

## REDUCED AROMATIC JET FUELS

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At present time growing demand and more severe quality specifications are observed for the jet fuels. The reasons of these are the growing aviation and the more conscious environmental requirements. The expansion of aviation featured the last two decades, especially the 2% at the beginning of the reviewed period approaches 15%, if we calculate in the point of passenger kilometers the driven passages with vehicles, buses, railroads and jets.

It can not be left from focus that aviation generates only 2% of the CO<sub>2</sub> emission of the world. This value can grow only for 3% to 2050, moreover it generates 12% of the CO<sub>2</sub> emission of the full transportation section, for comparison the public way transport generates 76% of the CO<sub>2</sub> emission.

One of the greatest problems is the jets that fly at one time more than 1500 kilometers, because aviation produces 80% of the greenhouse gases. But there are no other alternatives for bridging these distances in the transport section.

The quality of the jet fuels is improvable with reducing their sulphur- and aromatic content. The hydrogenation of the aromatic content of the jet fuels to naphthenic hydrocarbons can produce products that are environment-friendly, they have high energy content, lower density, which contributes to satisfying the growing demands.

Our aim was to study the possibilities of producing low sulphur and aromatic content jet fuels in a catalytic way. On a transient metal catalyst we studied the possibilities of quality improving of Russian crude oil based petroleum fraction depending on the change of the operating parameters (temperature, pressure, liquid hourly space velocity, volume ratio).

With 1800 mg/kg sulphur content petroleum on the NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst we carried out the experiments at 200–340°C, 20–50 bar pressure, 1.0–3.0 cm<sup>3</sup>/cm<sup>3</sup>h liquid hourly space velocity and 200–400 Nm<sup>3</sup>/m<sup>3</sup> hydrogen/hydrocarbon ratio.

Based on the quality parameters of the liquid products we found that we made from the Russian based petroleum in the adequate technological conditions products which have lower sulphur content than 10 mg/kg and which have reduced aromatic content, so these are excellent jet fuels, and their stack gases damage the environment less.

We blended bioparaffins to the products of the catalytic experiments. We reached products with lower aromatic content than 5%.

**Keywords:** jet fuel, hydrodesulphurization, bioparaffin, aromatic saturation

### Introduction

Recent demands for jet fuels have shown significant increase in the last 20 years. (Fig. 1) [1]. This was generated by the constant growing of aviation. In addition the quality requirements of jet fuels get more tightened. This was generated by the more severe environmental regulations and the increasing quality requirements. For the production of the jet fuels with good burning properties low aromatic hydrocarbons fractions are mainly suitable [1, 2, 3].

The expansion of aviation featured the last two decades, especially the 2% at the beginning of the reviewed period approaches 15, calculating passenger kilometres the driven passages vehicles, buses, railroads and jets.

It can not be left from focus that aviation generates only 2% of the CO<sub>2</sub> emission of the world [5, 6]. This value can grow only for 3% to 2050, moreover it generates 12% of the CO<sub>2</sub> emission of the full

transportation section, for comparison the public way transport generates 76% of the CO<sub>2</sub> emission [4, 7, 8].

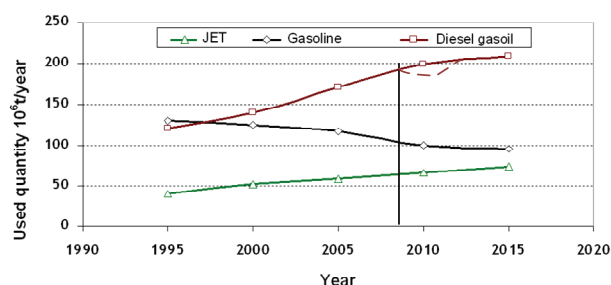


Figure 1: Quantity demands of fuels (EU-27) [1]

One of the greatest problems is the jets that fly at one time more than 1500 kilometres, because aviation produces 80% of the greenhouse gases. The reason of it the reserve fuel is let in the atmosphere at the end of the flying, so the formation of green house effect is

increased. But there are no alternatives for bridging these distances in the transport section [9, 10].

Recently the properties of gasolines and diesel gas oils got continuously more severe, so the properties of jet fuels will become more severe, too. So now some people study the possibilities of producing low aromatic and low sulphur content jet fuels in a heterogeneous catalytic way [2, 7, 8].

In our present jet fuels are produced from different origin feedstocks. With the increasing demand more feedstocks must be in the focus. With using these feedstocks environmental friendly (low sulphur- and

aromatic content) and good performance fuels are productable (Fig. 2) [1-6, 11, 12].

