

Investigation of Isoparaffin Rich Alternative Fuel Production

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In this paper isomerization of C₁₂-C₂₀ paraffin mixture produced from sunflower oil was investigated over 0.5% Pt/SAPO-11 catalyst at 260-400°C, 20-80 bar, 0.5-4.0 h⁻¹ LHSV and 400 Nm³/m³ H₂/HC ratio. It was concluded that at the favourable operational parameters (determined in compromise by the product yield, the ratio of mono and multibranched paraffins, the ratio of individual monobranched paraffins and the place of branchings) (T = 360°C, p = 40-50 bar, LHSV 0.75-1.0 h⁻¹ and H₂/HC = 400 Nm³/m³) high isoparaffin containing mixtures were produced with high liquid yield (>90%) and high isoparaffin selectivity. The cetane numbers of these products were 76-88 units (EU Standard value is ≥ 51), and the cold filter plugging points were between -5 and -13°C.

1. Introduction

Because of the increasing population of the world and the industrial development the need for Diesel fuel is continuously increasing, but the sources of the fossil energy are depleting (Dembras, 2009). Consequently the importance of bio fuels has increased. Besides them mainly the production of normal and isoparaffins is expedient, which are the most favourable compounds of the Diesel fuels regarding the service and human biological properties. Normal paraffin rich mixtures can be produced from different sources of triglycerides, but these have to be isomerised to reach favourable cold flow properties products. The hydroisomerization of bioparaffin mixtures is reported only a few paper (e.g. Hancsók, et al. 2007a; 2007b; Kasza, et al., 2010) and mentioned in some patent (e.g. WO 2008/058664 A1, US 2007/0006523 A1, WO 2008/101945), wherein the formation of individual isoparaffins were not investigated.

For the isomerization of bio-origin C₁₂ - C₂₀ paraffins currently the different noble metal containing zeolites (ZSM-5, ZSM-22, ZSM-23), silica-alumina-phosphates (SAPO-11, SAPO-31, SAPO-41) and mesoporous materials (MCM-41, Al-MCM-41) seem to be the most suitable (Perego and Bianchi, 2010), namely the isomerization take place in sufficient degree (60-90%) at high yield (91-97%) because of their mild acidity. The degree of isomerization, the yield and composition of products depend highly on the characteristics of the applied catalyst, the operational parameters and the composition of the feedstock. The best isoparaffins for Diesel fuels regarding the service properties are that ones which have one methyl branching at central position along the carbon chain, because by increase of number and length of alkyl side chain the cetane number

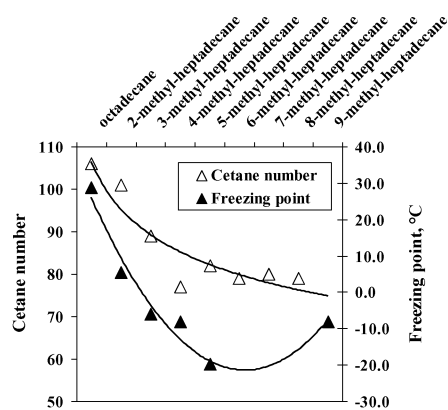


Figure 1: The cetane number and the freezing point of octadecanes

significantly decrease (e.g. n-hexadecane: 100; methyl-pentadecanes: 73-87; dimethyl-tetradecanes: 40-61), furthermore the cold flow properties decline by shifting the position of the methyl branching to the end of the chain (e.g. freezing point: 2-methyl-heptadecane: +5.5°C, 5-methyl-heptadecane: -19.8°C) (Fig. 1). Out of the tubular pore zeolites with 10-membered ring mono-methyl paraffins could be produced with high selectivity over the platinum containing SAPO-11 catalyst (Kasza, 2010), those combustion and cold flow properties can widely satisfy the expectations of the Diesel blending components.

2. Experimental

The aim of our experimental work was investigation the effect of process parameters [temperature, pressure, liquid hourly space velocity (LHSV), hydrogen/hydrocarbon ratio (H_2/HC)] on yield of products and ratios of isomers of heptadecane and octadecane furthermore their effect on the service properties (cetane number, freezing point) during the isomerization of n-paraffin mixture produced from sunflower oil over 0.5% Pt/SAPO-11 catalyst found to be suitable for the isomerization of bioparaffins (Hancsók, 2007a).

