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TECHNOLOGY****PHYSICO-CHEMICAL ANALYSIS OF ALCOHOL-KEROSENE BLEND FOR  
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**ABSTRACT**

The aim of work is the research and development of new types of aviation fuels in particular obtaining alcohol-kerosene type fuels.

This paper shows a full description of the product, based on its physical and chemical properties, with emphasis on blend advantages.

Isopropanol retards fuel combustion, prevents knocking, and has almost zero NO emissions; it also controls rapid heat release and acts as emulsifier for water in kerosene.

Preparation of isopropanol-kerosene aviation fuel was fast and easy. Except for flash point, the isopropanol addition doesn't change physical and rheological properties of kerosene, but greatly improves the freezing point of fuel.

**KEYWORDS:** isopropanol, kerosene, analysis**INTRODUCTION**

Alternative jet fuels are vehicular fuel that is not entirely derived from petroleum, as natural gas, an alcohol mixture or hydrogen. These fuels are very similar in performance to conventional jet fuel, but have almost zero sulfur and aromatics. This may result in lower particulate exhaust emissions. In addition, alternative fuels exhibit excellent low-temperature properties, maintaining a low viscosity at lower ambient temperatures. Thermal stability properties are also improved, resulting in less fuel system deposits. Alternative fuels have very good performance, and have already been in use for many years. It will be easy to supplement current jet fuel supplies with alternative derived fuel. If the additional CO<sub>2</sub> that is produced during the manufacturing process can be captured and permanently sequestered, alternative fuel could be a good near-term supplement.

Alternative aviation fuels are receiving considerable attention from researchers and policy makers alike, as a potential means to reduce greenhouse gas emissions while increasing and diversifying fuel supplies. Moreover, alternative jet fuels are generally superior to petroleum-based fuels in terms of their impacts on air quality when combusted. However, the production of alternative aviation fuels may come at a cost. For example, bio-based fuel production could compete with food production; increased agricultural activity could strain freshwater reservoirs and pollute rivers and oceans. Fuel production may be prohibitively expensive if the biomass yield is insufficient, biomass availability limited, or the conversion technology inefficient or capital-intensive.

The importance of aviation in modern world in general cannot be overemphasized. It is currently the fastest transport, which greatly accelerates and improves the global trade cooperation between the countries and solves the problem of global tourism.

There are many areas of the world economy using aviation transport quite a lot. Annually more than 2.5 billion passengers uses air transport. The number of people employed in the air industry is more than 33 million.

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Increasing fuel efficiency has always been a priority for aeronautical engineers. Engines were improved, and double-circuit and after turbofan engines were patented. Compared with the first mass passenger jets late 1950s and 1960s, modern airliners became more economical by almost 70%.

Nowadays, hydrocarbon reserves on the planet are reducing and their prices have opposite dynamics. In fact, it is not always possible to predict their prices, which makes it complicated for air companies to achieve their budget planning. This is the reality and the future is not optimistic.

Crude oil and its refining are one of the major ecological pollutants, with long-term negative impact on the environment.

In the recent years, due to the rising prices of petroleum products, alternative fuels are increasingly gaining interest and there are many efforts to find the appropriate composition and raw materials for new fuels.

Alternative jet fuels' greenhouse gas impact must be comprehensively assessed because greenhouse gas emissions differ between pathways and feedstocks, and not all candidate fuels decrease greenhouse gas emissions on a well-to-wake, or lifecycle, basis. The overall sustainability impact of alternative fuels must be addressed using a multi-criteria approach that considers technical, environmental, and economic aspects.

The Kerosene/Jet Fuel category covers substances and finished products commonly referred to by the generic term "kerosene". The generic term "kerosene" is used to describe the fraction of crude oil that boils approximately in the range of 150 to 290°C and consists of hydrocarbons approximately in the range of C<sub>9</sub>-C<sub>16</sub>. Kerosenes are the lighter end of a group of petroleum substances known as middle distillates, the heavier end being gas oils. The predominant use of kerosene in the U.S.A. is aviation turbine fuel for civilian (using Jet A or Jet A-1) and military (using JP-8 or JP-5) aircraft. Kerosenes are also used as diesel fuel, domestic heating fuel, and illuminating kerosene. Kerosene-based fuels differ from each other in performance specifications (primarily freezing point or sulfur concentration) and minor amounts of performance additives that may be added (generally less than 0.1% v/v) [1,2].

While kerosenes are similar in composition, the precise composition of a specific kerosene-range refinery stream depends on the crude oil from which the kerosene was derived and on the refinery processes used for its production. Because they are complex petroleum derived hydrocarbons, substances in this category are typically not defined by detailed compositional data but instead 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/cm<sup>3</sup> 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].

Regardless of crude oil source or processing history, kerosene's major components are branched and straight chain alkanes and naphthenes (cycloalkanes), which normally account for at least 70% by volume. Aromatic hydrocarbons in this boiling range, such as alkylbenzenes (single ring) and alkyl naphthalenes (double ring), do not normally exceed 25% by volume of kerosene streams. Olefins are usually not present at more than 5% by volume [5].

The flash point of kerosene is between 37 and 65°C, and its auto ignition temperature is 220°C. The pour point of kerosene depends on grade, with commercial aviation fuel standardized at -47°C. Heat of combustion of kerosene is similar to that of diesel; its lower heating value is 43.1 MJ/kg (around 18,500 Btu/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 Kazakhstan market by using alcohol-kerosene blends. The presented solution is easy, feasible, cheap, and environmental-friendly.

