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# Branched ketone biofuels as blending agents for Jet-A1 aviation kerosene

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## KEYWORDS

Butanol, Aviation, Biofuel, Biorefinery, Kerosene, Jet

## ABSTRACT

In this investigation a range of ketone biofuels produced from the alkylation of isoamyl alcohol and isobutanol were examined as potential blending agents with Jet A-1 aviation kerosene. The fuels were synthesised under solvent-free conditions using a Pd/C catalyst with  $K_3PO_4$ , previously reported for the alkylation of acetone, butanol, ethanol (ABE) fermentation mixtures. Reasonable yields and selectivity were achieved for branched alkylation products with up to 61 % produced from isoamyl alcohol and 64 % from isobutanol. The key aviation fuel properties of the mixtures were tested unblended and in 50% and 20% blends with Jet A-1 aviation kerosene. The freezing point of the fuels were all found to be below the required  $-47\text{ }^\circ\text{C}$  irrespective of blend or the temperature of the reaction. The energy density of the unblended fuels ranged between 30.4-41.36 MJ/kg depending on the temperature of the reaction and whether remaining alcohols were removed. While this is below the HHV of the Jet A-1 used (45.69 MJ/kg) the energy density of the 50% and 20% blends were more suitable with the isoamyl alcohol derived fuels having a maximum HHV of 44.31 MJ/kg at 50% blending and 44.99 MJ/kg at 20% blend with Jet A-1. The fuels derived from isoamyl alcohol produced above  $140\text{ }^\circ\text{C}$  were found to satisfy the flash point criterion ( $>38\text{ }^\circ\text{C}$ ) of the Jet A-1 specification, though the isobutanol derived fuels did not, producing fuels with flash points between  $33\text{ }^\circ\text{C}$  and  $35\text{ }^\circ\text{C}$ . The kinematic viscosity of the fuels were also tested at  $-20\text{ }^\circ\text{C}$ . Unblended only a few of the fuels analysed met the maximum viscosity requirement at  $-20\text{ }^\circ\text{C}$  of  $8\text{ mm}^2\text{ s}^{-1}$ , though this fuel property was improved substantially on blending with jet fuel. This work demonstrates that ketones produced from isoamyl alcohol through a simple alkylation have the potential to be used as blending agents with Jet A-1.

## INTRODUCTION

The aviation industry contributes approximately 2% of anthropogenic greenhouse gases and as such is under increasing global pressure to reduce carbon emissions through increasingly strict targets.<sup>1</sup> The development of renewable aviation biofuels, suitable for blending with aviation kerosene is therefore a key priority. Suitable aviation biofuels must possess a number of characteristics such as a high energy density, good atomisation, an ability to be relit at altitude though a low explosive risk on the ground, a suitably low viscosity, an extremely low freezing point and good chemical stability. The fuel should also be reasonably non-toxic and be widely available.<sup>2-6</sup>

While the hydroprocessing of lipids offers a suitable route to hydrocarbons, edible oils compete with arable land, promote deforestation and are not produced in suitable quantities. A more promising route to second generation biofuels is *via* fermentation of lignocellulosic biomass.<sup>7</sup> While the technology to produce second generation bioethanol is becoming established, the low energy density and high water affinity of ethanol have led to the development of alternatives such as n-butanol,<sup>8</sup> isoamyl alcohol and isobutanol.<sup>9, 10</sup> Despite the increased energy density of these compounds over ethanol, the water affinity, low flash point and low boiling point make these unsuitable for aviation without further upgrading.

Recently the alkylation of butanol, with acetone and ethanol, has been investigated as a potential method for the production of longer chain components more suitable for the current fuel market.<sup>11</sup> ABE products comprise both the nucleophilic  $\alpha$ -carbons of the acetone and the electrophilic  $\alpha$ -carbons of the alcohol. These paired functionalities enable the construction of higher alkanes from two, three and four-carbon precursors by the alkylation of acetone with the electrophilic alcohols. The alkylation results in the formation of long-chain ketones in the C<sub>5</sub> to C<sub>11</sub> range, which may be deoxygenated to paraffins suitable as components in gasoline.<sup>12</sup>

Guillena and co-workers investigated the double alkylation of acetone under transition-metal catalysed conditions.<sup>13, 14</sup> They hypothesised that two possible side reactions could occur in a transition metal-catalysed alkylation of acetone with primary alcohols; (i) self-condensation of the alcohol to the corresponding aldehyde (Guerbet reaction)<sup>15</sup> and (ii) combination of acetone to form diacetone alcohol, mesityl oxide, and other products.<sup>16</sup> Other work on the conversion of ABE includes their catalytic upgrading to ketones using hydrotalcite (HT) supported copper(II) and Pd(0) catalysts with integration of isopropanol from engineered strains of acetobutylicum.<sup>17</sup> The sequential condensation of butanol to Guerbet alcohol and subsequent alkylation of acetone by the Guerbet product has been demonstrated using HT supported ruthenium catalysts,<sup>18-21</sup> though the corresponding ketones were only obtained in a 20 % yield. A bimetallic HT supported Pd/Ru catalyst was shown to offer modest improvement on this yield. Where butanol was used as the reaction medium yield of the ketone was shown to increase to 58%.<sup>17</sup>

However, the straight chain ketones produced from the upgrading of these ABE mixtures have too high freezing points to be considered for aviation, while the derived hydrocarbons are only suitable for gasoline applications due to the low flash point. In this investigation the suitability of producing ketones with superior low temperature properties was examined by introducing branching into the ketone chain. This was achieved through the alkylation of isobutanol and isoamyl alcohol with acetone. The key fuel parameters of both the unpurified alcohol/ketone product mixtures and the mixtures after removal of remaining alcohol were assessed.

