RESEARCH ARTICLE

Evaluation of bio-acetal as a sustainable alternative jet fuel

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Abstract: The European Council's strict regulation on carbon dioxide (CO_2) emission-allowances for all flights taking off and landing on EU countries has encouraged the development of bio-jet fuels from plant oil due to its advantage of carbon neutrality. The common production methods of bio-jet fuel involve the thermo-chemical cracking of plant oil into short carbon chain fragments of around C8 to C10 compounds. This is often conducted at high reaction temperature and pressure.

In the present study a milder approach using ozonization and electrolysis has been applied for the cracking of fatty acid methyl esters derived from sunflower oil, and the acceptability of the reaction products in bio-blend jet fuel was evaluated. The major chemical compounds generated were aldehydes, but the thermal stability of these compounds was too poor to be utilized as a bio-jet fuel. Acetal, which can be derived from aldehyde, has a high thermal stability and at the same time its flash point, specific energy and freezing point are comparable to that of Jet A-1 fuel. A 10 % blend of 1,1- dimethoxynonane (acetal derived from nonanal) did not change the important fuel properties of Jet A-1. The high thermal stability of this blend was also confirmed.

Keywords: Bio-acetal, bio-jet fuel, double bond cracking, evaluation, jet fuel property.

INTRODUCTION

Carbon dioxide emissions from international aviation are not covered by the Kyoto Protocol, and are not included in any national emission reduction frameworks. In the recent years, however, emissions have increased much faster than what had been projected. Air travel is the world's fastest growing source of greenhouse gases like carbon dioxide, which causes climate change. Globally the world's commercial jet aircraft fleet generates more than 700 million tons of carbon dioxide (CO_2) per year, which is the world's major greenhouse gas (Capoccitti *et al.*, 2010). This is about 2 % of the total anthropogenic CO_2 emissions in 1992 or about 13 % of the CO_2 emissions from all transportation sources. Aircraft emissions of CO_2 will continue to grow between 2000 and 2050 by a factor in the range of 2.0 – 3.6 depending on the scenario (Owen *et al.*, 2010).

The European Commission has recommended the International Civil Aviation Organization (ICAO) to facilitate the development and adoption of global emission reduction measures for their sectors by the end of 2010. The European Parliament voted to include a law on emission trading scheme (ETS) to cut down greenhouse gases. According to this law airlines will have to cut its CO_2 emission by 8 % from 2013 onwards (BBC, 2008). This directive came into force in 2012. Prescribing the mean of emissions between 2004 and 2006 as the emission standard of airlines, the cap for the year 2012 was 97 % of the emission standard and in 2013 it became 95 % (Hodgkinson *et al.*, 2008). This strict regulation has encouraged the development of bio-jet fuels with its advantage of carbon neutrality. On the 24th of February 2008, the Virgin Atlantic Airways Ltd., succeeded in the first demonstration flight using bio-jet fuel made from coconut oil and babassu palm oil. The flight was from Heathrow Airport, London to Amsterdam using Boeing 747 with a blend of 20 % biofuel and 80 % Jet A-1 (kerosene) in one of its four engines. After this test flight, the Continental Airlines, Air New Zealand and Japan Airlines conducted test flights using bio-blend jet fuels prepared from the so-called second-generation biofuel feedstock such as *Camelina*, *Jatropha* and algae.

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Almost all production processes of bio-jet fuel using second-generation feedstock, are based on the cracking of plant oil using hydrogen gas under high pressure and high temperature (Bezergianni *et al*., 2009; Kinder & Rahmes, 2009). In a previous study, a new cracking method using ozonization and electrolysis, which can be operated under normal temperature and atmospheric pressure has been developed (Soriano *et al*., 2005). Here, we have investigated the acceptability of the reaction products as blending compounds for jet fuel by comparing their major fuel properties with the quality standard of Jet A-1.

METHODS AND MATERIALS

Transestrification and ozonization procedures

High oleic sunflower oil with 85.5 % oleic acid content (Showa Sungyo Co. Ltd., Tokyo, Japan) was used. The transestrification for methyl oleate production and its ozonization was carried out as described in a previous study (Soriano *et al*., 2003).