Role of produce jet fuels from triglycerides on catalytic way will be more important in the near future. During the hydrogenation, the formed normal- and iso-paraffin hydrocarbons have suitable energetically and low temperature properties

Near the hydrogenation of triglycerides two other renewable feedstock processing technology can get role in the future; one produces different fuels with transformation and hydrogenation of lignocelluloids, while the other is the Fischer-Tropsch synthesis, which is applied in our present and processes synthesis gas from biomass.

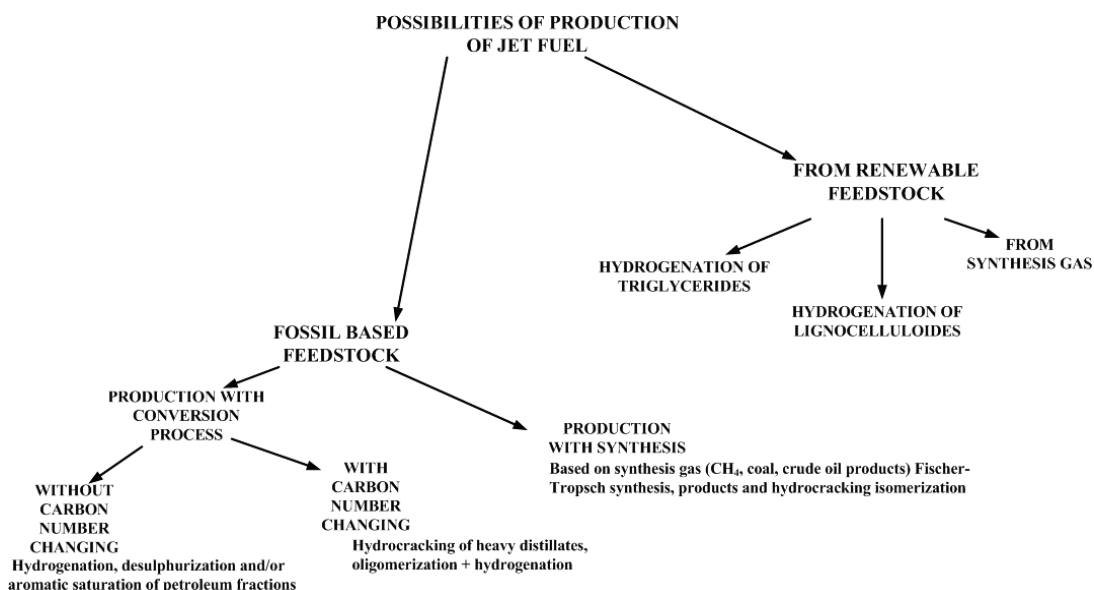


Figure 2: Classification of jet fuel production possibilities

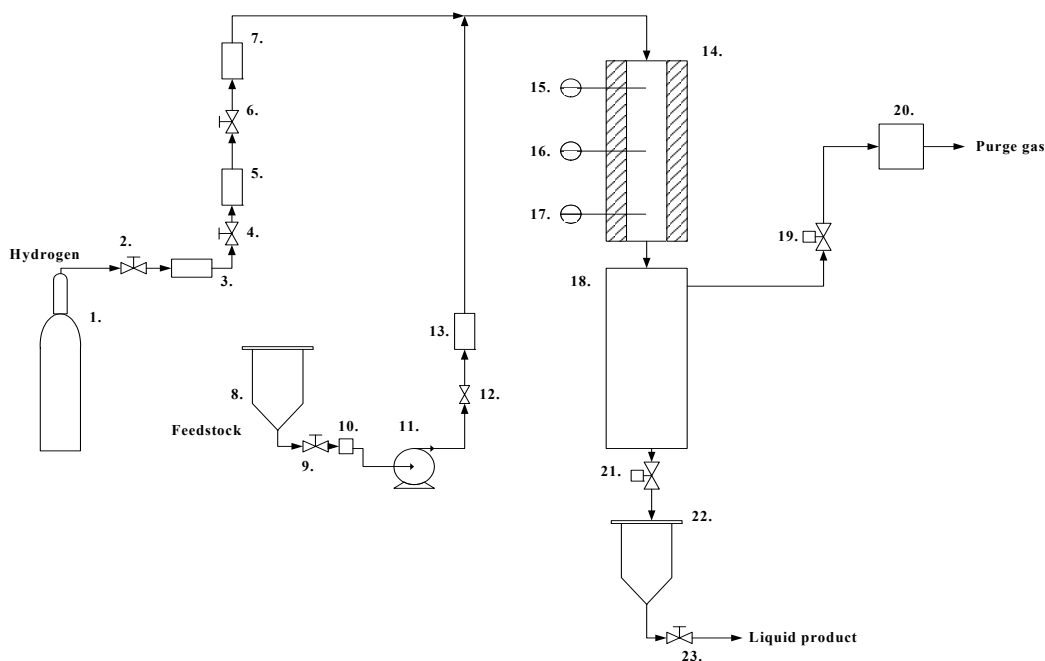


Figure 3: The applied experimental apparatus

- 1: bottle-storage; 2, 4, 6: non-return valves; 3, 5: gas reducers; 7: gas flow controller; 8: feedstock vessel; 10: filter; 11: feedstock pump; 12: throttle valve, 13: flow meter; 14: reactor; 15, 16, 17: thermometers; 18: separator; 19: pneumatic valve; 20: gas-meter; 21: magnetic valve; 22: product receiver; 23: liquid product outlet

## Experimental

Our aim was to study the possibilities of producing low sulphur and aromatic content jet fuels in a catalytic way with hydrogenation of a petroleum fraction. We studied the effect of the process parameters to the product yield and quality. Our further aim was to study kerosene boiling point range paraffin mixture, produced with catalytic hydrogenation of triglycerides, as a possible jet fuel blending component.

### Experimental apparatus

The heterogeneous catalytic hydrogenation experiments for aromatic saturation were carried out in a reactor system which contained all of the important apparatus and units that can be found in a reactor loop of an industrial desulphurizer and aromatic hydrogenation plant. The simplified process flow diagram of the apparatus is shown in *Fig. 3*. The effective volume of the reactor was 100 cm<sup>3</sup>.

### Used materials

During the experiments we used a NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst, which is suitable for the desulphurization of gas oils. Before the starting of the experiments we loaded 60 cm<sup>3</sup> (56.79 g) catalyst into the middle sector of the reactor. The preparation of the new not activated catalyst we carried out by the activation method, that is made at the Department after the loading.