## EXPERIMENTAL METHODS

### MATERIALS

All chemicals (isoamyl alcohol >98%, isobutanol >99%, acetone >99.9%, potassium phosphate tribasic >98%, 5 wt% Pd/C) were purchased from Sigma Aldrich and used without further purification.

### METHODS

#### ALKYLATION REACTIONS

To a 350 mL stainless steel stirred pressure vessel (Parr Instruments, USA) was added 5.67g Pd/C (5 wt% Pd) and 64.40 g  $K_3PO_4$ . To this was then added 1.782 mol of alcohol substrate with 0.891 mol acetone. The vessel was then sealed and stirring commenced at 320 rpm. Heating was ramped to 120 °C, 140 °C or 160 °C at a rate of 3 °C/min. The reaction was allowed to proceed for 20 hours. On reaction, the contents of the reactor were then filtered twice to remove all heterogeneous catalyst and base. Reactions were undertaken in triplicate and the standard deviation calculated.

Reaction profiles were obtained by analysing aliquots obtained from the stirred pressure vessel, using GC-MS. The GC-MS used was an Agilent 7890A Gas Chromatograph coupled to an Agilent 5975C inert MSD with Triple Axis Detector. The machine was fitted with a DB-FFAP nitroterephthalic-acid-modified polyethylene glycol column and a He mobile phase (flow rate: 1.2 mL min<sup>-1</sup>) coupled with an Agilent 5977A inert MSD with Triple Axis Detector. A portion of the fuel samples (approximately 50 mg) was initially dissolved in 10 mL dioxane and 1 µL of this solution was loaded onto the column, pre-heated to 150 C. This temperature was held for 5 min and then heated to 250 °C at a rate of 4 °C min<sup>-1</sup> and then held for 2 min. The % areas, used as a quantitative method of analysis were calculated from the GC-FID chromatograph and compared against an internal standard.

## REMOVAL OF ALCOHOLS

For isoamyl alcohol mixtures, remaining alcohols were removed via vacuum distillation by removal of a mid boiling fraction at 70 °C (condenser inlet temperature) under a reduced pressure of 112 mmhg. The remaining alcohols in the unpurified mixture were predominantly found to be unreacted alcohol substrate by <sup>1</sup>H NMR. The other fractions (lower and higher boiling) were determined to contain negligible quantities of alcohols by <sup>1</sup>H NMR and were recombined to constitute 'alcohol free' fuels. .

An analogous process was carried out for the isobutanol mixtures however the removed fraction was obtained at 50 °C (condenser inlet temperature), and a pressure of 112 mmhg.

## FUEL PROPERTIES

Viscosities were determined in accordance with ASTM D445 using a Canon-Fenske capillary kinematic viscometer. Temperature modulation was achieved using a refrigeration unit. Samples within the viscometer were allowed to rest at the required temperature for a minimum of 5 minutes prior to viscosity measurement to allow temperature equilibration. The standard error was found to be lower than  $\pm 0.073 \text{ mm}^2\text{s}^{-1}$  at -20 °C,  $\pm 0.128 \text{ mm}^2\text{s}^{-1}$  at 20 °C and  $\pm 0.100 \text{ mm}^2\text{s}^{-1}$  at 40 °C.

Melting points of the fuels were determined visually by cooling of 1.5 cm<sup>3</sup> vials of the samples in a low temperature freezer, and periodically checking to see if the melting point had been surpassed. The samples were allowed to rest at each temperature for a minimum of 10 minutes in order to allow equilibration of sample and freezer temperatures. All melting points tested were found to have no more than 1 °C standard experimental error.

Energy content of fuels was determined in accordance with ASTM D3338 using an IKA C1 automatic bomb calorimeter. Approximately 0.3 g of each sample was used. The error of measurements was found to be <0.5 %.

Flash points of each sample were determined in accordance with ASTM D56/IP 170 using a Stanhope-Seta 99880-0 Flashcheck, tag, closed cup flash point machine. All flash point measurements were measured to an accuracy of  $\pm 1$  °C or better.

## RESULTS AND DISCUSSION

The products of the isoamyl alkylation (IAP) and isobutyl alkylation (IBP) were synthesised according to literature precedent.<sup>11</sup> The component products were determined by GC-MS spectroscopy. In each instance, alcohol and acetone substrates were used in a 2:1 molar ratio, with the intention that a double alkylation product in the carbon range C<sub>11-15</sub> would be achieved.

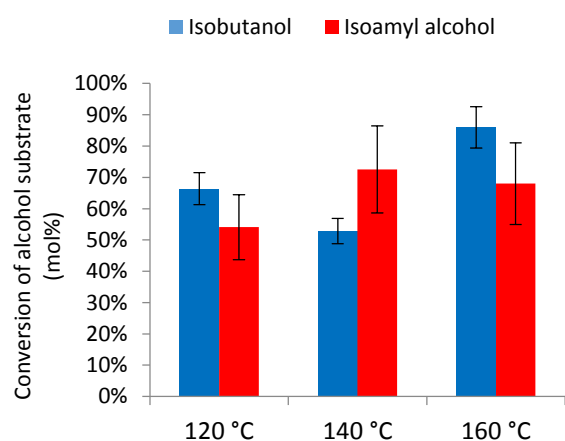


Figure 1: Conversion of starting alcohol substrates for reactions at varying temperatures. Error bars are given as standard deviation ( $n=3$ ).



