CHEMICAL ENGINEERING TRANSACTIONS Volume 21, 2010
Editor J. J. Klemeš, H. L. Lam, P. S. Varbanov
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DOI: 10.3303/CET1021220

Catalytic Conversion of Fischer-Tropsch Waxes

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Nowadays, the application of fuels and lubricants produced from renewable feedstocks has come to the front because of serious environmental problems and ambiguity of crude oil supply. In this paper mesoporous Pt/AlSBA-15 catalysts with different platinum contents were investigated and it was found that catalysts having 0.5 wt. % platinum showed the best results in the production of gas oil and base oil fractions with high isoparaffin content from Fischer-Tropsch wax. The selectivity of the target product fractions was high, and based on these facts the selective isomerization of the Fischer-Tropsch wax can be a new application area of the Pt/AlSBA-15 catalyst.

1. Introduction

Nowadays, the application of fuels and lubricants produced from renewable feedstocks has come to the front because of serious environmental problems (e.g. greenhouse effect) and ambiguity of crude oil supply (e.g. import dependence). In the integrated Fischer-Tropsch synthesis (Figure 1) liquid hydrocarbons („synthetic crude”) and subsequently fuels, base oils and other special products are produced from natural gas, coal, hydrocarbons, biomass and wastes through synthesis gas in three main steps. The Fischer-Tropsch wax (60-80% of the Fischer-Tropsch products) produced of synthesis gas of different sources is a mixture of high molecular weight (C_{20}-C_{60}) n-paraffins, which is solid at normal conditions. The products (fuels and base oils) made of this paraffin mixture is of high quality, less harmfull to environment (practically zero sulphur- and nitrogen content, low aromatic content, excellent application properties) and do not demand changes in the fuel supply infrastructure and in the engine constructions (Perego et al., 2009; Sousa-Aguiar et al., 2005; Hancsók 2004, Gamba et al. 2010).

The final step of the integrated Fischer-Tropsch technology is the upgrading and separation of the product mixtures with different compositions and quality. It is possible to produce the above mentioned high quality products with isomerization and/or hydrocracking from Fischer-Tropsch paraffin mixture, partly with the production of hydrocarbons with lower hydrocarbon chain and lower pour point and partly with the production of branched hydrocarbons with the same chain length. As the gaseous and

Please cite this article as: Pölczmann G., Szegedi A., Valyon J., Wollmann A and Hancsók J., (2010), Catalytic conversion of Fischer-Tropsch waxes, Chemical Engineering Transactions, 21, 1315-1320 DOI: 10.3303/CET1021220

naphta products are formed during hydrocracking in significant volume (8-12 % and 10-20 %) the selectivity of the product mixture is low. Accordingly it is very important to develop a catalytic system (identification of the proper catalysts and the advantageous process parameters) that can be applied to produce the appropriate mixture of gas oil and base oil with selective isomerization (skeletal arrangement) and with high isoparaffin selectivity (Zhou et al. 2004, Vosloo 2001, Bouchy et al. 2009).