Electrolysis of ozonized methyl oleate

Ozone reacts very specifically with the -CH=HC- bond and forms ozonide (1,2,4-trioxolane), which is easily decomposed by chemical and other methods under reductive atmosphere (Bailey, 1978). In the present study, electro-reduction was employed to cleave the double bond. Constant voltage electrolysis was conducted by applying 50 V and 1 A in 50 mL of completely ozonized methyl oleate using Cu plates as electrodes (45 x 30 mm) with a spacing of 5 mm. A mixture of methanol and acetic acid (1:1 volume ratio) was used as the proton donor. The amount of proton donor added corresponded to a sample/proton donor ratio of 2.5 : 1 (v/v). $NaClO_4$ was used as the supporting electrolyte. The extent of the cleavage of ozonide (expressed as percentage cleavage) was calculated from the ^1H NMR integration values of the signal at 5.17 and 3.7 ppm corresponding to the protons of the trioxolane rings and the methyl protons of the ester moiety, respectively.

Vacuum distillation and analysis of fuel properties of distillate blend jet fuels

After electrolysis, the reaction mixture was subjected to vacuum distillation (Tokaseiki Co. Ltd., Model AD-1160NSR, Kanagawa, Japan) under 5 and 10 hPa. The distillate in the boiling range of 25 °C at 10 hPa – 115 °C at 5 hPa (corresponds to 150 – 275 °C under atmospheric pressure) was then mixed with Jet A-1 fuel (Idemitsu Kosan Co. Ltd., Japan) at volume ratios of 10 % and

20 %. The important fuel properties such as flash point and freeze point of the blend jet fuels were submitted for analysis (K.K. SVC Tokyo Company, Kanagawa, Japan) according to the Japanese industrial standard methods.

NMR analysis

For ^1H NMR and ^{13}C NMR spectroscopy, about 30 mg of the sample was dissolved in $CDCl_3$ containing TMS as standard. Both spectra were obtained using the Bruker Avance 600 Spectrometer (Karlsruhe, Germany). A trace amount of $CHCl_3$ in the solvent used exhibits signals at 7.26 and 77.0 ppm in ^1H and ^{13}C NMR, respectively.

Preparation of 1,1-dimethyloxynonane (acetal) from nonanal (aldehyde)

Commercially available nonanal (Wako Pure Chemical Industries Ltd., Osaka City, Japan) was used for the preparation of 1,1-dimethyloxynonane. Approximately 61 mmol of nonanal was placed in a 500 mL glass reactor followed by 400 mmol of acetic acid (99.9 % purity) and 3.1 mol dehydrated methanol. The reaction was conducted for 9 h at 60 °C. In order to determine the necessary reaction time for acetal production, 3 mL of reaction mixture was sampled every 90 min, immediately extracted with diethyl ether and washed 3 times with distilled water. After decantation, the diethyl ether was dried with magnesium sulphate. The final product was obtained by removing diethyl ether using a rotary evaporator. It was then analysed by Gas Chromatography (GC) after dilution with chloroform.

RESULTS AND DISCUSSION

Basic idea for the production of bio-jet fuel from plant oil

In the early stage of the development of bio-jet fuel, attempts were made to mix biodiesel derived from plant oil with fossil jet fuel. In 2003 Dunn has reported on blend jet fuel prepared with soybean biodiesel and JP-8. The freeze point of JP-8 (− 48 °C) was increased to −24 °C by a 10 % blend of soybean biodiesel (with a freeze point of + 5 °C). This resulted in a significant change in the cold flow property, which is one of the most important jet fuel properties. This showed that just simple mixing of biodiesel with fossil jet fuel is not enough to produce a reliable (i.e., good cold flow property) product.