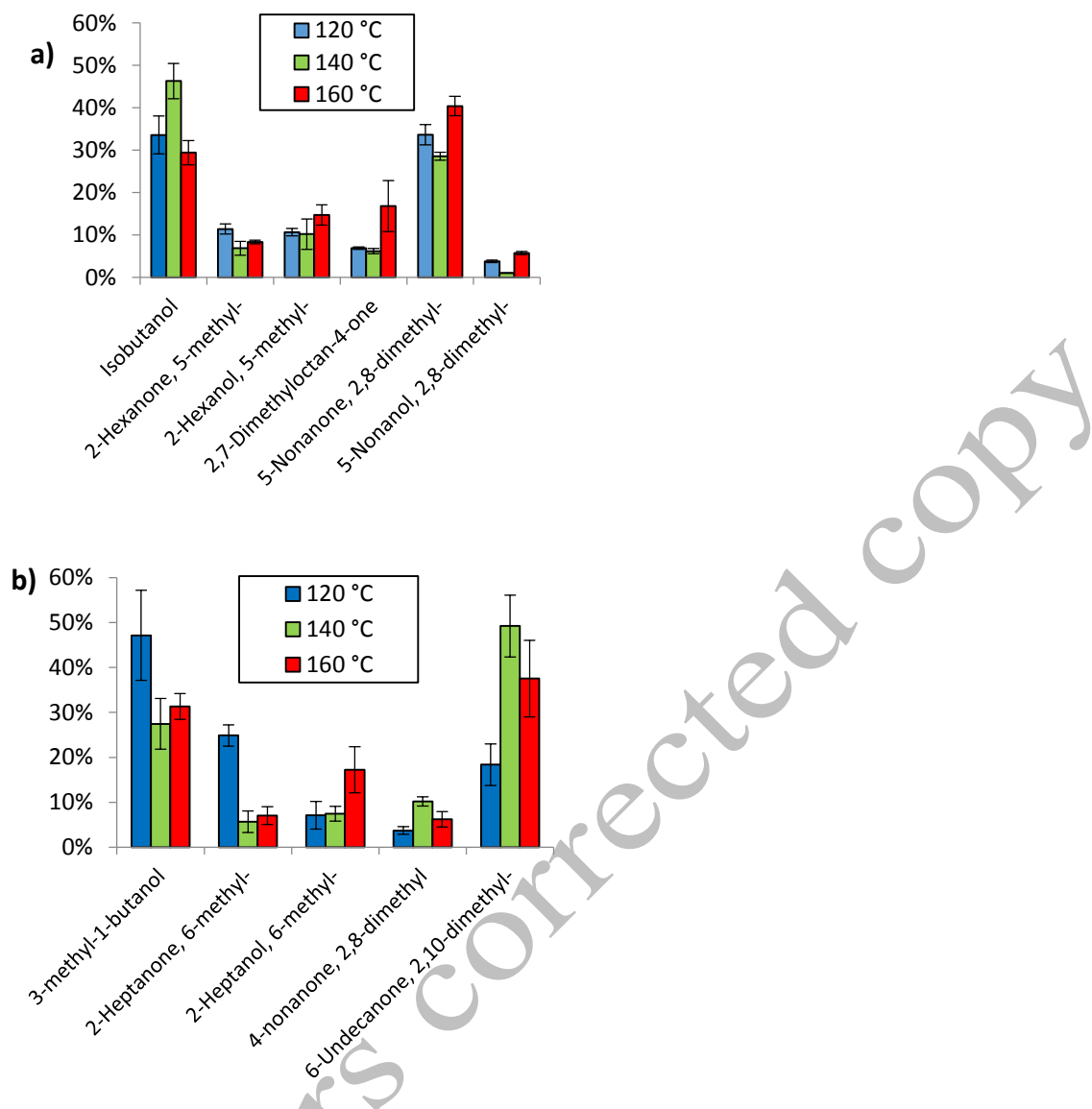


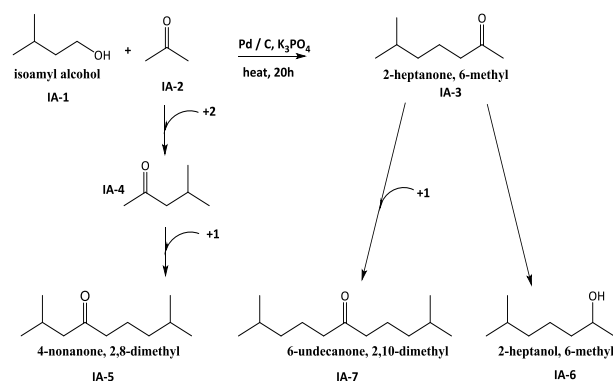
Figure 2: Product distribution of the branched alcohol reactions at 120 °C, 140 °C and 160 °C, 20 h, 0.3 mol% Pd catalyst. Where a) shows isobutanol-acetone alkylation reactions and b) shows the reaction of isoamyl alcohol. Standard deviation ( $n=3$ ) are presented as error bars.

Variation of product mixture composition at different reaction temperatures was observed (Figure 1). In the case of isobutanol-acetone alkylation, conversion of isobutanol to an alkylated product is 66%, 54% and 71% for reaction temperatures 120, 140 and 160 °C, respectively, showing a lower conversion at the mid-temperature than at lower or higher temperatures. With increasing temperature, the quantity of the single alkylate, 5-methyl-2-

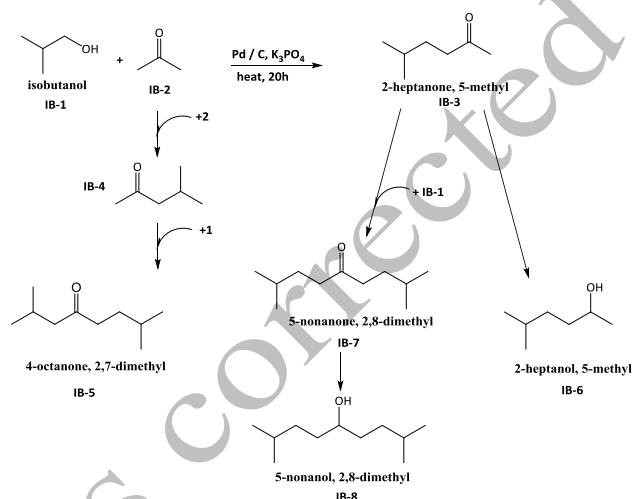
hexanone (as a proportion of non isobutanol products), decreases approximately linearly with increasing temperature. This single alkylate constitutes 17 % of products at 120 °C and 10 % at 160 °C. The opposite trend is observed for 2,7-dimethyl-4-octanone which depends on the initial self-condensation of acetone to form mesityl oxide, which increases with increasing temperature. It is thought that at the higher temperature there is relatively rapid self-condensation of the acetone to form mesityl oxide, which is then available for further alkylation with the available isobutanol. At lower temperatures, the self-condensation of acetone is less favoured, resulting in a longer residence time of acetone in the reaction solution, and thus greater proliferation of the acetone-isobutanol alkylation.

