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Potential renewable oxygenated biofuels for the aviation and road transport sectors

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1. Introduction

Due to the increasing pressure to reduce greenhouse gases and the concerns over the increasing scarcity of fossil fuels replacing road or aviation transport fuels with more sustainable alternatives is a pressing scientific and engineering challenge. In the short to medium term replacements must be of the sort that can be used within the current infrastructure to allow a smooth transition to low carbon economies. One alternative fuel is biodiesel, the fatty acid methyl esters (FAMEs) derived from vegetable, animal or waste oils. However, there are four key issues which make biodiesel a poor replacement for mineral diesel:

1. There is insufficient land to produce enough oil feedstock to replace diesel fuel and feed a growing global population.

2. The fatty acid profile of biodiesel, and therefore the fuel properties are highly variable and dependent on the source and growing conditions.

3. As a consequence of containing polyunsaturated esters biodiesel has poor oxidative stability.

4. Biodiesel also contains long chain saturated and monounsaturated esters leading to poor low temperature properties.

These issues lead to adverse consequences. The feedstock is not sufficient to meet more than a fraction of demand, engines cannot be adapted to the fuel due to the variability in fuel performance, higher blending cannot be used in colder climates and without effective antioxidants polymeric gums and solid material are produced that can, if present in the fuel prior to combustion, block the fuel filters and injectors and reduce the efficiency of the engine [1]. For the next generation of biofuels to be effective these issues must be addressed. Potential solutions to these four key issues are:

1. The fuel could be derived from cellulosic sources, which is far more abundant and can be grown on marginal land or collected from waste food.
2. The fuels must have a known molecular formula, like bioethanol, that behaves predictably regardless of the feedstock source.
3. The fuel must contain no polyunsaturated components to reduce the oxidative instability.
4. To improve the low temperature behaviour the fuel must contain shorter chain saturates or monounsaturated components.

One potential method of converting cellulosic biomass is through fermentation. Generally fermentation is used to produce bioalcohols and currently there are a number of industrial ventures producing ethanol or butanol from cellulose and hemicelluloses [16, 17]. Alcohols are not the only oxygenated fuels to have been investigated as a replacement to fossil fuels. Ethers, produced by the dehydration of alcohols have been shown to be effective blending additives with petrol [18].

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1   Substituted fufurals and furans can be produced by the acid hydrolysis of cellulose and catalytic

2   chemical upgrading [19]. These compounds are suitable for use in spark ignition engines, and the

3   effect of blending on the petrol properties has been assessed [20]. Another major product from the

4   acid hydrolysis of cellulose is levulinic acid. Christensen *et. al.* examined levulinate esters as diesel

5   blend components [8]. In this study they found that though ethyl levulinate was a poor additive

6   being relatively immiscible with diesel, butyl levulinate was miscible, had an extremely low melting

7   point, and with a cetane improver additive gave a similar performance to straight diesel fuel when

8   used in a 20% volumetric blend.

9   Though biodiesel can be used in a gas turbine engine, the poor low temperature properties

10   make it unsuitable for the aviation sector where the fuel must have a freezing point of -47 °C or

11   below. Though *n*-butanol and dibutyl ether have been suggested as possible alternatives for the

12   aviation sector the flash points, 35 °C and 25 °C respectively, are too low compared to the DEF STAN

13   91-91 (Jet A-1) minimum of 38°C [21, 22]. A further possibility for converting cellulose is though

14   fermentation to a range of short chain acids. Ethyl acetate, ethyl propionate and ethyl butyrate have

15   been shown to be suitable fuels for a Homogeneous Charge Compression Ignition (HCCI) engine,

16   though they ignite more slowly than ethanol [23]. There are many other acids that can be produced

17   industrially or have the potential to be by fermentation (table 1). Due to the acidity and high melting

18   points the acids must be esterified prior to use, though this is achievable by a low energy chemical

19   step and these compounds can be transformed into short chain esters with the potential to be used

20   as liquid transport fuels.

21   In this study a range of organic acids, that can potentially be produced in one step from biomass

22   via fermentation were esterified with either *n*-butanol or ethanol. The properties of these fuels were

23   then compared to other oxygenated biofuels and relevant hydrocarbons. The suitability of these

24   compounds as replacements for aviation, diesel or petrol fuels was assessed.

