0	14.7	13.6	27.8	4.2	4.7	10.6	6.0	5.95	14.38	21.88
C16:1	1.5	1.3	3.4	0.2	0.2	0.1	2.0	-	0.39	1.57
C17:0	0.3	0.2	0.4	0.1	-	0.1	1.5	nd	nd	nd
C17:1	0.2	0.2	0.3	0.2	0.2	0.1	0.4	nd	nd	nd
C18:0	8.5	7.9	14.9	1.9	1.7	4.1	12.7	2.07	4.26	17.03
C18:1	51.9	53.7	47.0	60.7	61.1	24.2	38.9	60.34	57.17	45.12
C18:2	17.1	17.2	1.3	19.3	19.6	52.5	8.5	20.87	17.08	8.05
C18:3	3.0	3.0	0.7	9.9	9.5	7.9	14.7	8.15	2.08	1.09
C20:0	0.5	0.5	1.0	0.7	0.6	0.2	0.4	0.61	0.53	-
C20:1	0.8	0.9	0.8	1.5	1.4	0.2	-	1.27	0.88	-
C20:2	-	0.1	0.6	0.1	0.1	-	-	nd	nd	nd
C20:5	-	-	-	-	-	-	3.9	nd	nd	nd
C22:0	0.3	0.2	-	0.4	0.3	-	-	0.34	0.67	-
C22:1	-	-	-	0.3	0.3	-	-	0.19	-	-
C24:0	-	0.1	-	0.2	0.1	-	-	nd	nd	nd
C24:1	-	-	-	0.2	0.1	-	-	nd	nd	nd
NI	-	0.2	0.6	-	-	-	9.6	0.12	2.15	3.06
Total Δ0	25.3	23.3	45.1	7.5	7.5	15.1	22.1	9.06	20.25	41.11
Total Δ1	54.6	56.2	51.7	63.2	63.3	24.5	41.2	61.80	58.44	46.69
Total Δ2	17.1	17.3	1.3	19.4	19.7	52.5	8.5	20.87	17.08	8.05
Total Δ3	3.0	3.0	0.7	9.9	9.5	7.9	14.7	8.15	2.08	1.09
Total Δ5	-	-	-	-	-	-	3.9	-	-	-
PV (meq O_2/kg)	39	28	54	62	5	32	3	3.4	9.3	-
AV (mg KOH/g)	0.42	0.43	0.30	0.25	0.13	0.03	2.23	0.37	0.36	0.26
BAPE	23	23	3	39	39	68	54*	37	21	10
OSI IP (h)	0.5	0.4	0.8	1.3	6.1	0.8	0.2	9.2	8.0	0.7

NI: not identified; -: not detectable; nd: not determined; xU: undistilled sample; *: not accounting for NIs

OSI IP determination of biodiesel blends

Under the EN 14112 procedure, the OSI instrument heats the fuel to 110 °C and feeds air through the sample cell at a rate of 10 litres per hour. Under those conditions, we observed considerable evaporation of petrodiesel in the biodiesel ester blends even after just an hour (Table 5). Normally, a small reduction of the sample's volume during the procedure would induce a slight acceleration of the oxidation process and shorten the OSI IP measurements to a certain degree. However, in the biodiesel ester blends, the diminution of the sample volume caused by the partial evaporation of the volatile fraction of petrodiesel led to an important concentration of biodiesel esters and resulted in greatly accelerated oxidative degradation and OSI IP measurements. The distillation curve of the ULSD sample used is shown in Figure 3.

Table 5 – Mass loss of sample during OSI IP determination

		Mass loss at determination time					
Sample	**Testing temp.**	**0.5 h**	**1 h**	**2 h**	**3 h**	**4 h**	**4 h**
ULSD	25 °C	2.1%	4.3%	7.5%	10.6%	13.4%	15.8%
B20	25 °C	1.9%	3.7%	6.5%	9.2%	11.5%	13.5%
ULSD	110 °C	10.5%	17.1%	25.6%	33.5%	40.4%	46.2%
B20	110 °C	10.8%	16.9%	25.9%	33.4%	37.9%	41.0%

