The Oligomerization of Olefin Hydrocarbons in Light FCC Naphtha on Ion Exchange Resin Catalyst

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In our experimental work our aim was the investigation of the possibility to convert olefin hydrocarbons of a light FCC naphtha fraction with oligomerization. In this framework, we studied the production possibilities of higher carbon number isoolefin rich motor fuel blending components, with oligomerization of the C_4-C_6 olefin content of the feedstock on water-containing acidic ion exchange resin catalysts. From the studied catalysts the ion exchange resin showed the highest oligomerization activity: the conversion of the olefins was 90.9 % and the share of oligomer products was 29.0 %. After hydrogenation of the C_8-C_{16} isoolefin mixture, the octane number of gasoline product is around 100, the JET product has high energy content and low crystallization point, the cetane number of gas oil product is high and it has a good CFPP (cold filter plugging point). So with these two catalytic steps valuable products can be produced from light olefin-containing refinery by-products.

1. Introduction

The oil refinery developments are primarily motivated by the environmental protection and economical efforts in the past decade. The quality requirements of motor fuels were tightened significantly, which are targeting the reduction of harmful material emission of the vehicles. The high degree of reduction of the sulphur and aromatic content were the most important. The growing motor fuel demand of the world makes it necessary to develop new technologies for producing different motor fuels (gasoline, jet, and diesel gas oil) or to improve the existing ones. Because of all these effects in the case of gasolines and diesel gas oils the useage of environmentally friendly, relatively "clean burning", and practically heteroatom-free, high n- and i-paraffin containing blending fractions in a larger quantity came into front. From the options which from the lower value light hydrocarbons (C_3-C_6 paraffins and olefins) are producing heavier and more valuable products (gasoline or middle distillate) have great importance. Therefore the oligomerization technologies which are flexible from the point of the product composition will be more important than the conventional solutions (e.g. alkylation, production of ethers). During oligomerization from these olefins isoolefins in different boiling point ranges (depending on the degree of oligomerization compounds in the gasoline, jet or diesel gas oil boiling point range are formed) can be produced, which can be converted into isoparaffins after hydrogenation. Therefore with the application of this technology the gasoline- JET-diesel gas oil flexibility of the oil refinery can be enhanced greatly.

The feedstock of oligomerization can be the fractions rich in light olefin (3-6 carbon number) produced as by-products during the fluid catalytic cracking (FCC) and other thermal technologies in relatively

large quantities. The blending of these fractions in motor fuels is limited because of its high olefin content and vapour pressure. Therefore the separate conversion of these olefins is required.

Until now the oligomerization was studied with the application of different catalysts, like solid phosphoric acid (Prinsloo, 2006), zeolits (Yoon et al., 2008; Grieken et al., 2008), ionic liquids (Gu et al., 2003; Fehér et al., 2012), and metal-oxides (Tzompantzi et al., 2009).

A part of the olefins, which is formed in oil refineries, is used for producing ethers (e.g.: methyl-tercier-buthyl-ether – MTBE). The importance of MTBE has been reduced due to the environmental and health risks (Hancsók et al., 2003). The application of the acidic cation exchange resin catalysts can be a good solution from that aspect that with the limited MTBE use there is a great quantity of till unused capacity with the ion exchange catalyst, from which only a part will be converted to bio-ETBE (ethyl-tercier-buthyl-ether) plant.

The ion exchange resins are catalysts that are regenerable and applied in different hydrocarbon processes. The acidic ion exchange resins, which are available commercially, have different acidic strength, depending on the type of the contained acidic group (e.g.: $-SO_3H$, $-COOH$). First of all the sulphonic acid group containing catalysts can be the most suitable for the aim of oligomerization from these catalysts. The studies of the oligomerization of isobutene were carried out with different commercial ion exchange resin catalysts. On the studied catalyst they reached different conversions (90-100 %), and different selectivity of dimers (5-10 %), trimers (75-95 %), and tetramers (2-6 %) (Alcantara et al., 2000). The achieved results correlated with the acidic capacity, the type of the function group and the structure of the applied catalysts. Some papers studied especially the possibilities of producing dimers (Marchionna et al., 2001; Ouni et al., 2006), but there are some papers which worked on the possibilities of producing trimers, too (Alcantara et al., 2000; Yoon et al., 2006; Hauge et al. 2005). But these experiments were carried out with model compounds (isobutene), not with the materials available in the industry.

