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# Fuel Production from Fischer-Tropsch Paraffin Mixtures

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Hydrocracking of biomass-based Fischer-Tropsch paraffin mixtures was studied on Pt/H-Beta and Pt/H-ZSM-5 catalysts in the temperature range of 225 - 350 °C, at 40 bar total pressure, LHSV = 1.0 $h^{-1}$, and hydrogen to hydrocarbon ratio of 600 $Ndm^3/dm^3$. Two waxes having different carbon number distribution were investigated. The yields of gas, gasoline, and middle distillate fractions obtained from $C_{13}$ - $C_{69}$ and the $C_{16}$ - $C_{45}$ paraffin mixtures were determined. The selectivity of the two catalysts was compared at about the same $C_{21+}$ conversion that was controlled by selecting the right reaction temperature. The hydrocracking/hydroisomerization activity of the catalysts reflected their Brønsted acidity. Catalyst Pt/H-Beta showed significant hydrocracking/hydroisomerization activity at 225 - 275 °C, whereas similar activity was attained only at 300 - 350 °C using catalyst Pt/H-ZSM-5. The higher reaction temperature increased the gas yield on expense of the yield of gasoline and middle distillates. Due to shape selectivity substantially less branched chain hydrocarbon product was formed over the Pt/H-ZSM-5 than over the Pt/H-Beta catalyst.

## 1. Introduction

Concentration of harmful pollutants related to transportation can be reduced by using alternative fuels that are free of sulfur and aromatics, have excellent burning properties and high hydrogen content in the constituent molecules (Eller et al., 2016). The use of environment-friendly biomass/waste based alternative fuels is encouraged by the European Union (EU, 2009) and also by several international organizations (IATA, 2015). As a consequence, the significance of Fischer-Tropsch synthesis is continuously increasing (Ail and Dasappa, 2016). The products of Fischer-Tropsch synthesis are practically free from aromatics and heteroatoms. About 40 - 45 wt.% of the product from the Low-Temperature Fischer-Tropsch synthesis is a solid, less valuable, n-paraffin rich mixture, the so-called Fischer-Tropsch wax (FT wax). Due to its high pour point, this portion of the product cannot be used directly as engine fuel (Maitlis and de Klerk, 2013); however, by hydrocracking the heavy paraffin wax components the yield of fuel quality products and the economics of the overall process are also improved. Hydrocracking is usually accompanied by hydroisomerization, which results in branched-chain hydrocarbons having burning properties similar to those of n-paraffins. Monobranched isomers reduce the freezing point of JET fuel and the pour point of gasoil and base oil fractions (Hancsók et al., 2014). In earlier studies, hydroconversion was mainly carried out using model paraffin mixtures in batch reactor using (Regali et al., 2013) over bifunctional supported transition metal/noble metal catalysts. Various oxides were applied as support, such as, $SiO_2$-$Al_2O_3$ (Lee et al., 2011), sulfated metal-oxide, and tungsten-oxide-zirconia (Zhou et al., 2003). Only a few studies report about the use of real Fischer-Tropsch feedstock and continuously operated reactor (Schablitzky et al., 2011). The knowledge about the effects of strong solid acid supports, such as acidic zeolites is rather limited (Hanaoka et al., 2015). Therefore, in the present study bifunctional Pt/H-Beta and Pt/H-ZSM-5 catalysts were synthetized and studied in the hydrocracking of biomass-based, real Fischer-Tropsch paraffin mixtures.

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## 2. Experimental part

### 2.1. Feedstock

FT waxes (WAX A and WAX B) having different carbon number distribution were used as feedstock (Figure 1). Both mixtures contained mainly $C_{21+}$ n-paraffins. The density, the congealing point, and the $C_{21+}$ hydrocarbon content of WAX A were 910 kg/m$^3$, 78 °C, and 80.7 wt.%, respectively. The corresponding properties of WAX B were 940 kg/m$^3$, 84 °C and 99.2 wt.%.