2. Experimental Section

2.1 Materials

Acetic acid, propionic acid, butyric acid, oxalic acid, malonic acid, succinic acid, malic acid, itaconic acid, fumaric acid, citric acid, ethanol, n-butanol, ethyl acetate, ethyl butyrate, butyl butyrate, ethyl levulinate, butyl levulinate, butyl lactate and butyl butyrl lactate were purchased from Sigma-Aldrich, UK and were used without further purification. Kerosene, diesel and petrol were bought from standard fuel suppliers. Deuterated solvents (CDCl$_3$, D$_2$O) for ^{1}H NMR analysis were purchased from Fluorochem.

2.2 Methods

2.2.1 Esterification

Diethyl fumarate, diethyl malate, diethyl malonate, diethyl succinate, diethyl oxalate, ethyl propionate and triethyl citrate were synthesised according to the following method. A round bottom flask was charged with the appropriate acid (0.3 mol), ethanol (138 g, 175 ml, 3 mol) and 3 wt% (with respect to the starting acid) of H$_2$SO$_4$ to catalyse the esterification. The reaction mixtures were stirred under reflux for 24 hours. On reaction, the mixtures were washed with distilled water (4 × 50 ml) to remove the sulphuric acid as well as any unreacted acid and ethanol. The resulting fuel was purified by removing any excess alcohol or water under reduced pressure. The product, was established by ^{1}H NMR to be >99% pure. Butyl acetate, butyl propionate, dibutyl fumarate, dibutyl itaconate, dibutyl malate, dibutyl malonate, dibutyl succinate dibutyl oxalate and tributyl citrate were synthesized in an identical manner, except for the substitution of n-butanol (222.2 g, 3 mol) instead of ethanol.

To test their cetane number and tribology properties, dibutyl fumarate, dibutyl malonate, and dibutyl succinate were synthesised on a ~1 l scale via a simple esterification reaction. A 2L round

bottom flask was charged with the appropriate acid (5.85 mol), *n*-butanol (962 g, 1190 ml, 13 mol), and approximately 3 wt% (with respect to the acid) of H_2SO_4. The reaction mixtures were left heating under reflux overnight. The mixtures were washed with distilled water (4 × 250 ml) to remove the sulphuric acid as well as any unreacted acid. The resulting fuel was purified by removing any excess alcohol or water under reduced pressure. The product purity (>99%) was establish by ^{1}H NMR. Diethyl succinate was synthesised in an identical manner, except for the addition of ethanol (598 g, 758 ml, 13 mol) instead of n-butanol.

2.2.2 Kinematic viscosity

The kinematic viscosities of all promising esterified fuel products were measured with calibrated

Canon-Fenske Routine Viscometers No. 75 and 150, in accordance with standard test methods set

out in ASTM D445 and ISO 3104 at 40 °C or -20 °C where appropriate.

2.2.3 Blending studies

The esterified fuel products were mixed in a 50:50 blend with the relevant hydrocarbon fuel to

determine miscibility. Those found not to be miscible with current fuels were added drop wise until

the mixture became translucent to determine their solubility in the relevant hydrocarbon fuel.

On establishing that the fuels were miscible the fuel mixtures were held in a cold bath and the

temperature reduced by 5 °C and held for 10 minutes until the cloud point of the relevant

hydrocarbon fuel was reached.

2.2.4 Energy content

The energy content of promising fuels products (specifically diethyl succinate, dibutyl succinate,

dibutyl malonate, dibutyl oxalate, dibutyl fumarate, butyl lactate, butyl butyrate and butyl

1 butyryllactate) were measured using a Parr 1341 Plain Oxygen Bomb Calorimeter, in accordance

2 with ASTM D240.

3

4 **2.2.5 Oxidation studies**

5 A 10 ml round bottom flask was charged with 5 ml of the fuel, these were dibutyl succinate, diethyl

6 succinate, dibutyl itaconate, dibutyl fumarate and rapeseed methyl ester (see supporting

7 information for full specification). The flask was placed in an oil bath at the required temperature

8 (110°C) and the compounds were mechanically stirred at a constant rate, subjected to constant light

9 intensity and constant airflow for 24 hours. The resulting mixture was analysed by ^{1}H NMR and GC-

10 MS.

11

12 **2.2.6 Cetane number, octane number and tribology**

13 Cetane number (CN) analysis and tribology studies were conducted by Saybolt, United Kingdom Ltd.

14 The cetane number was ascertained using a Co-operative Fuel Research (CFR) engine to the testing

15 standard ISO 5165. The lubricity was ascertained by using a High Frequency Reciprocating Rig (HFRR)

16 and measuring the corrected wear scar diameter at 60 °C, this conforms to the test method ISO

17 12156-1. The research octane number (RON) of butyl butyrate was conducted by Intertek testing, UK

18 on a R.O.N. engine to the testing standard EN ISO 5164.