We given the properties of the feedstock for the catalytic experiments in *Table 1*. This is produced from Russian crude oil with distillation by MOL Plc.

*Table 1:* Quality properties of the used petroleum fraction

Appearance	Clear, transparent and sediment free
Aromatic content, %	
Monoaromatic	17.9
Diaromatic	3.8
Mercaptan sulphur content, %	0.01
Total sulphur content, mg/kg	1800
Density on 15 °C, g/cm <sup>3</sup>	0.8083
Crystallization point, °C	-43
Heating value, MJ/kg	42.37
Smoke point, mm	23.4

*Table 2* contains the main quality properties of the alternate origin blending component (paraffin mixture), that we used at the blending of jet fuel.

*Table 2:* Main properties of the alternate based jet fuel blending components (C<sub>10</sub>-C<sub>12</sub> paraffin mixture)

Density, g/cm <sup>3</sup>	0.7404
Sulphur content, mg/kg	<1
Aromatic content, %	<0.1
Heating value, MJ/kg	43.2
Crystallization point, °C	-52

### Process parameters of the catalytic experiments

The circumstances of the catalytic experiment are given in *Table 3*.

*Table 3:* Applied process parameters during the catalytic experiments

Temperature, °C	200–380
Pressure, bar	20–50
H <sub>2</sub> /hydrocarbon volume ratio, Nm <sup>3</sup> /m <sup>3</sup>	400
LHSV, cm <sup>3</sup> /cm <sup>3</sup> h	1.0–3.0

## Methods

We determined the quality properties of the feedstock and the liquid products with standards, given in this table.

*Table 4:* Standard test methods of the feedstock and liquid products

Property	Standard number
Appearance	MSZ 10870:1995
Density on 15°C, g/cm <sup>3</sup>	EN 12185:1998
Sulphur content	EN 14596:2007
	EN 20846:2004
Aromatic content	EN 12916:2000
Hydrocarbon-group analysis (IR)	MSZ 09.60134
Smoke point	MSZ 970:1984
Crystallization point	EN 2047:1986
Distillation properties	EN 3405:2000

## Results and discussion

The yield of the liquid products were greater than 96%, which is very preferable for the main product (*Fig. 4*). The loss comes from the cracking reactions and from the H<sub>2</sub>S, that is formed during the desulphurization reactions.

