

Production of Bio Gas Oil from Bioparaffins over Pt/SAPO-11

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In this paper a new field of the application of Pt/SAPO-11 catalyst is introduced. The isomerization of C₁₂-C₂₀ paraffin mixtures produced from rapeseed oil was investigated over different platinum containing (0.2; 0.3; 0.4; 0.5; 0.7; 1.0 %) SAPO-11 catalysts at 300-400°C, 30-80 bar; 0.5-4.0 h⁻¹ LHSV and 200-800 Nm³/m³ H₂/HC ratio. It was concluded that economically the most favourable results (high isomer content at high yield) could be obtained using SAPO-11 catalyst with 0.4 % platinum content. At the favourable operational parameters (determined in compromise by the product yield, the ratio of mono- and multibranched paraffins, the place of branchings) (T= 360 °C; p=50-60 bar; LHSV 1.0-1.5 h⁻¹, H₂/HC = 350 Nm³/m³) high isoparaffin containing mixtures were produced with high liquid yield (>90%) and high i-C₁₂-i-C₂₀ selectivity. The cetane numbers of these products were 75-85 units (EU Standard value is ≥51), and the cold filter plugging points were between -2 and -11 °C.

1. Introduction

The energy demand of the world is continually increasing because of the industrial and population growth. Consequently the importance of biofuels has increased in the last decade (Hayes, 2009). Another important reason is the lower CO₂ emission of biofuels relative to conventional fuels regarding the whole life cycle.

Nowadays the transesterified vegetable oils (biodiesels) are mainly used as a renewable diesel fuel blending component, which has several disadvantages [e.g. depositions in the fuel system and the combustion chamber; bad storage (oxidation and heat) stability because of the olefinic double bonds; aptitude to water intake; hydrolysis sensitivity of the ester bonds, which generate corrosive acids; etc.] (Hancsók et al., 2007), consequently the maximum blending quantity of the fatty acid methyl esters is limited to 7.0 V/V% in the EN 590:2009 standard by the suggestion of the car manufacturers.

Consequently the quantity of biofuels could only be increased by using hydrocarbons with different conformation (e.g. mixtures of paraffins) produced from triglycerides, fatty acid, etc., which satisfies better the application requirements of the diesel vehicles (engines) (Hancsók et al., 2007). However, these paraffin mixtures (mainly n-C₁₂ – n-C₂₀) have unfavourable cold flow properties (CFPP) (e.g. n-C₁₆ : +17 °C), accordingly

these need to be chemically converted to lower freezing point compounds. It could be realised by hydrocracking and/or by isomerisation. In the previous case lower cetane number products could be obtained with low yield (<80-85 %). Because of these it is expedient to isomerise them to high cetane number (65-75) isoparaffins with lower freezing point (e.g. 5-methyl-pentadecane: -31 °C). In the literature the isomerization activities of different catalysts were tested with mainly model compounds (n-decane, n-hexadecane) (Deldari, 2005; Elangovan and Hartmann, 2003). However, a few papers are published about the isomerization of real feeds as the mixtures of mainly heptadecane, octadecane and some oxygen containing compounds. Accordingly, the aim of our experimental work was the investigation of isomerization of n-paraffin mixtures produced by hydrogenation of triglycerides. Based on the results of our pre-experiments the Pt/SAPO-11 catalyst was the most favourable among the several investigated catalysts regarding their activity and selectivity (Gergely et al., 2001). In this paper the results of our experiments applying paraffin mixture with new composition on Pt/SAPO-11 catalysts with different platinum content are presented.

2. Experimental

The aim of our experimental work was the investigation of production possibilities of bio gas oil with good flow properties by catalytic paraffin conversion from high n-paraffin containing mixture produced from rapeseed oil by catalytic hydrogenation. Besides, our objective was to determine the effects of the platinum content (0.2-1.0%) of the used Pt/SAPO-11 catalysts thus the effect of the ratio of metallic/acidic sites and of the favourable operational parameters (temperature, pressure, space velocity, hydrogen/feed ratio) on the yield and quality of the products. The measurements were carried out in a high pressure flow apparatus. Reaction conditions were as follows: 300-380°C; pressure: 30-80 bar; LHSV: 0.5-4.0 h⁻¹, H₂/HC ratio: 200-800 m³/m³. Products were analyzed according to EU and ASTM standards and GC-MS.