19

20 **3. Results and Discussion**

21 **3.1 Properties of the pure compounds**

22 To initially screen the products for their effectiveness as fuels, the melting point, flash point,

23 kinematic viscosity and density were taken into account and compared to the equivalent

24 hydrocarbon fuel (tables 2 - 4). Ethyl acetate has an extremely low melting point and flash point

6

1   making it suitable as a petrol replacement as opposed to butyl acetate where the flash point is too

2   high for an effective replacement to petrol but too low for use as a diesel or aviation fuel. Ethyl and

3   butyl propionate were similarly dismissed. Butyl butyrate has a flash point above the minimum

4   required in the aviation standard and a melting point far lower than kerosene making it a potential

5   biofuel for this application.

6   Most of the monoesters exhibit flash points below the minimum of 55°C for diesel fuel. Ethyl

7   lactate, butyl lactate and butyl butyryllactate, all have higher flash points which fall within the diesel

8   fuel specification, however, the viscosity of ethyl lactate is too low to be considered as a

9   replacement for diesel fuel. Similarly diethyl oxalate and diethyl malonate have viscosities that are

10   too low to act as a replacement for diesel, where diethyl malate, dibutyl malate, diethyl fumarate

11   and diethyl itaconate have too high melting points. The viscosity and the melting point of a

12   compound is greatly increased if inter molecular bonding, such as hydrogen bonding or dipole

13   interactions are possible. For this reason the most successful potential fuels in this regard have no

14   alcohol groups and tend to have longer butyl rather than shorter ethyl chains. Though viscosity can

15   be altered with additives such as low molecular weight organic polymers, the need for further

16   additives would drive the cost of these alternative fuels up, it is likely that only blending with the

17   correct fuel would therefore be an option.

18   The butyl substituted succinate, oxalate, fumarate, malonate and itaconate all fall within the

19   ASTM D975 and EN 590 diesel specification and were therefore investigated for their further fuel

20   properties. Triethyl and tributyl citrate were found to be too viscous to be used as a replacement for

21   hydrocarbon fuels and would only be able to be used as an alternative fuel at low blend levels with

22   mineral diesel. A further stipulation in the Jet A1 standards is the kinematic viscosity of the fuels at -

23   20 °C. This must be no more than 8 mm^2s^{-1}, butyl butyrate, diethyl malonate, dibutyl malonate, butyl

24   levulinate and ethyl levulinate were therefore tested (fig. 1).

1   The viscosity of diethyl malonate and butyl butyrate falls within the Jet A-1 aviation

2   specification though dibutyl malonate is far too viscous at the temperature required to be

3   considered a suitable replacement. The previously reported ethyl and butyl levulinate both fall

4   within the Jet A1 specification.

5

6   **3.2 Miscibility of the esters**

7   All the promising fuel products were tested for their miscibility with the appropriate hydrocarbon

8   fuel (table 5). All fuels derived from fermentation – with the exception of diethyl malonate – were

9   completely miscible with the desirable hydrocarbon at room temperature, this is in contrast to ethyl

10   levulinate. None of the fuels tested were found to have a high mass solubility with water, however

11   dibutyl succinate and dibutyl fumarate show less water solubility and are therefore more promising

12   fuel substitutes than butyl lactate or diethyl succinate. It seems likely that the increase in

13   hydrophobicity caused by the longer alkyl chain is necessary to produce a reasonable substitute for

14   hydrocarbon fuels.