Based on the measurements with HPLC, total aromatic content of products decreased with the rising of the temperature (*Fig. 5*). The quantity of the decreasing, so the effectiveness of the aromatic saturation was the

highest at 340 °C and 50 bar pressure. At the same time on temperature 360 °C the aromatic concentration of the products was higher than at 340 °C. The reason is the exothermic aromatic saturation reactions are inhibited by the thermodynamically inhibition.

The saturation of monoaromatics comes to the foreground at 280 °C (Fig. 6), until this temperature high desulphurization and hydrogenation of diaromatics are typical. Above 280 °C the hydrogenation activity of studied NiMo/Al<sub>2</sub>O<sub>3</sub> is increased very well.

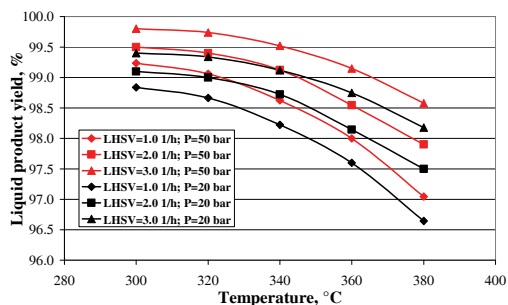


Figure 4: Yield of the liquid products (H<sub>2</sub>/HC ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>)

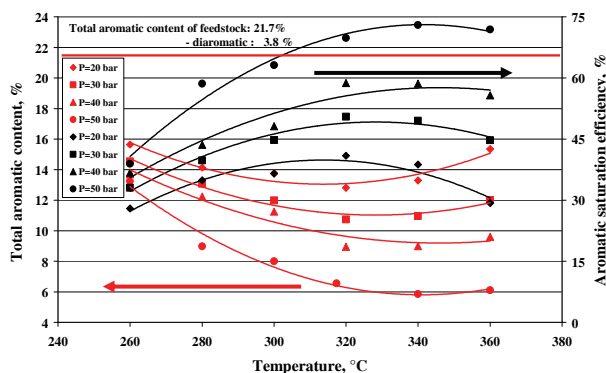


Figure 5: Changing of the total aromatic content of products as a function of the temperature (LHSV: 1.0 1/h, H<sub>2</sub>/HC ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>)

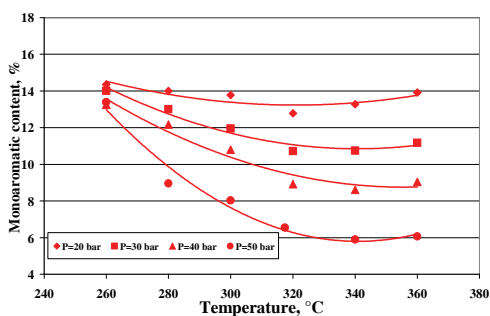


Figure 6: Changing of the monoaromatic content of products as a function of the temperature (LHSV: 1.0 1/h, H<sub>2</sub>/HC ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>)

We studied with infrared spectroscopy the hydrocarbon-group composition of the products, to determine what hydrocarbons are formed from the aromatic content of the feedstock. The values of this test method are not equal with the HPLC aromatic content values, but they give correct information about the composition of the hydrogenated products. The share of n- and isoparaffin

hydrocarbon-groups changed a little during the experiments (Table 5). Oppositely the cycloparaffin content of the products are increased compared to the cycloparaffin content of the feedstock, the rate of this was equal with the decreasing of the aromatic content (Fig. 7). Based on this we determined the aromatic content of the feedstock is hydrogenated to cycloparaffin hydrocarbons, so ring opening reactions did not work or worked in low rate and resulted linear paraffins.

This hydrogenation is very preferable, because cycloparaffins are not just environmental friendly, but they have better energetic properties and lower crystallization point than that aromatics with the same carbon number (Table 6).

Table 5: n- and i-paraffin contents of products based on IR test

n- and i-paraffin content, % LHSV=1.0-2.0 1/h; H <sub>2</sub> /CH ratio: 400 Nm <sup>3</sup> /m <sup>3</sup>					
T, °C	280	300	320	340	360
p, bar					
20	51.9	51.2	51.6	51.6	51.9
30	52.2	52.2	51.6	51.6	51.8
40	52.2	52.2	51.6	51.6	51.8
50	52.1	51.6	51.6	51.6	51.8