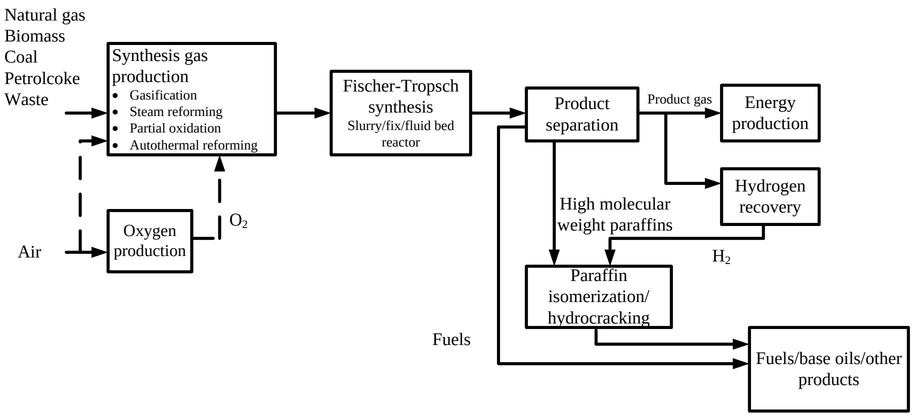

Figure 1: The integrated Fischer-Tropsch synthesis

Isomerization of high molecular weight n-paraffins can be effectively carried out on bifunctional catalysts. The metal content has the hydrogenating-dehydrogenating function and the acidic active sites of the carrier are responsible for the activation of the C-C and C-H bonds with carbo-cationic mechanism. There are only a few indications about the application of metal catalysts on mesoporous supports in the literature (Deldari 2005, Rosetti et al. 2009). Consequently our objective was to investigate some Pt/AlSBA-15 (SBA: Santa Barbara Amorphous) catalysts which have not been investigated in detail in this reaction system yet.

2. Experimental

2.1 Objectives

In our experiments the applicability and catalytic activity of AlSBA-15 catalyst with different (0.3-1.0 %) platinum contents and different metallic/acidic active site ratios were investigated for the selective isomerisation of Fischer-Tropsch paraffins. The effect of the process parameter combinations (pressure, temperature, liquid hour space velocity, H_2/hydrocarbon volume ratio) on the yield and composition of the products were also investigated.

2.2 Feedstock

The feedstock of our experiments was a paraffin mixture produced from biomass-based synthesis gas with Fischer-Tropsch synthesis (sulphur content < 5 mg/kg, pour point = 72 °C, nitrogen content = 12 mg/kg). The paraffin composition of the feedstock is shown in Figure 2.

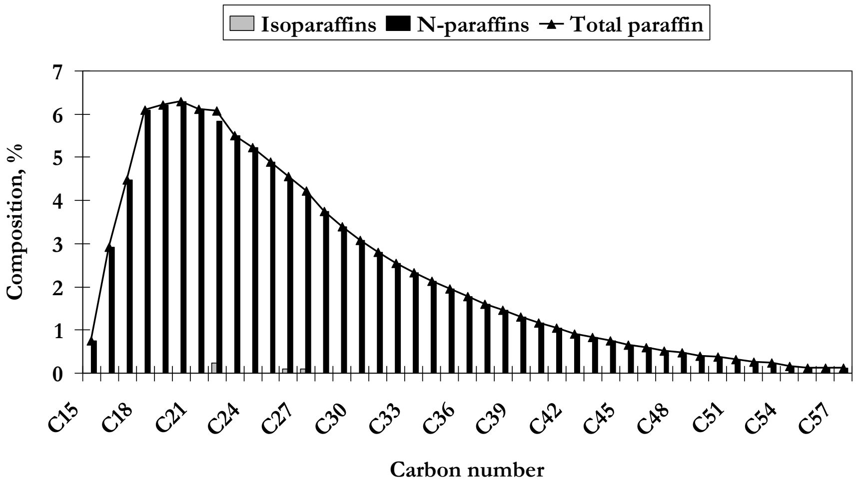

Figure 2: The paraffin composition of the feedstock

2.3 Catalyst

The parent Al-SBA-15 support was prepared according to the procedure of Vinu et al. Pt was loaded by incipient wetness impregnation method in the form of $Pt(NH_3)_4(OH)_2 \bullet xH_2O$ precursor. In the experimental reactor the appropriate liquid distribution was attained by the application of quartz pieces under and above the catalyst bed. The activation of the catalyst was made at 450 °C in hydrogen flow. The main characteristics of the catalysts are presented in Table 1.

Table 1 The main characteristics of the applied catalysts

Properties	*Value*
Platinum content, wt. %	0.3-1.0
Acidity, NH_3/g	0.6-0.65
BET area, m^2/g	470
Average pore diameter, nm	3.6
Si/Al ratio	17.8

2.4 Experimental equipment

Catalytic experiments were made in a high-pressure microreactor system in continuous operation and on a catalyst with steady-state activity. The heating of the reactor was made by an adjustable ceramic jacket. Minimum 80 °C temperature was maintained in the whole system because of the risk of chilling (the feedstock was solid at room temperature).