Alcohol-kerosene blends are potentially highly important for Kazakhstan's economy because the following reasons:

- The necessity to reduce pollution is growing every day and became important problem for Kazakhstan;

- The price for iso-propanol is relatively low in Kazakhstan and therefore the production of alcohol-kerosene blends is practical and profitable.

## MATERIALS AND METHODS

### Preparation of isopropanol-kerosene blend

In order to prepare the blend fuel, KazMunaiGaz kerosene and Sigma-Aldrich iso-propanol were used. The quality of feedstock is important for the quality of final blend. The used raw materials have the properties described in Table 1 and 2.

**Table 1 Properties of iso-propanol used for the blend**

Property	Value
Formula	C <sub>3</sub> H <sub>8</sub> O
Molar mass, g/mol	60.1
Density at 20°C, g/cm <sup>3</sup>	0.786
Melting point, °C	-89
Boiling point, °C	82.6
Acidity, pKa	16.5
Refractive index	1.3776
Viscosity, cP	
at 15°C	2.86
at 25°C	1.96
at 30°C	1.77
Vapor Pressure, mmHg	33
Flash point, °C	12
Freezing point, °C	-88.33

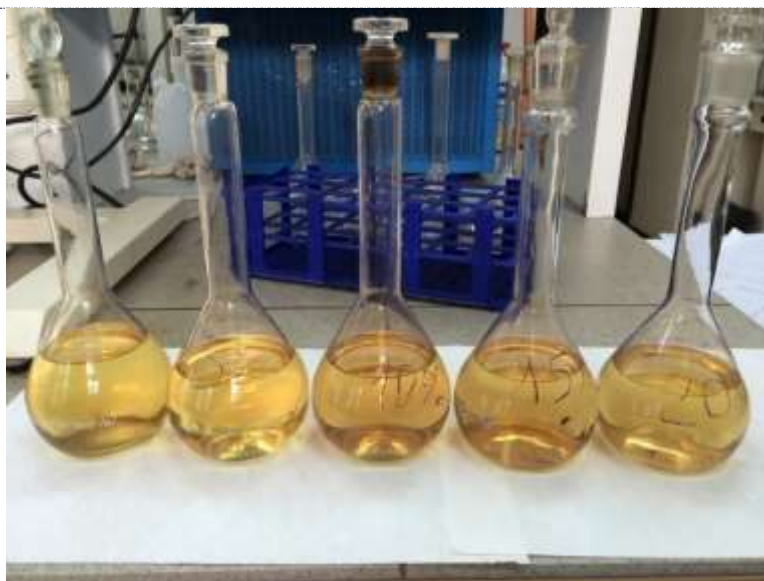
**Table 2 Properties of kerosene used for the blend**

Property, units	Value
Density at 15°C, g/cm <sup>3</sup>	0.7879
Kinematic viscosity, cP	
At 15°C	2.0481
At 40°C	1.3331
Distillation, °C	
IBP	125
10% volume	154
50% volume	203
90% volume	228
Flash point, °C	39
Freezing point, °C	-40

Literature reported that isopropanol retards fuel combustion, prevents knocking, and has almost zero NO emissions; it also controls rapid heat release [13]. Isopropanol is also expected to decrease the freezing point of kerosene, but decreasing the flash point and the initial boiling point. Isopropanol acts as an emulsifier for water in kerosene.

Preparation was done by simple mixing at room temperature, at 1000 rpm mechanic stirrer for 0.5 h each sample, due to the fact that both components are fully miscible at room temperature, and no emulsifier is needed.

The resulting samples had the appearance shown in Figure 1. There was no significant change in turbidity, appearance, or color with isopropanol addition.



*Figure 1 Comparative photo of kerosene and isopropanol-kerosene blends*

### Experimental Procedure

In order to draw a complete characterization of samples, several important features were analyzed. The LS-MS was performed with a Bruker Solaris equipment, using an eluent formed by a mixture of n-hexane and isopropanol, with argon as carrier gas. Physical and chemical properties were determined according to ASTM determination methods shown in table 3.

*Table 3 Test methods used for sample characterization*

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

Literature reported an indirect method for the estimation of heat of combustion for kerosene, taken into account its specific gravity [14]:

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

where  $d$  is specific gravity, calculated with the formula:

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

According to [14], aniline point helps to the estimation of combustion performance of kerosene, expressed as aniline gravity, calculated with the following formula:

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

where  ${}^\circ API$  is the specific gravity, and  $AP$  is the aniline point.

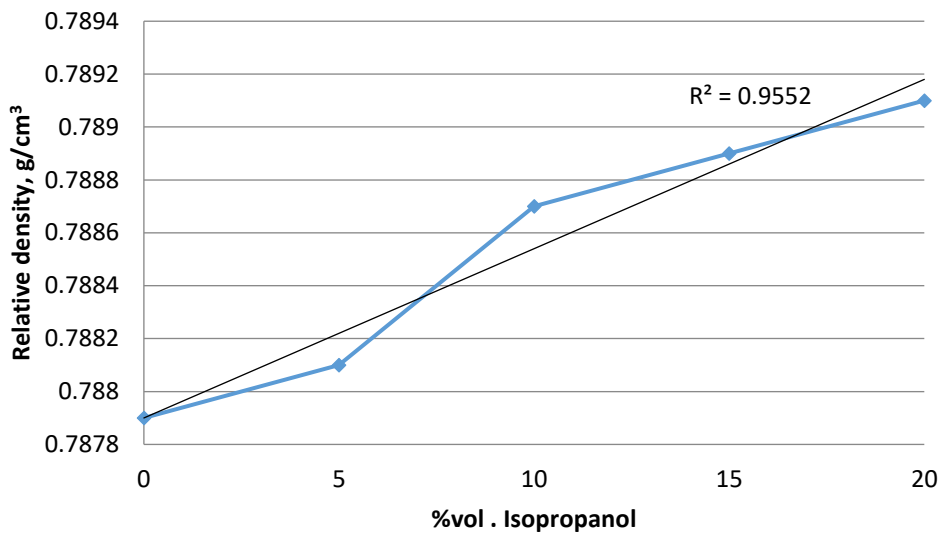
The flash point was calculated using the API method, which has a 5° error, for comparison, with the following formula [14]:

