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JET Fuel Production from High Molecular Weight Fischer-Tropsch Paraffin Mixture

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The quality requirements of fuels have significantly increased in the last 20 years. Furthermore, the demand for fuels produced from non-edible plants or waste biomass has become more important, due to more stringent environmental protection and political regulations. Fuel blending components are also produced from synthesis gas by Fischer-Tropsch synthesis. The boiling point of the 40 - 45 % of Low-Temperature Fischer-Tropsch product is higher than 370 °C, so-called Fischer-Tropsch wax. The wax is less valuable commercially, thus it is appropriate to hydrocrack it to more valuable liquid hydrocarbons, having lower molecular weight. In case of hydrocracking hydroisomerization also take place. Isoparaffins have advantageous performance properties; they burn clean relative to aromatic hydrocarbons, and they are desirable components of fuels. In our experimental work we investigated the fuel purpose hydrocracking of high molecular weight Fischer-Tropsch wax on Pt/H-ZSM5, Pt/H-Beta and Pt/H-[BAl]MCM22 zeolite catalysts. The main properties of feedstock were the followings: carbon number range: C_{13}-C_{69}, C_{21+} hydrocarbon content: > 99 %, pour point: 84 °C. The main products were gases (10 - 48 %) and gasoline (10 - 60 %) on the tested catalysts. The C_{21-} product – formed on Pt/H-Beta zeolite – contained 85 % isoparaffin hydrocarbon, while on the Pt/H-[BAl]MCM22 and Pt/H-ZSM5 zeolite took place isomerization in smaller degree (iso/n-paraffin ratio: 2 - 3 and 0.5 - 0.6, respectively). In our experiments we could produce fuel components – belonging to different boiling point range – with good yield and we observed shape selective effects and special selectivity as well, due to specific structural of zeolites.

1. Introduction

Nowadays the production and utilization of fuels - produced from renewable sources - have come to the front because of the increasing fuel consumption, more stringent environmental regulations (lower sulphur and aromatic content) and crude oil dependency of some countries. The utilization of alternative fuels in transportation is requested by political regulations both in the European Union and around the World. The European Union specifies the use of renewable energy to 10 % in transportation by 2020 (EU, 2009). In order to reduce the harmful effects significant steps have been also taken in the last years in the aviation sector. In 2009 The European Parliament decided to involve the aviation into the European Emission Trading System (EU ETS) from 2012 (EU, 2008). In 2009 the International Air Transport Association (IATA) also declared ambitious goals (growing of fuel consumption efficiency by 1.5 % annually by 2020, achieving a carbon neutral growth by 2020, and reducing the CO_2 emission by 50 % relative to 2005 level by 2050) (IATA, 2015). In order to achieve the stated objectives, the use of biofuels, which burn cleaner and have lower harmful emission during the entire lifecycle, is also required. Biocomponents of gasoline and diesel fuel are mainly produced nowadays from edible plants which raises many questions (Pölczmann et al., 2016). Alternative fuels can be also produced from biomass based synthesis gas by Fischer-Tropsch synthesis (Eller et al., 2014). Due to the political regulations, environmental protection, and favourable properties of the products (absence of sulphur and aromatic compounds) an increasing interest has stimulated toward Fischer-Tropsch synthesis (Hu et al., 2012). The 40 - 45 % of the product of Fischer-Tropsch synthesis is less valuable so-called Fischer-Tropsch

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wax, which is the mixture of high molecular weight n-paraffin hydrocarbons (Maitlis and de Klerk, 2013). The wax is solid at ambient temperature and it has high pour point. For its quality improvement fluid catalytic cracking and hydrocracking are used. The olefin concentration of the fluid catalytic cracking product is high (> 15 - 30 %). Olefins worsen the storage stability of fuels, thus they are not allowed components in JET fuels (Srivastava and Hancsók, 2014). The concentration of olefin hydrocarbons is limited in gasoline as well. In olefin hydrogenation processes straight chain paraffins are produced, which reduce the octane number (Hancsók et al., 2011). The other possible method for Fischer-Tropsch wax quality improvement is hydrocracking, where hydroisomerization takes place, too. The combustion of the product - containing isoparaffins in high amount - is more complete (e.g. isoparaffins burn cleaner than aromatic hydrocarbons), they improve the octane number of gasoline, reduce the freezing point of JET fuels, and in the case of diesel fuel the result is lower coldfilter plugging point (CFPP) (Hancsók et al., 2014). Hydrocracking of high molecular weight Fischer-Tropsch waxes have already been investigated by several groups. The feedstocks of these experiments were mainly model compounds, which catalytic conversion was investigated in batch reactors (Hanaoka et al., 2015) but some researchers made experiments in fixed bed reactors, too (Regali et al., 2014). In the literature some research groups can be found who also made experiments with real Fischer-Tropsch feedstock (Kim et al., 2012), but only limited information is available about experiments at continuous operation.