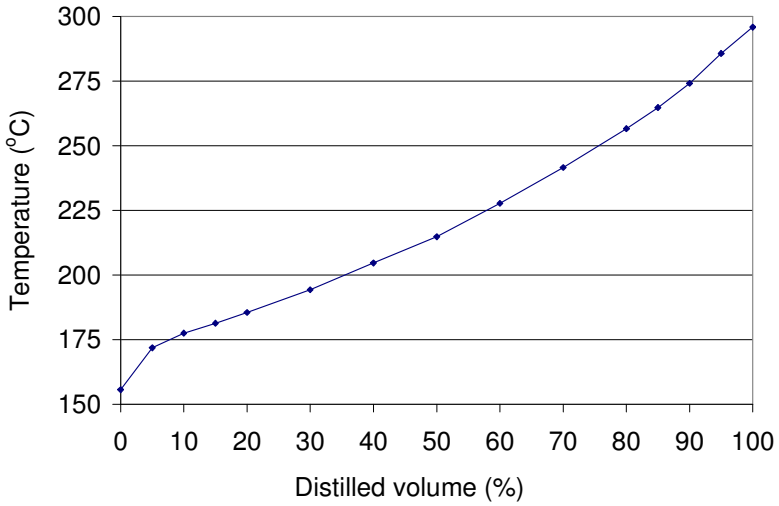

Figure 3 – Distillation curve of the ULSD sample

Attempts were made to modify the test's parameters in order to obtain valid OSI IP with samples containing a good proportion of volatile compounds. We lowered the air flow and the sample cell temperature and raised the sample volume in order to try to minimise the evaporation of the sample's volatile fraction. Even with no heating of the sample cell and minimum airflow allowable by the instrument (7 litres per hour), significant evaporation of the biodiesel blend samples was observed.

OSI IP determination of biodiesel containing methanol

During the study, questions arose concerning the effect of residual methanol content on OSI IP. It was thought by some that methanol content could affect measured OSI IP in a very important way due to the evaporation effect and presence of methanol in the apparatus conductivity cell. In order to check that effect, we prepared blends of the RAP-EN sample with different proportions of methanol (from 0.3 to 10 %) and tested those for OSI IP. Two sets of results were produced: one at constant sample weight and another where the evaporation of methanol was taken into account to give a constant sample weight after complete evaporation of the methanol. The results are presented in Table 6.

Table 6 – Effect of methanol content (% MeOH) on OSI IP

% MeOH (% v/v)	**Sample weight** (g)	**OSI IP EN 14112** (h)
0%	3.00	4.5
0.3%	3.00	4.6
1.0%	3.00	4.6
3.0%	3.00	4.3
5.0%	3.00	4.4
10.0%	3.00	4.2
0.3%	3.01	4.2
1.0%	3.03	4.2
3.0%	3.09	3.9
5.0%	3.15	4.1
10.0%	3.30	4.0

Even at 10 % methanol content, the OSI IP measurements were not greatly affected. It was concluded that methanol content normally met in the biodiesel industry wouldn't influence OSI IP measurements in a significant way.

DISCUSSION

Effect of initial peroxide value on OSI IP

The initial peroxide value of biodiesel esters samples was plotted vs. their OSI IP (Figure 4). Due to the poor precision of the method at low OSI IP, and since most samples showed results under 1 h, we could not use the data to determine whether or not there was a correlation with initial PV.

