

Preliminary Experimental Analysis of Alcohol-Kerosene Blend for Commercial Aviation

*Turysbay Miras, Toncu, Dana-Cristina***

*School of Chemical Engineering Kazakh-British Technical University 59 Tole-bi, Almaty,
050000 KAZAKHSTAN*

ABSTRACT: *The aim of this work is to provide insight into alcohol-kerosene fuels and their promising use as an alternative in commercial aviation. A detailed chemical and physical experimental analysis is drawn, with a focus on the advantage of the isopropanol-kerosene blend. Despite reported beneficial isopropanol effects on retarding fuel combustion, knocking prevention, and much lower emissions, few investigations managed to offer clear prospects for such an alternative commercial aviation fuel. The ease of mixing with kerosene and the advantage of improved freezing points overcome negative effects of volatility and corrosion for low isopropanol percentage and makes it a strong candidate for alternative jet fuels.*

KEYWORDS: *Isopropanol; Kerosene; Aviation; Alternative; Experiment.*

INTRODUCTION

Alternative jet fuels have gained importance since they may not be entirely derived from petroleum, but still present very similar in performance to conventional jet fuel, and the advantage of almost zero sulphur and aromatics. Their use promises lower particulate exhaust emissions, and additional excellent low-temperature properties, such as low viscosity at lower ambient temperatures. The improved thermal stability properties translate into less fuel system deposits. Alternative fuels demonstrating very good performance have already been in use for years, making it easier to supply current jet fuel demands. When the additional CO₂ that is produced during the manufacturing process can be captured and permanently sequestered, alternative fuel seems a good near-term solution [1-12].

With the huge number of air passengers annually, and many more employed in the sector, air transport has received a lot of attention from researchers and companies, with the accent on increasing fuel efficiency, lowering pollutant emissions, decreasing costs [13-21]. Recently, high fluctuations in petroleum products' prices shifted the interest towards alternative jet fuels, with less greenhouse gas impact and improved composition.

Kerosene covers both substances and finished products, most commonly used to describe the fraction of crude oil that boils approximately in the range of 150 to 290°C and consists of hydrocarbons in the range of C₉-C₁₆. The predominant use of kerosene is aviation turbine fuel for civilian (using Jet A or Jet A-1) and military (using JP-8 or JP-5) aircraft. Other uses include diesel fuel,

* To whom correspondence should be addressed.

+ E-mail: dtoncu@gmail.com

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domestic heating fuel, and illuminating kerosene. Kerosene-based fuels differ from each other in performance specifications (primarily freezing point or sulphur concentration) and minor amounts of performance additives that may be added (less than 0.1% v/v) [1,2].

With relatively similar basic composition, kerosenes derived from specific refinery stream depend on the crude oil from which it was separated and on the processes used for production. Due to its complex petroleum-derived hydrocarbon composition, this category is rather defined by process history, physical properties, and product-use specifications [3].

Kerosene is a thin, clear liquid formed from hydrocarbons obtained from the fractional distillation of petroleum between 150°C and 275°C, resulting in a mixture with a density of 0.78–0.81 g/cm³ composed of carbon chains that typically contain between 6 and 16 carbon atoms per molecule. It is miscible in petroleum solvents but immiscible in water [4].

Irrespective of crude oil source and processing history, kerosene's major components are branched and straight chain alkanes and naphthenes (cycloalkanes), normally accounting for at least 70% volume. Aromatic hydrocarbons in this boiling range, such as alkylbenzenes (single ring) and alkylnaphthalenes (double ring), do not normally exceed 25% volume of kerosene streams. Olefins are usually not present at more than 5% volume [5]. The flash point of kerosene is between 37 and 65 °C, and its autoignition temperature is 220°C. The pour point of kerosene depends on grade, and for commercial aviation fuel is standardized at -47°C. The heat of combustion of kerosene is similar to that of diesel; its lower heating value is 43.1MJ/kg (around 18,500Btu/lb), and its higher heating value is 46.2 MJ/kg [6].

The purpose of this work is to show the competitiveness of innovative fuel in the Kazakhstan market. Alcohol-kerosene blends constitute an easy, feasible, cheap, and environmental-friendly solution, on an emerging market with climate particularities in Central Asia.