2. Experimental

The aim of our experimental work was to produce isoolefin-rich products from the olefin content of light FCC-naphtha with oligomerization on an acidic ion exchange resin catalyst; which products can be used as blending components for different motor fuels after hydrogenation.

2.1 Experimental setup

We carried out our experiments not with individual olefins, but a fraction of FCC-naphtha separated with distillation (boiling point range: 30.6-88.0 °C, density at 15.6 °C: 0.6561 g/cm^3) (Table 1.). We cut the feedstock with distillation. The applied redistilled feedstock contained 35.0 % unsaturated components (mainly C_5-C_6 hydrocarbons), which were important from the point of view of oligomerization.

Table 1: The composition of the applied feedstock

Hydrocarbons	Quantity, m/m %	Hydrocarbons	Quantity, m/m %
C_4 hydrocarbons	0.7	Hexane-isomers	15.9
n-pentane	4.6	C_6-olefins	8.8
Isopentane	34.4	C_6-naphthenes	2.6
C_5-olefins	25.6	Benzene	1.2
Cyclopentane	0.6	C_7 and heavier hydrocarbons	4.4
n-hexane	1.2		

We carried out the experiments in a laboratory, high pressure reactor system. The effective volume of the fixed bed reactor was 100 cm^3. This equipment included the main apparatus and machines which can be found in an industrial plant too.

We carried out the experiments on acidic cation exchange resin type catalyst (Table 2). We loaded 80 cm^3 catalysts into the reactor.

Table 2: The main properties of ion exchange resin catalysts

Properties	Value		
	„A" catalyst	„B" catalyst	„C" catalyst
Acidity, eq/kg	>5,1	>4,7	>4,9
Surface area, m^2/g	15-25	38	28
Average pore size, Å	250-400	354	568
Porosity, cm^3/g	0,15-0,30	0,36	0,45

We have determined the process parameters based on literature data and our earlier experiments. The investigated temperature range was: 80-130 °C, pressure range: 15-30 bar, liquid hour space velocity: 0.5-2.0 h^{-1}.

We thermostated the feedstock at nearly 0-5 °C in the storing- and feeding burettes for all of the experiments. The measurements on the ion exchange resin were carried out in nitrogen atmosphere. We started the experiment when the system was in steady-state.

We examined the composition of the liquid hydrocarbon products with gas chromatography method (Thermo Finnigan Trace GC), which contained a PONA column (Varian CP-Sil PONA CB FS 50×0.21×0.5). Based on the gas chromatogram of the product we determined the olefin conversion for the olefin content of the feedstock, the quantity of heavier products in liquid product (the fraction or share of oligomeric products; unit: the absolute%) and the share of C_8-C_{11} and C_{12+} hydrocarbons for the oligomeric products (C_8-C_{11} and C_{12+} selectivity; unit: relative %). These datas characterized the oligomerization reactions that take place.

2.2 Results and dicussion

In our experiments, we examined the oligomerization activity of three different water-containing acidic ion exchange resin catalyst in a wide range of process parameters. Based on these results, we found that the yield of liquid products in all experimental points was above 99%, i.e. there are no significant cracking reactions in the studied temperature range. The olefin conversion had a maximum in the studied range of parameters at 120-130 °C in case of all three catalysts (Figure 1-3). At 130 °C, particularly at small LHSV, the olefin conversion decreased. This may be due to the exothermicity of oligomerization reaction, so after the initial kinetic inhibition there will be thermodynamic inhibition at higher temperatures. Furthermore, we found that above 120 °C the structure of the ion-exchange resin catalyst may be damaged, degraded. According to Hauge et al. (2005) the sulfonic groups of ion-exchange resins they examined at 115 °C are damaged and the catalyst was not stable, however, the catalysts we studied remained active at higher temperatures, so their maximum stable operating temperature is ca. 10 °C higher. The highest olefins conversion (90.9 %) we achieved in case of "B" catalyst which have the largest surface (38 m^2/g) and the lowest acidity (>4.7 eq/kg), at 130 ° C, 30 bar pressure and 2.0 h^{-1} LHSV.

At a constant temperature reducing the LHSV the olefin conversion increased at higher temperatures, but under 100 °C it was reduced. This probably is related to the water content of the resin. The resin lost the water above 100 °C significantly; therefore is necessary more LHSV under 100 °C to replace the water on the surface of catalyst, the feedstock can access to the active sites of the catalyst.