2. Experimental part

According to the previously mentioned, the aim of our experimental work was to study the hydrocrackability of high molecular weight Fischer-Tropsch paraffin mixture on Pt/H-Beta, Pt/H-[BAl]MCM22 and Pt/H-ZSM5 zeolite catalysts.

2.1 Feedstock

The commercially available FT wax contained more than 99 % C_{21+} hydrocarbons (Figure 1). The pour point and density of it were 84 °C and 940 kg/m^3.

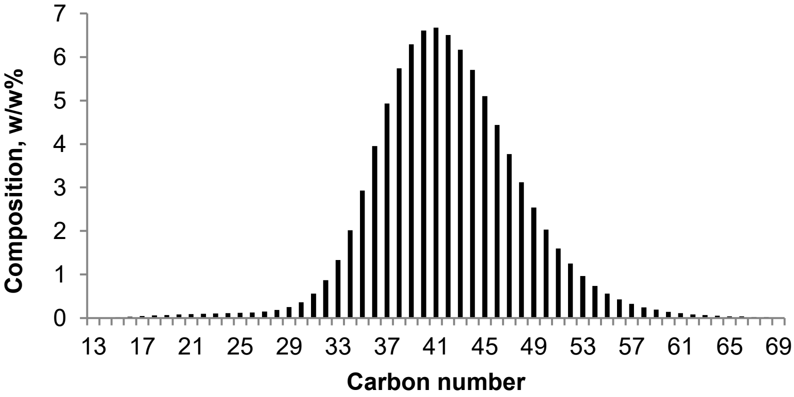

Figure 1: The n-paraffin hydrocarbon distribution of the feedstock

2.2 Catalysts

MCM22 zeolite was prepared by hydrothermal synthesis applying a stainless steel autoclave. The composition of synthesis gel was: 1 SiO_2 : 0.0196 Al_2O_3 : 0.0834 B_2O_3 : 0.078 Na_2O : 0.253 Na_2SO_4 : 0.517 hexamethyleneimine (HMI) : 42.5 H_2O, B/Al = 4.25. The temperature and time of crystallization were 145 °C and 10 days. The preparation of Beta zeolite was made according to ref. (Wadlinger et. al, 1967) at 135 °C for 9 days. Preparation of ZSM5 zeolite was also made by hydrothermal synthesis at 140 °C for 7 days. The synthesis gel composition was the following: 80 SiO_2 : 1 Al_2O_3 : 7.7 Na_2O : 18 Na_2SO_4 : 14.8 propylamine (PA): 1200 H_2O. After crystallization the products were recovered from the gel solution by filtration and washed with deionized water till reaching pH 7. After washing the samples were dried at 50 °C and calcined at 550 °C for 3 h, then convert to H-form by ion-exchange with ammonium-chloride solution. The form of Pt was prepared by incipient wetness with ($Pt(NH_3)_4(OH)_2 \bullet H_2O$) for 4 - 6 h. The disruption of Pt-complex was made by temperature programmed heating.

The main properties of catalysts – containing 50 % binding components – are summarized in Table 1. The BET surface of samples was measured at the temperature of liquid nitrogen (-196 °C) by Quantachrome Autosorb type automatized gas adsorption equipment. The surface was determined from the measured nitrogen adsorption isotherm. Prior to the measurement the samples were out-gassed by evacuation at 150 °C for 12 h. The concentration of Brønsted acid sites was determined by NH_3 temperature programmed desorption method. During the measurement catalyst samples were heated from 180 °C to 650 °C, and ammonia - absorbed in water - was titrated continuously with 0.1 M HCl solution. The ammonia released between 180 and 650 °C was taken as equivalent with the Brønsted acid site concentration of the sample.

Table 1: The main properties of catalysts

Properties	Pt/H-ZSM5	Pt/H-Beta	Pt/H-[BAl]MCM22
Pt-content, w/w%	0.5	0.5	0.5
Al-content, mmol/g	0.025	0	0.013
Na-content, mmol/g	0.584	1.855	0.498
BET surface, m^2/g	425	620	428
Si/Al ratio	27.6	13.0	25.5
NH_4^+ ion exchange capacity, mmol/g	0.39	1.20	0.84

2.3 Catalytic experiments

Catalytic experiments were carried out in a high-pressure microreactor system (Figure 2) at continuous operation. Prior to the experiments into the reactor 1.8 cm^3 (1.0 g) catalyst was placed (particle size: 0.315 - 0.80 mm) and activated in-situ by reduction at 450 °C in hydrogen flow (P = 15 bar). Experiments were carried out in the temperature range of 250 - 350 °C, while pressure (40 bar), hydrogen / hydrocarbon ratio (600 Ndm^3/dm^3) and liquid hourly space velocity (1.0 h^{-1}) were constant.

