



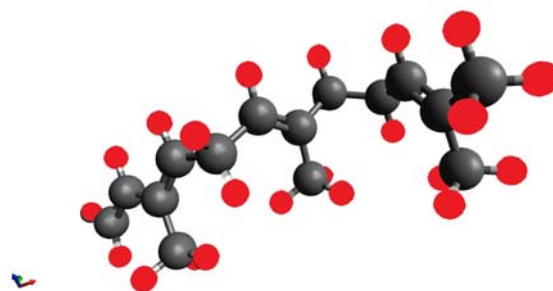
## BIOJET FROM SUGAR DERIVATIVES

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This study shows the research using the  $\alpha$  and  $\beta$  farnesene mixtures to obtain the biojet fuel. Hydrotreating experiments were made at 60 bar pressure,  $1\text{h}^{-1}$  hourly space velocity, 350, and 370 °C for Co-Mo/ $\gamma\text{Al}_2\text{O}_3$  and 170°C for Pt/active charcoal catalysts. Also, this paper has focused on the influence of the catalyst and of the hydrotreating conditions on the composition and the properties of the biojet obtained in conformity with the Jet A1 quality standards required by ASTM D1655.



### INTRODUCTION

The air transportation sector knows a rapid evolution and integration in the daily life, being the fastest method of transportation for passengers. The evolution of this sector led to a continuous demand of fuel for the gas turbines that power most commercial airplanes. In 2018, the total demand for jet fuel has grown to 356 billion liters, while in 2019 the demand went to 375 billion liters, on a rise with 5.3 %.<sup>1</sup>

The demand for fuel can be associated with the rise in passenger transport: from 4.09 billion in 2017 to 4.358 billion in 2018, with the market aiming for a rise in numbers of 5 to 6 % per year for the next 20 years. Besides the passenger air transportation, the air freight transportation is starting to gain an importance, especially for the merchandise that's being bought and sold online.<sup>2,3</sup>

Currently, the primary fuel used for powering airplane gas turbines is a petroleum fraction called kerosene, which is formed out of a mixture of

hydrocarbons ( $\text{C}_8\text{-C}_{16}$ ), with a majority made out of paraffins which are characterized by a high specific energy, smokeless burn and no traces of particle matter when burnt. Out of the paraffinic hydrocarbons, it's preferred to have those with a branched structure because they have a lower freezing point. Also, the naphthenic hydrocarbons found in kerosene have a good burning and cold flowing characteristics. The aromatic content like alkylbenzenes is limited to a 20-25 % because aromatics have a low specific energy per unit of volume, generate smoke while burning and generate large quantities of particle matter.<sup>2,3</sup> A drastic reduction in aromatic content would improve significantly the quality characteristics of jet fuel but it would also increase the costs of the due to a more severe hydrotreating done by refiners and it will generate problems in the running the gas turbine because a low content of aromatics is desirable for maintaining the elasticity of gaskets which would prevent any fuel leaks.<sup>4,5</sup>

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The quality requirements for jet fuel have become much more rigorous over the years. The reason for these restrictions is strongly linked to the environmental impact and the increasing requirement for more performant fuels for the aviation industry. The most widely used standard for jet fuel Jet A fuel is ASTM D1655, which defines the main requirements for composition, volatility, composition, thermal stability, cold flow properties etc.

Usage of fossil fuels is a great challenge due to increase demand for fuels while the petroleum resources are shrinking. The supply and demand imbalance are toppled by the instability of oil barrel price and the environmental impact generated by the usage of fossil fuels which result in more CO<sub>2</sub> emissions (the main greenhouse gas responsible for global warming). By burning 1 kg of jet fuel, it's generated 3.2 kg of CO<sub>2</sub>, which makes the aviation industry responsible for about 2 % of the global CO<sub>2</sub> emissions.<sup>6</sup>

The aviation industry uses a smaller quantity of fossil fuel than the land and maritime transportation, the CO<sub>2</sub> emissions generated by the aviation industry still remain a challenge for the future since for the other modes of transportation there are other alternatives with different types of energy that can fuel transportation, while the aviation industry will continue to use liquid fuels.