For the refining of petroleum, a continuous steady state fractional distillation is employed, and components having different boiling points are withdrawn at specific

outlets along the height of the column. The crude oil fractions with higher boiling points generally have more carbon atoms. The average carbon number of kerosene, which is a major component of jet fuels is 10 and exhibits a boiling point ranging from 170 – 250 °C (Figure 1). The boiling range for C14 diesel is 240 - 350 °C. Plant oil, which is a triglyceride consists of three fatty acids with a long carbon chain of C16 and C18. Therefore, in order to produce a kerosene-like hydrocarbon from plant oil, the fatty acids should be cracked into shorter chains of around C8 – C10.

Unsaturated fatty acids have carbon-carbon double bonds (-CH=HC-) in their molecules, i.e., oleic acid
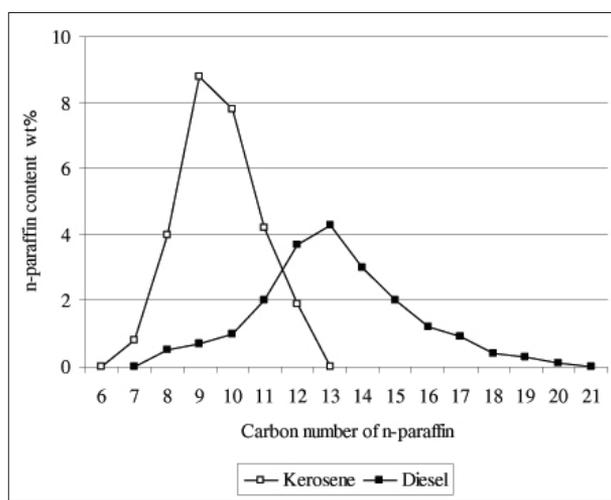

Figure 1: Average carbon number of kerosene and diesel oil

with C18 has one -CH=CH- at the 9th carbon and it is indicated by C18:1; linoleic acid with C18 (C18:2) has two -CH=HC- at the 9th and the 12th carbon as shown in Figure 2. If the double bond of oleic acid can be successfully cleaved, we can get two C9 chemical compounds. In the case of linoleic acid we can get C9,
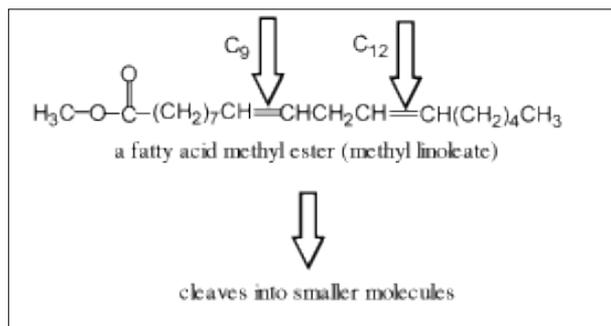

Figure 2: Carbon-carbon double bond for selective cracking

C3 and C6. The objective of this study was to use these double bonds for selective cracking of long carbon chains of fatty acids. In a previous study a new technology has been developed to cleave these double bonds under normal temperature and atmospheric pressure through ozonization and electrolysis (Soriano *et al*., 2006).

Chemical compounds obtained from electro-reductive cracking of -C=C- double bond of methyl oleate and fractional distillation of the reaction mixture

During the research on electro-reductive cracking, the nature of the products formed and whether they are acceptable as blending compounds for the preparation of bio-blend jet fuel was not examined. Therefore, using ^{13}C NMR analysis we first investigated the chemical compounds generated from the electro-reductive cracking of methyl oleate. As seen in Figure 3, aldehyde, acetal and alkene were formed but aldehyde
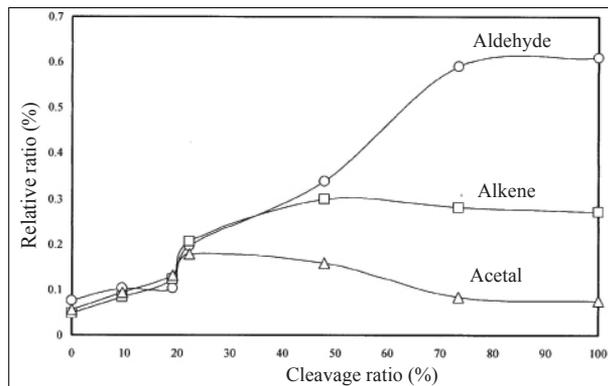