2.1. Apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor of 100 cm³ effective volume. It contains all the equipment and devices applied in the reactor system of an industrial heterogeneous catalytic plant. The experiments were carried out in continuous operation with steady-state activity catalyst.

2.2. Materials

During our heterogenic catalytic experiments normal paraffin mixture (CFPP = 23°C; hydrocarbons: C₁₇: 6.8 %, n-C₁₇: 27.3 %, i-C₁₇: 0.5 %, n-C₁₈: 63.5%, i-C₁₈: 1.0 %, C₁₈₊: 0.9%) produced with high yield (84.6%) from Hungarian rapeseed oil (palmitic acid: 4.8%, stearic acid: 1.5 %, oleic acid: 62.1 %, linoleic acid: 21.6 %, linolenic acid: 7.5 %, other fatty acids: 2.5 %; cetane number: 43.5; iodine number: 109g I₂/ 100 g; CFPP: 32°C) over special hydrotreating catalysts was used as feedstock. The properties of the feedstock and the products were measured according to standard methods. The catalysts of 0.2-1.0 wt% Pt-content were prepared as described and characterized according to HU 225 912 patent (Gergely et al., 2001). The synthesized SAPO-11 microporous molecular sieve was impregnated with Pt(NH₃)₄Cl₂ solution. Prior to the activity measurements the catalysts were pretreated in situ.

3. Results

3.1. Product yields

During our experiments the values of the process parameters were varied in wide ranges. Our aim was that the yields of the organic products be higher than 80 %, by this way there is no high degree of cracking, which could quickly deactivate the catalysts. Furthermore in case of industrial application the yields should be at least 90-95 %. The most favourable results (high isomer content at high yield) were obtained when using SAPO-11 catalyst with 0.4 % platinum content (Figure 1). The reason of this was that up to 0.4 % the platinum content increased significantly the isomer content of the product, because the increase of the number of the hydrogenation/dehydrogenation active sites promoted the isomerisation and the fast hydrogenation of the carbocations (intermediate products), consequently retarded the decomposition of those. The further increase of platinum content had no effect. So in this article the detailed introduction of the experimental results and the valuation of these are presented in case of 0.4 % platinum containing SAPO-11.

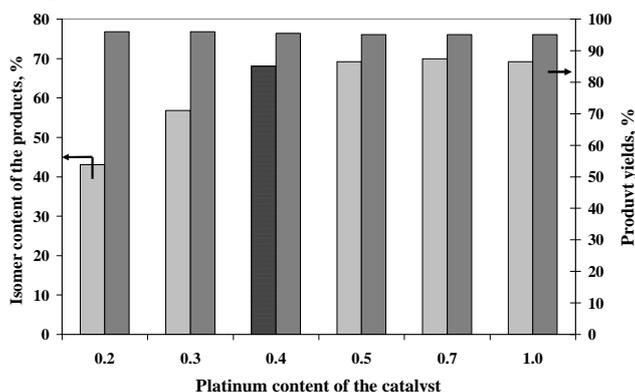


Figure 1: The yield and the isomer content of the target products in the function of platinum content of the catalysts ($T = 360^{\circ}\text{C}$, $p = 40 \text{ bar}$, $H_2/\text{HC ratio} = 400 \text{ Nm}^3/\text{m}^3$)

The yields of the products decreased by increasing the temperature and by decreasing the liquid space hourly velocity (Figure 2) and the pressure (Figure 3). The decrease of hydrogen/feed ratio below $400 \text{ Nm}^3/\text{m}^3$ had the same effect. These were caused by the hydrocracking reactions taking place beside the isomerisation in higher and higher degree. Consequently the yields of the gas products changed oppositely. The reason of these processes was that the reaction rate of skeletal isomerisation and also the cracking reactions were augmented by the increase of the temperature; with decreasing the hydrogen pressure the partial pressure of hydrocarbons increased, consequently the degree of hydrogenation of the instable iso-carbeniumions decreased, so those could be easily decomposed; the same effect prevailed in case of the decrease of the hydrogen/feed ratio; by the decrease of the liquid space velocity the flow rate of the feed on the surface of the catalyst particles dropped, the desorption of the branched molecules from the active sites was slowed down, so the degree of the cracking could increase.