We found that the olefin conversion values are slightly lower than the others by the model experiments performed. The reason for this was that the industrial material contained in relatively large quantities of not reactive materials from the point of oligomerization (about 66 % paraffinic and cyclic compounds).

In function of the pressure the olefin conversion increased slightly in the case of different catalysts (Figure 4), because of in fluid state the increasing of pressure has a smaller influence to the olefin conversion.
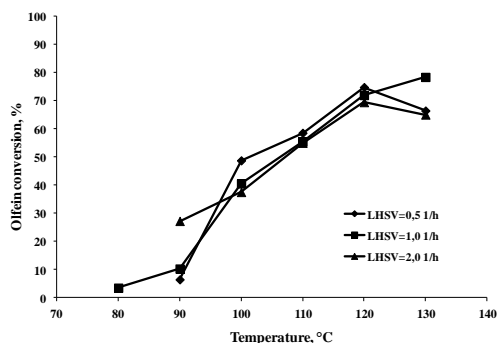
Figure 1: The change of olefin conversion in function of temperature in case of "A" catalyst (P= 30 bar)
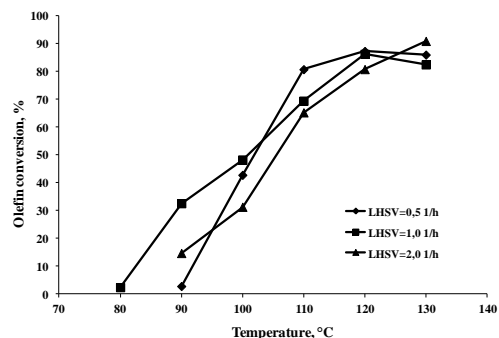

Figure 2: The change of olefin conversion in function of temperature in case of "B" catalyst (P= 30 bar)
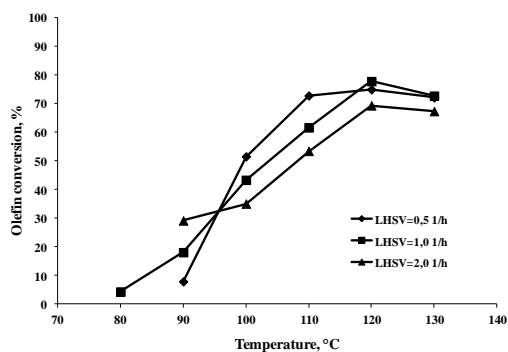

Figure 3: The change of olefin conversion in function of temperature in case of "C" catalyst (P= 30 bar)
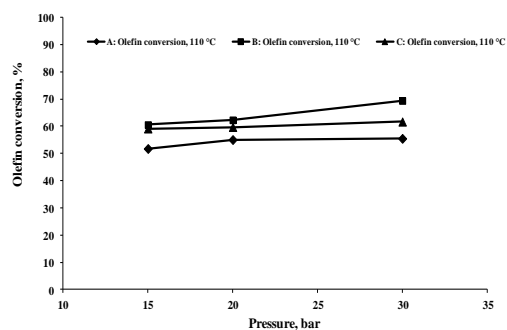

Figure 4: The olefin conversion in function of pressure in case of different catalysts (LHSV= 1.0 h^{-1})

The share of oligomers in the product has maximum at 120 °C in function of temperature in case of "B" catalyst (Figure 5). The highest share of oligomer (29.0 abs%) we achieved at 30 bar pressure and 1.0 h-1 LHSV. The amount of C8-C11 fraction in all cases exceeded the amount of C12+. The C12+ selectivity at different LHSV changes in different ways; at 0.5 and 1.0 h-1 LHSV has a maximum, compared at 2.0 h-1 LHSV has at 130 °C in the range of studied parameters; the highest value was (27.9 %) at 120 °C, 30 bar, 1.0 h-1 LHSV (Figure 6). The C12+ selectivity was at lower temperatures in case of relatively higher in case of olefin conversion was also low. The reason was probably that because the water content of the resin inhibits the formation of higher degree of oligomerization product. This is consistent with the findings in the publications of other authors (Alonso et al., 2010, 2011).