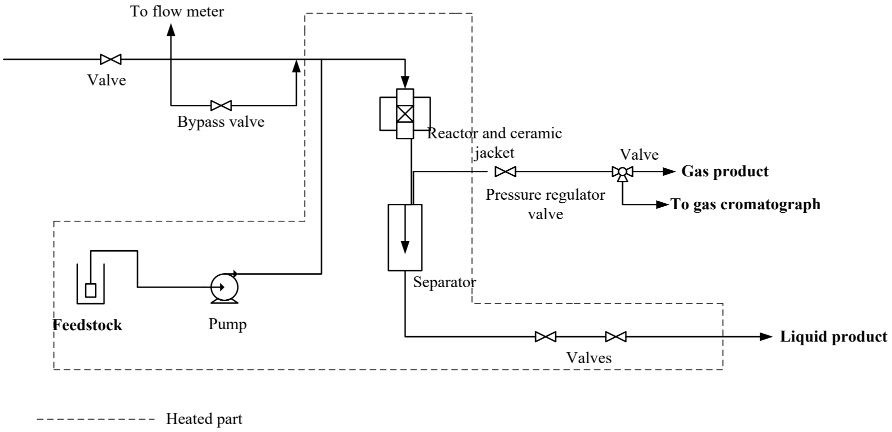

Figure 2: The scheme of experimental equipment

2.4 Analytical methods

The composition of the feedstock and reaction products were analysed by gas chromatographs. The qualitative and quantitative analysis of gas products were made by Chrompack CP 9001 gas chromatograph with flame ionization detector (Equity-1 column, at 35 °C). To the liquid product analysis GC-MS method was used (Shimadzu GC-2010, DB-1HT column, 8 min at 35 °C, heating to 240 °C with 8 °C/min, then heating with 10 °C/min to 350 °C and 15 min at 350 °C).

3. Results and discussion

The activity of Pt/H-ZSM5 and Pt/H-[BAl]MCM22 catalysts were low under 300 °C, while on Pt/H-Beta zeolite catalyst – having higher Brønsted acid concentration – almost full conversion could be observed at 275 °C. With increasing the temperature the yield of gas products and the C_3 and C_4 content also increased. This finding can be explained by the higher cracking activity of the catalysts at higher temperature. The highest gas product's yield (45 %) was observed on Pt/H-[BAl]MCM22 zeolite at 350 °C. On Pt/H-Beta and Pt/H-[BAl]MCM22 catalysts the gas product contained in highest amount of isobutane, suggesting that the hydrocracking took place after the hydroizomerization of high molecular weight paraffins (the isobutane is produced by β-scission of the branched carbenium ion intermediate) or further hydroisomerization of the cracking products took also place. In the case of Pt/H-ZSM5 catalyst the gas product contained n-butane in the highest amount (23 %). On the Pt/H-[BAl]MCM22 zeolite the isobutane yield was 4.9 - 20.0 %, while the gas product produced on the higher Brønsted acidity Pt/H-Beta zeolite contained 1.4 - 20.4 %. On the examined catalysts the produced amount of methane and ethane was very small or zero suggesting that hydrogenolysis of the C-C bonds did not proceed. Probably, the hydroisomerization and hydrocracking mainly took place in the pores. The yield of liquid products decreased with increasing the temperature (Table 2).

Table 2: Liquid product (C_{5+}) yields as a function of C_{21+} conversion

	Pt/H-[BAl]MCM22[a]	Pt/H-[BAl]MCM22[b]	Pt/H-[BAl]MCM22[c]
C_{21+} conversion, %	22.7	71.4	95.5
C_{5+} yield, %	91.4	66.8	55.0
	Pt/H-ZSM5[a]	Pt/H-ZSM5[b]	Pt/H-ZSM5[c]
C_{21+} conversion, %	20.1	68.9	93.4
C_{5+} yield, %	93.2	70.2	55.4
	Pt/H-Beta[d]	Pt/H-Beta[e]	Pt/H-Beta[f]
C_{21+} conversion, %	22.4	69.2	92.1
C_{5+} yield, %	98.3	87.5	73.3