The few studies carried out on isopropanol for alternative fuels reported its effects on fuel combustion retard, knocking prevention, and almost zero NO emissions; as it controls rapid heat release: 2 degrees spark timing delay implies a 10% decrease in NO_x emissions, but also reduction of HC and CO, while improving soot emission as well by lowering air/fuel

temperatures and preventing premature explosion [13, 22, 23]. Isopropanol is also expected to decrease the freezing point of kerosene but at the expense of decreasing the flash point and the initial boiling point. Isopropanol acts as an emulsifier for water in kerosene, reducing the negative effects of condensed water in fuel tanks.

Alcohol-kerosene blends show great promise for Kazakhstan's economy:

- Pollution decrease in Kazakhstan;
- Practical and profitable iso-propanol production in Kazakhstan.

MATERIALS AND METHODS

Preparation of isopropanol-kerosene blend

KazMunaiGaz kerosene and Sigma-Aldrich iso-propanol were used for the mixture preparation. The used raw materials are described in Table 1 and 2.

Preparation involved mixing at room temperature, with 1000 rpm mechanic stirrer for 0,5 h. It is important to note that both components are fully miscible at room temperature, and no emulsifier is needed. The resulting samples had the appearance shown in Fig. 1. There was no significant change in turbidity, appearance, or color with isopropanol addition.

Experimental Procedure

For a better characterization of samples, several important features were analyzed. The Liquid Chromatography-Mass Spectrometry analysis (LC-MS) was performed with a Bruker Solaris equipment, using an eluent formed by a mixture of n-hexane and isopropanol, with argon as a carrier gas. Then Gas Chromatography-Mass Spectrometry (GC-MS) was carried out also with Bruker Solaris equipment to determine the isopropanol influence on low molecular mass hydrocarbons present in kerosene. LC-MS was chosen to detect components that may be impossible to analyze with GC-MS, by expanding the range of organic compounds identified in the samples, including the thermally unstable, charged and non-volatile ones. Corroborated with distillation, it offered a better understanding of isopropanol effect.

Physical and chemical properties were determined according to ASTM determination methods named in Table 3.

Because no direct determination of combustion properties was available, an indirect method was used

Table 1: Properties of iso-propanol used for the blend.

| Property, u.m. | Value |
|--|---------------------------------|
| Formula | C ₃ H ₈ O |
| Molar mass, g/mol | 60,1 |
| Density at 20°C, g/cm ³ | 0,786 |
| Melting point, °C | -89 |
| Boiling point, °C | 82,6 |
| Acidity, pKa | 16,5 |
| Refractive index | 1,3776 |
| Viscosity, cP at 15°C at 25°C at 30°C | 2,86 1,96 1,77 |
| Vapor Pressure, mmHg | 33 |
| Flash point, °C | 12 |
| Freezing point, °C | -88,33 |

Table 2: Properties of kerosene used for the blend.

| Property, units | Value |
|---|--------------------------|
| Density at 15°C, g/cm ³ | 0,7879 |
| Kinematic viscosity, cP At 15°C At 40°C | 2,0481 1,3331 |
| Distillation, °C IBP 10% volume 50% volume 90% volume | 125 154 203 228 |
| Flash point, °C | 39 |
| Freezing point, °C | -40 |

**Fig.1: Comparative photo of kerosene and isopropanol-kerosene blends.**

Table 3: Test methods.

| Characteristic | Determination Method |
|--------------------------------------|----------------------|
| Distillation at atmospheric pressure | ASTM D86-04 |
| Density | ASTM D1217-93(98) |
| Flash point | ASTM D56-02a |
| Aniline point | ASTM D611-04 |
| Kinematic viscosity | ASTM D445-04 |
| Freezing point | ASTM D5901-03 |

for the estimation of the heat of combustion for kerosene, based on the experimentally found specific gravity [14]:

$$Q = 12400 - 2100 \cdot d^2 \quad (1)$$

where d is specific gravity and can be calculated with the formula:

$$d = \frac{141.5}{d_{15}^{1.5}} - 131.5 \quad (2)$$

Also, the aniline point was used to estimate the combustion performance of kerosene expressed as aniline gravity, calculated with the following formula [14]:

$$AGP = ^\circ API \cdot AP \quad (3)$$

where $^\circ API$ is the specific gravity, and AP is the aniline point. As the lowest temperature at which equal volumes of fuel and aniline are miscible, the aniline point is inversely proportional to the aromatic content, while paraffinic content results in high aniline point.