The Engler distillation curves of products are compared to the distillation curve of feedstock on Figure 7. The running of the curves reflects to the previous evaluation. The smoothing of Engler distillation curves would indicate the presence of reconverting reactions. However they clearly show that the running of curves is staged according to the formation of different degree of oligomers. The liquid hydrocarbon product in a advantageous case contain about 28 V/V% gasoline-, 16 V/V% JET- and 14 V/V% gasoil boiling point range oligomeric products beside the feedstock fraction.
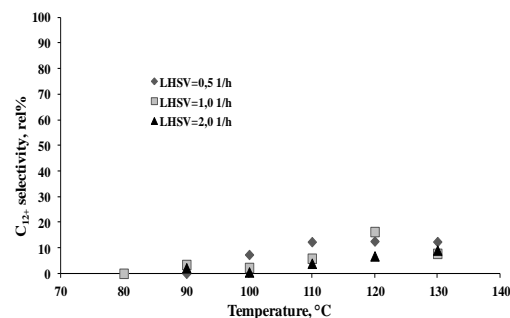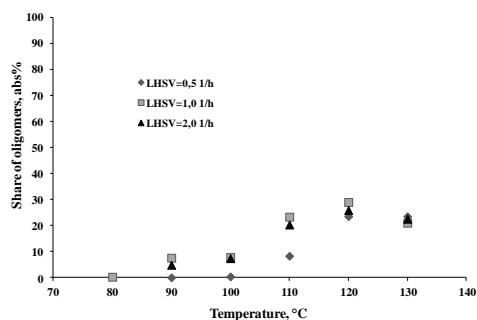
Figure 5: The share of oligomers in function of temperature on „B" catalyst (P= 30 bar)

Figure 6: The change of C_{12+} selectivity in function of temperature (P= 30 bar)
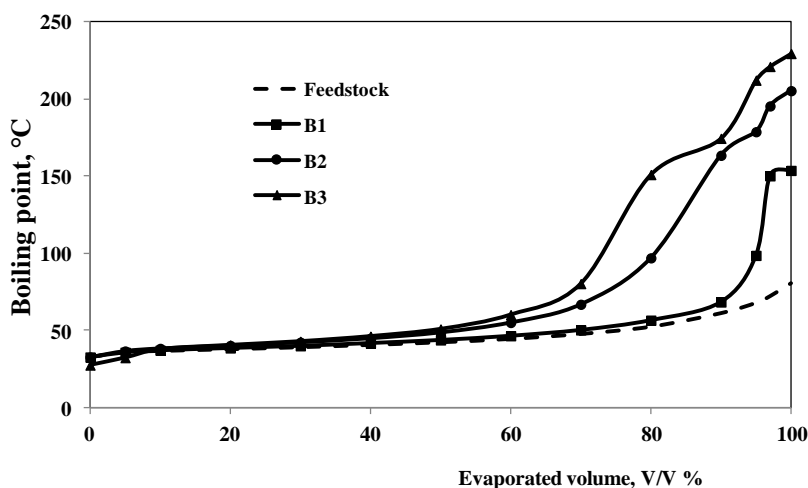

Figure 7: The comparison of the Engler distillation curve of the feedstock and of the typical products

3. Conclusions

The demand of increased use of motor fuels make necessary to research and develop such new processes, which are produced from less valuable materials blending components with appropriate quality.

In the course of experiments carried out with acidic ion exchange resin we performed our experiments with three different water containing catalyst. The highest olefin conversion (90.9 %) and the highest share of oligomeric products (29.0 abs%) we achieved on the "B" ion exchange resin, which has the highest surface and smallest acidity from the examined catalysts. In case of the "A" and "C" ion exchange resins the olefin conversions were significantly lower (78.4 % and 77.8 %). The favorable process parameter range was the following: 120 to 130 °C, 30 bar, 1.0 to 2.0 h^{-1}.

The feedstock contained high level of not reactive components from the point of oligomerization. However it still has been managed to convert the olefin content of feedstock. The presence of "inert" components may be one of the great advantages that generated exothermic reaction heat absorbed, making it easier to control the temperature, and the system is more stable.

The products cannot be applied directly as motor fuel blending components, because of their high olefin content. But with the catalytic hydrogenation isoparaffin-rich products can be produced with preferable quality. After the hydrogenation of C_8-C_{16} isoolefin mixture, the octane number of gasoline product is around 100, the JET product has high energy content (44,5 MJ/kg) and low crystallization point (-55 °C), the cetane number of gas oil product is high (>65) and it has a good CFPP (-15 °C) (cold filter plugging point). So with these two catalytic steps valuable products can be produced from light olefin containing by products of an oil refinery.

Acknowledgement

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