Figure 3: Relative ratio of compounds formed by cracking methyl oleate as a function of cleavage ratio of ozonized methyl oleate
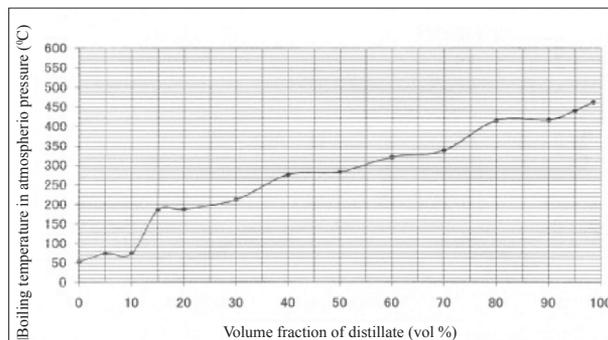

Figure 4: Distillation curve of the reaction mixture formed by electro-reductive cracking (temperature of vertical axis corresponds to atmospheric pressure calculated from actual pressure and temperature during vacuum distillation.)

Table 1: Fuel properties of Jet A-1 blended with distillate in the boiling range of 150 − 275 ºC

Test properties	Jet A-1 standard values	10 % distillate blended with Jet A-1	20 % distillate blended with Jet A-1
Density (at 15 ºC) (g/L)	0.775 − 0.840	0.785	0.791
Viscosity (at 40 ºC) (mm²/s)	0.71	0.70	0.77
Flash point (ºC)	≥ 38.0	38.5	39
Freezing point (ºC)	≤ - 47.0	-52.0	- 52.0
Acid value (mg KOH/g)	≤ 0.015	2.66	2.66

was the major product at the final stage of electrolysis. The relative ratio of these compounds were calculated from ^{13}C NMR integration values of the signal at 203, 139, 105 and 174 ppm corresponding to the carbons of aldehyde, alkene, acetal and methyl ester, respectively. Nonanal and methyl 9-oxononanoate may represent the C9 aldehyde derived by the cleavage of -C=C- double bond of methyl oleate.

After electrolysis the reaction mixture was subjected to vacuum distillation at 5 and 10 hPa. The distillation curve is shown in Figure 4. The initial vapourization of volatile compounds under atmospheric pressure occurred around 51 ºC, but a terminal temperature of 460 ºC (± 260 ºC at 5 hPa) was required to recover all the components. Aldehyde is known to polymerize at a temperature higher than 150 ºC and this may be the reason for the high final temperature. Considering the temperature range of Jet A-1, where the initial and terminal boiling points are 155.0 and 247.0 ºC, respectively, the distillate in the boiling range of 150 – 275 ºC was collected and mixed with Jet A-1 fuel at volume ratios of 10 % and 20 %. The significant fuel properties of these blends were then examined.

Table 1 compares the properties of the prepared fuel blends with the standard values. The freezing point, flash point, density and viscosity, even in the 20 % blend were in the satisfactory range based on Jet A-1 qualities. However, the acid values were extremely high. This could be due to the presence of aldehydes in high concentrations in the distillate, since it can be converted into acids during distillation as well.

**Selection of stable chemical compounds derived from aldehyde**

Judging from the increase in acid value and polymerization during distillation due to the presence of aldehydes, the thermal stability of the electrolysis product was considered not acceptable for bio-jet fuel. However

esters and acetals, which can be derived from aldehyde are known as stable chemical compounds (Moens *et al.*, 2009). Therefore, for the purpose of comparison, methyl esters were prepared using six different saturated fatty acids with a carbon number of C8 – C18. Figure 5 shows the flash point data, which indicated an increasing value with increasing carbon number of saturated methyl ester. The minimum flash point of standard Jet A-1 is 38.0 ºC, and the flash point of commercially available Jet A-1 is around 43 ºC. Based on these requirements, only methyl octanoate (C8) appeared promising but still at a high value of 80 ºC. The freezing point and specific energy of methyl octanoate were measured and these were found to be -24.3 ºC and 39.2 MJ/kg, respectively. Although the specific energy is almost comparable with the Jet A-1 standard of 42.8 MJ/kg, the freezing point is much higher than the maximum standard of -47.0 ºC. Based on these evaluations it was concluded that the middle chain fatty acid methyl esters were unsuitable as a blending compound for jet fuel.