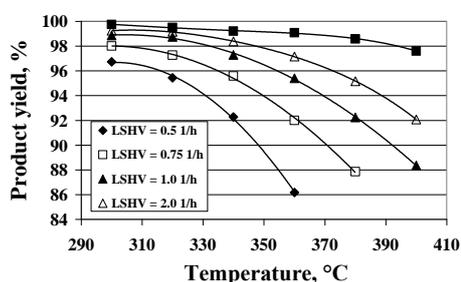


Figure 2: The yields of products in function of the temperature ($p = 40$ bar, H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

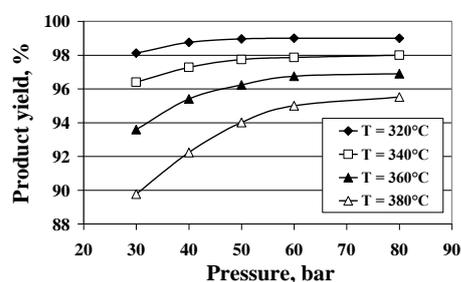


Figure 3: The yields of products in function of the pressure ($LSHV = 1.0 \text{ h}^{-1}$, H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

3.2. The composition of the products

The products obtained during the heterogeneous catalytic conversion contained in the highest degree (85-92 %) C_{17} and C_{18} hydrocarbons, furthermore lower compounds (C_{10} - C_{16}) in the gas oil boiling range (180-360 °C) in various quantities depending on the operational parameters, and some heavier compounds (C_{19+}), as well. In the C_{10} - C_{18} fraction the changing of the concentration of the iso- and normal paraffins was detected exactly, so the rate of conversion (skeletal isomerisation) was well-trailed in function of the process parameters. The concentration of the isomerised hydrocarbon increased significantly above 320 °C, but above 360 °C it started to decrease because of the increase of the cracking. This effect was intensified by the decrease of the liquid space velocity. (Figure 4Fig). Up to 360 °C the increase of the pressure had a negative effect on the isomer content of the product as it reduced the partial pressure of the hydrocarbons, which slowed down the isomerisation reactions; but above 360 °C the increased reaction rate could balance the decreased partial pressure, which is favourable regarding the mitigation of the cracking reactions as well. (Figure 5).

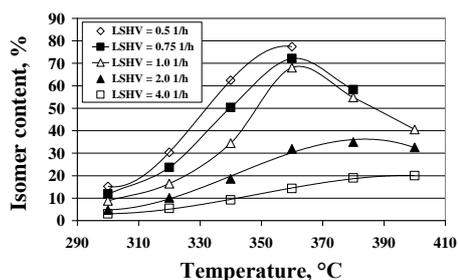


Figure 4: The total isomer content of the product in function of the temperature ($p = 40$ bar, H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

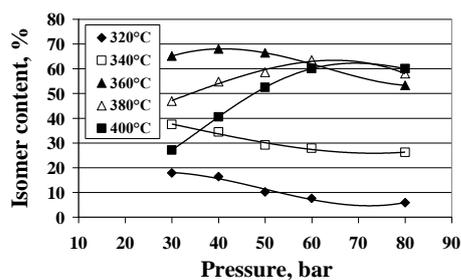


Figure 5: The total isomer content of the product in function of the pressure ($LSHV=1.0 \text{ h}^{-1}$, H_2/HC ratio= $400 \text{ Nm}^3/\text{m}^3$)

The increase of the H_2 /feed ratio had a positive effect on the isomer content of the products, especially at 360°C and higher temperature), where above $400 \text{ Nm}^3/\text{m}^3$ H_2 /hydrocarbon ratio could cut significantly the degree of hydrocracking which

depressed the isomer yield. But the utilisation of $600 \text{ Nm}^3/\text{m}^3$ and higher H_2/feed ratio in case of 360°C and lower temperature decreased the isomer yield as the partial pressure of hydrocarbons were decreased, consequently the degree of conversion decreased as well.

3.3. The investigation of the performance properties of the products

The cold filter plugging point (CFPP) of the Diesel fuels is a very important performance property, as the paraffin crystals precipitated by decreasing temperature could cause operational disorders or unserviceability of the fuel supply system of the engine. The CFPP values of the product are presented in Figure 6 as a function of the temperature. The reason of the decrease of the CFPP values of the product by increasing the temperature was mainly the increasing quantity of iso-paraffins – namely the iso-paraffins have more favourable freezing points – and furthermore that the lighter hydrocarbons generated in the hydrocracking reactions have a lower freezing point, consequently these improve the CFPP values.