In order to fulfill the environmental challenges for CO<sub>2</sub> emission reduction, the usage of biofuels as components in fossil fuels is a better alternative. As a consequence, EU and IATA have formulated directives (*i.e.*: 2009/28/EC) which recommend a usage of 10 % biojet, which should improve the energetic efficiency by 1.5 % and drop the CO<sub>2</sub> emissions by 50 % on a timeframe between 2010 to 2050.<sup>7</sup>

Based on the yearly growth of air traffic, usage of biojet from biomass with the aim of protecting the environment and reducing the operating costs is a solution widely debated on the globe.

There are many processes which convert the biomass in jet fuel substitutes. Biomass derived bio-oils are processed and converted in bio-jet through hydrotreatment processes, including deoxygenation, isomerization and hydrocracking reactions. The most well-known Oil-to-Jet (OTJ) processes Hydroprocessed Renewable Jet (HRJ) and Hydroprocessed Esters and Fatty Acids (HEFA).<sup>8-10</sup>

Through these methods, the biofuel obtained is called "green jet" and is formed out of paraffins with 8 to 18 carbon atoms, has no sulfur and a low content of aromatics, which allows this fuel to be mixed in bleedings up to 50 %. These technologies

have the advantage that can be easily integrated into the hydrotreatment processes in refineries, which can process vegetable oils and petroleum fractions at a reduced cost.

Another method of obtaining biojet is through the Gas-to-Jet (GTJ) method, through which the biomass of different types – especially the agricultural waste, food industry waste etc can be gasified into a synthesis gas (Syngas) which is processed further through Fischer-Tropsch and results a liquid hydrocarbon compatible with jet fuel.<sup>11,12</sup>

A third technology for obtaining biojet is called Alcohol-to-Jet, which is sometimes called Alcohol-to-Jet Synthetic Paraffinic Kerosene (ATJ-SPK) which utilizes in the synthesis process C<sub>2</sub>-C<sub>4</sub> alcohols (ethanol and isobutanol) obtained through aerobic fermentation of biomass.<sup>5,13</sup>

A fourth technology used for obtaining biojet is Sugar-to-Jet (STJ). This technology uses the bioconversion of sugars from biomass, resulting from the aerobic fermentation a ramified sesquiterpene comprised from 3 isopren monomer units, called farnesene. The process has been turned to industrial scale by Amyris and transforms glucose and sucrose from biomass (especially sugar cane) through fermentation by genetically modified yeasts (*saccharomyces cerevisiae*) into farnesene which are separated through distillation to a purity of 96-97 %, after which they are saturated with hydrogen into a isoparaffin with 15 carbons called farnesan, an ideal component for biojet that is sometimes called Synthesized Iso-Paraffins (SIP).<sup>14,15</sup> Other researchers have studied the obtaining of β-farnesene from a two-stage biotransformation of waste cooking oils.<sup>16</sup>

Farnesan has been identified as a suitable replacement for jet fuel due to its good cold flow properties, high specific energy and low emissions in particle matter and Green House Gases (GHG).<sup>17</sup>

The raw material, farnesene, are obtained from biomass components like sugars and glucose through fermentation by genetically modified yeasts.

Polycyclic or macrocyclic sesquiterpenes have higher densities and energy density, which recommends them as bio components which can be mixed with fossil jet fuel and used as fuel for the aviation industry, civilian, military or rocket fuel.

The current paper presents the research done on obtaining high quality bio-jet components through hydrotreating of farnesene. Also, the current paper investigates the influence of the catalyst and of the hydrotreating conditions on the composition and the characteristics of the biojet obtained in accordance with the Jet A1 quality standards required by ASTM D1655.

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In this study we use an innovative way to obtain sesquiterpenes as compounds of the biojet by hydroconversion.

## EXPERIMENTAL

The raw material used for these experiments were a mixture of  $\alpha$  and  $\beta$  farnesene produced by Sigma Aldrich. The main characteristics of their product are presented in Table 1, while the molecular structure is presented in Fig. 1.

Two catalysts have been used: an industrial mild hydrocracking catalyst: Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and a catalyst of 0.5 % Pt/Active charcoal. The textural characteristics (specific surface, volume and average diameter of pores) have been determined based on the isotherms of adsorption-desorption of nitrogen using the Autosorb 1 Quantacrome laboratory machine. The specific surface has been calculated using the BET equation in the linear part of the adsorption isotherm

while the volume and average diameter of pores has been determined using the BJH method on the desorption part of the isotherms with hysteresis. The strength and distribution of acidity of the catalyst have been determined through thermodesorption with diethylamine.