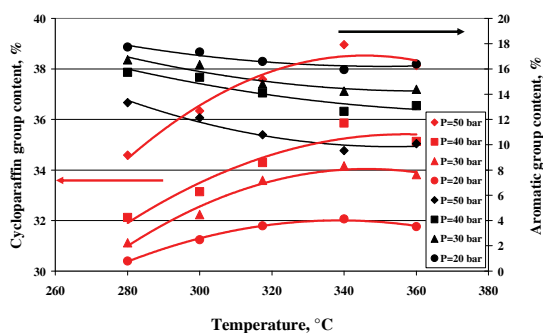


Figure 7: Changing of the cycloparaffin-group content of products as a function of the temperature (LHSV: 1.0 1/h, H<sub>2</sub>/HC ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>)

Table 6: Heating values and crystallization points of aromatics and cycloparaffins with the same carbon number

	Heating value, MJ/kg	Crystallization point, °C
n-pentyl-benzene	34.1	-43
n-pentyl-ciklohexane	36.5	-58
n-hexyl-benzene	34.1	-42
n-hexyl-ciklohexane	36.5	-52
n-heptyl-benzene	34.2	-40
n-heptyl-ciklohexane	36.6	-47

The legal sulphur content of jet fuels is maximum 3000 mg/kg. In the near future this value will be decreased. So it composed a part of our experimental work to study the effect of the different process parameters to the sulphur content of the products. At the mildest process parameters (T: 200°C, p: 20 bar, LHSV: 3.0 1/h) sulphur content of the product decreased well compared to the feedstock. With increasing of the temperature and the pressure

sulphur content of the products decreased further (Fig. 8 and 9). At low LHSV (1.0 1/h) and on 20 bar we approached lower sulphur content than 10 mg/kg, which is the specification for gasolines and diesel gas oils in the European Union. On 50 bar pressure and on 280 °C sulphur content of the product decreased under 50 mg/kg, while on 300 °C and 1.0 1/h LHSV it didn't exceed 10 mg/kg, moreover increased LHSV to 3.0 1/h it didn't exceed 200 mg/kg.

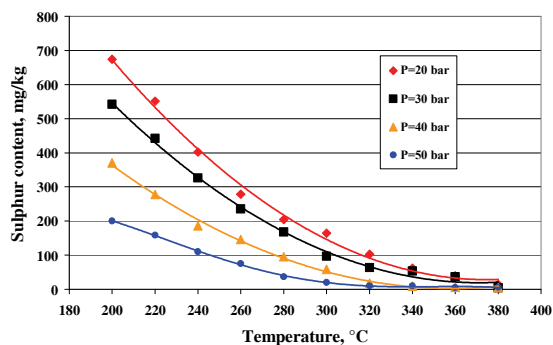


Figure 8: Changing of the sulphur content as a function of the temperature (LHSV: 1.0 1/h,  $H_2/CH$  ratio:  $400 \text{ Nm}^3/\text{m}^3$ )

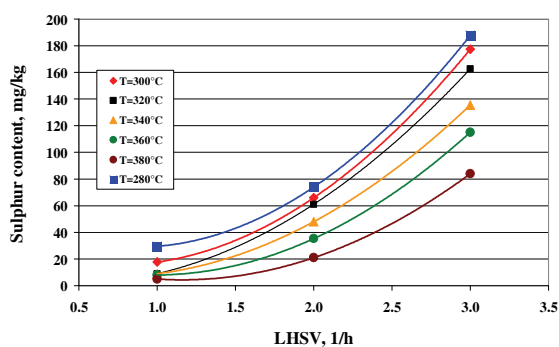


Figure 9: Changing of the sulphur content as a function of the LHSV (P: 50 bar,  $H_2/CH$  ratio:  $400 \text{ Nm}^3/\text{m}^3$ )

We introduced some of the performance properties of the products – smoke point, crystallization point.

Aromatic hydrocarbon content of the middle distillate influences value of smoke point decisively. Aromatics burns smoke flame by their lower hydrogen-carbon ratio, than the cycloparaffins and paraffins with higher hydrogen-carbon ratio. On Fig. 10 hydrogenation of aromatic hydrocarbons smoke point value increased well. On 320 °C the some point values of the products exceeded the standardized minimum 25 mm. This is given by the cycloparaffins with better flaming properties, that are formed during the hydrogenation reactions.

Crystallization point of products decreased continuously compared to the crystallization point of feedstock ( $-50.5 \text{ °C}$ – $-51.5 \text{ °C}$ ) by the high hydrogenation of aromatics. Decreasing of crystallization point is favourable, the current stand standard prescribes maximum  $-47 \text{ °C}$  (Fig. 11).