The flash point can be experimentally determined either directly or by calculation with the API method, which has a 5° error, with the following formula [14]:

$$T_f = \frac{1}{-0.02421 + \frac{2.84947}{T_{10}} + 0.00342541 \ln T_{10}} \quad (4)$$

where T_{10} is the temperature at the 10% volume distilled point on ASTM D 86 curve, in K.

Devices and Equipment

As shown in Table 3, the experimental analysis implied the use of the following devices and equipment:

- Tag closed cup tester for flash point, as described by ASTM D56, consisting of a gas burner, bath stand

for a gas burner, overflow bath, test cup, thermometers for cup and bath, oil chamber, flame tip, and flame size bead;

- Apparatus for distillation of petroleum products and liquid fuels at atmospheric pressure, as requested by ASTM D86, formed by a distilling flask with a thermometer inside a bath on top of a burner, and a graduated cylinder for distilled fractions;

- Bingham pycnometer for density and relative density (specific gravity), as stated by ASTM D1217, and Mettler-Toledo balance;

- Calibrated glass capillary viscometers, and their holders, thermostats, thermometers, and chronometers, according to ASTM D445;

- Heat resistant, 25 mm diameter and 150 mm length, aniline point test tube, designated in ASTM D611, with inner stirrer and thermometer;

- Automated optical method apparatus for aviation fuels' freezing point, consisting of a test chamber with jacketed test tube supported in a jacketed enclosure configuration that cools and heats the test samples, and a nitrogen purge collar as part of the closure assembly for the test chamber, preventing moisture from combining with the sample, and circulating bath, as described in ASTM D5901.

RESULTS AND DISCUSSIONS

Fig. 2 shows that the density of the samples hardly increases with the amount of alcohol in the mixture, because both components have similar densities, and differences may be due to 0-2% experimental errors. Such results support the idea of using isopropanol-kerosene blends in current engines without any modifications.

Fig. 3 represents the distillation curve, under atmospheric pressure, and it points out isopropanol decreased the initial

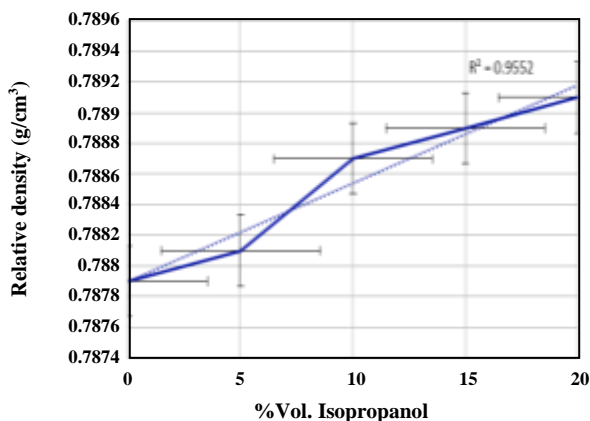


Fig. 2: Density variation with isopropanol content (including error bars).

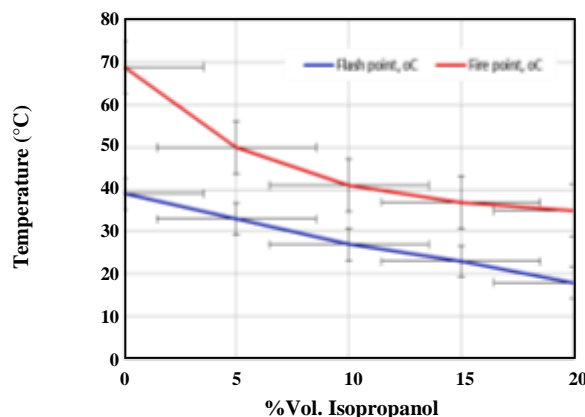


Fig. 4: Flash and fire points of samples.