$$T_f = \frac{1}{-0.02421 + \frac{2.84947}{T_{10}} + 0.0034254 \ln T_{10}} \quad (4)$$

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

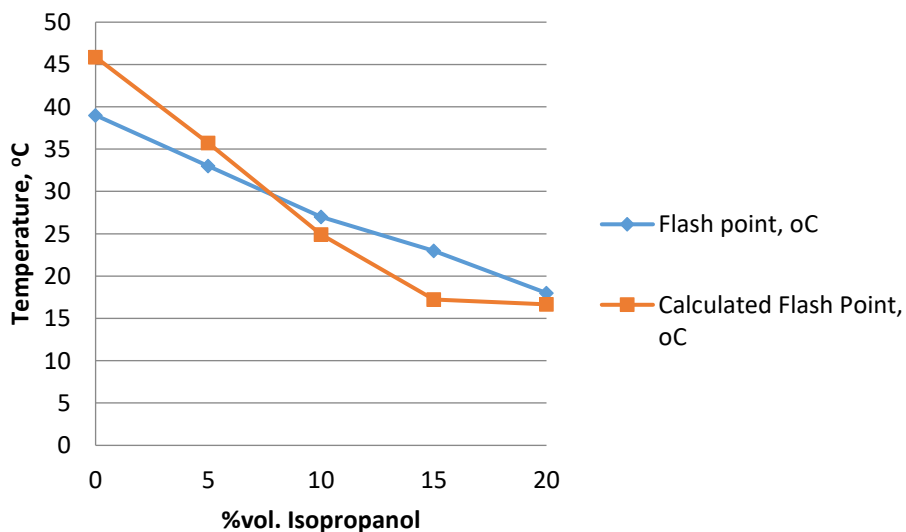
**RESULTS AND DISCUSSIONS**

Figure 2 shows the density variation of blends. It can be seen that the density of the samples barely increases with the amount of alcohol in the mixture. The reason is that both components have similar densities, and the noticed difference may be due to error, which still stays in the 0-2% admissible range.



*Figure 2 Density variation with isopropanol content*

As the distillation curves of all samples were drawn, it was possible to compare the estimated and the determined flash points. The temperatures corresponding to 10% volume distilled were 154, 142, 136, 126, and 120°C, respectively. From Figure 3, it can be noticed that there is a difference around the 5° error between the analytical and experimental values.



*Figure 3 Calculated and determined flash point of samples*

When plotted against isopropanol content, flash and fire points exhibit a decrease with increasing alcohol content, due to the low flash point of isopropanol, that is just 12°C (Fig.4). Taking into account the fire danger, it could be concluded that there would be two solutions in order to overcome this inconvenient: isopropanol content must be limited to 5% volume, or different stabilization additive for flash and fire point must be chosen to correct the inappropriate values.

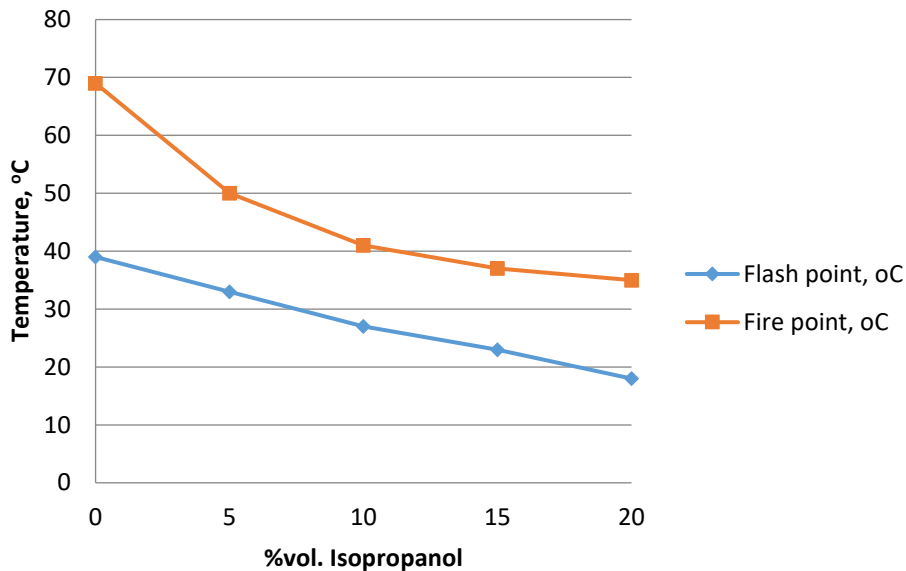


Figure 4 Flash and fire points of the samples

Results plotted in Figure 5 show that kinematic viscosity decreases with increasing isopropanol content because of the difference of components viscosity and ability to wet the walls. The change in kinematic viscosity of blend with isopropanol content may be due to the rearrangement of molecules, further reactions between components, especially alkyl radicals and low paraffins, leading to a decrease in viscosity and further sliding between molecules, with the overall effect of improving rheological behavior of blends. The figure also shows an expected decrease in viscosity with increasing temperature.