### The micro-pilot plant

The experiments of hydrotreating has been performed in a micropilot unit (Fig.2), in a fixed bed reactor (length of 0,5 m, inside diameter of 25 mm, volume of 200 cm<sup>3</sup>) at 60 bar pressure, 1 h<sup>-1</sup> hourly space velocity and 1000 cm<sup>3</sup>/cm<sup>3</sup>.H<sub>2</sub>/feedstock ratio. An amount of 50 cm<sup>3</sup> catalyst was loaded in the middle of the reactor. The top and the bottom of the reactor were filled each with 75 cm<sup>3</sup> of inert glass beads which average diameter of 1-2 mm. The temperature was measured with an automatic system using two thermocouples inserted into reactor. The reactor work in quasi-isothermal regime, the temperature decreasing with 4-5°C from inlet to outlet. The temperature reaction was fixed in correlation with catalysts: 350, and 370°C for Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 170°C for Pt/active charcoal.

The resulted products from the farnesene hydrotreating experiments have been analyzed by GS-MS method, on a CP-3800 Triple Quad Agilent Technologies system.

For the identification and the analysis of the products, we used the NIST database. The analysis parameters of the GC/MS are presented in Table 2.

The characteristics of the catalysts used are showed in Table 3.

Table 1

Farnesene specification

Refractive index at 20°C	1.482
Specific gravity	0.865
Molecular Weight	204.35
Flash point	119.2

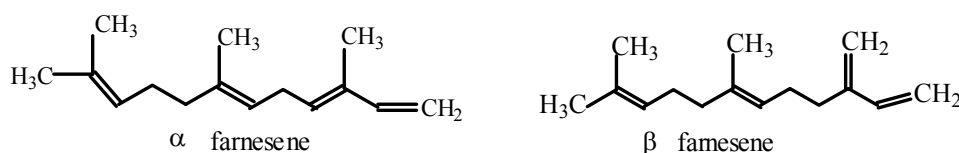


Fig. 1 –  $\alpha$  and  $\beta$  farnesene structure.

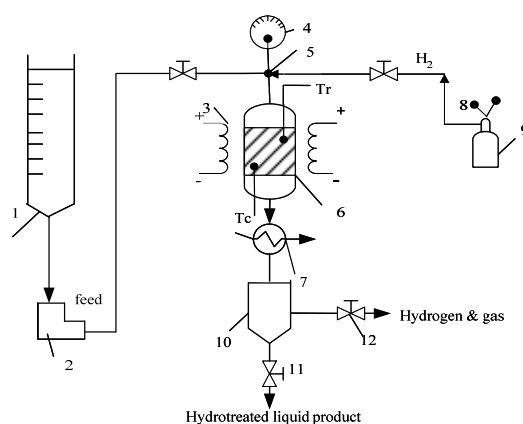


Fig. 2 – The hydrotreating micropilot.

(1.feedstock burette; 2. metering pump, 3. electric heater, 4.-gauge, 5. mixture point H<sub>2</sub> + feedstock, 6. reactor, 7. water cooler, 8. pressure controller; 9. H<sub>2</sub> tank, 10. separator, 11. valve exhaust products, 12. valve exhaust gas + H<sub>2</sub>, T<sub>R</sub>-thermoresistance, thermocouple T<sub>C</sub>)

Table 2

The Parameters of the GC/MS Analysis

Method GS	Method MS
Column DB-WAX (L=30m, D=250 $\mu$ m, d=0.25 $\mu$ m)	Collision cell: QQQ; Flow Quench Gas (He) = 2,2 mL/min; Flow rate of collision gas: (N <sub>2</sub> ) = 1.5 mL/min;
Oven program: 50°C for 1 min., then 7 °C/min. Up to 180 °C	Type of source: EI;
Carrier gas: He, flow rate 1mL/min	Electrons energy: 70 eV;
Injector temperature: 250 °C	Source temperature: 230°C;
	Auxiliary source: 280°C
Volume injected: 0,5 $\mu$ L	Type of chromatogram: TIC

Table 3

The catalysts properties

Catalyst	Surface Area m <sup>2</sup> /g	Pore Volume cm <sup>3</sup> /g	Pore diameter, nm	Acidic strength Milliequivalent/g catalyst			Acidic strength distribution, %		
				Weak	Medium	Strong	Weak	Medium	Strong
Co-Mo/ $\gamma$ Al <sub>2</sub> O <sub>3</sub>	219.3	0.423	5.4	0.850	0.760	0.085	50.14	44.83	5.03
0,5% Pt/Active Charcoal	132.07	0.132	3.279	0.405	0.554	0.187	35.34	48.35	16.31

## RESULTS AND DISCUSSION

The experimental results obtained after the hydrotreating of farnesene on the CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts are presented in, Fig. 3. and Fig. 4.