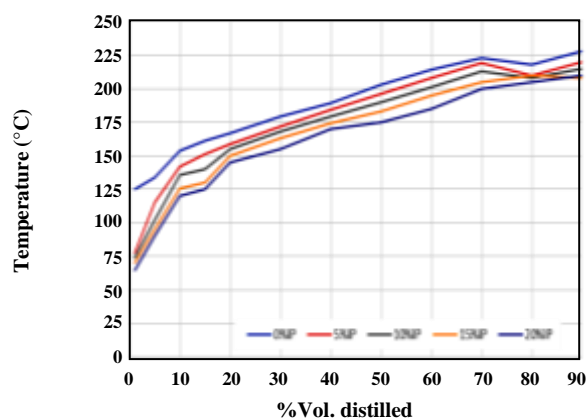


Fig. 3: Distillation curve for analyzed samples

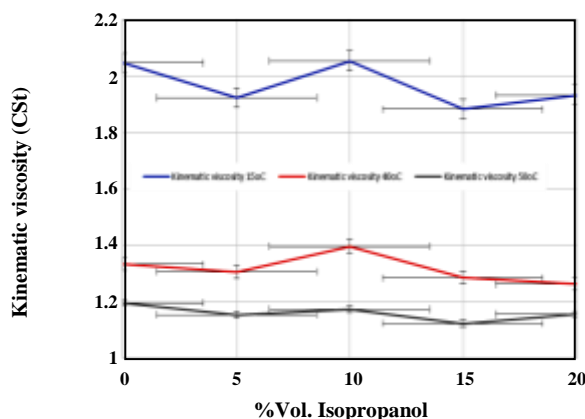


Fig. 5: Kinematic viscosity of samples.

the boiling point of the blends, together with an overall shift towards lower distillation range for the whole distilled samples. The distillation curves preserved the same general shape. The 50°C difference in initial boiling point from zero to 20% vol. isopropanol suggests a change of light molecular mass components, because of reaction with isopropanol or oxidative degradation, which would later become clear by GC-MS spectrometry. The presence of shorter-chain alkanes and alkenes (C₈-C₁₀) and light aromatic compounds at early points of distillation was confirmed. One important implication of vapor rising temperatures suggested by initial distillation, behavior regards the ease of starting the jet engine, especially in cold weather, and points out the high volatility of isopropanol-kerosene blends.

The distillation curves of all samples allowed the estimation of flash points with temperatures corresponding to 10% volume distilled (154, 142, 136, 126, and 120°C, respectively) and equation (4).

Fig. 4 presents the variation in flash and fire points, in degrees Celsius, with isopropanol content. The properties exhibit a decrease with increasing alcohol content, as isopropanol flash point is just 12°C. To overcome the fire danger and high flammability, isopropanol content must be limited to 5% volume, or different stabilization additive for flash and fire point must be chosen to correct their values.

Fig. 5 shows that kinematic viscosity decreases with increasing isopropanol content because of the difference of components viscosity and ability to wet the walls. Such change in kinematic viscosity with isopropanol content may occur because of molecules rearrangement, reactions between components, especially alkyl radicals and low paraffin that lead to a decrease in viscosity and further sliding between molecules, with the global effect of improving rheological properties for blends. The expected decrease in viscosity with increasing temperature

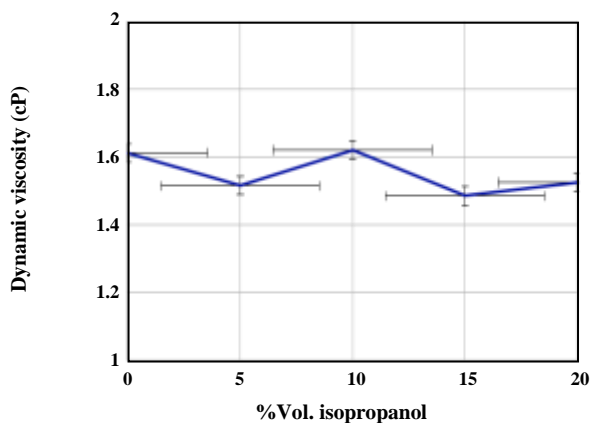


Fig. 6: Dynamic viscosity of blends.

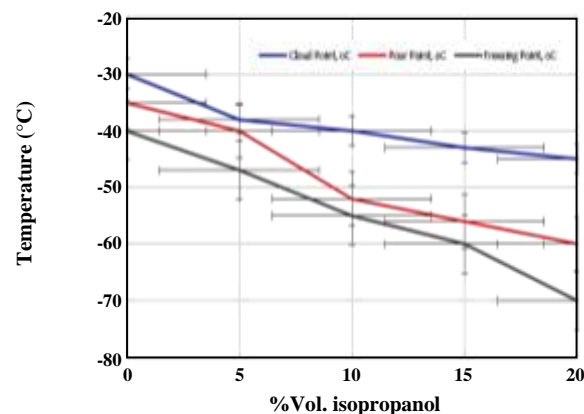


Fig. 8: Comparison of cloud, pour and freezing points.