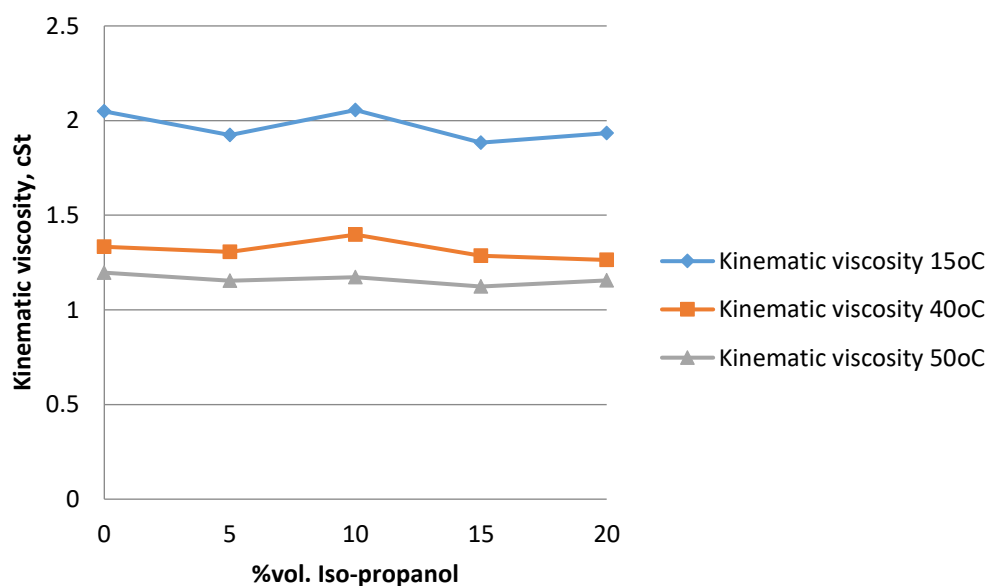


Figure 5 Kinematic viscosity variation with temperature and isopropanol content

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From figure 7, it can be seen that the dynamic viscosity slightly increases with increasing isopropanol in the mixture, because of the difference in kinematic viscosity and density of components. Dynamic viscosity is the product between kinematic viscosity and density.

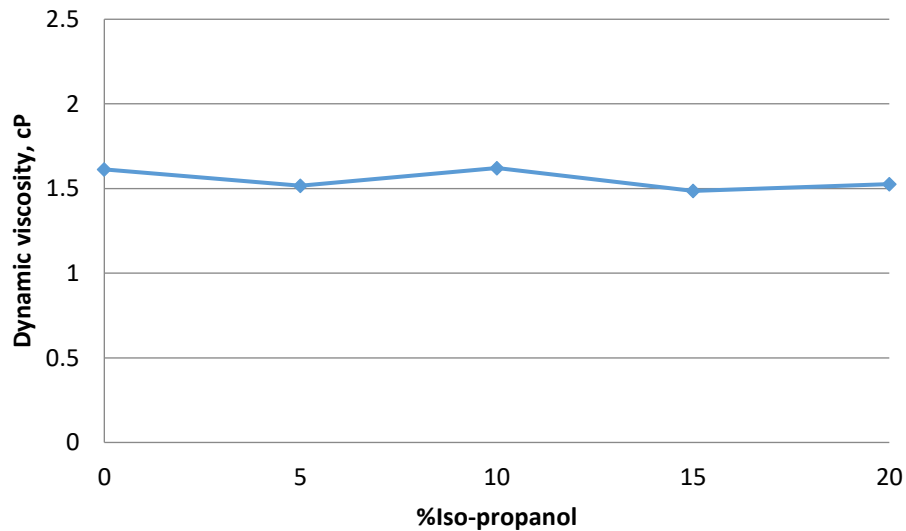


Figure 7 Dynamic viscosity of blends

From the distillation curve, under atmospheric pressure, it was noticed that the isopropanol decreased the initial boiling point of the blends, together with an overall shift towards lower distillation range for the whole distilled samples (Figure 8).