In the case of isoamyl alcohol products conversion of the alcohol substrate is 54 %, 73 % and 68 % for 120, 140 and 160 °C, respectively. At the lower temperature, there is a notably lower proportion of double alkylate products (34% of alkylate products) formed relative to shorter chain, single alkylates such as the single alkylate, 6-methyl-2-heptanone (46% of alkylate products). At the higher temperatures the product distribution is shifted towards double alkylation with 68 % and 55 % 2,10-dimethyl-6-undecanone at 140 and 160 °C respectively as opposed to 34 % at 120 °C (excluding alcohol substrate). Conversion to alkylates which are then reduced to alcohols appears to be favoured to a small degree at higher temperatures.

Between the two alcohol substrates, conversion to double alkylates is marginally favoured at higher temperatures, however the self condensation of acetone to a mesityl oxide intermediate inhibits selectivity for the double alcohol-acetone coupled product.



**Scheme 1:** Alkylation of isoamyl alcohol with acetone. Formation of side product (IA5) is shown competing with the formation of products IA3, IA6 and IA7.



**Scheme 2:** Alkylation of isobutanol with acetone. Similarly to scheme 1, the self-coupling of acetone and subsequent production of product IB5 competes with production of products IB3, IB6, IB7 and IB8.

In this reaction isoamyl alcohol is oxidised to the corresponding aldehyde, producing hydrogen, this then undergoes nucleophilic attack at the  $\alpha$ -carbon by acetone, releasing  $\text{H}_2\text{O}$  to produce IA3 (Scheme 1). The alkylated product is subsequently reduced by the ‘borrowed hydrogen’. A competing pathway involves the condensation of acetone to produce compound

IA4 which then undergoes alkylation via the same mechanism to yield IA5. Compound IA3 either undergoes reduction and becomes trapped as the corresponding alcohol, IA6, or undergoes a further alkylation through nucleophilic attack at the  $\alpha$ -carbon to produce the double alkylate, IA7. Isobutanol undergoes an analogous reaction to that of the isoamyl alcohol alkylation, however there is more evidence of reduction of the double alkylate, IB7, to produce the corresponding alcohol, IB8 (Scheme 2).

Isoamyl alcohol does not exhibit the same pattern of higher efficiency at lower temperatures with respect to alkylation with acetone under the conditions used, but rather at 140 °C. At this temperature there is a marked propensity for the formation of the double alkylation product, 2,10-dimethyl-6-undecanone (IA7), which accounts for 49% of the final product mixture, compared to just 18% and 38% for the reactions run at 120 °C and 160 °C respectively. Potentially the increase in temperature from 120 °C to 140 °C allows for a faster oxidation of the alcohol to the corresponding aldehyde, allowing the alkylation reaction to proceed, however, when the temperature is increased above 140 °C to 160 °C, the reduction of the ketone to the corresponding alcohol is expedited, effectively halting further alkylation.

To assess the efficiency of the catalyst the reaction profile of the alkylation reactions were determined. The reaction profile of the isoamyl alcohol reaction at 140 °C is given in figure 3. From the reaction profile, it is evident that most of the conversion of isoamyl alcohol occurs within the first four hours. As expected, the reaction appears to proceed sequentially through the initial coupling of acetone and isoamyl alcohol to produce 6-methyl-2-heptanone, IA3, which is then available to couple with another isoamyl alcohol molecule to yield the double alkylation product, 2,10-dimethylundecan-6-one (IA7). Whilst the production of these two ketones occurs with obvious interdependence, the concurrently occurring reaction to produce 2,8-dimethylnonan-4-one (IA5) does not show dependence on any other product. This suggests that acetone self-couples to produce 4-methylpentan-2-one, IA4, before coupling with isoamyl

alcohol rather than acetone coupling with 6-methyl-2-heptanone. The production of the alcohol derivative, 6-methyl-2-heptanol is presumably due to the reduction of the ketone, and proceeds at the greatest rate between 1 and 2 hours, when there is the greatest availability of the ketone. Catalyst recycle tests suggest that only a minimal amount of activity is retained (data not shown). It is therefore likely that it is a combination of the depletion of acetone and catalyst deactivation that causes conversion rate to slow dramatically after 4 hours.

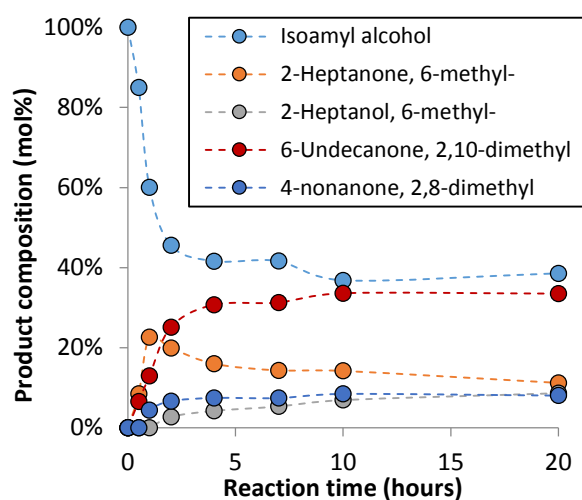


Figure 3: Reaction profile for the alkylation of isoamyl alcohol at 140 °C, in a stirred autoclave. Isoamyl alcohol 1.8mol, acetone 0.9mol,  $K_3PO_4$  0.3mol, 0.3wt% Pd (5.783g 5wt% dry basis Pd/C) over 20 hours.