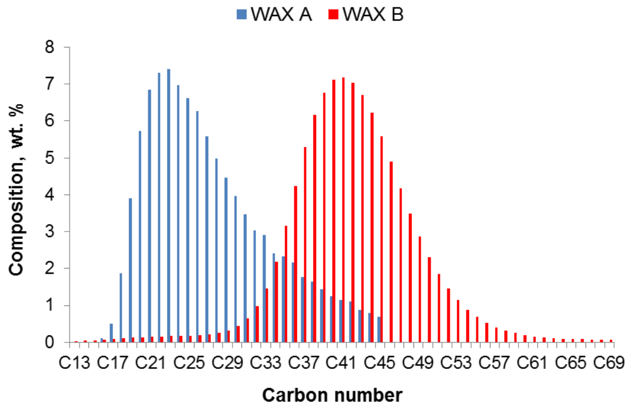

*Figure 1: Carbon number distribution of the feedstock FT waxes*

### 2.2. Catalyst preparation

Beta- and ZSM-5 zeolites were prepared by using aqueous solution of structure directing agent tetraethylammonium hydroxide and propyl-amine, respectively. The crystalline product of the synthesis was washed with deionized water to neutral pH, then dried and calcined at 550 °C in order to remove the template molecules from the zeolite structure. The thus obtained Na-zeolite was transformed into $NH_4$-form by liquid phase ion exchange. The H-form was obtained by thermal decomposition of the $NH_4$-zeolite. Each H-zeolite was loaded with 0.5 wt.% platinum. The suspension of $Pt(NH_3)_4(OH)_2$ solution and H-zeolite was stirred at room temperature for 4 h, the excess water was evaporated on a water bath, and then the sample was dried at 50 °C. Decomposition of the Pt precursor compound was affected by calcination at 480 °C. In order to provide proper mechanical strength, Pt/H-zeolites were mixed with aluminium oxyhydroxide solution then dried and calcined. After calcination, the formulated catalyst contained 50 wt.% of γ-alumina binder.

### 2.3. Catalyst characterization

The concentration of Brønsted acid sites was determined by measuring the temperature-programmed ammonia evolution from the $NH_4$-zeolite by heating the sample from 180 °C to 650 °C in nitrogen flow. The released ammonia was absorbed in water and titrated continuously with 0.1 M HCl solution. The ammonium released between 180 and 650 °C was taken as equivalent with the Brønsted acid site concentration (mmol $NH_3/g_{zeolite}$) of the sample. The different acid sites (Brønsted and Lewis acid sites) were characterized by pyridine adsorption. The self-supporting pellet of the catalyst sample was placed into the sample holder of an infrared cell and was activated in-situ in oxygen stream at 500 °C. After evacuation, the temperature of the cell was lowered to 200 °C and sample was contacted with 5 mbar of pyridine vapor. The temperature was lowered to 100 °C, pyridine vapor was removed from the cell by evacuation, and then the spectrum of adsorbed pyridine was collected at room temperature. The specific surface area of the catalyst samples was determined from the nitrogen adsorption isotherm measured at -196 °C.

### 2.4. Catalytic experiments

Before catalytic runs, catalysts were activated in-situ in a flow-through tube reactor (Tomasek et al., 2016) by reduction at 450 °C in hydrogen flow. Experiments were carried out in continuous operation mode in the temperature range of 225 - 350 °C, and at constant 40 bar total pressure, $H_2$ to hydrocarbon ratio of 600 Ndm$^3$/dm$^3$, and LHSV = 1.0 h$^{-1}$. The composition of the feedstock and the product mixtures were analyzed by GC. The qualitative and quantitative analysis of the gas phase product was determined by a GC equipped with a flame ionization detector and Equity-1 column, whereas liquid product was analyzed by GC-MS equipped with a Rxi-5Sil MS column (Restek).