15   To be considered as a suitable substitute, novel biofuels must also be fully miscible at the

16   lowest temperatures that the fuels will be used at. To examine this, the biofuels were blended with

17   the appropriate fossil fuel in a 50:50 volumetric mix. Butyl butyryllactate, dibutyl oxalate, dibutyl

18   malonate, dibutyl succinate and dibutyl fumarate remained miscible down to -19 °C i.e. the cloud

19   point of the mineral diesel used in this study. Butyl levulinate was found to separate at sub-zero

20   temperatures from the diesel fuel and from aviation kerosene. The kerosene compatible fuel butyl

21   butyrate remained miscible up to -47 °C, when the cloud point of the fuel was reached. Dibutyl

22   malonate was not miscible at these temperatures, demonstrating the further unsuitability of this

23   fuel for the aviation sector.

24

3.3 Energy content

Bioethanol has a far lower volumetric energy density than petrol therefore reducing the range of the

vehicle. Biodiesel has a higher energy density more akin to diesel, though it is still slightly reduced

depending on the source and FAME profile. In this study the energy density of the fuels were

examined by bomb calorimetry (fig. 2). All the fuels tested have a lower energy density per unit

weight than the fossil fuels. However, this discrepancy is far less pronounced by volumetric fuel

density due to the higher densities of the oxygenates. The diesters tested all have a similar energy

density, the lowest is diethyl succinate followed by dibutyl oxalate, dibutyl malonate and dibutyl

succinate, with this trend of increasing energy density reflecting the decreasing oxygen content. All

the fuels tested have a higher energy density than ethanol though only butyl butyrate and dibutyl

succinate have a comparable energy content to *n*-butanol. The energy density of the rapeseed

methyl ester used in this study was found to be higher than all the novel fuels tested albeit slightly

lower than the mineral diesel.

3.4 Oxidative stability

The oxidative stability of biofuels such as biodiesel is generally measured by the Rancimat test where

the fuel is heated to 110 °C under a steady flow of air (10 L h^{-1}). The volatiles, mainly small organic

acids, are collected in a water trap and the conductivity of this is measured [29]. To examine the

stability of the fuels in this study, the samples were held under Rancimat like conditions but were

analysed using ^{1}H NMR after 24 hours reaction time. The oxidation was then compared to rapeseed

methyl ester (fig. 3). None of the saturated or monounsaturated esters had changed over the 24

hour period, unlike RME where over 90% of the unsaturated components had degraded over the

timeframe. The main mechanism of oxidation of these types of compounds proceeds with the

formation of a radical hydrocarbon species on the bisallylic carbon, the double bonds will then

1 isomerise into a more stable conjugated structure, this radical reacts with oxygen to form a variety

2 of oxygenated intermediates [30]. As the conjugated structure is necessary to stabilise the system,

3 monounsaturated and saturated esters are far more stable than the polyunsaturated esters present

4 in most vegetable oils.

5

6 **3.5 Toxicity**

7 Though not regulated through the aviation or road transport standards toxicity is a consideration in

8 the design of novel biofuels. A comparison of the toxicity of the proposed fermentation fuels with

9 their hydrocarbon counterparts was undertaken by reference to the material safety datasheets

10 (MSDS). It was found that dibutyl succinate, diethyl succinate, butyl butyrate, dibutyl fumarate and

11 dibutyl malonate are more benign than their hydrocarbon counterparts [31]. Dibutyl oxalate,

12 however, can cause skin irritation, allergic reaction, serious eye damage or respiratory irritation. As

13 such dibutyl oxalate was not considered suitable for further study.

14

15 **3.6 Lubricity of the diesel substitutes**

16 The standard test to measure the lubricating performance of fuels set out in the ASTM D6079 and

17 EN 590 is by the HFRR (High Frequency Reciprocating Rig) method. In this method a hardened steel

18 ball vibrates against a steel plate immersed in the test fuel. The wear scar diameter of the plate is

19 then assessed against a reference fuel. In this study the four potential diesel substitutes were

20 examined by HFRR (ISO 12156-1) to quantify the fuel lubricant performance (fig. 4). Boundary

21 lubricants tend to be similar to surfactants and have polar and non-polar groups. The polar groups

22 such as those containing oxygen, nitrogen or sulphur become attracted to the metal or metal oxide

23 surface, the non-polar group then extends away from this surface creating a malleable organic layer

24 allowing the parts to move across one another with reduced friction. Esters have been shown to be

1   moderately effective polar groups [32], and as such biodiesel has been demonstrated to have

2   excellent properties as a lubricant due to the polar ester group and hydrophobic fatty chain [33]. The

3   esters tested throughout this report all fall within the EN and ASTM specifications for lubricity,

4   though the butyl substituted esters are more effective than diethyl succinate presumably due to the

5   increased hydrophobicity of the butyl over the ethyl group. Dibutyl succinate demonstrated the best

6   lubricity, and could potentially be used as a lubricity improving additive.