The data from Fig. 3 and Fig. 4 presents a composition contrary to the expectations. It's concluded that instead of obtaining mostly isoparaffins – as it was expected, it was obtained alkylbenzenes and naphthene. Moreover, instead of obtaining hydrocarbons with 15 atoms of carbon, the results showed hydrocarbons with 6 to 9 carbons. These results are justified by the strong unsaturated structure of the farnesene which allow a fast cyclisation, in the presence of a CoMo catalyst on an alumina support which has a metallic and weak acidic function. The acidity of the catalyst determined thermo-gravimetric highlights the weak strength acidic centers with (50.14 %) and medium strength acidic centers (44.83 %).

The bifunctional character of the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst promotes cyclisation and hydrogenation-dehydrogenation reactions. Also, the same catalyst promotes hydrocracking reactions, which explains the presence of light products.

The double bonds of the farnesene structure are located in the 1-6, 2-7 and 6-10 position and allow an easy cyclisation to monocyclic structures of the

bisabolene type, which subsequently through dehydrogenation-hydrogenation reactions, hydrocracks and generates alkyl aromatic structures Fig. 5 a, alkyl naphthenic or other condensed structures of the alkyl tetralin structure Fig. 5 b.

With the increase of the reaction temperature, the hydrocracking reaction intensifies and leads to formation of more alkyl benzenes with 7-10 carbons in molecule. Following the cyclisation reactions and hydrogenation, alkyl naphthene are formed with 5 and 6 carbons in cycle, with a yield lower in comparison with the alkyl aromatics. Regarding the chemical composition, the product resulted from the hydroconversion of the farnesene on the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst can become an aromatic component necessary in the formulation of the Jet A1 jet fuel for which the content of aromatic hydrocarbons imposed by the ASTM D1655 standard is of a maximum of 20 to 25 %.

It was observed that alkyl aromatic compounds which were predominantly obtained at 350°C have many alkyl groups and short chain and alkyl tetralin which is also obtained at 350°C has a high heating value and a freezing point below -40 degrees.

Cyclic compounds were obtained in higher amounts at 370°C, the temperature increase led to a higher content of alkyl cycloalkanes which have a good behavior in jet fuel.