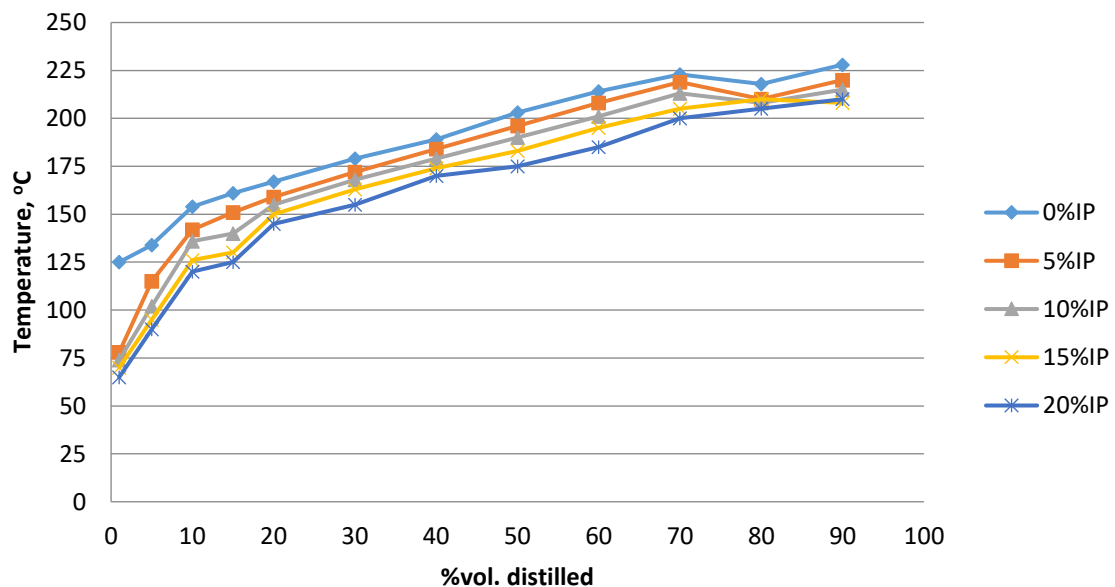


Figure 8 Distillation curve for kerosene

Figure 9 shows the evolution of heat of combustion for blends with isopropanol content. Due to the small difference in density, the calculated heat of combustion has only 0.03% difference for 20% volume isopropanol. Another aspect of the variation in heat of combustion is the linear trend, also a result of the linear decrease in density with increasing isopropanol content. The variation of heat of combustion with isopropanol content, though



small, underlines the effect of this constituent on combustion delay, knocking prevention, and better heat release reported in literature [13].

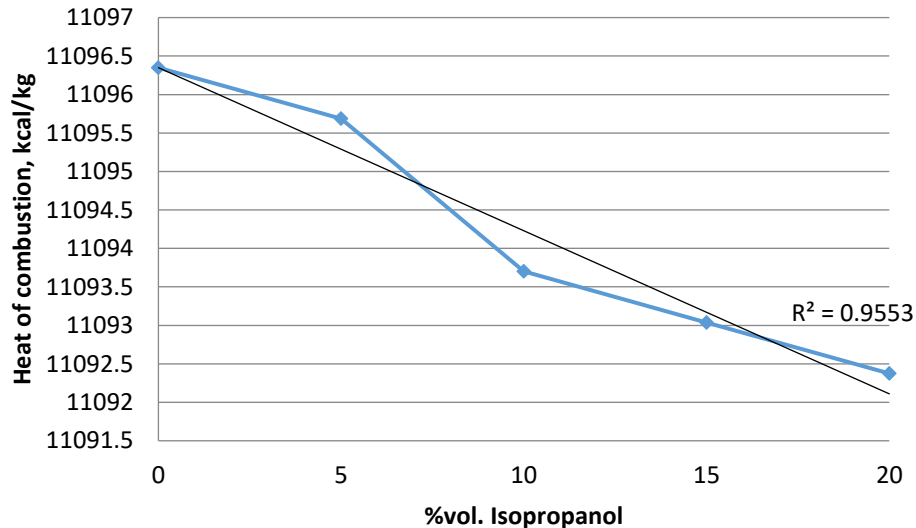


Figure 9 Calculated heat of combustion of blends

As seen in figure 10, freezing, pour and cloud points decrease with increasing volume of alcohol. The reason is the low freezing point of iso-propanol, causing depletion in freezing points almost proportional to its percentage in blends. The positive effect of isopropanol on the kerosene blend 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. Corroborating with heat of combustion, it explains the retard in fuel combustion and knocking prevention previously reported [13].

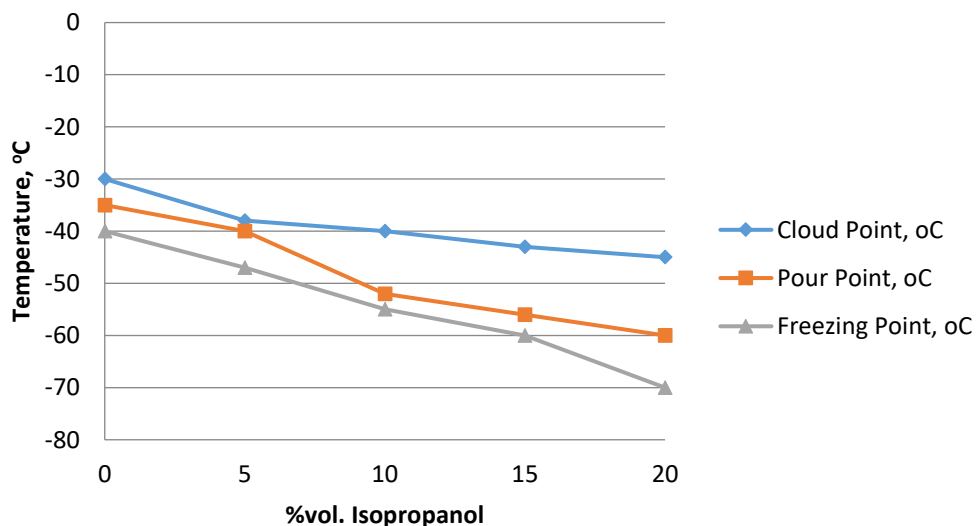
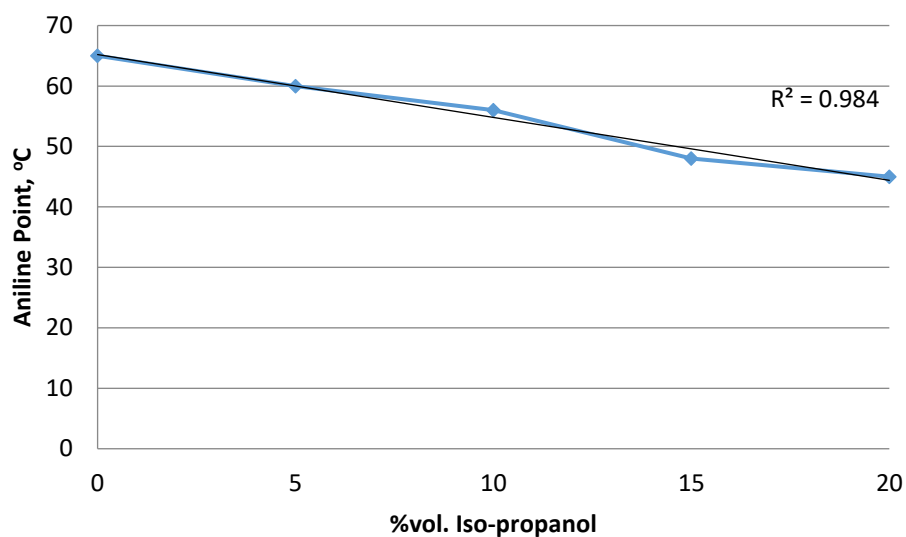