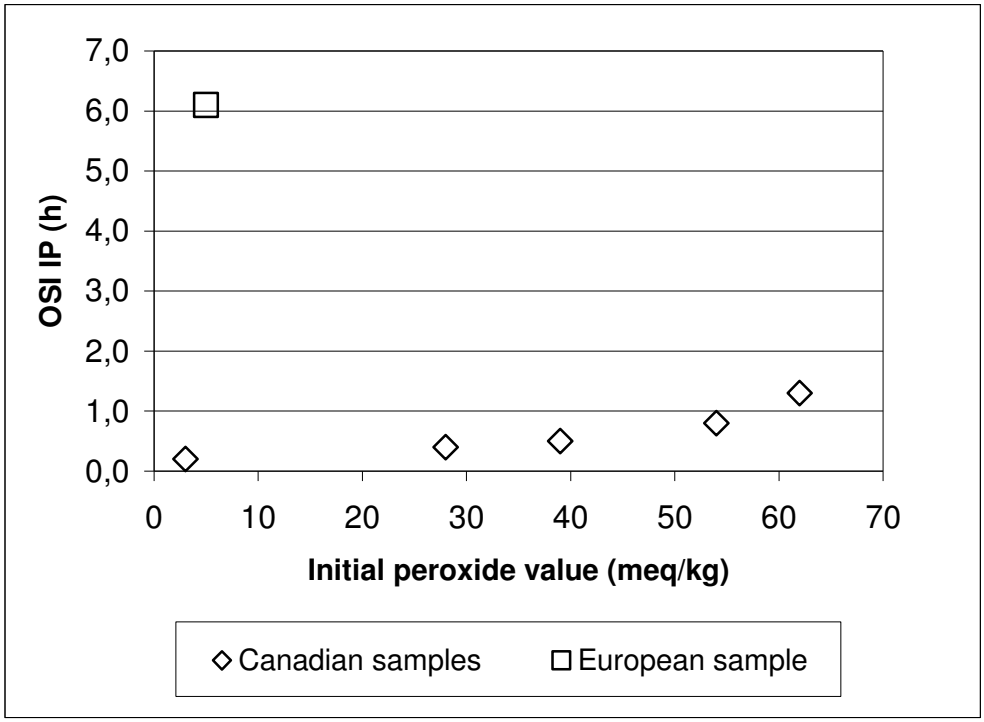

Figure 4 – OSI IP vs. initial peroxide value for the biodiesel ester samples tested

Oxidative degradation is a combination of multiple successive chemical reactions that form a degradation pathway. The formation of radicals and hydroperoxides is the first step of oxidative degradation. This reaction usually proceeds at higher speed rates than the following degradation reactions, which leads to an “accumulation” of peroxides and an increased peroxide number. In addition, the hydroperoxide formation speed is also a function of the availability of reactive alkenes. During ageing, the availability of remaining reactive alkenes will diminish and, consequently, the hydroperoxide production rate will decrease. If the consumption rate of hydroperoxides into further degradation pathways

remains constant, the combination of those two factors will lead to a general scenario where the peroxide number will rise over time to a maximum, then start to decrease.[15] It is known that the peroxide value maximum occurs at earlier stages of oxidation in more polyunsaturated oils because their hydroperoxides decompose more readily.

Consequently, it is not advisable to try to use a single PV determination as an indication of oxidation, because 1) different feedstock will display different hydroperoxide content maxima and 2) it is not possible to determine the position of the value on the general PV evolution curve (going up or going down). Only the variation of PV over time on the same sample could give some indication of the state of oxidation of that sample, but even then, interpretation of the results could be misleading. For example, slow evolution of PV could be as much the indication of great stability or complete oxidation.

One interesting point to note is that the FIS sample we tested displayed a very low PV while having the lowest stability of the lot. On the other hand, the RAP-EU sample displayed a similarly low PV, but had a significantly higher OSI IP (6h) than the other samples. This example illustrates well why PV alone cannot be used as a predictor of oxidation stability without having followed its evolution from the moment the sample was produced.

In this case, the most probable explanation for this observation is that the two samples were at a different stage of their oxidation. The FIS sample, having a high content in polyunsaturates, probably already had gone through the first steps of oxidation and was further along the oxidation process (Figure 5) while the RAP-EU sample had not, possibly because it is more resistant to the formation of radicals and hydroperoxides due to its content in natural or synthetic antioxidants. Unfortunately, the project resources did not allow for a measure of antioxidants in the samples.

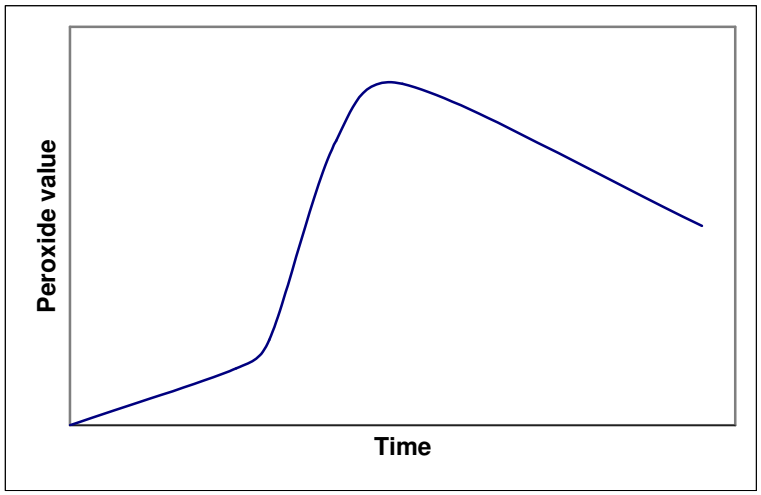

Figure 5 – Example of PV evolution over time during normal fat oxidation

Effect of initial acid value on OSI IP

Within the limited number of samples that were tested, we encountered samples displaying low OSI IP with either very high or very low acid values, while the only sample displaying high OSI IP (European sample) had a fairly low level of acidity. The initial acid value of biodiesel esters samples was plotted vs. their OSI IP to determine if a correlation could be drawn (Figure 6), but that exercise was inconclusive. Either the acid value is not a very important factor for oxidation stability, or it is important only in combination with other parameters.