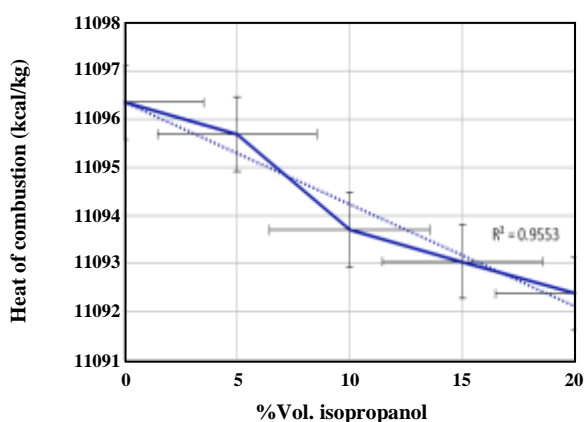


Fig. 7: The Calculated heat of combustion for samples.

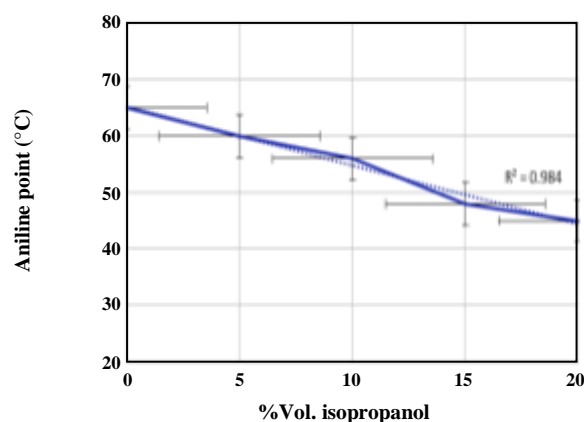


Fig. 9: Aniline point of blends.

is also visible. It can also be noticed that 5 % isopropanol doesn't induce a high volatility in the kerosene-based jet fuel.

Fig. 6 shows the dynamic viscosity of samples slightly increasing with increasing isopropanol content, due to the difference in kinematic viscosity and density of components. Dynamic viscosity is the product between kinematic viscosity and density.

Fig. 7 shows the calculated heat of combustion for kerosene and its mixtures with various percentages of isopropanol content. Since the differences in density of all samples are small, also the difference in calculated heat of combustion is only 0.03% difference, even for 20% volume isopropanol. There is, however, a linear variation in heat of combustion, because of the linear decrease in density with increasing isopropanol content.

Fig. 8 shows freezing, pour and cloud points of samples, as they decrease with increasing alcohol content. Iso-propanol has a low freezing point, and its presence

results in a decrease in freezing points in blends samples. Such a behavior may be regarded as positive under low-temperature conditions, making its use suitable for use in Arctic regions and during winter, with additional consequences in lessening clogging in filters and pipes when water crystals form and corrosion problems associated with water presence appear.

Fig. 9 shows the aniline point of samples. There is a reduction in aniline point with growing alcohol content. It indicates a decrease in aromatic hydrocarbon content of alcohol-kerosene blends. The analysis is consistent with LS-MS and GC-MS, indicating no poly-aromatic compound in kerosene, and cyclic hydrocarbons in iso-propanol mixtures. It is also consistent with the low density that samples exhibit, all signs of the low-aromatic content of base kerosene and even lower aromatic content of mixtures. Such blends would comply with standard criteria of limited aromatic content, while their

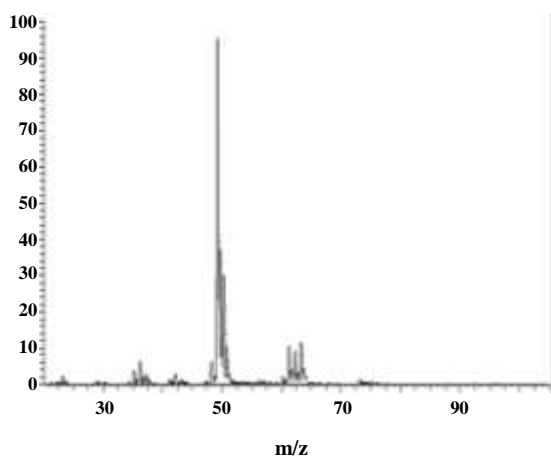


Fig. 10: Kerosene spectrum.