7

8   **3.7 Octane and cetane number of the relevant fuel substitutes**

9   Cetane number (CN) is an important metric in determining the ignition quality of fuels used in

10   compression-ignition engines. The higher the CN the more easily the fuel ignites in the combustion

11   chamber. Though the CN requirements of an engine depend on its size, load and speed, there are

12   minimum levels set out in the standards that a fuel must conform to. These are 40 by the US

13   standard ASTM D975 and 51 by the European standard EN 590. Though fuels with excessively high

14   CN can produce increased levels of PM, more problematic is when the cetane number is too low.

15   Fuels with low cetane numbers can produce excessive NO_x and PM emissions as well as reducing the

16   engine efficiency [34]. In this study the cetane number of the four diesel like fuels was analysed on a

17   CFR engine according to the standard test procedure ISO 5165 (fig. 5). The cetane number of a fuel is

18   dependent on a range of physical and molecular properties. It has previously been shown that for

19   longer chain esters an increase in the molecular weight or carbon number of the fuel, increases the

20   cetane number substantially [35]. However, this trend is not observed with the esters examined over

21   the course of this project as both diethyl succinate (C_8) and dibutyl succinate (C_{12}) have the same

22   cetane number. In a further study, the carbon number of an ester was shown to only moderately

23   correlate with cetane number and a host of other factors such as the boiling point, melting point,

24   heat of combustion, refractive index and density were all shown to have an effect, though density

1   and the boiling point were found to have the highest correlations [36]. Higher densities and lower

2   boiling points correlated with lower cetane numbers. All the esters screened for their cetane

3   number in this study had densities far higher than diesel fuel and much reduced boiling points

4   indicative of low cetane number fuels.

5   The cetane numbers for the four fuels do not vary greatly depending on stucture. As with

6   ethyl and butyl levulinate which have a CN of 5 and 14 respectively [8], the CN is too low to be used

7   as a fuel without either blending with the corresponding diesel fuel or using additives such as 2-

8   ethylhexyl nitrate, to improve the combustion characteristics. Christensen et. al. estimated that

9   when blending butyl levulinate in a 20% volumetric blend (B20) with diesel fuel the cetane was

10   roughtly double that of the pure ester. A further increase in the cetane number was acheived by

11   adding 2-EHN, at 1584 ppm bringing the B20 blend up to ASTM standards [8]. It is likely that similar

12   methods would need to be employed with the diester fuels.

13   The octane number, a measure of the fuel performance in spark ignition engines, is inversely

14   proportional to the cetane number. Though other physical properties make these fuels unsuitable as

15   petroelum substitutes without blending, the poor cetane numbers (and hence good octane rating)

16   mean that these fuels could potentially be used as octane improving additives in blends with petrol.

17   Ethyl acetate has an octane rating of 116 [37], over the course of this study butyl butyrate was

18   found to have a similarly suitable research octane rating of 97.3, higher than the minimum of 95 set

19   out in the EN 228, making it an ideal candidate as a gasoline or aviation fuel substitute.

20

21   **3.8 Prospective costs of the feedstock acids**

22   The expense of the acids will be a large factor in whether the esters presented in this report will

23   become biofuels used in the future. At present the acids described in this investigation are

24   manufactured on a smaller scale than the bioalochols or biodiesel. These range from over 1.7 million

tonnes of citric acid produced by fermentation in 2007 to the production of malonic acid by

fermentation which has yet to be industrialised [38]. At present the cost of the acids reflect this scale

of production, where citric acid costs near $1.00 kg^{-1} [38], itaconic acid costs near $2.00 kg^{-1} and

succinic acid costs at present between $ 5.00-9.00 kg^{-1} [39, 40]. However, the cost of succinic acid

has been predicted to fall to between $0.50 -1.00 kg^{-1} or even lower when the wide scale

manufacture of this acid by fermentation becomes the norm [40,41]. While these costs are

prohibitively high at present they have the potential to be reduced substantially by economies of

scale.