## 3. Results and discussion

The main properties of the catalyst samples studied are summarized in Table 1. The framework aluminum content ($Al_F$) of H-Beta is significantly higher than that of H-ZSM-5. In accordance, more than three times higher $NH_4^+$ exchange capacity was observed for the Beta zeolite than for the ZSM-5 zeolite. Since the $NH_4^+$ exchange capacity was taken as equivalent with the Brønsted acid site concentration of the samples, it follows that the concentration of Brønsted acid sites is more than three times higher in the H-Beta zeolite than in the H-ZSM-5.

*Table 1: Main properties of the synthesized catalysts*

| Properties | Pt/H-Beta | Pt/H-ZSM-5 |
|---|---|---|
| Na content, mmol/g | 0.0 | 0.025 |
| $Al_{tot.}$ content, mmol/g | 1.855 | 0.584 |
| Specific surface area, $m^2/g$ | 620 | 425 |
| $Si/Al_F$ molar ratio | 12.6 | 41.3 |
| $NH_4^+$ exchange capacity, mmol/g | 1.2 | 0.39 |

Figure 2 shows the FT-IR spectra of adsorbed pyridine on H-Beta and H-ZSM-5 zeolites. Absorption band appearing at 1545 $cm^{-1}$ is characteristic of pyridinium ions formed on Brønsted acid sites, whereas the band at 1454 $cm^{-1}$ can be assigned to pyridine molecules coordinately bound to Lewis acid sites (Parry, 1963). Both H-Beta and H-ZSM-5 zeolites contain Brønsted (B) and Lewis (L) acid sites. However, the relative intensity of the absorption bands characteristic of pyridinium ions suggest that the concentration of Brønsted acid sites in H-Beta zeolite is about three times higher than in H-ZSM-5. These results are in accordance with the $NH_4^+$ ion exchange capacities (Table 1).

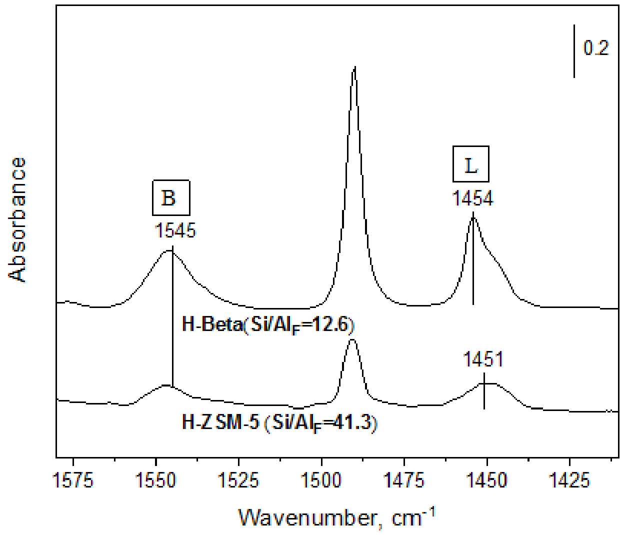

*Figure 2: FT-IR spectra of pyridine adsorbed on the H-form of Beta and ZSM-5 zeolites*

The activity of Pt/H-ZSM-5 zeolite was low in the hydrocracking of both paraffin waxes at temperatures lower than 300 °C, whereas the Pt/H-Beta zeolite catalyst, having higher Brønsted acid site concentration was active already in the temperature range of 225 - 275 °C. The yield of gas phase products was higher at higher reaction temperatures over both catalysts (Table 2), which can be attributed to acceleration of secondary hydrocracking processes at higher temperatures. The product gas contained mainly propane and butanes (n-butane and isobutane). In accordance with expectations (Sie, 1993), methane and ethane were practically absent from the product mixture. These light products ($C_1$ - $C_2$) were not produced even at higher temperatures (350 °C), suggesting that C - C bond hydrogenolysis did not proceed over metallic sites, but the hydrocracking and hydroisomerization reactions did proceed in the pores of zeolites. On the Pt/H-Beta catalyst the product gas contained isobutane in high concentration, whereas higher amount of propane and n-butane were produced over the Pt/H-ZSM-5 catalyst (Table 2). The lower isobutane selectivity of ZSM-5 zeolite can be attributed to shape selective effects. The product selectivity within the relatively narrow pores of zeolite ZSM-5 does not favor the formation of branched hydrocarbons having larger critical diameter than the straight chain paraffin molecules.