All remaining acetone was removed from the resulting fuel mixtures through distillation resulting in the isoamyl product (IAP) and isobutanol product (IBP) fuels. These ketone/alcohol mixtures were blended with aviation kerosene (Jet A-1) and the fuel properties examined.

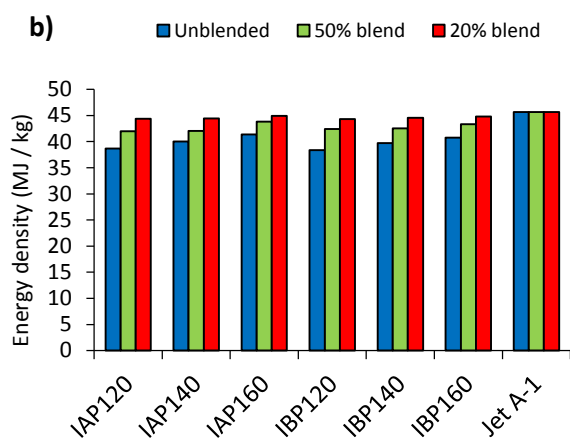
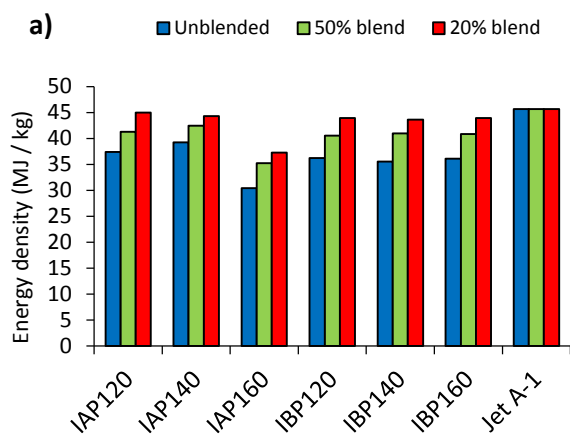


Figure 4: Higher heating values of the isoamyl (IAP) and isobutyl (IBP) fuel products and their blends (100%, 50% and 20% with Jet A-1) where a) is the fuel mixtures including the alcohols b) shows the HHV of the fuel blends where the parent alcohols have been removed.

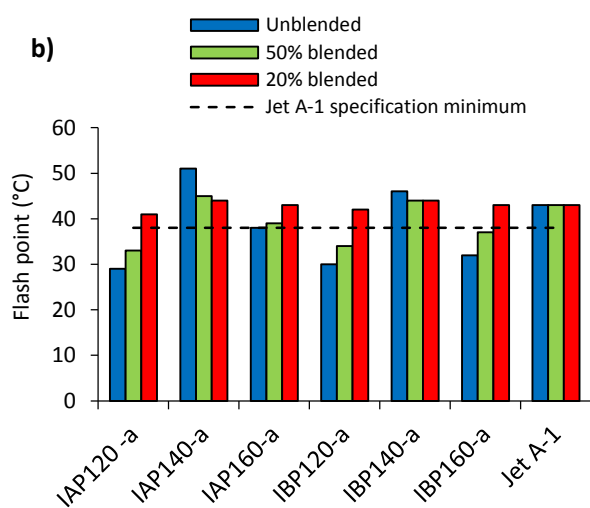
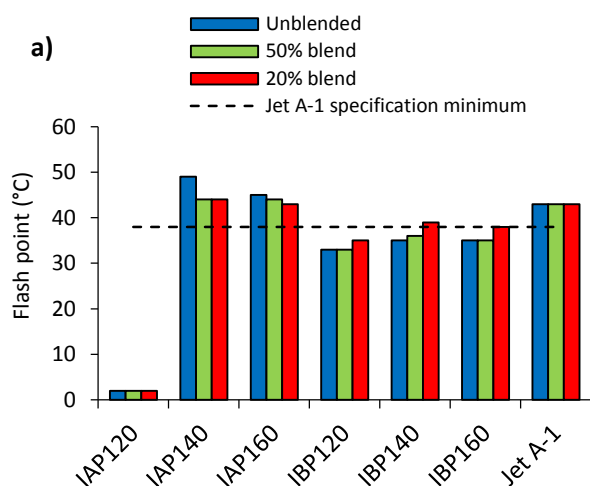


Figure 5: Flash point of the isoamyl (IAP) and isobutyl (IBP) fuel products and their blends (100%, 50% and 20% with Jet A-1) where a) is the fuel mixtures including the alcohols b) shows the flash point of the fuel blends where the parent alcohols have been removed.