4. Conclusion

Butyl butyrate was found to be compatible with petrol and has similar properties to the recently

published alternative fuel substitutes ethyl acetate, ethyl propionate and ethyl butyrate, mentioned

in the introduction section. Unlike these fuels, butyl butyrate was also compatible with kerosene

with a melting point below -47 °C and a flash point above 38 °C, as well as remaining miscible with

kerosene at low temperatures. As such butyl butyrate is a promising additive for the aviation sector,

though more work is needed in this area to examine the effects that these types of oxygenated fuels

have on the operation of an aircraft, especially at low operating temperatures. The major application

for the fermentation esters presented in this paper are as blending agents with mineral diesel. Four

potential fermentation products could be used as a blend with diesel fuel; dibutyl succinate, dibutyl

malonate, dibutyl fumarate and diethyl succinate. Each of these fuels had a suitable kinematic

viscosity, flash point, melting point and miscibility with diesel. The energy density of each fuel was

roughly 80% that of diesel and though the cetane numbers were low, cetane improver additives and

blending down with diesel fuel can be used to bring this up to specification. As these fuels have a

1   defined structure, irrespective of the feedstock source, the engine could potentially be adapted to

2   more easily run on this type of biofuel.

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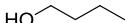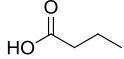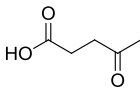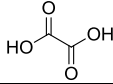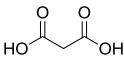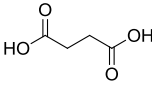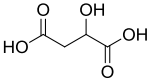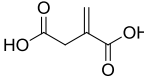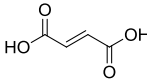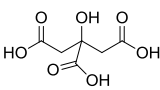
Product	Structure	Example organism
Ethanol		*Saccharomyces cerevisiae,* [2]
n-Butanol		*Clostridium acetobutylicum,* [3]
Acetic acid		*Acetobacter aceti,* [4]
Propionic acid		*Propionibacterium acidipropionici,* [5]
Butyric acid		*Clostridium tyrobutyricum,* [6]
L-Lactic acid		*Rhizopus oryzae,* [7]
Levulinic acid		by the acid hydrolysis of cellulose, [8]
Oxalic acid		*Aspergillus niger,* [9]
Malonic acid		*Cerrena unicolor,* [10]
Succinic acid		*Actinobacillus succinogenes,* [11]
Malic acid		*Aspergillus flavus,* [12]
Itaconic acid		*Aspergillus terreus,* [13]
Fumaric acid		*Rhizopus arrhizus,* [14]
Citric acid		*Aspergillus niger,* [15]

1   *Table 1. Possible fermentation products derived from cellulosic biomass*

2

Product	Flash point (°C)	Melting point (°C)	Cloud point (°C)	Pour point (°C)	Boiling point (°C)	K. viscosity @ 40 °C (mm^2/s)	Density @ 15 °C (g/cm^3)
Diesel	min 55	-	-15 - 5	-35 - -15	360 (95% recov.)	2.00 - 4.50	0.820 - 0.845
Kerosene (Jet A-1)	min 38	min -47	-	-	max 300 (100% recov.)	max 8.00 (@ -20°C)	0.775 - 0.840
Petrol	-43	-	-57	-	max 210 (100% recov.)	0.37-0.44 (@ 20°C)	0.720 - 0.775
Bioethanol	8.9	-114	-	-	72.6	1.5 (@ 20°C)	0.794
Biobutanol	35	-90	-	-	118	3.6 (@ 20°C)	0.814
Biodiesel (RME)	min 120	N/A	-3 -15	-5 - 10	315 - 350	3.50-5.00	0.860 - 0.900

1   *Table 2. Properties of fuels commonly used throughout the EU,* values listed correspond to Diesel (EN 590) ,

2   Kerosene (Jet A1 standard), Petrol (EN 228) and RME (EN 14214) where appropriate *[8, 18, 22, 24-27]*

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Product	Flash point (°C)	M.pt (°C)	B.pt. (°C)	K. viscosity @ 40 °C (mm^2/s)	Density @ 15 °C (g/cm^3)
Ethyl acetate	-3.3	-84	77	0.43	0.91
Butyl acetate	22	-78	126	0.71	0.87
Ethyl propionate	12	-73	95	0.73	0.89
Butyl propionate	38	-90	146	0.76	0.88
Ethyl butyrate	19	-98	122	0.70	0.87
Butyl butyrate	49	-91	165	0.90	0.87
Ethyl levulinate	78	<-60, [8]	206	1.52	1.01
Butyl levulinate	98	<-60, [8]	238	2.03	0.97
Ethyl lactate	55	-26	154	1.64	1.03
Butyl lactate	69	-28	170	2.24	0.98
Butyl butyryllactate	125	<-50	272	2.23	0.99