*Table 2: Gas yields and share of $C_3$-$C_4$ hydrocarbons*

| Yields, wt.% | Pt/H-Beta[a] | | Pt/H-ZSM-5[b] | |
|---|---|---|---|---|
| | WAX A | WAX B | WAX A | WAX B |
| Total gas | 1.1-12.6 | 1.7-26.7 | 7.9-45.1 | 6.8-44.5 |
| Propane | 6.2-8.2 | 2.4-9.1 | 44.2-43.9 | 21.8-28.3 |
| Isobutane | 86.1-85.2 | 80.7-76.8 | 17.9-19.1 | 12.2-19.1 |
| n-Butane | 7.7-6.5 | 16.9-14.1 | 37.6-36.1 | 65.5-52.3 |

[a] 225 - 275 °C, [b] 300 - 350 °C

The results of hydrocracking experiments carried out over Pt/H-Beta and Pt/H-ZSM-5 catalysts with the two waxes are shown in Figure 3. In general, higher $C_{21+}$ conversions were observed with the higher average molecular weight feedstock WAX B, than with the lower average molecular weight feedstock WAX A (cf. conversion curves *a-b* and *c-d* in Figure 3). The higher conversions are clearly attributed to the higher reactivity of longer chain hydrocarbons (Wojciechowski, 1998).

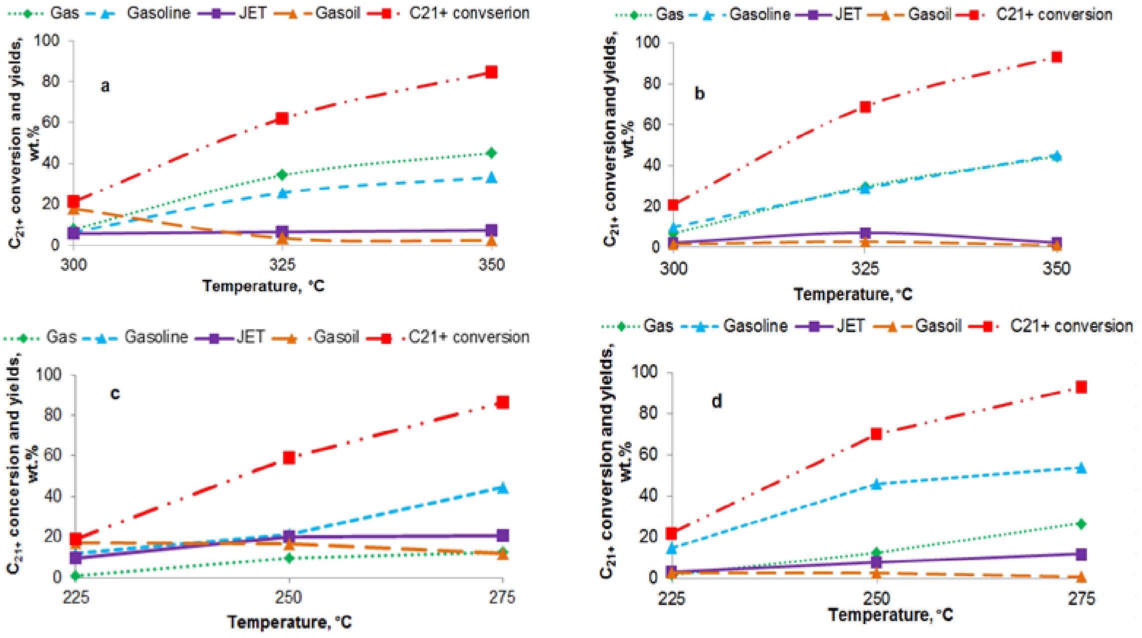

*Figure 3: $C_{21+}$ conversion and product yields determined on (a,b) Pt/H-ZSM5 and (c,d) Pt/H-Beta with feedstock (a,c) WAX A and (b,d) WAX B*