In the case of acetal, several interesting fuel applications have been mentioned in literature. These
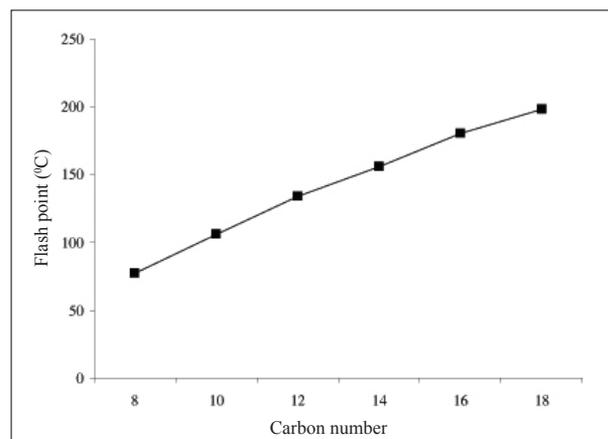
Figure 5: Effect of carbon number on flash point of saturated fatty acid methyl ester

include (a) an alternative fuel to methanol in fuel cell system (Savadogo, 2001); (b) a biodiesel fuel component (Garcia *et al*., 2008) and (c) an anti-freezing agent for biodiesel (Mushrush *et al*., 1997; Silva *et al*., 2010). Acetal is derived by the condensation reaction between carbonyl compound and alcohol through hemiacetal as shown in equation 1. The reaction is reversible, therefore an excess amount of alcohol is required to get a high yield of acetal (Ranu *et al*., 2004).
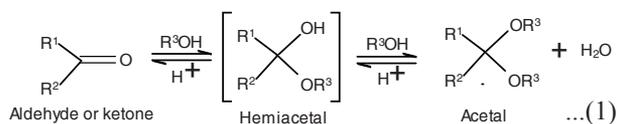
In order to evaluate the acceptability of acetal in bio-blend jet fuel without any disturbance from contaminants

generated from electrolytic cracking of methyl ester of sunflower oil, we first derived acetal from pure aldehyde. Figure 6 shows the time course of 1,1-dimethoxynonane (DMN) formation from nonanal (NN). Nonanal quickly dropped and attained a steady concentration in 90 min. The compound indicated as 'other products' must be hemiacetal, and it shows a typical reaction pattern of an intermediate. The other unknown compounds indicated as 'NN like' were also detected, and their retention times in GC analysis were similar to nonanal. The yield of acetal was almost 90 %, but the residual nonanal was also present at a considerable level of 3 %.
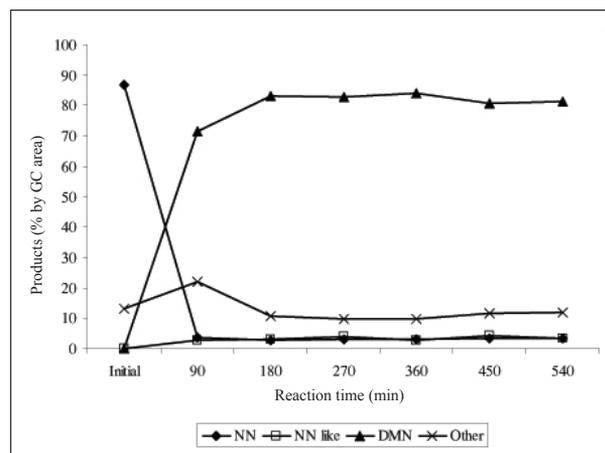
Table 2: Fuel properties of 1,1 dimethoxynonane ($C_{11}H_{24}O_2$)