In function of the pressure up to 360°C the CFPP values increased by the increase of the pressure, as the isomer content of the product decreased in this range, above 360°C this values decreased by increasing the temperature, as in this range the increase of the pressure protected the isoparaffins to be cracked (Figure 7), resulting a lower freezing point. In function of the H_2/feed ratio the CFPP values of the products were practically unchanged. Above 360°C the decrease of this ratio below $400 \text{ Nm}^3/\text{m}^3$ caused the decomposition of branched hydrocarbons, consequently the CFPP values were higher.

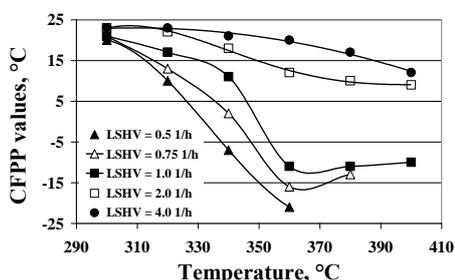


Figure 6: The CFPP values of the products in function of the temperature ($p = 40 \text{ bar}$, H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

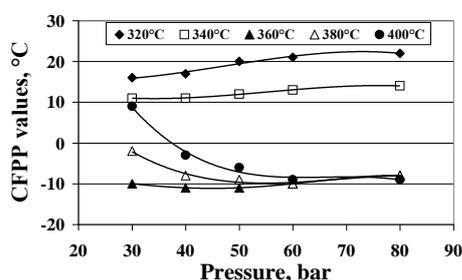


Figure 7: The CFPP values of the products in function of the pressure ($\text{LSHV}=1.0 \text{ h}^{-1}$, H_2/HC ratio= $400 \text{ Nm}^3/\text{m}^3$)

The changing of the concentration of the different isomers was investigated as well. It was determined that by the increase of the temperature the concentration of multibranching isomers was increased. The reason of that is that the reaction rate of mono-branched paraffins increased at higher temperature, so multibranching paraffins could be formed in consecutive reactions. These components affect the cold flow properties favourably, but another important performance property, the cetane number is by far more unfavourable in case of these components. In consequence the cetane numbers of the products decreased continually through the higher degree of catalytic conversion relative to the feedstock (101 units), but these reached in every case at the favourable process parameters (determined in compromise by the product yield, the

ratio of mono- and multibranched paraffins, the place of branchings) the 76-88 units, which are significantly overtop the 51 units specified in the current standard (Figure 8).

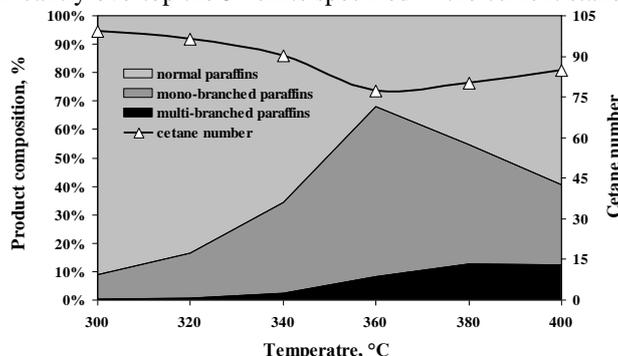


Figure 8: The composition and the estimated cetane number of the products in function of the temperature ($LHSV = 1,0 h^{-1}$, $p = 40 bar$, H_2/HC ratio = $400 Nm^3/m^3$)

4. Conclusions

According to our results SAPO-11 catalysts with different platinum content are suitable for the isomerisation of paraffin mixture derived from the hydrogenation of rapeseed oil. The most favourable results were obtained on 0.4% Pt/SAPO-11 catalyst. The products contained isoparaffins in high amount, which were mainly mono-methylparaffins, which have high cetane number (76-88 unit) and favourable cold flow properties (between -2 and -11 °C). The favourable process parameters ($T = 350-360^\circ C$; $P = 50-60 bar$; $LHSV = 1.0-1.5 h^{-1}$, $H_2/HC = 350 Nm^3/m^3$) were determined by the evaluation of the liquid product selectivity (liquid yield > 90 %), the isoparaffin selectivity (> 68 %) and furthermore, by the product composition of the performance properties.

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