2.1 Apparatus

The experiments were carried out in continuous operation with steady-state activity catalyst 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 catalytic hydrogenation plant (Hancsók, 2007a).

2.2 Materials

During our heterogenic catalytic experiments normal paraffin mixture (CFPP = +23°C; hydrocarbons: C₁₇₋: 6.3%; i-C₁₇: 0.3%; n-C₁₇: 46.7%; i-C₁₈: 0.4%; n-C₁₈: 43.3%; C₁₉₊: 2.0%, content of oxygenic compounds : 0.06%, oxygen content : 68 mg/kg) produced from Hungarian sunflower oil over commercial type hydrotreating catalyst was used as feedstock. The catalyst of 0.5 wt% Pt-content was prepared as described and characterized earlier (Hancsók, 2007a). The synthesized SAPO-11 microporous molecular sieve was impregnated with Pt(NH₃)₄Cl₂ solution. Prior to the activity measurements the catalyst was pre-treated in situ in hydrogen flow.

2.3 Methods

The properties of the feedstock and the products were measured according to methods specified in the EN 590:2009 standard. The composition of those, the concentration of

the normal and isoparaffins were determined on DB-1HT (Agilent) capillary column (30 m x 0,32 mm x 0,1 μm) using Shimadzu 2010 GC.

3. Results

3.1 Product yields

During our experiments the values of the process parameters were varied in wide range $T = 260\text{-}400^\circ\text{C}$, $p = 20\text{-}80$ bar, $\text{LHSV} = 0.5\text{-}4.0$ h^{-1} , $\text{H}_2/\text{HC} = 400$ Nm^3/m^3) to investigate isomerization reactions. Yields of the products decreased by increasing the temperature and by decreasing the liquid hourly space velocity (Fig. 2) and the pressure (Fig. 3).

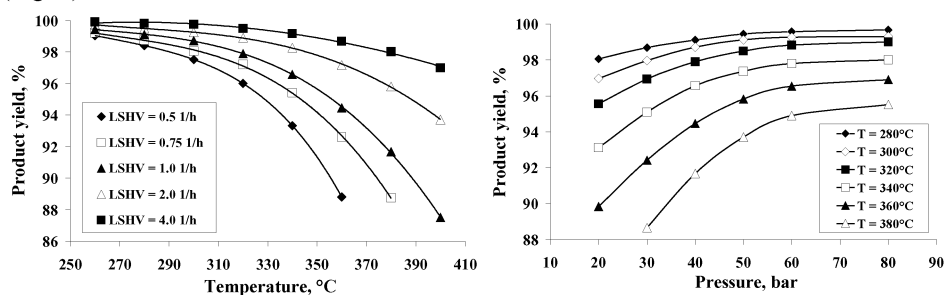


Figure 2: The yields of products in function of the temperature ($p = 40$ bar, H_2/HC ratio = 400 Nm^3/m^3)

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

These were caused by the hydrocracking reactions taking place simultaneously the isomerization in higher and higher degree, namely by increase of the temperature the reaction rate of skeletal isomerization the cracking reactions were augmented. By the decrease of the liquid space velocity the flow rate of the hydrocarbons on the surface of the catalyst particles dropped, namely the contact time increase, the desorption of the branched molecules from the active sites was slowed down, so the degree of the cracking could increased. By decrease of the hydrogen pressure the partial pressure of hydrocarbons increased, consequently the degree of hydrogenation of the instable iso carbenium ions decreased, so those could be easily decomposed.

3.2 Composition of the products

The products obtained during the heterogeneous catalytic conversion (85-92%) C_{17} and C_{18} hydrocarbons contained in the highest degree, furthermore other hydrocarbons in the gas oil boiling range ($\text{C}_{10}\text{-C}_{16}$ and $\text{C}_{19}\text{-C}_{24}$). The concentration of the isomerised paraffins 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 (Fig. 4). The further increase of temperature ($>360^\circ\text{C}$) could increase the isomer content of the product only at pressure of 60-80 bar, because in these cases the partial pressure of hydrogen was high enough to roll back the cracking reactions where the number of moles is increasing (Fig. 5).