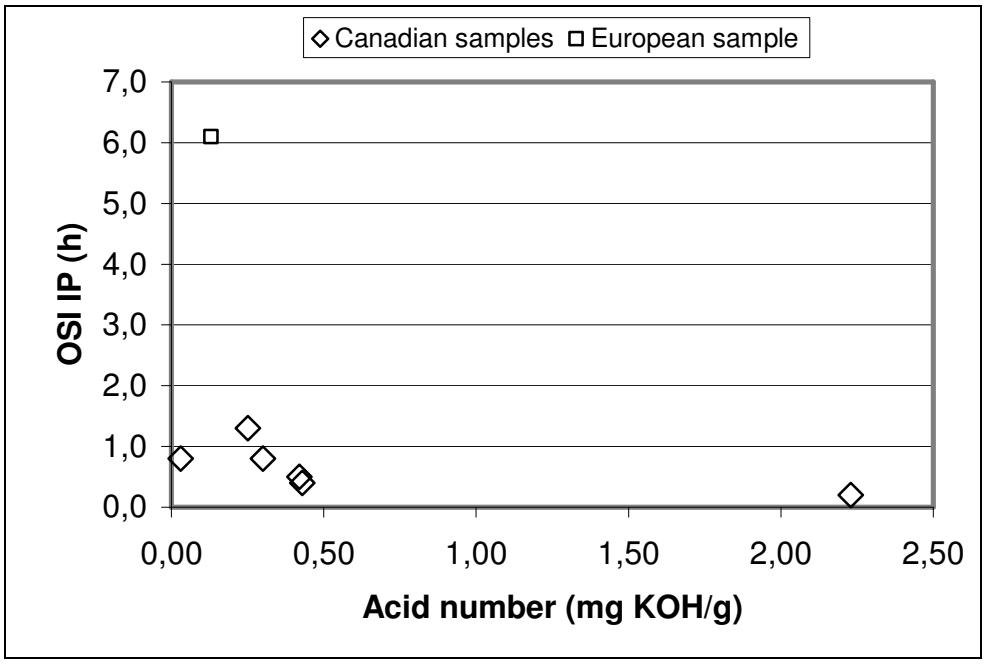

Figure 6 – OSI IP vs. acid value for the biodiesel ester samples tested

Effect of fatty acid distribution on OSI IP

As shown in Table 3, all Canadian biodiesel ester samples displayed OSI IP of less than 2 hours. Figure 7 indicates the OSI IP results obtained for the 36 different biodiesel samples reported by OLEOTEK (6), BIOSTAB (4) and NREL (26). Of those 36 samples, only 4 (11%) fall above the 6 h requirement specified in EN 14214 fuel standard (vertical dotted line).

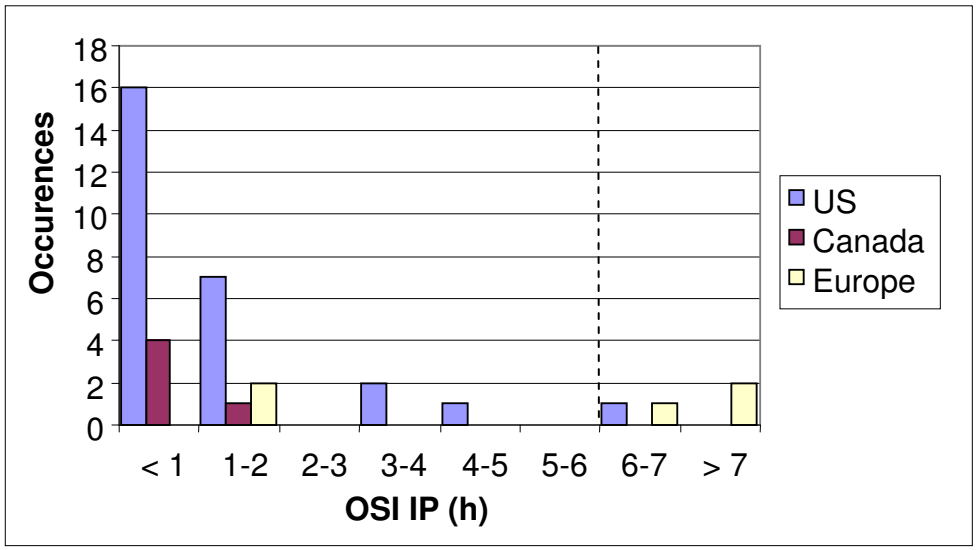

Figure 7 – OSI IP for American, Canadian, and European biodiesels

The differences in oxidation stability between the biodiesel samples could also be attributed to the type of feedstock used to make the biodiesel esters. The chemical composition of the biodiesel esters depends on the chemical composition of the feedstock that was used to produce them. Some feedstock types have chemical compositions that make them more sensitive to oxidation, while others have chemical compositions that make them more resilient to oxidation. As shown in the introduction, sensitivity to oxidation is usually linked with the presence, quantity, and configuration of unsaturated bonds in the fatty acid composition of the biodiesel as well as other factors (antioxidants, impurities, sample age).