Figure 10 - Comparison of cloud, pour and freezing points

Figure 11 shows the aniline point variation with isopropanol content, revealing a decrease in aniline point with increasing alcohol content. The evolution is due to the decrease in aromatic hydrocarbon content of the overall blend, as a direct result of isopropanol addition.

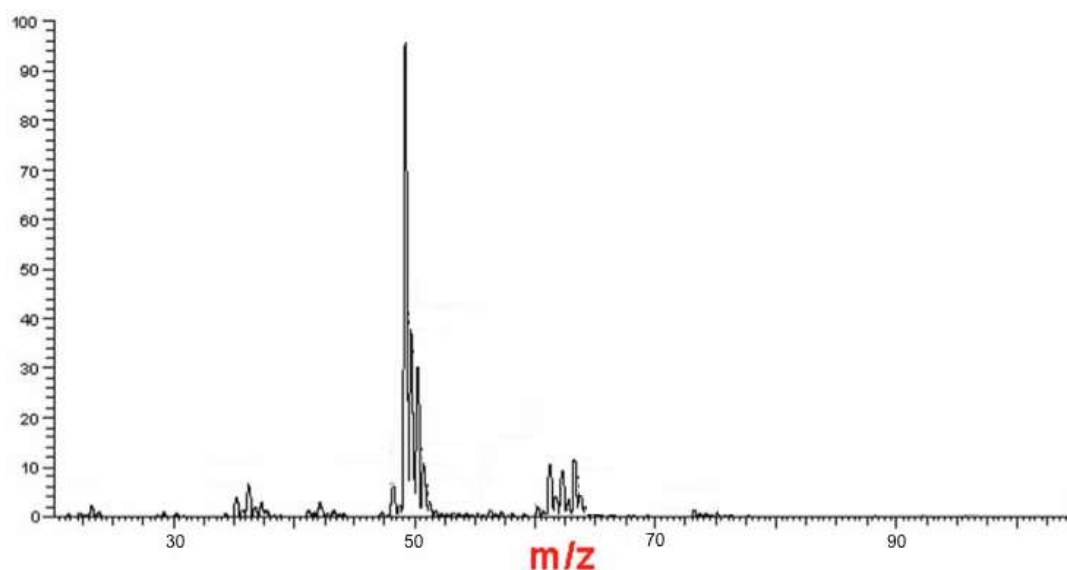




*Figure 11 Aniline point of blends*

LC-MS spectra revealed the relative concentration of hydrocarbons contained in kerosene, and the change with isopropanol addition. The mass-to-charge ratio  $m/z$  in respect to relative abundance for the analyzed samples are shown in Figure 12-16. The TIC curve as well as the retention time versus intensity were not available, therefore it was not possible to perform the precise identification of chemical species and their concentration from peak areas. However, several observations could be done, using NIST database:

- The raw kerosene used for blends contains few low molecular weight hydrocarbons, the most abundant hydrocarbons being, in increasing  $m/z$  order, benzene, *n*- and *i*- pentane, pentane-3-one, 2 methylbutane, 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.
- There are no polyaromatic hydrocarbons in the kerosene used for blending ( $m/z$  higher than 200).
- With increasing isopropanol content, methanol, benzyl alcohol, cyclohexanol appear in the mixture, revealing a reaction between isopropanol and the hydrocarbons inside kerosene, especially between low molecular mass and alkyl radicals connected to aromatic rings, as well as alcohol formation with cycloparaffins and aromatics.