Regarding the ratio of liquid hydrocarbon fractions (Figure 3), a higher amount (10 - 54 wt.%) of gasoline fraction ($C_5$ - $C_9$) was produced from the higher average molecular weight WAX B than from WAX A (6.4 - 44.4 wt.%). Middle distillates (JET + Gasoil, $C_{10}$ - $C_{21}$), however, were produced from WAX B and WAX A in an amount of 3.6 - 12.6 wt.% and 9.7 - 36.5 wt.%, respectively. Therefore, under identical experimental conditions the ratio of the gasoline fraction to middle distillates is always higher with WAX B having higher average molecular weight than with WAX A (Table 3). The ratio of JET fraction to the gasoil fraction ($C_{10}$ - $C_{14}$/$C_{15}$ - $C_{21}$) within the middle distillates changed similarly (Table 3).

*Table 3: Product ratios*

| | Pt/H-Beta[a] | | Pt/H-ZSM5[b] | |
|---|---|---|---|---|
| | WAX A | WAX B | WAX A | WAX B |
| Gasoline/Middle distillates ratio | 0.3-1.4 | 2.6-4.3 | 0.3-3.4 | 2.5-12.7 |
| JET/Gasoil ratio | 0.6-1.7 | 1.3-14.6 | 0.3-3.1 | 1.5-2.3 |

[a] at 225 and 275 °C; [b] at 300 and 350 °C

The carbon number distribution of the products obtained on Pt/H-Beta and Pt/H-ZSM-5 catalysts are shown in Figure 4. Starting from WAX A, the product distribution clearly shifts towards the lower carbon numbers ($C_5$ - $C_9$ hydrocarbons) on the Pt/H-ZSM-5 catalyst (cf. Figure 4, part *a* and *c*), which is less discernible for WAX B (Figure 4, part *b* and *d*). The observed shift of the product distribution towards lower carbon numbers on Pt/H-ZSM-5 can be attributed to the higher reaction temperature (325 °C), needed to reach the same conversion level than over Pt/H-Beta catalyst. At 325 °C the contribution of secondary hydrocracking reactions is probably more significant than at lower temperature (250 °C) applied for the Pt/H-Beta zeolite, which is also supported by the higher gas yields obtained over Pt/H-ZSM-5 catalysts (see the $C_1$ - $C_4$ yields in Figure 4). It also should be noted, however, that secondary reactions could be more significant in the relatively narrow pores of ZSM-5 zeolite due to the slower product diffusion and thus longer residence time of primary hydrocracking products within the pores.