The European yellow grease-derived biodiesel ester sample displayed better stability than the samples produced in Canada. When comparing the composition and characteristics of these two biodiesel esters however (Table 7), we cannot pinpoint any reason for such an important difference between the oxidation stability of the two samples. The fatty acid composition of the two samples displays slight differences, but, in our opinion, not enough to justify such a difference in oxidation stability as confirmed by the identical BAPE values. The acid value of the YG1 and YG2 samples is slightly higher than that of the UU sample, but again, we are of the opinion that such a relatively small difference cannot cause such a difference in OSI IP.

Table 7 – Comparison of yellow grease-derived biodiesel ester samples

Sample	C16:0	C16:1	C18:0	C18:1	C18:2	C18:3	Total Δ0	Total Δ1	Total Δ2	Total Δ3	Peroxide val. (meq O_2/kg)	Acid value (mg KOH/g)	OSI IP (h)
YG1	14.7	1.5	8.5	51.9	17.1	3.0	25.3	54.6	17.1	3.0	39	0.42	0.5
YG2	13.6	1.3	7.9	53.7	17.2	3.0	23.3	56.2	17.3	3.0	28	0.43	0.4
UU	14.38	0.39	4.26	57.17	17.08	2.08	20.25	58.44	17.08	2.08	9.3	0.36	8.0

Note: Data extracted from Table 4

Also interesting to note is the difference in oxidation stability between the rapeseed oil-derived esters sample made in Europe and the Canola oil-derived ester sample made in Canada. Again, it is difficult to pinpoint the exact reason for this radical difference in oxidation stability. As shown in Table 8 and Figure 8, the composition analyses made on the tested samples do not warrant such a difference in oxidation stability. Also, one will note that the fatty acid composition of Canola and rapeseed oil-derived fatty esters are very similar, even if we were expecting an important difference in erucic acid content (C22:1). After inquiry, it was been established that the European rapeseed used to make the RAP-EU sample was in fact Canola rapeseed grown in Europe. That explained why there was virtually no erucic acid found in the RAP-EU sample and the great similarities with the CAN sample.

Table 8 – Comparison of Canola and rapeseed oil-derived biodiesel ester samples

Sample	C16:0	C18:0	C18:1	C18:2	C18:3	C20:1	C22:0	C22:1	Total Δ0	Total Δ1	Total Δ2	Total Δ3	Peroxide val. (meq O_2/kg)	Acid value (mg KOH/g)	OSI IP (h)
CAN	4.2	1.9	60.7	19.3	9.9	1.5	0.4	0.3	7.5	63.2	19.4	9.9	62	0.25	1.3
RAP	4.7	1.7	61.1	19.6	9.5	1.4	0.3	0.3	7.5	63.3	19.7	9.5	5	0.13	6.1
RU	5.95	2.07	60.34	20.87	8.15	1.27	0.34	0.19	9.06	61.80	20.87	8.15	3.4	0.37	9.2