*Figure 12 Spectrum of kerosene*

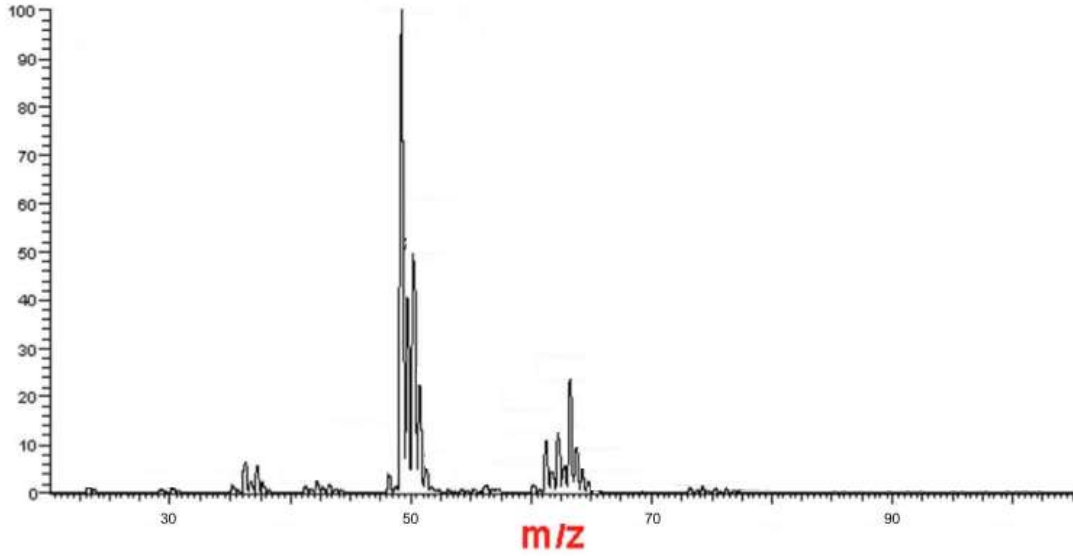


Figure 13 Spectrum of 5% volume isopropanol blend

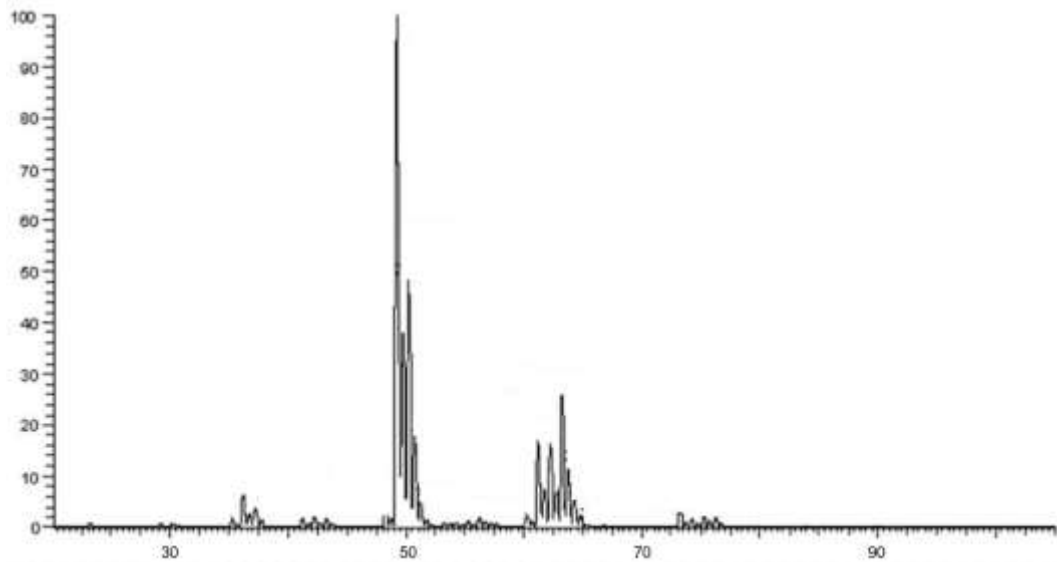
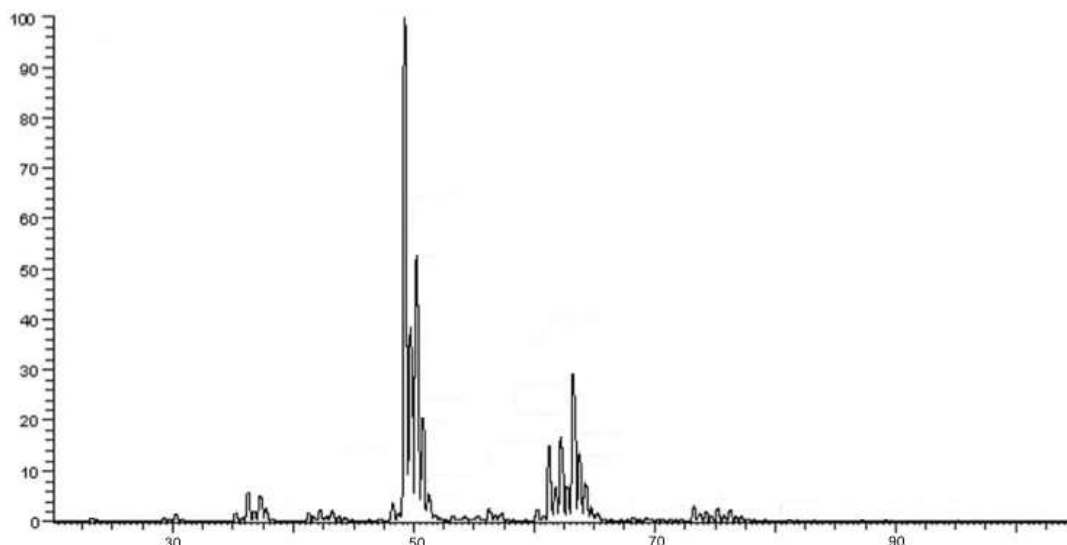
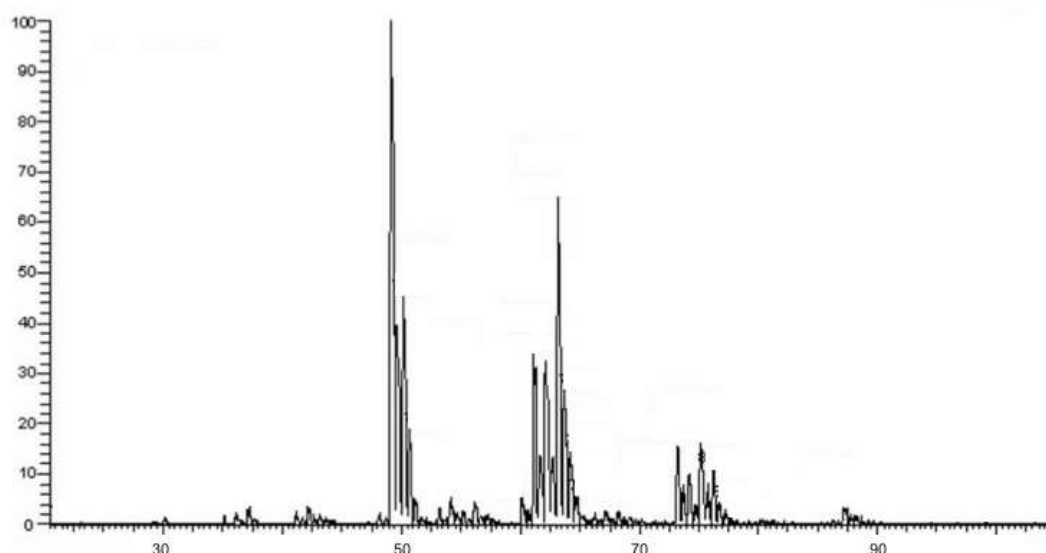