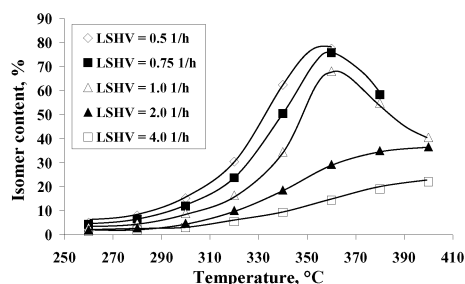


Figure 4: The total isomer content of the product in function of the temperature ($p = 40 \text{ bar}$, $H_2/HC \text{ ratio} = 400 \text{ Nm}^3/\text{m}^3$)

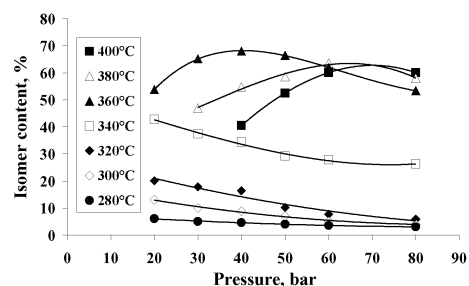


Figure 5: The total isomer content of the product in function of the pressure ($LHSV=1.0h^{-1}$, $H_2/HC \text{ ratio}=400\text{Nm}^3/\text{m}^3$)

3.3 Distribution of the isoparaffins

Product mixtures contained mainly the isomers of heptadecane and octadecane in the highest quantity, which were mainly mono-methyl paraffins. In the lowest concentration 4-methyl isomers generated (Fig. 5). The concentration of multibranched isoparaffins started to increase above 360°C , but it didn't reached 25% above 400°C either because of their cracking. For the isomerization of bioparaffins Pt/HZSM-22 found to be similarly high selectivity (Hancsók et al., 2007b). In case of this catalyst the isomerization reactions and the distribution of the products were investigated in detail in laboratory scale using inert diluent (n-heptane) (Claude and Martens 2000, Claude et al., 2001). According with our results the authors concluded that isomerization of paraffins could take place through "pore mouth" (methyl branching at the end of the carbon chain) and "key lock" (methyl branching at central position) modes of physisorption (Fig. 6). As a resultant of the two adsorption mode the concentration of the isomers has maximum at the branching position of 2 and 5-8 (Fig. 7), and it causes the mentioned minima at the position of 4.

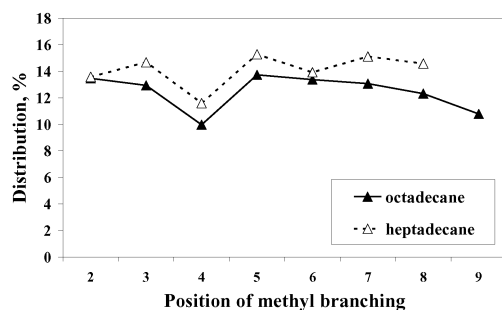


Figure 5: Distribution of methylalkanes ($T = 360^\circ\text{C}$, $p = 40 \text{ bar}$, $LHSV = 1.0 \text{ h}^{-1}$, $H_2/HC \text{ ratio} = 400 \text{ Nm}^3/\text{m}^3$)

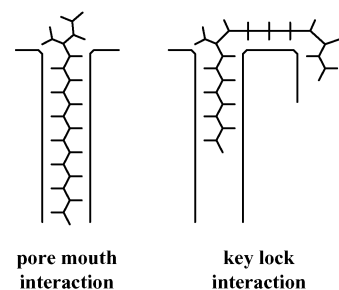


Fig. 6: Schemes of pore mouth and key lock interactions of octadecane on SAPO-11 zeolite

Based on our experimental results it was also concluded that in case of the methyl-heptadecanes by increasing the temperature the concentration of the 4-methyl-heptadecane increased, while that of the 2-methyl-heptadecane decreased (Fig. 8), probably because of the increasing degree of the “key lock” catalysis, namely the isomerization take place at higher degree by “key lock” adsorption.