Note: Data extracted from Table 4

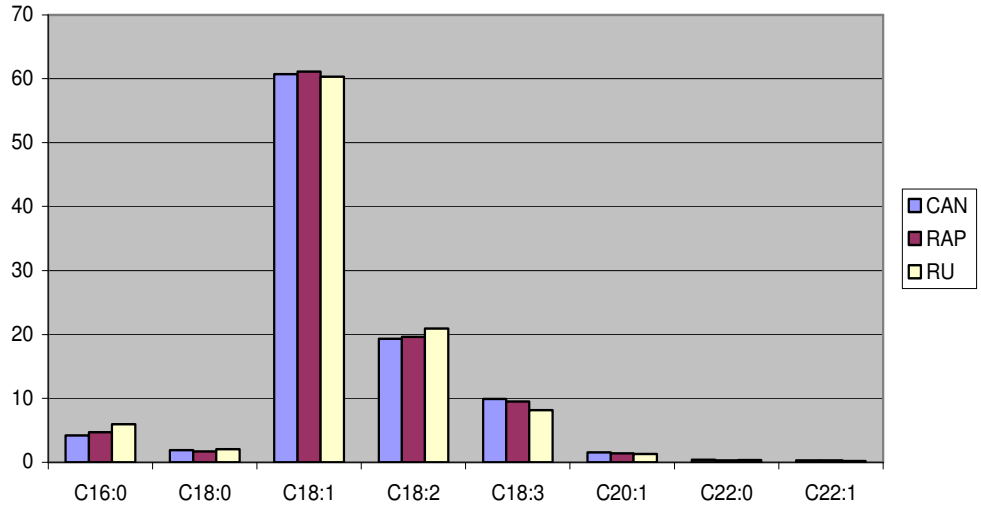

Figure 8 – Fatty acid composition of Canola and rapeseed oil-derived biodiesel ester samples

Based on fatty acid composition and acid value, we do not see any reason why Canola-derived fatty esters would have much lower oxidation stability than rapeseed-derived fatty esters. The acid value of the RU sample was higher than that of the CAN sample, yet its fatty acid composition was very similar.

These observations lead us to conclude that the fatty acid composition wasn't the major factor influencing the oxidation stability of these specific samples. The only conclusion we can reach at this point is that there is at least another parameter that affects the

oxidation stability in a much more important way, a parameter which has not been monitored in this study. Our best hypotheses at this moment are that the biodiesel samples tested have very different contents in natural or added antioxidants or that the production process would prove to be a more important parameter for oxidation stability than the actual fatty acid distribution of the biodiesel. If so, we should pay greater attention to parameters like trace metals, isomerizations induced by the process, process impurities, etc. These hypotheses have yet to be verified.

It is interesting to note that this “mystery” of significant and unexplainable oxidation stability differences between American and European vegetable oils has already been reported by Catherine Watkins and Albert Dijkstra in the deep-frying oil industry.[19,20] These authors came to the conclusion that the oil extraction processes could be the important parameter where oxidation stability is concerned.

Comparison of oxidation stability testing methods

This study demonstrated that the EN 14112 – OSI test method is not appropriate for testing samples containing volatile compounds, including petroleum diesel fuels. Thus, we looked for a standard test that could be suitable for volatile materials. A summary of existing oxidation stability tests is given in Table 9.

Table 9 – Comparison of some oxidation stability testing methods

Method	System	Atmosphere	Pressure or flow kPa or L/h	Temp. °C	Time	Catalysts (if any)	Added Water	Agitation	Measurement
ASTM D 525	Closed	O_2	700 kPa	100	ND	-	No	No	Time until pressure drops 14 kPa in 15 minutes
ASTM D 2112	Closed	O_2	620 kPa	140	ND	Copper wire	Yes	Yes (rotation)	Time until pressure drops 172 kPa
ASTM D 2272	Closed	O_2	620 kPa	150	ND	Copper wire	Yes	Yes (rotation)	Time until pressure drops 175 kPa
ASTM D 2274	Open	Bubbled O_2	3 L/h	95	16 h	-	No	Yes (bubbling)	Mass of filterable and adherent insoluble matter
ASTM D 4625	Open	Air	-	43	24 weeks	-	No	No	Mass of filterable and adherent insoluble matter
ASTM D 4742	Closed	O_2	620 kPa	160	ND	Metal naphtenates (Pb, Cu, Fe, Mn, Sn)	Yes	Yes (rotation)	Time until pressure break point
ASTM D 5304	Closed	O_2	800 kPa	90	16 h	-	No	No	Mass of filterable and adherent insoluble matter
ASTM D 6468	Open	Air	-	150	3 h	-	No	No	Light reflectance of filter charged with insoluble matter
ISO EN 14112	Open	Bubbled air	10 L/h	110	ND	-	No	Yes (bubbling)	Time until the conductivity increase in the detection cell accelerates

ASTM D 4625 simulates long-term storage above-ground, not the operating conditions of modern diesel engine vehicles. Although some users store fuel over long periods of time at near ambient temperatures before pouring it into a vehicle tank or leave it idle in the vehicle for a while (e.g., during a summer holiday period), it has been established by the BIOSTAB group that running vehicle conditions are more important causes of degradation than those prevalent in longer-term storage, and that a sample that is stable under running vehicle conditions most likely is stable under storage conditions too.