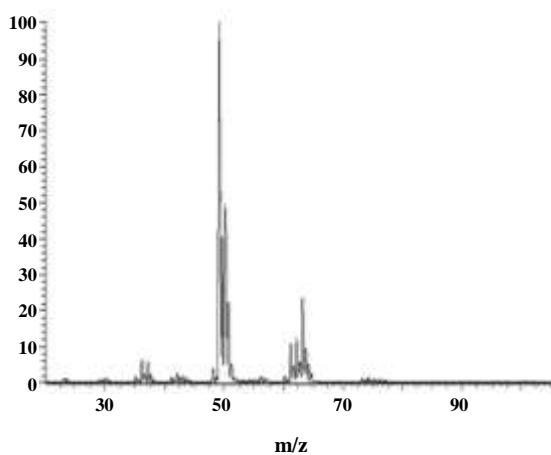


Fig. 11: 5% vol. isopropanol blend spectrum.

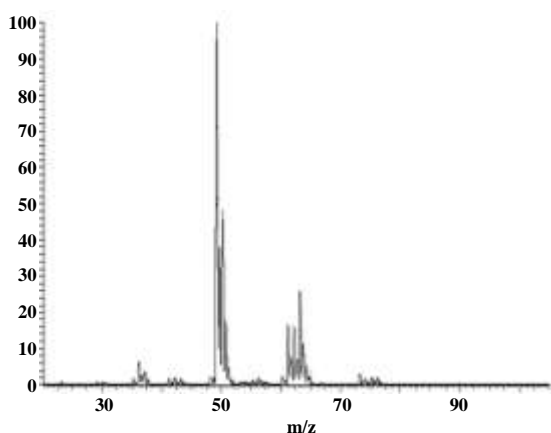


Fig. 12: 10% vol. isopropanol blend spectrum.

combustion behavior would satisfy commercial aviation demands.

LC-MS and GC-MS spectra were useful for component detection in kerosene and iso-propanol blends. Figs. 10-14 represent GC-MS-taken mass-to-charge ratio m/z versus the relative abundance of species in samples. The kerosene contains few low molecular weight hydrocarbons, especially benzene, *n*- and *i*-pentane, pentane-3-one, 2 methyl butane, pentane-2-one, *n*-dodecane, octane, 1-octene, trans-2-octene, cis-2-octene, cis-3-octene, cis-4-octene, trans-4-octene, cyclohexanol, *n*-tridecane, *n*-pentadecane, hexane, small amounts of phenyl cation. No polyaromatic hydrocarbons were detected in kerosene, as no m/z ratio exceeded 200. Reactions between kerosene components and iso-propanol were held responsible for a series of compounds detected in blends and with concentration increasing with alcohol content, such as methanol, benzyl alcohol, cyclohexanol. Reactions were more likely to occur between low molecular mass and alkyl radicals connected to aromatic rings, and alcohol formation with cyclo-paraffins and aromatics.

The comparison of isopropanol-kerosene blends with international standards becomes easier in the light of 2015 IATA Guidance Material for Sustainable Aviation Fuel Management and ASTM D7566 covering aviation turbine fuel that consists of conventional and synthetic blending components, together with Commercial Aviation Alternative Fuels Initiative [24, 25]. For Jet A1, ASTM D1655 contains the most comprehensive description.