a: 300 °C, b: 325 °C, c: 350 °C, d: 225 °C, e: 250 °C, f: 275 °C

The yields of gasoline fraction on the examined catalysts are compared on Figure 3 - 5. The C_5-C_{10} yields increased with increasing of the reaction temperature. The C_5-C_{10} yields were similar on Pt/H-[BAl]MCM22 and Pt/H-ZSM5 catalysts (10 - 48 %), while C_5-C_{10} hydrocarbons are produced in higher quantities on Pt/H-Beta catalyst (15 - 60 %). Besides the gasoline fraction yield we also determined the yield of middle distillates. On the tested catalysts middle distillates were not produced in such great amount as gasoline fraction. The yields of middle distillates changed between 2.4 – 8.0 %. The middle distillates yield above 70 % conversion decreased, suggesting that lighter compounds are formed from JET fuel and gas oil.

The isomer content of C_{21-} product increased as a function of C_{21+} conversion (Figure 6). On the Pt/H-ZSM5 zeolite catalyst did not take place hydroizomerization processes considerably. The degree of isomerization on the Pt/H-[BAl]MCM22 and Pt/H-Beta zeolites was higher significantly.

The highest iso/n-paraffin ratio (6 - 7) was observed on the Pt/H-Beta catalyst. This ratio was lower on Pt/H-[BAl]MCM22 (2 - 3) and Pt/H-ZSM5 (0.5 - 0.6) catalysts, consequently the Pt/H-Beta zeolite had the highest isomer selectivity of the tested catalysts. On the latter catalyst monobranched and multibranched isomers are also produced, while on Pt/H-ZSM5 zeolite beside the n-paraffin cracking product mainly monobranched isoparaffins could be identified in the reaction product. The observed differences in isomer content derived from the different structure of tested catalysts. The Pt/H-Beta zeolite –due to larger pore size – allowed the formation of multibranched isoparaffins and the fast diffusion of them from the pores; thus on this catalyst multibranched isomers produced in higher amount. In contrast, the channels of Pt/H-ZSM5 zeolite were probably too narrow to produce multibranched isoparaffins. Furthermore, due to the narrow channels the diffusion of produced monobranched isomers was limited, thus due to longer residence time they cracked in the pores of Pt/H-ZSM5 in higher degree than on the larger pore size Pt/H-Beta zeolite. Interestingly, on Pt/H-[BAl]MCM22 zeolite – contained narrower pores than Pt/H-ZSM5 catalyst – we got similarly significant amount mono- and multibranched isomers like on the Pt/H-Beta zeolite. This is probably due to the fact that the hydroisomerization took place on the large number of active centrums of surface cups can be found on the external surface of MCM22 zeolite.

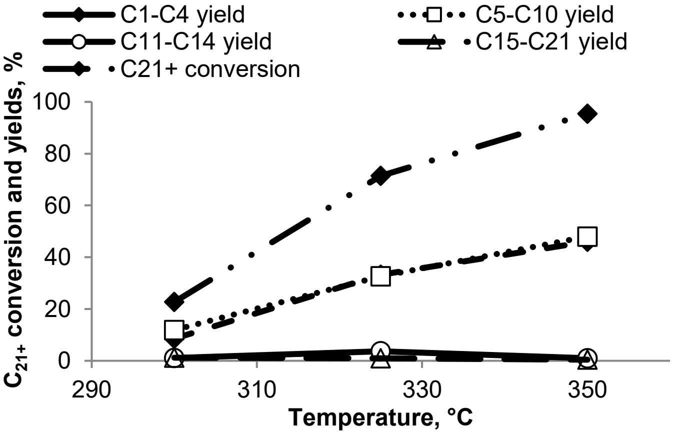

Figure 3: C21+ conversion and product yields as a function of temperature (Pt/H-[BAl]MCM22)

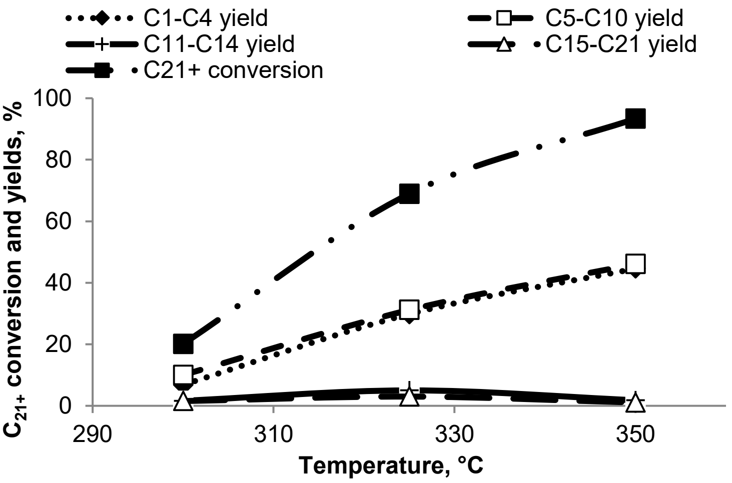

Figure 4: C21+ conversion and product yields as a function of temperature (Pt/H-ZSM5)