Test properties	Measured values (Jet A-1 standard)
Molecular weight (g)	188.3
Boiling point (ºC)	96 − 98
Density (g/L)	0.85 (0.775 − 0.840)
Flash point (ºC)	68 (≥ 38.0)
Ignition point (ºC)	194
Freezing point (ºC)	- 42.6 (≤ - 47.0)
Specific energy (MJ/kg)	39.7 (≥ 42.8)
Solubility	Insoluble in water

Figure 6: Time course of 1,1-dimethoxynonane (acetal) from nonanal (aldehyde) NN (nonanal); NN like (nonanal like compounds); DMN (dimethoxynonane) and other (other compounds)

Table 3: Fuel properties of 10 % acetal (1,1-dimethoxynonane)-blend Jet A-1

Test properties	Jet A-1 standard	Idemitsu Kosan Jet A-1	10 % acetal blended Jet A-1	Test method
Density (at 15 ºC) (g/L)	0.775 − 0.840	0.796	0.801	JIS K2249
Flash point (ºC)	≥ 38.0	42.5	43.5	JIS K2265
Specific energy (MJ/kg)	≥ 42.8	43.3	43.05	JIS K2279
Smoke point (mm)	≥ 25.0	25.5	25.0	JIS K2537
Existent gum (mg/100 mL)	≤ 7.0	0.0	0.0	JIS K2261
Freezing point (ºC)	≤ - 47.0	- 51.5	- 52.0	JIS K2276
Total sulphur (ppm)	≤ 3,000	310	280	JIS K2541
Viscosity (at -20 ºC) (mm²/s)	≤ 8.00	3.34	4.16	JIS K2241
Total acidity (mg KOH/g)	≤ 0.015	0.01	0.04	JIS K2501
Copper corrosion classification (at 100 ºC, 2h)	≤ 1	1a	1a	JIS K2513
Thermal stability (at 260 ºC)				JIS K2276
Filter pressure diff. hap	≤ 33.25	0.0	0.0	
Tube deposit rating visual	-	0	0	

The fuel properties of 1,1-dimethoxynonane obtained from nonanal are shown in Table 2. The freezing point and the specific energy, which were -42.6 ℃ and 39.7 MJ/kg were comparable with Jet A-1 standard.

An acetal blend Jet A-1 fuel was finally prepared by mixing 10 % of 1,1- dimethoxynonane. Significant fuel properties of this blend were analysed and then compared with those of the standard Jet A-1 and commercially available Jet A-1, which was employed for the preparation of blend jet fuel. As shown in Table 3, 10 % blending of 1,1- dimethoxynonane did not change the fuel properties of Jet A-1. The thermal stability was also within the acceptable range. The filter pressure difference was zero at the test temperature of 260 ℃. This indicates that the acetal was stable and did not induce any polymerization. The only limitation appears to be the slightly higher total acidity (acid value), which is probably caused by the residual nonanal in the crude 1,1- dimethoxynonane. This can be addressed by practical purification steps.

CONCLUSION

For the production of bio-jet fuel from plant oil, its fatty acid components should be cracked into shorter carbon chains around C8 to C10. In the present study, the reaction products formed by the cracking of fatty acids were investigated in order to assess whether they satisfy the quality standards of aviation fuels. The significant findings are as follows;

• The major chemical compound produced by the electro-reduction of ozonized methyl oleate was aldehyde, but its thermal stability was poor that the product may not be used as a blending compound for jet fuel.

• Ester and acetal, which can be derived from aldehyde were more thermally stable than their parent aldehydes. However, although the methyl ester with C8 (methyl octanonate) had a satisfactory flash point and a specific energy, its freezing point was too high.

• The fuel properties of 1,1-dimethoxynonane (the acetal derived from nonanal) are comparable to that of Jet A-1 standard and did not significantly affect the properties of Jet A-1 even at 10 % blending. The thermal stability of the blend was also acceptable. This indicates that acetal-based bio-jet fuel, which can be produced under milder and less energy-intensive reaction conditions, may be considered as an alternative aviation biofuel.

• A limitation regarding the high total acidity (acid value) of the acetal blend was apparent from the initial evaluations. This may be caused by the residual nonanal in the 1,1- dimethoxynonane.

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