2.5 Process parameters

The process parameters of our experiments were determined based on the results of our pre-experiments: temperature = 275-375 °C, pressure = 40-80 bar, liquid hour space velocity = 1.0-3.0 h^{-1}, H_2/hydrocarbon volume ratio = 400-800 Nm^3/m^3.

2.6 Analytical methods

The composition of the products was determined by gas chromatography. The main characteristics of the chromatographic analysis are presented in Table 2.

Table 2: Main characteristics of the gas chromatography analyses

	Liquid analysis	*Gas analysis*
Type of column	Agilent Tech DB-1HT	Supelco EQUITY-1
Detector	Flame ionization	Flame ionization

3. Results and Conclusions

The best catalytic results could be achieved by catalysts having 0.5 wt % platinum content. With increasing temperature the yield of the liquid products (C_{5+}) decreased, but until 325 °C this value was above 93 % in all cases (Figure 3). Increasing pressure shifted the hydrocracking reactions back (with the increasing number of moles) so it had a decreasing effect on the volume of the gas products. Lower contact time (higher liquid hour space velocity) had the same effect.

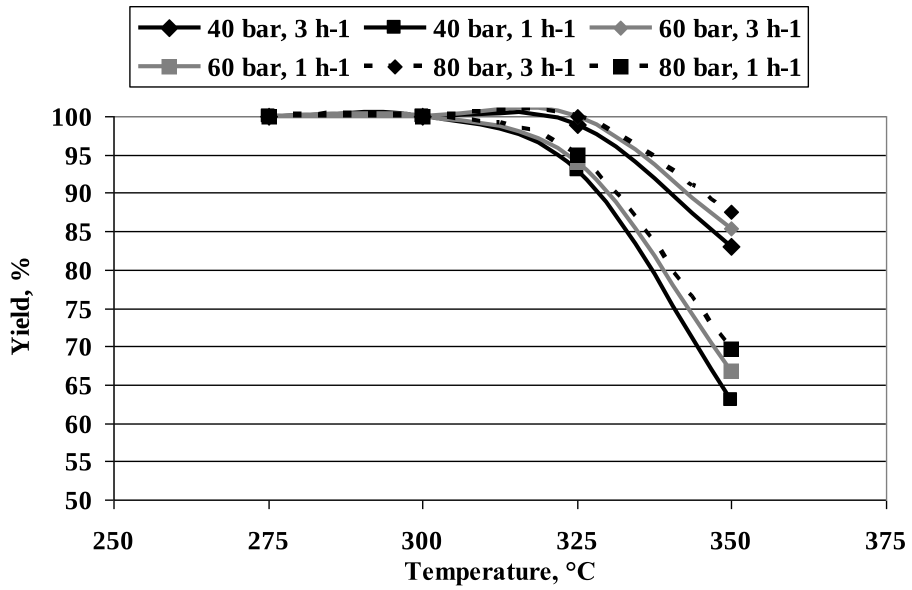

Figure 3 Changes in the yield of the liquid products (C5+) as a function of process parameters

The yield of the C_{5-} fractions as a function of different process parameters is shown in Figure 4. The produced amount of methane and ethane was very small or zero on all the catalysts. Increasing temperature increased the yield of propane and the higher molecular weight compounds, and in the gas products mainly branched isobutane could be identified indicating that cracking enacted partly after the isomerization reactions.