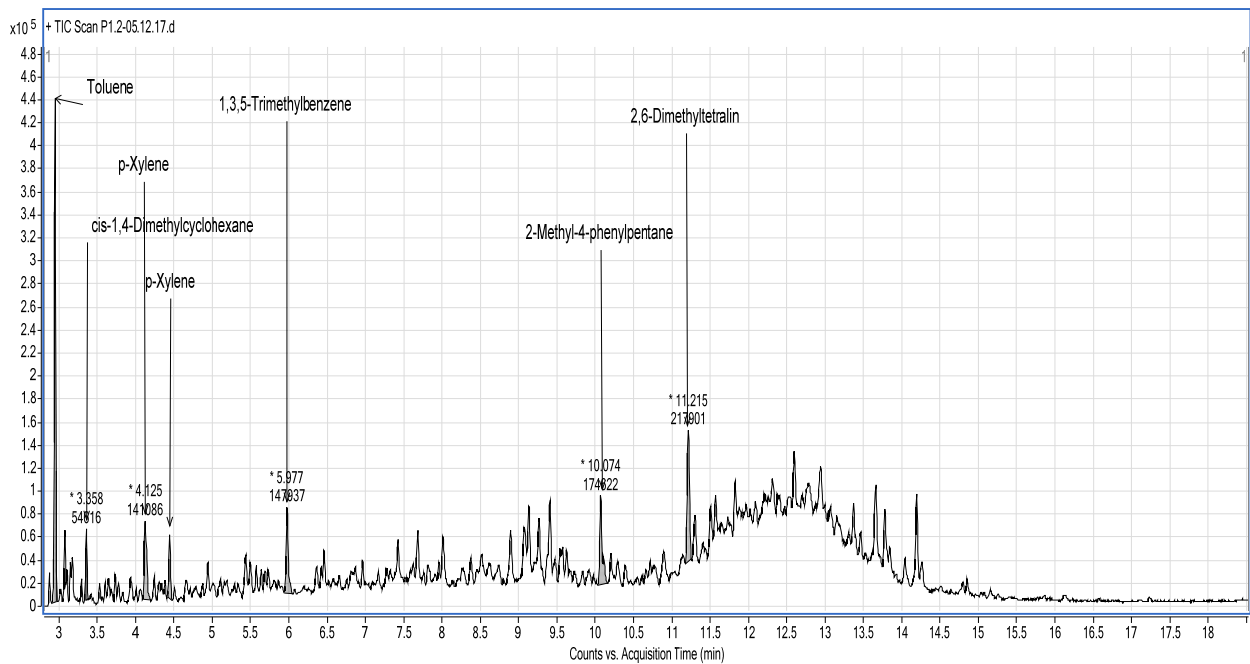


Fig. 3 – The composition of the product resulted from hydrotreating of the farnesene on the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst ( $t=350^{\circ}\text{C}$ ,  $P=60$  bar,  $w=1\text{h}^{-1}$ ).