Figure 14 Spectrum of 10% vol. isopropanol mixture



*Figure 15 Spectrum of 15% vol. isopropanol blend*



*Figure 16 Spectrum of 20% vol. isopropanol mixture*

## CONCLUSIONS

The motivation to develop alternate fuels for commercial aviation is twofold: First, with respect to near-term concerns, alternate fuels will relieve the worldwide pressure on crude oil derived fuels. This will help to stabilize price fluctuations. Secondly, with respect to mid-term concerns, alternate fuels should increase environmental performance of air transportation, including a substantial potential for reduction of CO<sub>2</sub> emissions over the life cycle. Thus, the ideal alternate fuel will fulfill both requirements: to relieve the worldwide pressure for crude oil derived fuels and to significantly reduce CO<sub>2</sub> emissions.

It has the potential to release pressure from pure crude oil derived fuels, without a long delay. However, it will not reduce CO<sub>2</sub> emissions over the entire life cycle. Moreover, if the additional process related CO<sub>2</sub>-emissions are not captured and sequestered, the total CO<sub>2</sub>-emissions may double.

Including future renewable derived bio-fuels and its blends with synthetic fuels, offer the promise of a complete replacement for crude oil derived fuels. In addition, for at least the CO<sub>2</sub>- emissions from the bio-derived fuel fraction, it offers the chance for an atmospheric neutral CO<sub>2</sub> balance fuel.

Isopropanol retards fuel combustion, prevents knocking, and has almost zero NO emissions; it also controls rapid heat release and acts as an emulsifier for water in kerosene.

Preparation for the innovative aviation fuel was fast and easy. Blends were done by simple mixing at room temperature, at 1000 rpm mechanic stirrer for 0.5 h each sample, due to the fact that both components are fully miscible at room temperature, and no emulsifier is needed.

From the laboratory work, the following conclusions can be drawn:

- There was no significant change in turbidity, appearance, or color with isopropanol addition;
- Density of the samples barely increases with the amount of alcohol in the mixture, because both components have similar densities;
- Flash and fire points exhibit a decrease with increasing alcohol content, due to the low flash point of isopropanol, that is just 12°C. There would be two solutions in order to overcome this inconvenient: isopropanol content must be limited to 5% volume, or different stabilization additive for flash and fire point must be chosen to correct the inappropriate values;
- Kinematic viscosity decreases with increasing isopropanol content because of the difference of components viscosity and ability to wet the walls. It may be due to the rearrangement of molecules, further reactions between components, especially alkyl radicals and low paraffins, leading to a decrease in viscosity and further sliding between molecules, with the overall effect of improving rheological behavior of blends.
- Regarding the distillation curve, under atmospheric pressure, the isopropanol decreased the initial boiling point of the blends, together with an overall shift towards lower distillation range for the whole distilled samples;
- Heat of combustion barely decreases with increasing amount of alcohol. The variation of heat of combustion with isopropanol content, though small, underlines the effect of this constituent on combustion delay, knocking prevention, and better heat release reported in literature;
- Freezing, pour and cloud points decrease with increasing volume of alcohol due to the low freezing point of isopropanol. The positive effect of isopropanol on the kerosene blend 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;
- There is a decrease in aniline point with increasing alcohol due to the decrease in aromatic hydrocarbon content of the overall blend.

From LC-MS, the following conclusions appear:

- The raw kerosene used for blends contains few low molecular weight hydrocarbons, the most abundant hydrocarbons being, in increasing m/z order, benzene, n- and i- pentane, pentane-3-one, 2 methylbutane, 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.
- There are no polyaromatic hydrocarbons in the kerosene used for blending (m/z higher than 200).
- With increasing isopropanol content, methanol, benzyl alcohol, cyclohexanol appear in the mixture, revealing a reaction between isopropanol and the hydrocarbons inside kerosene, especially between low molecular mass and alkyl radicals connected to aromatic rings, as well as alcohol formation with cycloparaffins and aromatics.

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