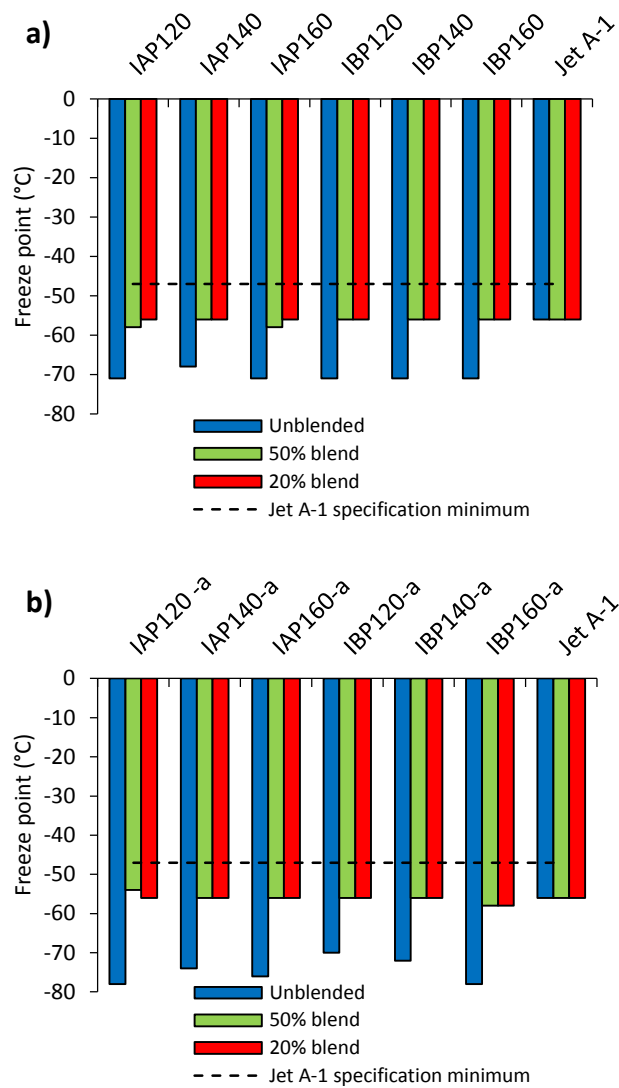


Figure 6: Freeze point of the isoamyl (IAP) and isobutyl (IBP) fuel products and their blends (100%, 50% and 20% with Jet A-1) where a) is the fuel mixtures including the alcohols b) shows the freeze point of the fuel blends where the parent alcohols have been removed.

The gravimetric energy density is an important metric, as it directly affects the efficiency obtained by using a particular fuel. The Jet A-1 specification stipulates a minimum lower heating value (LHV) of 42.8 MJ/kg. The higher heating value of Jet A-1 used in this study was



found to be 45.69 MJ/kg. Of the two alcohol derived fuels, isoamyl alcohol derivatives achieve the greatest energy density, with IAP140 without removal of substrate alcohol, exhibiting a HHV of 39.28 MJ/kg, corresponding to the higher level of double alkylated species (figure 3). When the remaining alcohol was removed, IAP160 exhibited a slightly higher HHV of 41.359 MJ/kg. The highest value shown by isobutanol derived fuels without removal of substrate alcohol is that of IBP120 at 36.21 MJ/kg however when the alcohol was removed, IBP160 exhibited the highest HHV at 40.760 MJ/kg. When substrate alcohols are removed, a positive correlation between reaction temperature and product mixture gravimetric energy content is observed. Removal of the alcohol substrates, in all cases, acts to increase the energy density of the product mixtures.

The closed cup flash point is a key metric with aviation fuel, the Jet A-1 specification stipulates that this temperature should be higher than 38 °C. The Jet A-1 used in this investigation was found to have a flash point of 43 °C (Figure 5). Of the synthetic, alcohol derived fuels, IAP140 and IAP160 were the only fuels to satisfy this criterion exhibiting flash point temperatures of 49 °C and 45 °C respectively. IAP120 exhibited a flash point of 33 °C when unblended with Jet A-1, rising to 36 °C at a 20 % blend level. Of the IBP fuels, IBP120 exhibited the lowest value, of 33 °C, with IBP140 and IBP160 both possessing flash point temperatures of 35 °C. IBP fuels do not therefore, satisfy the flash point criterion of the Jet A-1 specification. Upon removing the parent alcohols the flash point is increased for the majority of the samples, particularly in the case of IAP120, where unreacted substrate was depressing the flash point of the product mixture to below room temperature however, after substrate removal, the flash point was only increased to 29 °C. IBP140 without removal of remaining substrates did not satisfy the flash point criterion for jet fuel, however with removal it surpasses the required value, exhibiting a flash point of 46 °C for the unblended product mixture.

Excitingly, both the fuels with and without alcohols had extremely low freezing points with the unblended fuels all having a melting point between -68 °C and -78 °C (figure 6). This is a significant improvement on the straight chain ketones that fall between -43 °C – 14 °C (table 1). This dramatic improvement in the low temperature properties, is presumably attributable to the presence of branching in the constituent molecules. This branching acts to disrupt intermolecular interactions and thus suppresses the melting point temperature improving the cold flow characteristics.

Table 1 Fuel properties of straight chain ketone and alkane derivatives, the flash points and melting points were obtained from the Scifinder database,<sup>22</sup> kinematic viscosity was experimentally determined.

<b>Fuel</b>	<b>Flash Point (°C)</b>	<b>Melting Point (°C)</b>	<b>Kinematic viscosity @ -20°C (mm<sup>2</sup>s<sup>-1</sup>)</b>
6-Undecanone	88	14	solid
4-Nonanone	62	-16	solid
2-Heptanone	41	-42	2.09
Undecane	62	-26	4.02
Nonane	31	-53	1.98
Heptane	-4	-91	1.24

The kinematic viscosity of the novel fuels was measured at -20 °C, 20 °C and 40 °C (figure 7 and 8). The viscosity of the unblended IAP fuels is significantly above the minimum specified at -20 °C in the Jet A-1 specification. IAP140 exhibits the highest viscosity having a kinematic viscosity of 31.7 mm<sup>2</sup>s<sup>-1</sup>, with IAP160 slightly less viscous at 21.3 mm<sup>2</sup>s<sup>-1</sup> and IAP 120 less viscous again with a viscosity of 11.3 mm<sup>2</sup>s<sup>-1</sup>. This trend of varying viscosity reflects pattern of substrate conversion to higher molecular weight products.

