Full Length Article

Production process of di-amyl ether and its use as an additive in the formulation of aviation fuels

Renato Cataluña[a,*], Zeban Shah[a], Vanessa Venturi[a], Nattan R. Caetano[b], Bibiana Porto da Silva[b], Carla M.N. Azevedo[c], Rosângela da Silva[d], Paulo A.Z. Suarez[d], Lincoln P. Oliveira[d]

[a] Federal University of Rio Grande do Sul, Av. Bento Gonçalves 9500, 91501-970 Porto Alegre, RS, Brazil
[b] Federal University of Santa Maria, 97105-900 Santa Maria, RS, Brazil
[c] Pontifical Catholic University of Rio Grande do Sul, Av Ipiranga 6681, 90619-900 Porto Alegre, RS, Brazil
[d] Universidade de Brasília, Campus Universitário Darcy Ribeiro, 70910-900 Brasília, DF, Brazil

ABSTRACT

This work deals with the production of a high added value ether used as additive in aviation fuel. The ether was synthesized from the *iso*-amylenes present in the C₅, the five-carbon isomer cuts in petroleum distillates and the *iso*-amyl alcohol found in the fusel oil of the alcohol industry. Qualitative analyses like mass spectrometry and nuclear proton magnetic resonance spectroscopy confirmed the formation and structure of the proposed semi-renewable ether, the high molecular weight di-amyl ether (DAE). Optimization of the reaction parameters resulted in a conversion of the 48%, molar fraction, *iso*-amylenes when using an adiabatic profile reactor. By using this ether production and purification process, the final product showed 98% w/w of purity. The synthesized di-amyl ether presented physicochemical properties similar to the commercial aviation kerosene. The physico-chemical properties evaluation performed in the mixtures of di-amyl ether in aviation kerosene showed relevant improvements, such as reduction of the freezing point and increase of the oxidation reaction rate. The results showed this novel fuel has great potential to be used in gas propulsion turbines in commercial flights and is also strategic for military aircraft.

1. Introduction

In recent decades, there has been a considerable increase in the concentration of pollutants in the atmosphere, especially greenhouse gases. The share in anthropogenic carbon dioxide (CO_2) emissions from the aviation sector will rise above the current 2–3%, as a consequence of the expectation of the aviation industry growth up to 2035 [1–3]. Although the airline industry is 70% more efficient today than 40 years ago, the development of this sector should exceed the estimation of increase in fuel efficiency in the same period [4]. In addition, the decline of fossil fuel reserves has also fomented advances in the development of alternative fuels for aviation [5–8].

The most commonly used aviation fuels are kerosene-type obtained from petroleum. Many different types of kerosene are currently being produced. Jet fuel, aviation turbine fuel (ATF), or avtur, is a type of aviation fuel designed for use in aircraft powered by gas-turbine engines. It is colorless to straw-colored in appearance. The only other jet fuel commonly used in civilian turbine-engine powered aviation is Jet B, which is used for its enhanced cold-weather performance. Jet fuel is a mixture of a large number of different hydrocarbons. The range of their sizes (molecular weights or carbon numbers) is defined by the requirements for the product, such as the freezing or smoke point. Kerosene-type jet fuel (including Jet A and Jet A-1) has a carbon number distribution between about 8 and 16 (carbon atoms per molecule); wide-cut or naphtha-type jet fuel (including Jet B), between about 5 and 15. [9] Among these, the most employed kerosene is the commercial fuel Jet A-1 [10,11]. Civil aviation kerosene, also named as QAV-1, is compatible with the Jet A-1 specifications laid down by the AFQRJOS (Aviation Fuel Quality Requirements for Jointly Operated Systems) and complies with the National Petroleum, Natural Gas and Biofuel Agency specifications [12–16]. Taking into account the environmental factors along with economic issues a growing interest in developing alternative fuels for aviation using sustainable feedstock has been promoted [4,7,17,18]. The investigation in the jet fuel formulation focusing in the alternative fuels with similar properties to Jet A-1. Before a blend can be approved for use in aviation fuel, it must undergo extensive testing to show both that it is effective and that it does no harm to any other fuel properties.

Several approaches have been developed to produce jet fuels [6,11,19], including the hydrodeoxygenation of vegetable oils [20,21], Fischer Tropsch synthesis [22,23], catalytic conversion of sugars [24,25], synthesis from algae [26,27] and other procedures.

Knowledge of the good antiknock properties of some oxygenated compounds dates back to the 1930's, when improvements in aircraft performance resulted in a demand for fuels of increasingly higher antiknock performance [28]. In the beginning of the 80's methyl tertiary butyl ether (MTBE) started replacing tetra-ethyl lead as a gasoline additive worldwide. However, its use has been restricted because of its high solubility in water, toxic effect and the subsequent environmental and human health problems [29,30]. Due to their high octane numbers and low volatilities, *tert*-amyl-ethyl-ether (TAEE), *tert*-amyl-methyl-ether (TAME) and ethyl *tert*-butyl ether (ETBE) are considered as attractive alternatives to MTBE as gasoline blending oxygenates [31–35]. However, these ethers do not have volatility characteristics required to be used in aviation kerosene formulations. Several requirements must be met for the fuel to be classified as aviation fuel, among these requirements are: high energy density, aiming to maximize the reach and reduce the carried fuel load; rapid evaporation and atomization; low risk of explosion; appropriate viscosity; physical and chemical stability and low freezing point [4,36].