The modified ASTM D 2274 method is a filtration method where esters are heated to 95 °C and filtered in order to measure insoluble degradation products (mainly polymers) which can deposit on engine parts. However, whereas an insoluble fraction may precipitate and form deposits in pure fatty esters or specific blend ratios with petrodiesel, a soluble polymeric fraction may precipitate out of a blend containing a different ratio of petrodiesel and still form deposits on engine parts if the fatty ester / petrodiesel ratio is modified after testing. A method measuring the actual degradation products (polymers) in an aged fuel would be preferable if one is concerned about preventing formation of deposits with a pure fatty ester blend stock or with any blend ratio with petrodiesel that can be produced from that blend stock.

One will note that other oxidation test methods also have their shortcomings and drawbacks when used to evaluate the oxidation stability of samples containing volatile materials. Open-system tests lead to the same evaporation problems observed with the EN 14112 OSI test, so closed-system tests seem to be preferable for testing blends. However, one must ensure that the tests represent a suitable model able to reproduce the working conditions the fuel is submitted to, i.e. recirculation of the fuel between the diesel engine and the tank where its temperature rises after many cycles up to around 93 °C in the presence of air.[21] As the fuel moves through the primary and secondary pumps and the injector (which is cooled by the fuel), fuel temperature rises well above 93 °C.

With that objective in mind, one should also note that oxidative reaction mechanisms change between two different temperatures. Production of volatile organic compounds

such as formic and acetic acid from fatty acid derivatives, occurring at around 100 °C in the OSI test, does not occur at room temperature, for example.[22] Most test methods use a higher value than the real temperatures being simulated in order to accelerate the phenomena of interest without subjecting the sample to a temperature that would excessively activate reactions that occur at a much lower rate in real vehicle fuel systems. The choice of temperature is a matter of compromise between, on the one hand, realism and accuracy, and, on the other hand, the need for completing the measurement of quality within a time span short enough to be useful to suppliers and buyers who want to decide whether or not a delivery is acceptable. The same observations apply when catalysts are used to accelerate the oxidation test: some degradation pathways impossible to get without catalyst can happen. Thus, it is strongly recommended that the test temperature be around or slightly above 90 °C without catalyst.

Also, since the fuel is being circulated in the fuel systems between the engine and the fuel tank, it would be preferable for the chosen test to reproduces that movement which increases the contact between the fuel and the air.

Finally, one must ensure that the measurements obtained in the test correlate with the specific problems encountered in engines: filter plugging and lacquering of engine parts. While gravimetric filtering tests are suitable to detect insoluble and adherent sludge produced by oxidative degradation in a given blend ratio, the production of other degradation products may be masked by their partial (or complete) solubility in that same blend ratio. If the partial combustion of soluble degradation by-products can cause lacquering problems in the combustion chamber of the engine (injectors, pistons, etc.), indirect measurements of oxidation seem preferable, like oxygen absorption or degradation compound quantification techniques. Thus, gravimetric measurements of insoluble and adherent sludge will give different results depending on the fatty acid ester / petrodiesel ratio of a specific fuel and are not a good indication of the actual amount of oxidation by-products present in the fuel.

Of all tests found in the literature, none combines all the preferred conditions expressed herein: closed system, contact with oxygen (or air), temperature around 90-100 ^{o}C, no catalyst, no water, and agitation. Thus, a new test procedure is warranted to accurately evaluate the oxidation stability of fatty acid esters / petrodiesel blends.

CONCLUSIONS

Oxidative stability (OSI IP), peroxide value, and acid value were determined for 7 biodiesel samples made from different feedstock, 6 of which were Canadian in origin. Also, OSI IP measuring was attempted on biodiesel blends with petrodiesel.

It has been determined that even with modifications to the analytical method, diesel evaporation makes it unreliable to analyse the oxidative stability of biodiesel blends with the EN 14112 method (Rancimat). The absence of an existing method combining the proposed preferred conditions for determining oxidation stability of biodiesel blends warrants the development of a new method.

The OSI IP of samples contaminated with methanol was also measured. It was concluded that methanol content normally met in the biodiesel industry wouldn't influence OSI IP measurements in any significant way.

Peroxide value was not shown to be a predictor of oxidation stability. The only way to use PV in that regard would be to follow its evolution from production time to interpret the PV according to the sample's oxidation status.

Measures of acid value suggest that it is not a very important factor for oxidation stability, or that it is important only in combination with other parameters.

Finally, compositional data and calculated indices (BAPE) leads us to conclude that the fatty acid distribution is not the major factor causing the OSI IP differences observed between similar samples. This is especially obvious for the rapeseed / Canola samples and the yellow grease samples we tested. The main factor is more likely the presence of compounds other than fatty acids such as natural or synthetic antioxidants, residual catalyst, trace metals, isomerized oils or other impurities introduced during the process. However, these hypotheses could not be verified within the scope of this project.