In the case of Isoamyl alcohol, a significant reduction in the viscosity of product mixtures was achieved by removal of remaining alcohol substrate, with IAP140 and IAP160 showing a reduction in viscosity of approximately  $15\text{mm}^2\text{s}^{-1}$ . Upon blending with jet fuel, an expected suppression of viscosity was observed, with values gravitating towards that of Jet A-1.

The opposite relationship with conversion is observed in the viscosities of the three IBP mixtures, with IBP120, which shows the highest conversion to the higher MW products, exhibiting the lowest low temperature viscosity of the three fuels, with a viscosity of  $12.6\text{mm}^2\text{s}^{-1}$  compared to those of IBP140 and IBP160 with viscosities of  $16.8\text{mm}^2\text{s}^{-1}$  and  $16.4\text{mm}^2\text{s}^{-1}$  respectively. Whilst IBP120 exhibits a lower viscosity than its higher reaction temperature equivalents, it is still well above the maximum allowed viscosity in the Jet A-1 standard.

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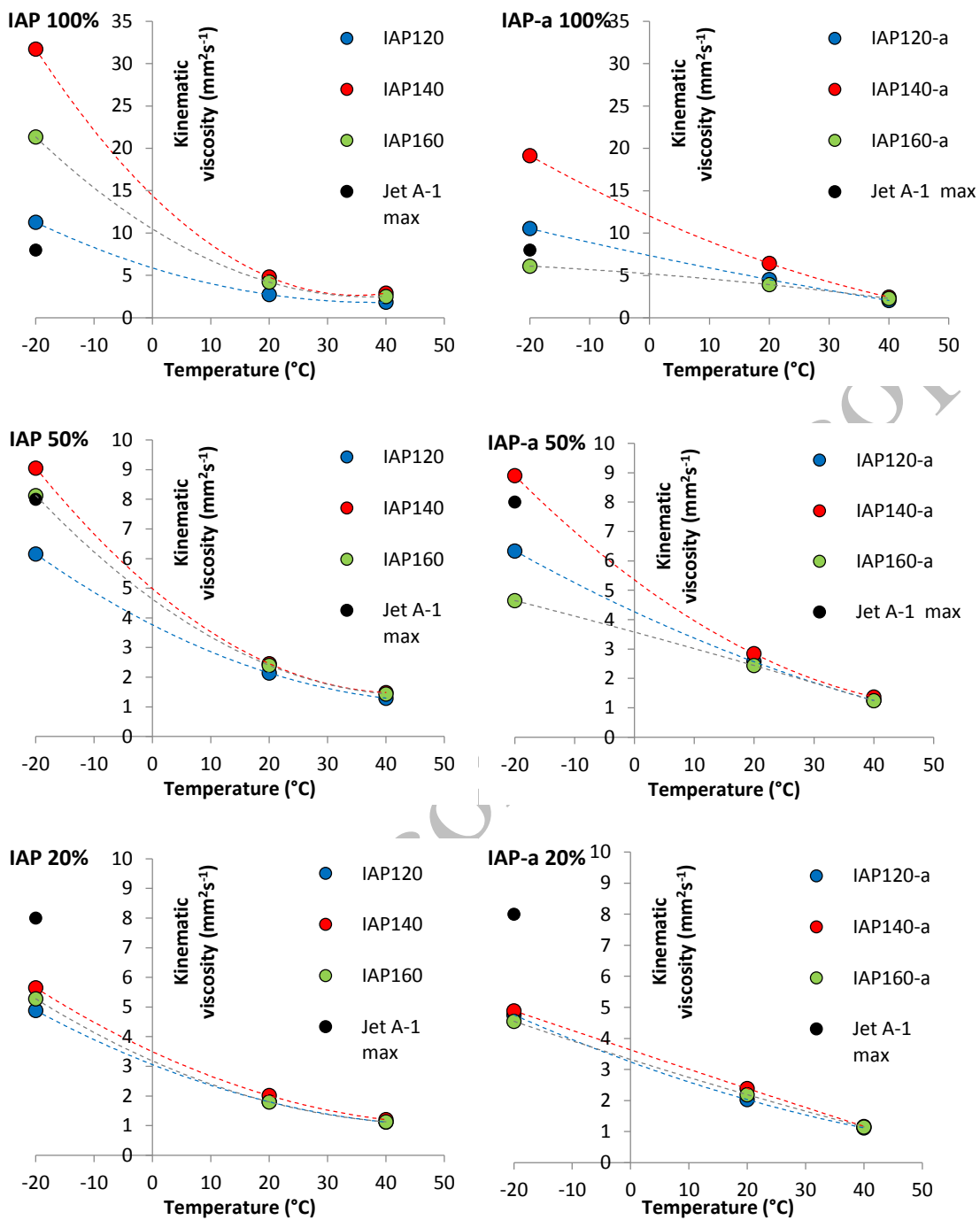


Figure 7: Kinematic viscosity of the isoamyl products (IAP) and the isoamyl fuel products with the alcohols removed (IAP-a), and their blends (100%, 50% and 20% with Jet A-1) in the temperature range  $-20\text{ }^{\circ}\text{C} - 40\text{ }^{\circ}\text{C}$ .