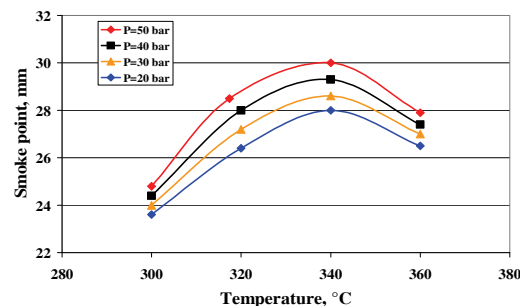


Figure 10: Changing of the smoke point as a function of the temperature ( $H_2/CH$  ratio:  $400 \text{ Nm}^3/\text{m}^3$ , LHSV: 1.0 1/h)

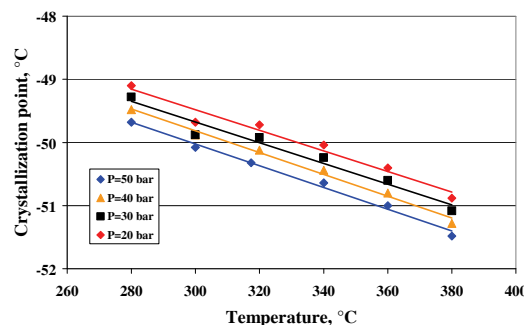


Figure 11: Changing of the smoke point as a function of the temperature (p= 50 bar, LHSV: 1.0 1/h)

We blended bioparaffin mixture to the products of catalytic experiment to study their effect to the aromatic content and performance properties.

We blended 10–30% bioparaffin to the product, that we reached at 340 °C, 50 bar and on 1.0 1/h, than we studied the important properties of these mixtures. As we decreased sulphur content of the products during the catalytic experiments, so sulphur content of product mixtures did not change significantly, moreover the studied performance properties did not change in important quantity, but at the same time aromatic content decreased under 5% (Table 7). Based on these results we determined, bioparaffin mixture from catalytic hydrogenation of triglycerides ( $C_{10}$ – $C_{12}$ ) do not worsen the properties of the crude oil based jet fuel.

Table 7: Effect of blending bioparaffin to properties of the products from the catalytic experiments

Property	Bioparaffin content, %			
	0	10	20	30
Density, $\text{g}/\text{cm}^3$	0.7998	0.7938	0.7878	0.7819
Sulphur content, $\text{mg}/\text{kg}$	9	8	7	6
Heating value, $\text{MJ}/\text{kg}$	43.0	43.1	43.1	43.1
Crystallization point, $^{\circ}\text{C}$	-51	-51	-51	-51
Aromatic content, %	5.9	5.3	4.7	4.1

## Results and discussion

Our aim was to produce low aromatic and sulphur content jet fuel, which has better energetically property, lower crystallization point, moreover its burning products damage the environment less by its changed hydrocarbon group composition during the hydrogenation. We studied the effect of the process parameters (T: 200–380 °C, p: 20–50 bar, LHSV: 1.0–3.0 h<sup>-1</sup>, H<sub>2</sub>/CH volume ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>) to the yield and quantity of the products, moreover we determined the preferable process parameters of the aromatic saturation and hydrodesulphurization.

We determined, the yield of the products was greater than 96.0%, which is very preferable. Increasing of the temperature and the pressure have significant effect to the aromatic saturation, liquid hourly space velocity has effect to the hydrodesulphurization. Total aromatic content of the products decreased to 340 °C, than with further temperature increasing hydrogenation of aromatics declined by the thermodynamically inhibition. Quantity of hydrodesulphurization did not change. Decreasing of aromatic hydrogenation caused by the thermodynamically inhibition by the high temperature. Aromatic hydrocarbons formed to cycloparaffins, they have better performance properties than aromatics.

Based on experimental results, the determined preferable process parameters for desulphurization and aromatic saturation are the following: temperature: 340 °C, pressure: 50 bar, liquid hourly space velocity: 1.0 h<sup>-1</sup>, H<sub>2</sub>/hydrocarbon ratio: 400 Nm<sup>3</sup>/m<sup>3</sup>. With these parameters, aromatic content of product was 5.9%, and the sulphur content was lower than 10 mg/kg. So, we produced successfully product, that has better properties than the prescriptions of the actual jet standard.

Blended 10–30% bioparaffins to the products that produced at the preferable process parameters, we determined, the aromatic content decreased from the investigated properties, the other properties did not change significantly.

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