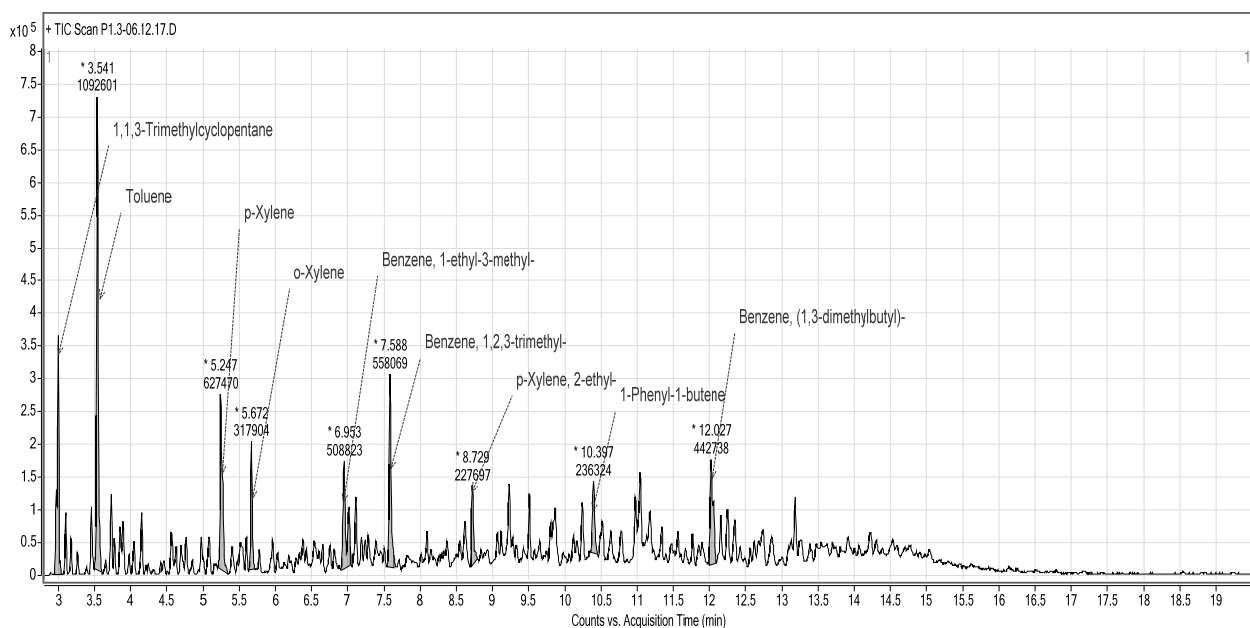
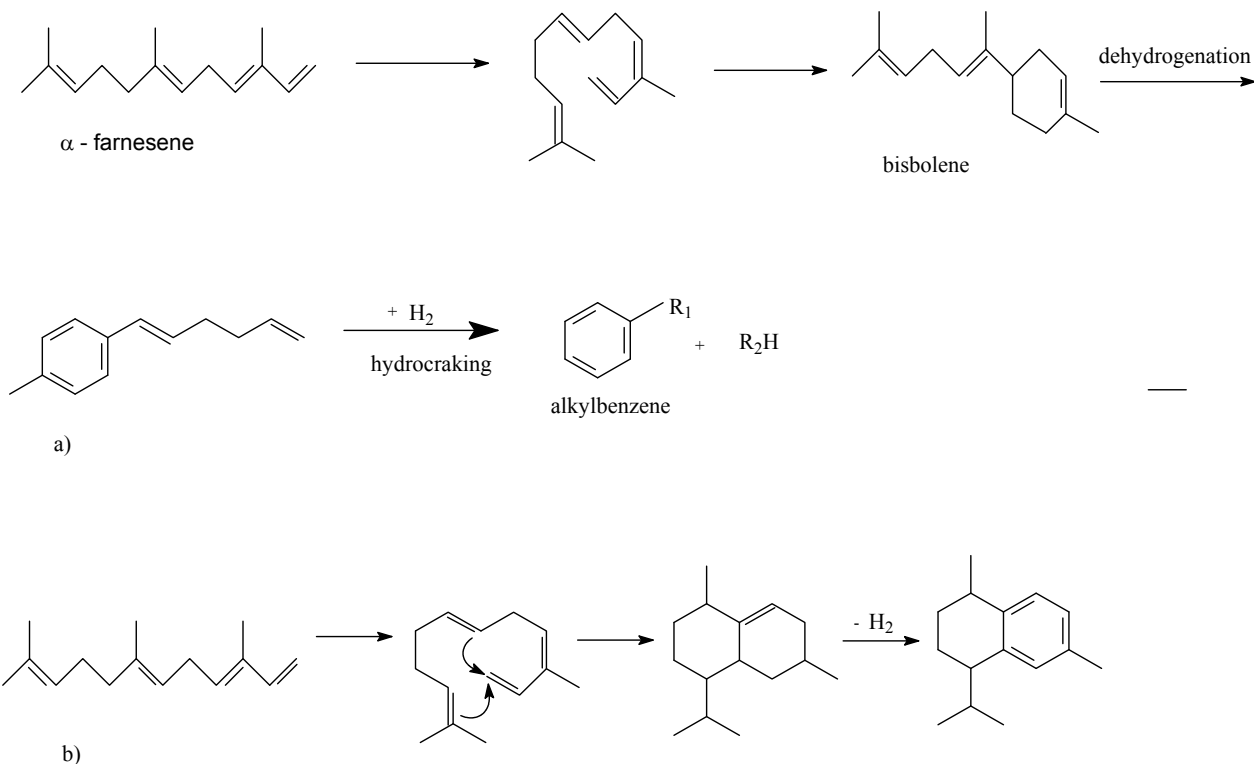
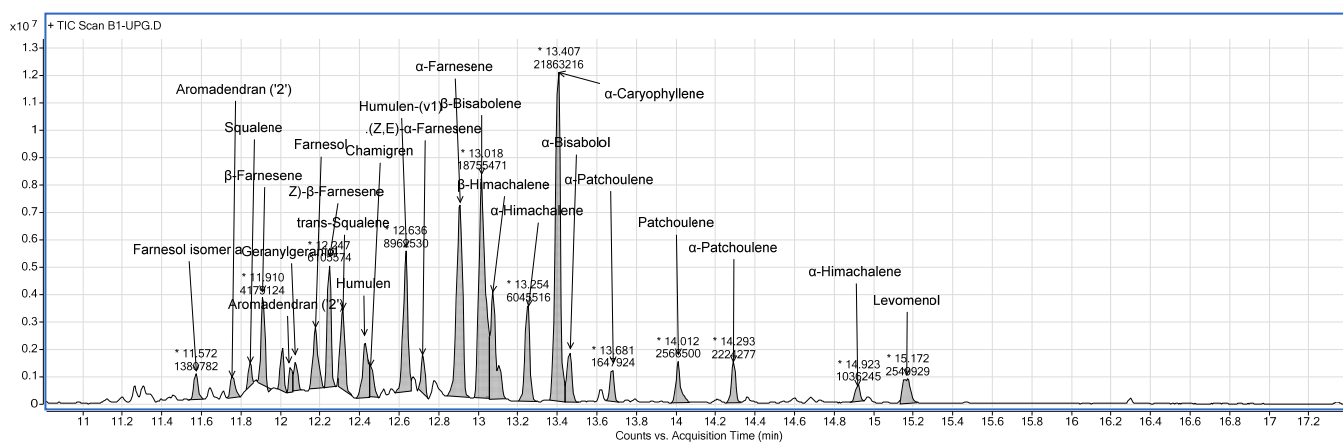


Fig. 4 – The composition of the product resulted from hydrofining of the farnesene on the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst ( $t=370^{\circ}\text{C}$ ,  $P=60$  bar,  $w=1\text{h}^{-1}$ ).