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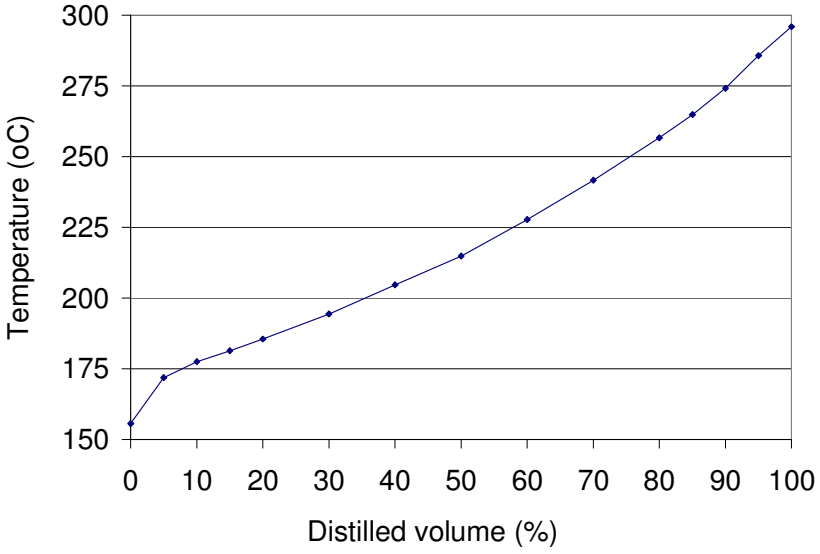
Sincere thanks are offered to the many people on the reviewing committee who have given their time providing comments on the drafts and assisting in many other ways. The contribution has been of inestimable value and is greatly appreciated. The fact that it has not been possible to respond to all the suggestions and comments individually is a matter of regret. Comments have all been considered and suggestions included to the greatest possible extent, while trying to keep the report of manageable length. The content of the report, including its errors and omissions, remains the responsibility of the authors.

ANNEXES

ULSD Certificate of Analysis

Test	Method	Result	Units
Density @ 15°C	ASTM D 4052	827	Kg/m^3
Kinematic viscosity @40°C	ASTM D 445	1.597	cSt
Organic sulphur	ASTM D 5453OS	16.5	ppm (w/w)
Organic nitrogen	ASTM D 4629ON	10.8	ppm (w/w)
Cloud point	ASTM D 2500	-58	°C
Pour point	ASTM D 97	<-60	°C
Cetane index	ASTM D 976	40.2	Index
Composition	ASTM D 1319-84		
Aromatics		14.2	% (v/v)
Olefins		2.5	% (v/v)
Saturates		83.3	% (v/v)
Lubricity @ 60°C, 44% rel. hum.	HFRR wear scar	607	microns



Distillation curve of the ULSD sample

Biodiesel Certificate of Analysis

Yellow grease methyl ester (YG1)

Test	Method	Result	Units
Flash point	ASTM D 93	165	^{o}C
Water and sediment	ASTM D 2709	0.015	%
Kinematic viscosity @40^{o}C	ASTM D 445	4.8	mm^{2}/sec
Sulfated ash	ASTM D 874	0.011	% (w/w)
Sulfur	ASTM D 2622	< 0.015	% (w/w)
Copper strip corrosion	ASTM D 130	1a	Index
Cetane index	ASTM D 613	58	Index
Cloud point	ASTM D 2500	+ 6	^{o}C
Carbon residue	ASTM D 4530	0.03	% (w/w)
Acid number	ASTM D 664	0.49	mg KOH/g
Free glycerin	ASTM D 6584	0.000	% (w/w)
Total glycerin	ASTM D 6584	0.197	% (w/w)

Tallow methyl ester (TAL)

Test	Method	Result	Units
Flash point	ASTM D 93	172	^{o}C
Water and sediment	ASTM D 2709	0.012	%
Kinematic viscosity @40^{o}C	ASTM D 445	4.6	mm^{2}/sec
Sulfated ash	ASTM D 874	---	% (w/w)
Sulfur	ASTM D 2622	< 0.015	% (w/w)
Copper strip corrosion	ASTM D 130	---	Index
Cetane index	ASTM D 613	---	Index
Cloud point	ASTM D 2500	+ 14	^{o}C
Carbon residue	ASTM D 4530	---	% (w/w)
Acid number	ASTM D 664	---	mg KOH/g
Free glycerin	ASTM D 6584	0.000	% (w/w)
Total glycerin	ASTM D 6584	0.146	% (w/w)

Other certificates of analysis were not available.

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