In the present study, a new process of production and purification, in semi-pilot scale, of the di-amyl ether (DAE), partially obtained from renewable source (semi-bio-ether) is reported. The DAE synthesis was performed for the first time in our laboratory [37–39]. Iso-amyl alcohol (present in the fusel oil from the distillation of ethanol from sugarcane) and a C_5 hydrocarbons cut (2-methyl-1-butene and 2-methyl-2-butene olefins provider) were used as reagents, in addition to resin Amberlyst 36 as a catalyst. The DAE was characterized and used as an additive in formulations with aviation kerosene (QAV-1), supplied by Petrobras. The physicochemical properties of fuel blends obtained by mixtures of DAE/QAV-1 (10%, 20% and 30% mass) were evaluated with respect to volatility, freezing point, viscosity and density [40,41]. These key fuel properties were compared with commercial aviation kerosene.

The main motivation of this work is to present the process of production of a new semi-renewable bio-ether and its performance as aviation fuel additive. The main characteristics of this ether are the low freezing point due to its branched structure and the high oxidation ration rate due to the presence of oxygen in its molecular structure.

2. Material and methods

2.1. Synthesis of di-amyl ether (DAE)

In the synthesis process of the di-amyl ether, iso-amyl alcohol (present in the fusel oil, an industrial residue obtained from the distillation of sugarcane ethanol) and C_5 hydrocarbons cut from thermal cracking of naphtha unit were used. The average molar composition of C_5 extracted hydrocarbons used in the DAE synthesis is shown in Table 1. The single reactive olefins in the DAE synthesis present in the reaction mixture are the olefins which have a tertiary carbon, i.e. 2-methyl-1-butene and 2-methyl-2-butene.

The resin *Amberlyst™* 36 (A-36), *Rohm and Haas France SAS*, were used as a catalyst in the DAE synthesis reaction, in the humidified form. The reaction system conditions itself, allowing the passage of *iso*-amyl alcohol to 80 °C. For this study, an adiabatic reaction system was used, followed by distillation purification steps. A liquid flow controller was employed in order to ensure the reactants charge flow in the reaction system.

The adiabatic reactor used has 1150 mL of internal volume, completely filled with the catalyst, which operates under 800 kPa. This reactor was fed by a cylinder containing a predetermined reagents mixture of the *iso*-amyl alcohol and C_5 hydrocarbon, under a pressure of 1.2 MPa. Fig. 1 shows a schematic diagram of the reaction system and the global flow of the reactor effluent purification system.

Table 1

The average molar composition of C_5 extracted hydrocarbons, obtained by gas chromatographic analysis using a flame ionization detector. Where C_4's, C_5's and C_6's represent the hydrocarbons with 4, 5 and 6 carbon atoms, respectively.

Chemical Components	(% mol)
C_4's	1.38
C_5's	15.72
Isopentane	12.30
2-methyl-1-butene	4.60
n-pentane	16.25
2-methyl-2-butene	17.50
Cyclopentene	15.65
Cyclopentane	14.30
C_6's	2.30

Since the synthesis reaction of the DAE is exothermic, the temperature control of the catalytic bed for an adiabatic reactor was carried out by adjusting the temperature of the reactor load. A backpressure valve ensured the pressure inside the reactor and an ice and salt cooling system was responsible for proper sampling of the reactor effluent. The synthesis reaction of DAE is an exothermic reaction that tends to equilibrium. Thus, the lower the temperature of the reaction system, the greater the conversion of the reagents into products. However, using low temperatures, the reaction rate decreases considerably, causing low space velocities to be used to achieve close-to-equilibrium conversions. Taking into account these requirements and based on a space velocities of $1.0 \, h^{-1}$, the temperature range between 40 and 45 °C was defined as an optimal operating condition for the adiabatic reactor and unit molar ratio, maintaining the reactor pressure at 800 kPa [39].

The DAE obtained was subjected to a fine purification system with several atmospheric distillation stages, in order to obtain a product purer than 98%. Distillation process, using packed columns (Fig. 1), were fed with controlled flow through liquid flow controllers. This system also promoted the recovery of the reagents for a second pass in the reaction system, which increases the final conversion rate.

In the first column of the purification system, the light weight compounds at the top (hydrocarbons inert in the reaction together with a small fraction of *iso*-amyl alcohol) were eliminated and at the bottom of the column, essentially, DAE and residual *iso*-amyl alcohol were obtained. The stream at the top should be reprocessed, representing the second reaction pass of the C_5 cut extracted, in order to exhaust it to the maximum, increasing the production yield. The stream at the bottom was processed in two other distillation stages, separating *iso*-amyl alcohol and DAE. The *iso*-amyl alcohol in the purification process of the DAE does not present adequate purity to pass through the reaction system. Thus, another distillation system was required to perform the rectification. In this way, the recovered alcohol was available to be reprocessed again in the system.

Quantitative analyses were performed applying gas chromatography coupled to a flame ionization detector (GC-FID, model Varian® 39 XL) with automatic injection, equipped with a CP-Sil PONA capillary column CB (dimethylpolysiloxane, 100 m × 0.25 mm × 0.25 µm) in order to monitor the DAE production and purification processes. The injected sample volume was 0.5 µL for a split ratio of 1:60. Helium was used as a carrier gas, with purity above 99%, provided by White Martins®. A heating system keeps the furnace on an isothermal condition over 10 min in 50 °C, followed by a heating rate $5 \, °C \, min^{-1}$ until the temperature reaches to 75 °C, initiating a new heating rate of $8 \, °C \, min^{-1}$ until 250 °C, remaining until the end of the analysis for 40 min.

The by-products of reaction were identified in a gas chromatograph with a four-pole mass detector (GC-MS, model Agilent® 6890 plus with MS 5973 N). HP-1 (dimethylpolysiloxane, 100 m × 0.25 mm × 0.5 µm) fused silica capillary column was used, initially at 35 °C for 15 min,