The chemical composition of the resulted product from the hydrogenation of the farnesene on the Pt/Active charcoal catalyst is presented in Fig. 6.

The hydrotreating of the farnesenes on the platinum catalyst has led to a mixture consisting mostly of monocyclic sesquiterpenes (C<sub>15</sub>H<sub>24</sub>)-type bisbolene or macro and multicyclic sesquiterpenes, with higher proportion are: longipinene, humulene,

himachalene, caryophyllene etc in the isomerized non-aromatic structure. The data from Fig. 6 shows a composition of hydrogenated farnesenes products on the Pt/active charcoal catalyst, made out of 46.97 % polycyclic sesquiterpenes, 16.09 % macrocyclic sesquiterpenes type humulene and its stereoisomers, 14.91 % monocyclic sesquiterpenes type bisabolene and the rest of the linear terpenes with 15 or 30 carbon atoms and alkyl cyclohexane.

Fig. 5 – Hydroconversion reaction of farnesene over CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst.Fig. 6 – Composition of the product obtained from the hydrotreated of farnesenes on the Pt /active charcoal catalyst ( $t=170^{\circ}\text{C}$ ,  $P=60$  bar,  $w=1\text{h}^{-1}$ ).

The dimerization of the farnesene has generated squalene, an isoolefin with 30 carbons. Monocyclic and multicyclic sesquiterpenes are formed through cyclisation, isomerisation and hydrogenation reactions. Fig. 7 shows the formation pattern of monocyclic sesquiterpenes with a cycle of six carbon atoms (bisbolene), with macrocycles (humulene), or bicyclic (carophyllene). The

presence of the conjugated double bonds in the farnesene favors cyclisation with a closing of the cycle in the 1-6 position and leading to formation of bisabolene, 1-10 with formation of macrocycles (germacrene) or 1-11 with formation of bicyclic sesquiterpenes ( $\beta$ - carophyllene) which can be isomerized to humulene.