1   *Table 3.* *Fuel properties of pure monoester fermentation products potentially derived from cellulosic biomass,*

2   *the kinematic viscosity was obtained experimentally all other data was obtained from a substance search from*

3   *the Scifinder website and references found within [28], unless otherwise stated.*

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Product	Flash point (°C)	M.pt (°C)	B.pt. (°C)	K. viscosity @ 40 °C (mm^2/s)	Density @ 15 °C (g/cm^3)
Diethyl oxalate	76	-41	185	1.31	1.07
Dibutyl oxalate	108	-30	240	2.16	1.05
Diethyl malonate	100	-50	199	1.47	1.05
Dibutyl malonate	117	-83	252	2.33	1.00
Diethyl succinate	100	-21	218	1.86	1.04
Dibutyl succinate	123	-29	274	2.91	0.99
Diethyl malate	85	<-50	281	5.68	1.15
Dibutyl malate	121	<-50	344	6.04	1.06
Diethyl itaconate	108	<-50	228	4.31	1.04
Dibutyl itaconate	142	<-50	307	3.28	0.99
Diethyl fumarate	93	1	214	3.95	1.07
Dibutyl fumarate	136	-18	280	3.56	1.00
Triethyl citrate	96	-55	294	14.10	1.18
Tributyl citrate	121	-20	390	13.88	1.08

1 **Table 4.** Fuel properties of pure diester fermentation products potentially derived from cellulosic biomass, the
2 kinematic viscosity was obtained experimentally all other data was obtained from a substance search from the
3 Scifinder website and references found within [28].

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Fuel	Petrol (25°C, g/L)	Diesel (25°C, g/L)	Kerosene (25°C, g/L)	Mass solubility in water pH 7, 25°C (g/L)
Ethyl acetate	M	-	-	39
Ethyl butyrate	M	-	-	8.5
Butyl butyrate	M	-	M	1.9
Ethyl levulinate	-	151.5	7.5	30
Butyl levulinate	-	M	M	6.4
Butyl lactate	-	M	-	38
Butyl butyryl lactate	-	M	-	0.91
Dibutyl oxalate	-	M	-	0.93
Diethyl malonate	-	-	53	21
Dibutyl malonate	-	M	M	0.91
Diethyl succinate	-	M	-	10
Dibutyl succinate	-	M	-	0.48
Dibutyl fumarate	-	M	-	0.43

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2   **Table 5.** Miscibility of the biofuels with the relevant fossil fuel and water, where M = completely miscible, - =
3   not applicable due to the incompatible fuel properties. The miscibility was found experimentally the mass
4   solubility was obtained from a substance search from the Scifinder website and references found within [28].
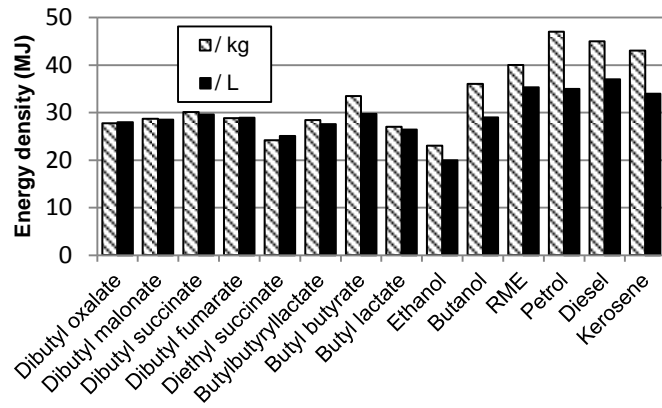
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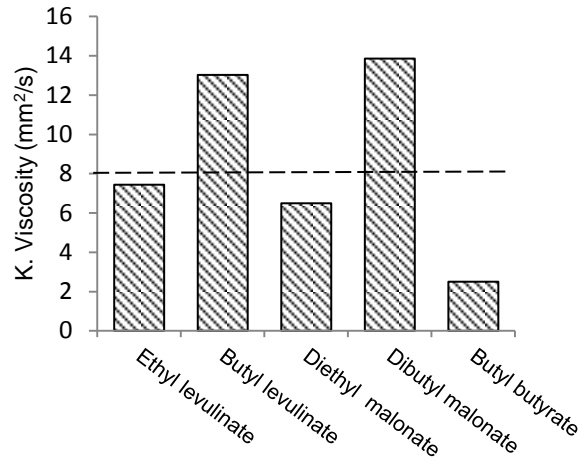
Fig 1. *Kinematic viscosity of the three potential aviation fuels at -20 °C, the dashed line indicates the maximum viscosity allowable in the Jet A-1 aviation standard [22]*