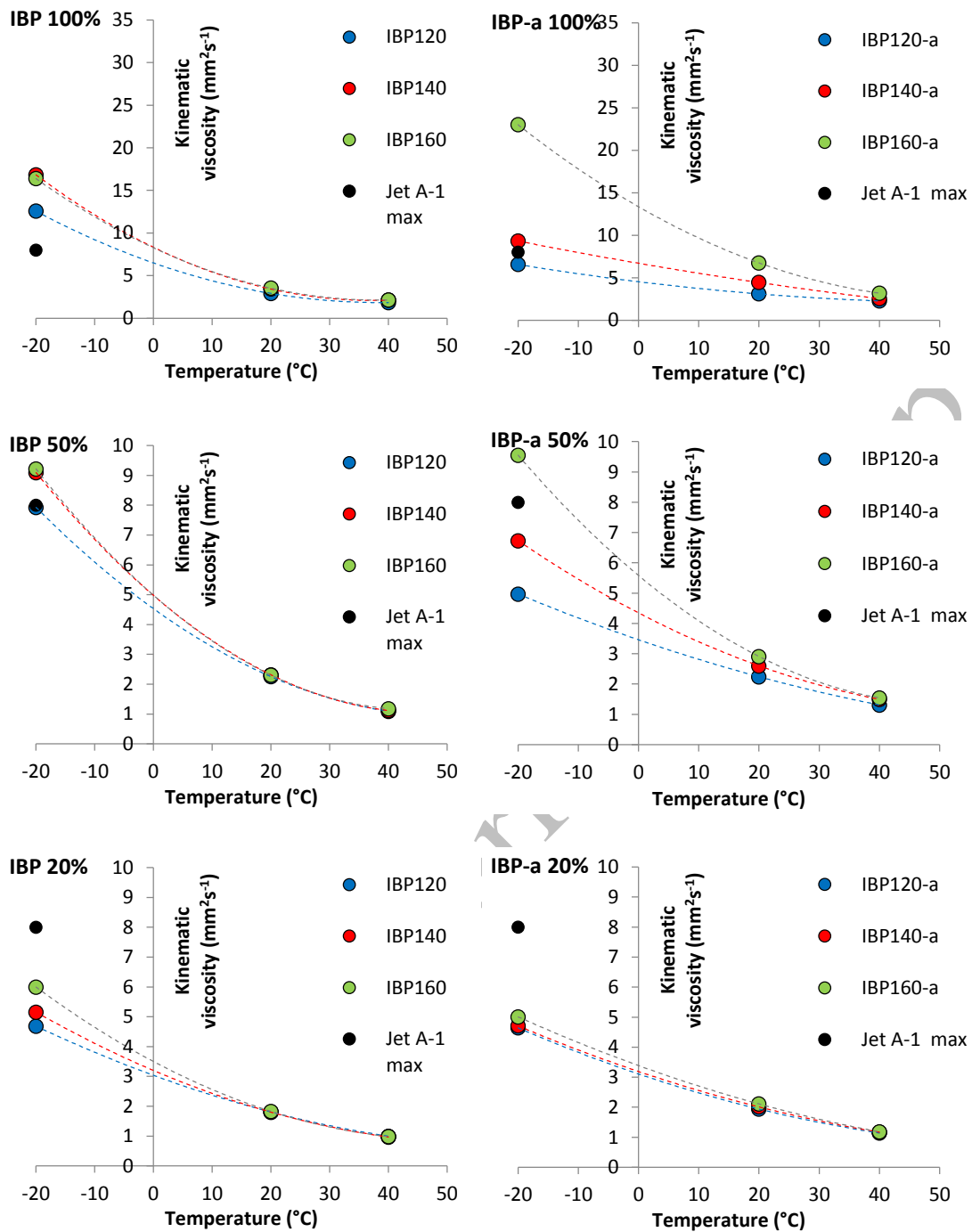


Figure 8: Kinematic viscosity of the isobutyl products (IBP) and the isobutyl fuel products with the alcohols removed (IBP-a), and their blends (100%, 50% and 20% with Jet A-1) in the temperature range -20 °C – 40 °C.

With unreacted alcohols left in situ, these fuels exceed the maximum allowed viscosity at -20 °C, arguably the maximum value for jet fuel is descriptive of conventional aviation kerosene, and that a slightly higher viscosity would not have a substantial detrimental effect on performance. Issues with pump wear and maintenance would have to be addressed as well as optimising fuel atomisation within the engine, however these should not be such great challenges so as to preclude the use of otherwise suitable aviation fuels. Alternatively the viscosity can be reduced by blending. The kinematic viscosity of all the fuels tested was reduced to between 7-9 mm<sup>2</sup> s<sup>-1</sup> at the 50% blend level, while at a 20 % blend level, all the product mixtures satisfy the Jet A-1 criterion. Where remaining alcohols are removed however, IAP160 and IBP120 were observed to satisfy the viscosity criterion for jet fuel, without blending and all fuels except IBP160 showed a reduction in viscosity at -20 °C.

## CONCLUSIONS

The solvent-free alkylation of branched alcohols with acetone resulted in complex mixtures of branched ketone fuels. These fuels were demonstrated to have superior low temperature properties in comparison to the straight chain ketones or the straight chain hydrocarbon derivatives and as such were deemed suitable for use as blending agents in aviation fuel. The conversions observed with the system used ranged between 54-73% for isoamyl alcohol derived products and 53-86% for isobutanol derived products with the Pd/C catalyst found to deactivate entirely after two uses. The energy density of isoamyl alcohol derivatives was found to be up to 39.3 MJ/Kg whilst isobutanol derivatives possess energy densities up to 36.1 MJ/Kg, while this lower than the allowable specification with blending this was increased substantially. The flash point temperatures were found to be between 44 °C and 49 °C for isoamyl alcohol derivatives, and slightly lower for isobutanol derivatives with values between 35 °C and 39 °C. Kinematic viscosities exhibited by the novel fuels were higher than the specification maximum for Jet A-1, exhibiting values of between 11.26 mm<sup>2</sup>s<sup>-1</sup> and

31.73 mm<sup>2</sup>s<sup>-1</sup> for isoamyl alcohol derivatives and between 12.56 mm<sup>2</sup>s<sup>-1</sup> and 16.84 mm<sup>2</sup>s<sup>-1</sup> for the isobutanol products. Removal of the parent alcohols from the fuel mix improved both the kinematic viscosity and flash points of the fuels.

## ACKNOWLEDGEMENTS

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