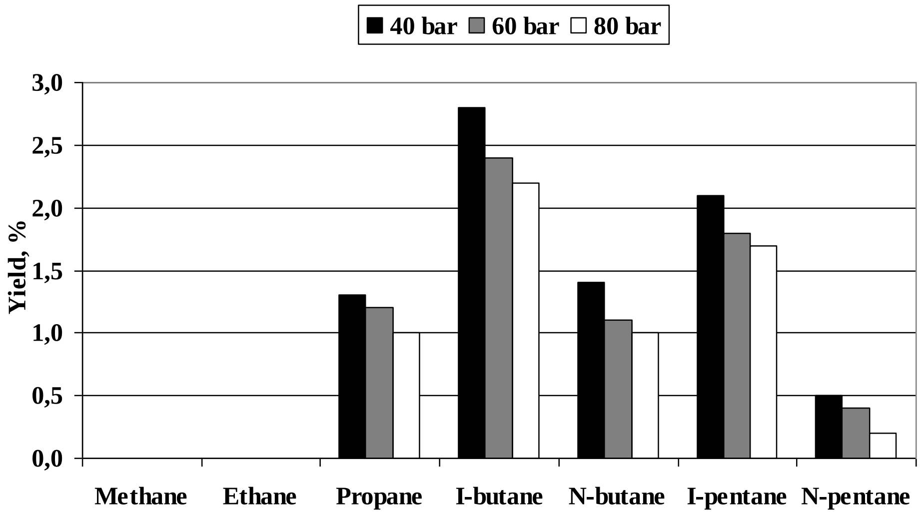

Figure 4: Composition of the C5- products as a function of process parameters (325 °C, LHSV: 1 h-1)

The yield of the produced C5+ fractions of the liquid products (C_6-C_{10}, C_{11}-C_{20}, C_{21}-C_{30} fractions) changed adversely with increasing temperature: the yield of C_6-C_{10} fraction increased, but the other two fractions decreased. Increasing the pressure forced back the amount of C_6-C_{10} fractions. The highest yield of C_{11}-C_{20} gas oil boiling point range target fraction was between 300-325 °C, the highest yield of C_{21}-C_{30} base oil boiling point range target fraction was between 275-300 °C.

The isoparaffin contents of the liquid products increased with increasing temperature and decreased with increasing pressure and LHSV while other parameters were kept constant (Figure 5). It is important to be noted that the isomer content of the liquid products was high and simultaneously the yield was significantly higher until 325 °C (>93%) than on other catalysts. So Pt/AlSBA-15 is a suitable catalyst for the isomerization and hydrocracking of Fischer-Tropsch waxes to produce mainly gas oil and base oil boiling range products.

Based on the isoparaffin contents of the different fractions it can be concluded that at advantageous process parameter combinations (T=300-325 °C, P=40-80 bar, LHSV=1,0-2,0 h^{-1}, and T=275-300 °C, P=40-80 bar, LHSV=1,0-2,0 h^{-1}) the catalyst was applicable to produce C_{11}-C_{20} and C_{21}-C_{30} fractions with high isoparaffin content (64.5-86.6 % and 35.1-59.7 %) with adequate yields (28.9-35.6 % and 45.2-57.8 %). It was found that the gas oil fractions having the lowest pour point were obtained in the case of high concentrations of 5-methyl isomers. The C_{21}-C_{30} fraction can be used as environmentally friendly, high viscosity index (VI ≥ 125) base oil. The activity and isomerisation selectivity of the catalyst having 0.5 wt % of platinum did not change after 240 hours time on stream experiment.

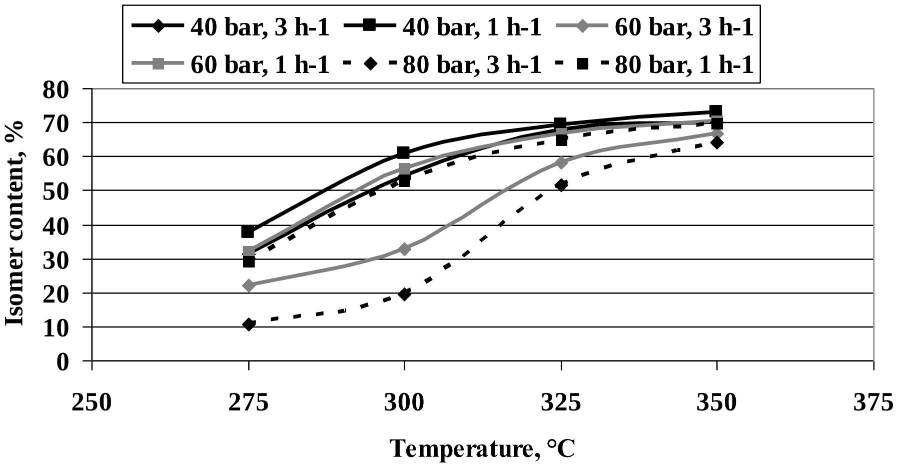

Figure 5: Effect of the process parameters on the isomer content of the products

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