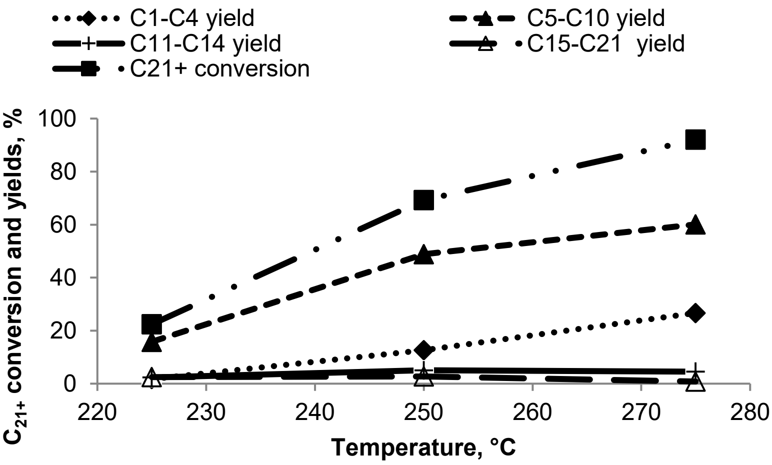

Figure 5: C21+ conversion and product yields as a function of temperature (Pt/H-Beta)

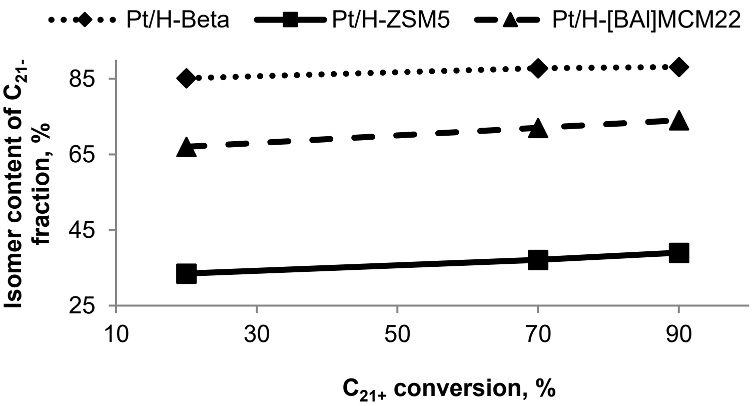

Figure 6: Isomer content of product as a function of C21+ conversion

4. Conclusion

We examined the hydrocracking possibility of high molecular weight Fischer-Tropsch paraffin mixture on Pt/H-Beta, Pt/H-ZSM5 and Pt/H-[BAl]MCM22 zeolite catalysts. Catalytic experiments were carried out in the temperature range of 250 - 350 °C, while the pressure (40 bar), the hydrogen / hydrocarbon ratio (600 Ndm^3/dm^3) and liquid hourly space velocity (1.0 h^{-1}) were constant. We determined the yields of liquid and gas products, and examined the yields of gasoline (C_5-C_{10}), JET (C_{11}-C_{14}) and gasoil (C_{15}-C_{21}) fractions as a function of temperature. During our experiments from the feedstock gases (1.7 - 45 %) and gasoline (10 - 60 %) are mainly produced; while the middle distillate yield was much lower (2.4 - 8.0 %). The Pt/H-ZSM5 and Pt/H-[BAl]MCM22 zeolite catalysts were not active under 300 °C. On Pt/H-Beta zeolite having higher Brønsted acidity almost full conversion was observed at 275 °C. The yield of liquid products decreased with increasing the temperature and C_{21+} conversion. The gas product produced on Pt/H-Beta and Pt/H-[BAl]MCM22 zeolites contained isobutane in highest amount, while on Pt/H-ZSM5 catalyst the amount of n-butane was the highest. The yield of C_5-C_{10} fraction increased with increasing of the temperature. During the experiments the isomer content of products increased as a function of C_{21+} conversion. On Pt/H-ZSM5 zeolite the isomer content was less significantly like on the Pt/H-Beta and Pt/H-[BAl]MCM22 catalysts. We ascribed the difference in isoparaffin content to the shape selective effect (Pt/H-ZSM5) and the special structure of the zeolite catalyst (Pt/H-[BAl]MCM22).

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