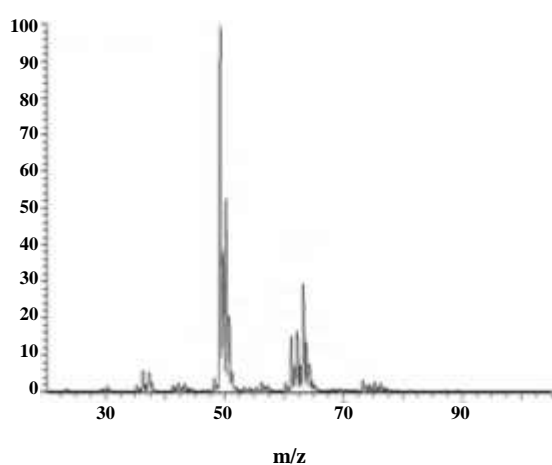
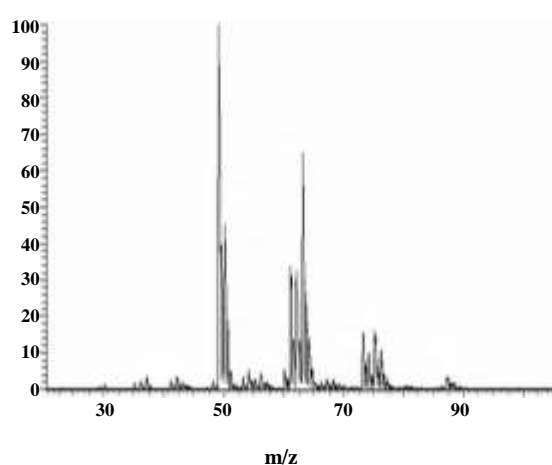
Table 4 summarizes 5% iso-propanol sample in comparison with standardized Jet A1 aviation fuel. Except for the flash point, all other values are inside the range stated in ASTM D1655. The 3°C difference in freezing point of blend accounts for 10% difference and may be easily corrected with other additives. The density stays inside the interval. Viscosity and freezing point are superior to those of Jet A1, signaling good thermal and rheological properties. The net heat of combustion is significantly improved. The high decrease in aniline point compared with a chemical composition in aromatics indicates the need of a different, maybe new method for the determination in the place of aniline point.

CONCLUSIONS

Alternative commercial aviation fuels have shown great promise for pollution and cost reduction. Alcohol-kerosene

Table 4: Comparative properties of Jet A1 and 5%vol. Iso-propanol-kerosene blend.

| Property, u.m. | ASTM D1655 | 5% vol. Iso-propanol-kerosene |
|--|----------------------|-------------------------------|
| Density at 15°C, kg/m ³ | 775 - 840 | 788 |
| Viscosity-20°C, mm ² /s | Max. 8 | 3,8 |
| Flash point, °C | Min. 38 | 35 |
| Freezing point, °C | Max. -47 | -67 |
| Distillation temperature, °C 10% recovered 90% recovered | Max. 205 Max. 300 | 142 220 |
| Aromatics, vol.% | Max. 25 | Max. 20 |
| Net heat of combustion, MJ/kg | Min. 42,8 | 46,45 |

**Fig. 13: 15% vol. isopropanol blend spectrum.****Fig. 14: 20% vol. isopropanol blend spectrum.**

blends and in particular isopropanol were the object of investigations revealing the positive effects on fuel combustion delay, knocking prevention, and almost zero NO emissions, with control over rapid heat release and water in kerosene emulsification.

Preparation of iso-propanol – kerosene alternative aviation fuel is fast, easy, and cost-effective mixing, as both components are fully miscible at room temperature, and no emulsifier is needed. Samples were ready for experiments after 0,5h of 1000 rpm mechanic stirring at room temperature.

There was no significant change in turbidity, appearance, or color with isopropanol addition with isopropanol addition.

Density doesn't undergo sensitive variation, and the estimated heat of combustion follows the same evolution with iso-propanol addition.

Flash and fire points decrease with increasing alcohol content, limiting the isopropanol content at 5% volume, or imposing a different additive for flash and fire point.

Kinematic viscosity decreases with increasing isopropanol content.

Isopropanol decreased the initial boiling point of the blends in the distillation under atmospheric pressure, together with an overall shift towards lower distillation range for the whole distilled samples.

Freezing, pour and cloud points decrease with increasing iso-propanol. The positive effect of alcohol on kerosene behavior under low-temperature conditions allows not only the use of such mixtures in Arctic regions and during winter, but also the reduction of clogging in filters and pipes due to the formation of water crystals, with following corrosion problems associated with water presence.

The kerosene contains few low molecular weight hydrocarbons, especially benzene, n- and i- pentane, pentane-3-one, 2 methyl butane, pentane-2-one, n-dodecane, octane, 1-octene, trans-2-octene, cis-2-octene, cis-3-octene, cis-4-octene, trans-4-octene, cyclohexanol, n-tridecane, n-pentadecane, hexane, small amounts of phenyl cation. No polyaromatic hydrocarbons were detected in kerosene, as no m/z ratio exceeded 200. Reactions between kerosene components and iso-propanol were held responsible for a series of compounds detected in blends and with concentration increasing with alcohol content, such as methanol, benzyl alcohol, cyclohexanol. Reactions were more likely to occur between low molecular mass and alkyl radicals connected to aromatic rings, and alcohol formation with cyclo-paraffins and aromatics.

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