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Fig 2. Volumetric and weight energy density for the potential biofuels derived from fermentation compared to
2 *the minimum energy densities found for aviation kerosene, mineral diesel and petrol.*
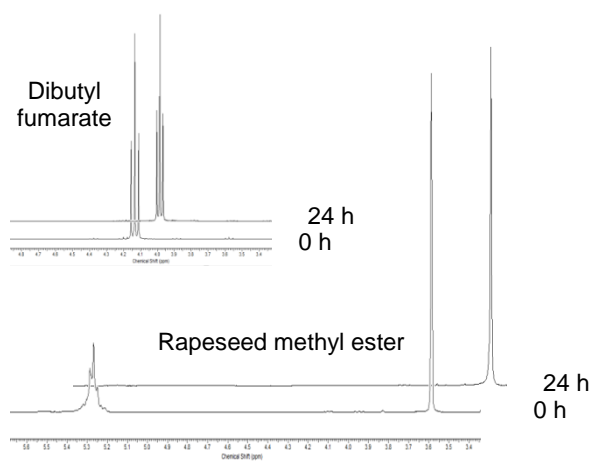3

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10   Fig 3. ^{1}H NMR spectra showing the degradation of the peak assignable to the double bonds in the oxidation of
11   dibutyl fumarate (δ 4.1 ppm) and rapeseed methyl ester (δ 5.3 ppm), after 24 hours at 110 °C.

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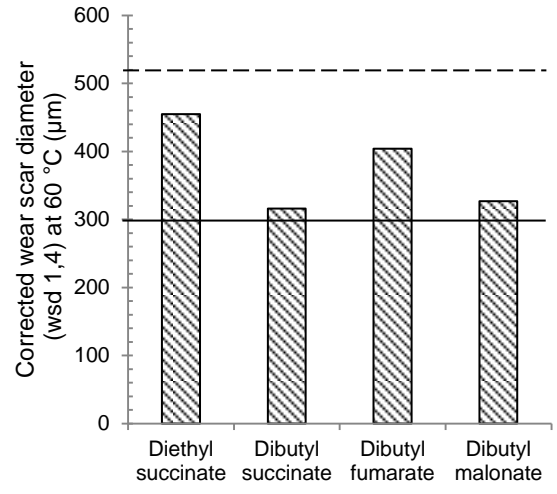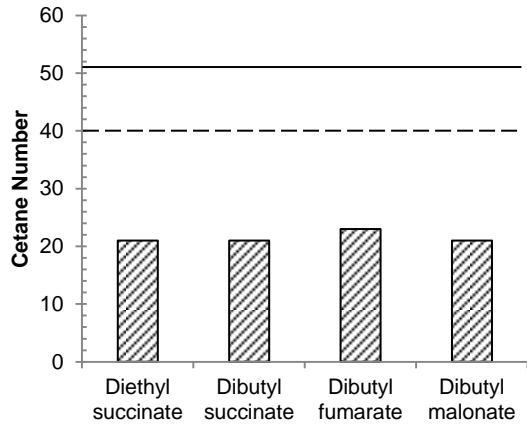1

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12   Fig 4. The corrected wear scar diameter as measured by HFRR, demonstrating the lubricity, for the
13   four likely diesel substitutes. The solid line shows the maximum allowable by EN 590, the dotted line
14   gives the maximum allowable by ASTM D975

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2   *Fig. 5 Cetane number for the four likely diesel substitutes, the solid line indicates the minimum required by EN*
3   *590, the dashed line by ASTM D975.*

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