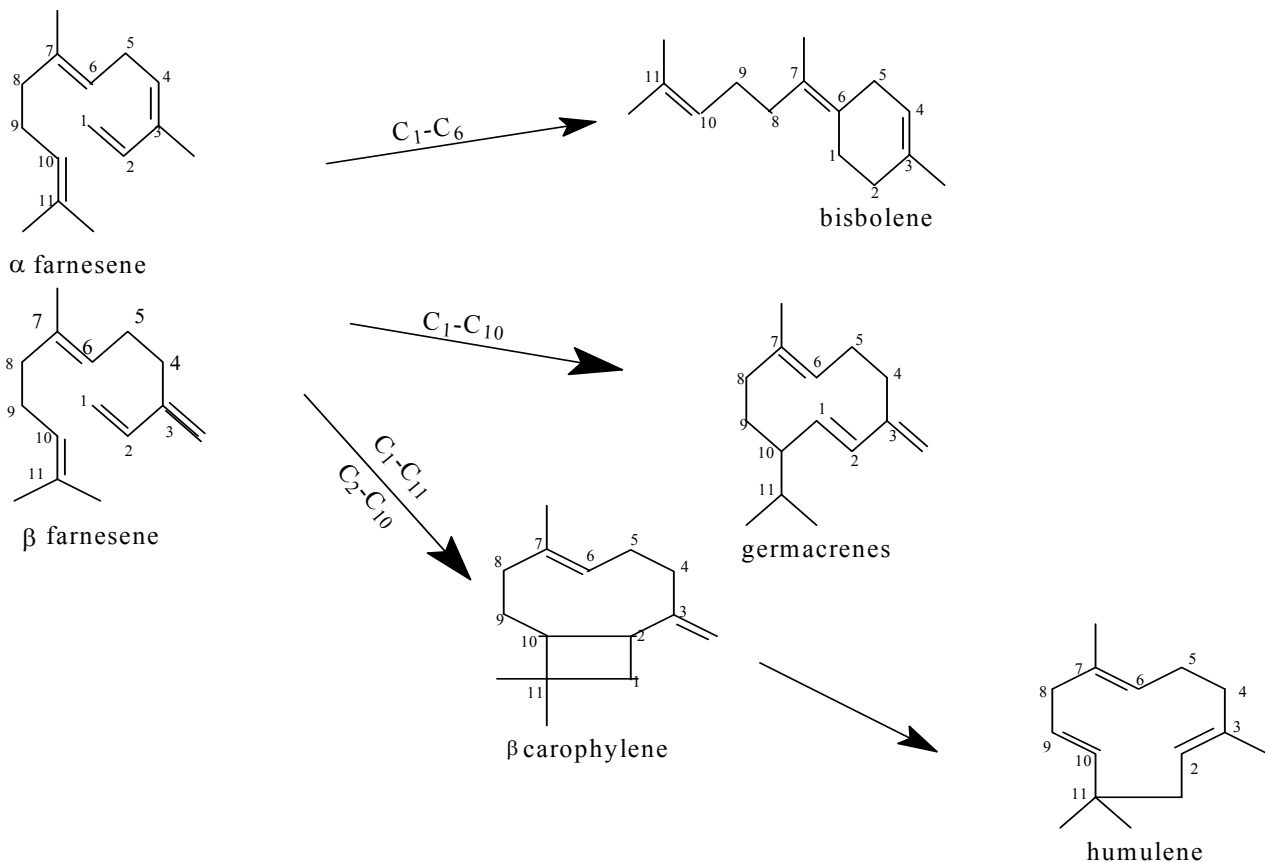


Fig. 7 – Sesquiterpenes formation by cyclization of farnesene.

The enthalpy of reactions presented above is determined as the difference between the sum of the binding energies that crack from the structure of the reactants and the sum of the binding energies that form in the structure of the reaction products, it demonstrates that the cyclization of farnesene is an endothermic reaction. Thus, for the bisabolene formation reaction, the heat of reaction is approximately 230 kJ / kmol.

The formation of polycyclic sesquiterpenes by cyclization, isomerization and hydrogenation reactions increases the density with 6% associated with the increase in heat of combustion per unit mass of fuel by 13% compared to the fossil jet.<sup>18</sup>

The number of carbons in the molecule, their polycyclic structure with olephinic functionality which determines the cold flow properties and high energy density, recommends the polycyclic sesquiterpenes as an alternative for biojet fuels used in reformulation of the jet fuels of the JP-8\Jet A-1 standard.

It is found that on the Pt catalyst weren't cracking reactions, but rather isomerizations, cyclizations, and dimerizations. The low temperature it is the main reason why the active centers did not conduct to cracking reactions.

Out of the two catalysts used for hydrogenation of the farnesenes, the most efficient is the one based on platinum because it favors the formation of mono and polycyclic sesquiterpenes or macrocyclic ones, which fall into the distillation limits of the jet fuel, have mostly an alkyl polycyclic structure, partially unsaturated, with low freezing points and very good combustion properties. The CoMo/ $\text{Al}_2\text{O}_3$  catalyst favors cyclisation and hydrocracking reactions of farnesenes, with the formation of alkyl benzenes with 7-10 carbons in the molecule and bicyclic ones of the alkyl tetralin type and lesser alkyl cyclohexane. The CoMo catalysts aren't recommended for the hydrogenation of the farnesenes because it transforms of the bio component in aromatics, which are limited in the composition of jet fuel to a maximum of 20 to 25 %.

## CONCLUSIONS

Sustainable biomass conversion into biojet represents a major opportunity for aircraft industry to resolve the fuel cost, energy supply, energy security and aviation emissions. Sesquiterpenes and sesquiterpene-derivate obtain from biomass by

fermentation represent a way to produce jet components, but with high costs due to the purification process.

Acyclic sesquiterpenes type farnesene or monocyclic sesquiterpenes type bisabolene or multicyclic and macrocyclic ones obtained through the hydroconversion process, through the cyclisation, isomerization and hydrocracking of farnesene constitute a viable alternative for obtaining biojet.

When using the CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst, it is found that the acid strength distribution, pore distribution and reaction conditions promoted cyclization and cracking reactions resulting in alkyl aromatics and alkyl cycloalkanes with one or more side chains.

The Pt catalyst favored other types of chemical reactions as: isomerizations, cyclizations, and dimerizations that led to low-freezing point compounds with high calorific value that can be used as jet fuel compounds.

The elaborated study shows that sesquiterpenes can be a viable solution for obtaining fuels with a high energy density, which can supply on a long term the needs of the aviation industry.

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