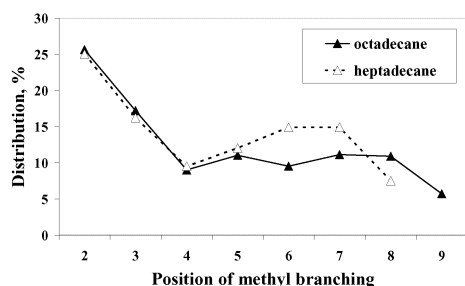


Figure 7: Distribution of methylalkanes ($T = 233^{\circ}\text{C}$, $P_{\text{H}_2}/P_{\text{HC}} = 13.1$)

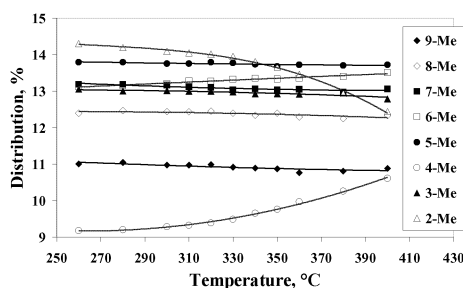


Figure 8: Distribution of the methyl-heptadecanes in products as a function of the temperature ($p = 40$ bar, $\text{LHSV} = 1.0$ h^{-1} , H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

By decreasing the LHSV the concentration of the isomers in the favourable positions (e.g. 2 and 5) decreased (Fig. 9), which happened with high probability because of the methyl shift conversion taking place mainly at higher contact time. By decreasing the hydrogen pressure the concentration of 2 and 3-methyl-heptadecans decreased, while that of the more central isomers increased (Fig. 10), because the degree of cracking reactions increase at higher hydrocarbon pressure, which could be happen with higher possibility in case of 2 and 3-methyl-heptadecans because of the longer time of their configurational diffusion from the pore.

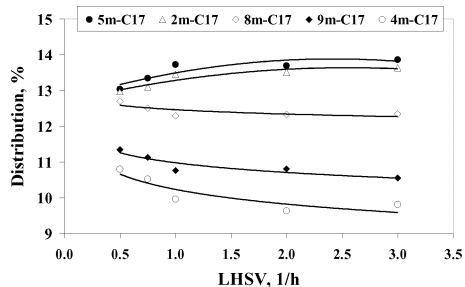


Figure 9: Distribution of methylheptadecanes in the product as a function of the LHSV ($T = 360^{\circ}\text{C}$, $p = 40$ bar, H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

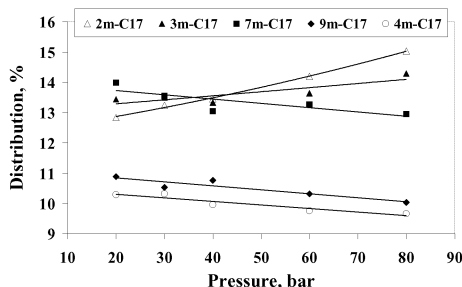


Figure 10: Distribution of the methylheptadecanes in the product as a function of the pressure ($T = 360^{\circ}\text{C}$, $\text{LHSV} = 1.0$ h^{-1} , H_2/HC ratio = $400 \text{ Nm}^3/\text{m}^3$)

According to abovementioned it can be concluded that the operational parameters have not only significant effect on the degree of isomerization but on the ratio of individual isoparaffins as well. The concentrations of the most unfavourable isomers regarding the cold flow properties decreased by increasing the temperature and decreasing the LHSV, which affected favourably the degree of isomerization, as well. The decrease of pressure was favourable to the formation of central isomers, but it was unfavourable regarding the yield, at the same time it can be advantageous regarding the installation and operational cost. On the other hand every effect which improved the cold flow property decreased the cetane number, which is unfavourable; consequently a compromise has to be made.

4. Conclusions

Based on the results the 0.5%Pt/SAPO-11 catalyst is suitable for the selective isomerization of paraffin mixture produced from sunflower oil. At the favourable process parameters ($T = 350\text{-}360^\circ\text{C}$, $p = 40$ bar, $\text{LHSV} = 0.75\text{-}1.0\text{ h}^{-1}$) determined by the product yield, total isoparaffin content and the ratio of individual isomers the cetane number of the mainly mono-methyl isomer containing products were high (76-88), and their cold flow properties are favourable (between -5 and -13°C). The obtained products are excellent Diesel fuel blending components.

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