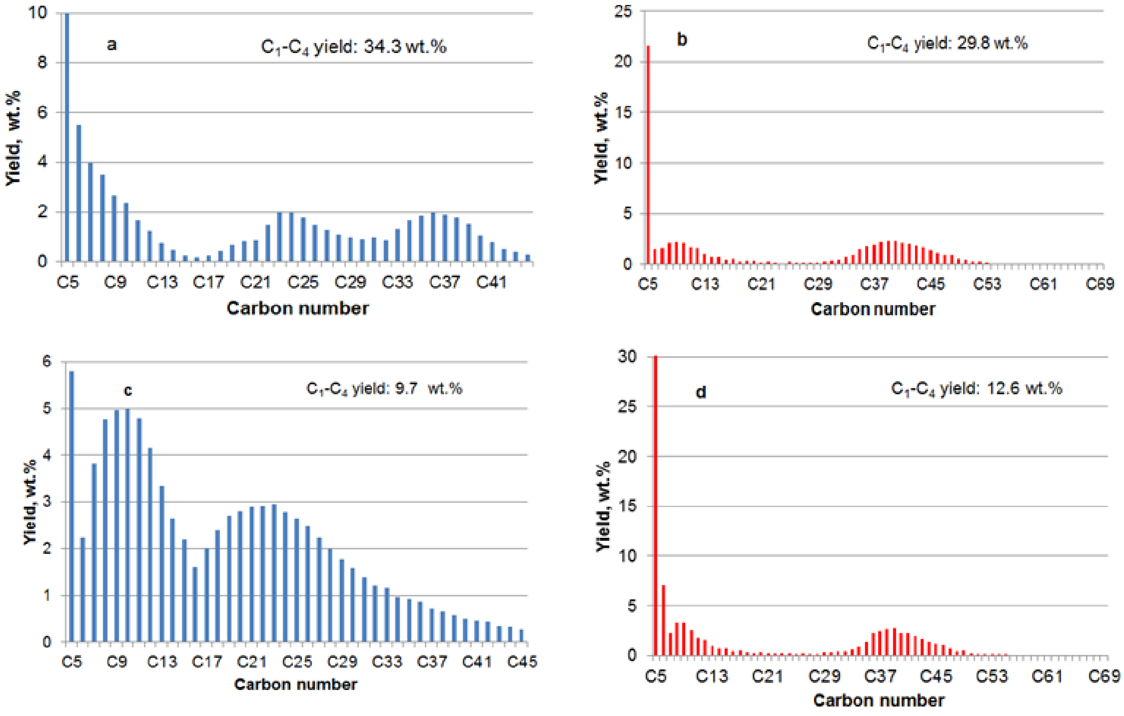

*Figure 4: Carbon number distribution of products obtained on (a,b) Pt/H-ZSM5 at 325 °C and (c,d) Pt/H-Beta at 250 °C with feedstock (a,c) WAX A and (b,d) WAX B*

## 4. Conclusions

Hydrocracking of biomass-based Fischer-Tropsch paraffin mixtures was studied on Pt/H-Beta and Pt/H-ZSM-5 catalysts at reaction temperatures of 225 - 350 °C, and constant 40 bar total pressure, LHSV = 1.0 $h^{-1}$, and $H_2$/hydrocarbon ratio of 600 $Ndm^3/dm^3$. The activity of Pt/H-ZSM-5 zeolite was low below 300 °C, whereas the Pt/H-Beta zeolite catalyst having higher Brønsted acid concentration was already active in the temperature range of 225 - 275 °C. The gas product produced on Pt/H-Beta zeolite contained mainly isobutane. On the Pt/H-ZSM-5 catalyst, higher amount of propane and mostly n-butane were produced, which was attributed to the shape selective effect (product type selectivity) of the ZSM-5 zeolite structure. Due to the higher reactivity of longer carbon chain paraffin hydrocarbons, higher $C_{21+}$ conversions and gasoline yields and lower middle distillate yields were observed for WAX B than for WAX A having lower average molecular weight. The product distribution was shifted towards the lower carbon numbers on the Pt/H-ZSM-5 catalyst. This was mainly attributed to the acceleration of secondary reactions at higher reaction temperature (325 °C) needed to reach the same conversion level than on the Pt/H-Beta catalyst. The slower diffusion of the primary products in the narrow channels of Pt/H-ZSM-5 and thus the longer residence time of the primary reaction products within the pores probably also contributed to the shift of the product distribution towards lower carbon numbers. Due to the lower required reaction temperatures and gas yields, the reaction can be carried out more advantageously on Pt/H-Beta zeolite, than on Pt/H-ZSM-5. At lower reaction temperatures, the operational cost of the process is also reduced significantly.

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