The Oligomerisation of High Olefin Containing Hydrocarbon Fractions on Ion Exchange Resin Catalyst

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Nowadays there is an increasingly important issue in refineries to increase the gasoline / middle distillate flexibility because of the ever-changing motor fuel demands. One possible way is to oligomerize light olefins (3-6 carbon atoms). There is a further advantage of the oligomerization technology that with the hydrogenation of the olefin-isoolefin mixture, formed as an intermediate product, high paraffin-isoparaffin containing products can be produced. In our experimental work we investigated the conversion possibilities with oligomerization of the C_4-C_6 olefin content of light FCC and more fractions with different composition on acidic ion exchange resin catalyst. The favourable application temperature of the ion exchange catalyst was 120-130 °C (P= 30 bar, LHSV= 1.0 h^{-1}). The available olefin conversion was also influenced by the composition of the feedstock. We achieved the best olefin conversion in the case of the feedstock with highest olefin content (olefin conversion: 91.5 %, C_{12+} selectivity: 31.2 %).

1. Introduction

Nowadays increase in the gasoline/middle distillate flexibility is an increasingly important issue for refineries because of the geographically- and ever-changing motor fuel demands. One of the possible ways is to oligomerize light olefins (3-6 carbon atoms). This technology is flexible regarding to the composition of the products, because blending components of different boiling point ranges [gasoline (C_7-C_{10}, middle distillate (C_{10}-C_{22})] can be produced in various shares by changing of the process parameters only. A further advantage of the oligomerization technology is that high n-paraffin-isoparaffin containing products can be produced with hydrogenation of the formed n-olefin-isoolefin mixture. The isoparaffins are environmentally friendly blending components of modern motor fuels, and their physico-chemical and performance properties are excellent, furthermore their blending ratio is not limited in any specifications (directive, standard). Thus, components with low sulphur, aromatic and olefin content can be produced in two steps corresponding to the current European standards and directives.

Potential feedstocks of oligomerization (hydrocarbon mixtures containing C_3-C_6 olefins in high concentration) are produced in high quantities as by-product in refinery and petrochemical processes; e.g. fluid catalytic cracking of distillates (FCC), fluid catalytic cracking of residues, steam reforming of hydrocarbons, delayed coking, cracking of waste plastic and other thermal cracking technologies, and Fischer-Tropsch synthesis. The production of more valuable hydrocarbons with higher carbon numbers from these low-value light hydrocarbons (C_3-C_6 olefins) is a high priority research area during the development of fuels for sustainable mobility.

Until now, the oligomerization of light olefins was studied by applying different types of catalysts. Nowadays several types of catalysts are examined for this purpose. In their experiments they used solid phosphoric acid (Prinsloo et al., 2006), ZSM-5 zeolite (Coelho et al., 2013), ionic liquid (Fehér et al., 2013). Ion exchange resins are regenerable, already used and proven catalysts in different hydrocarbon industrial processes (Zagorodni, 2007). The commercially available acidic ion exchange resins have different acidic strength (about 0.43 to 5.62 eqH$^+$kg^{-1} acid capacity) (Granollers et al., 2012) and depending on the type of acidic group to be contained (e.g. -SO_3H,-COOH) showed different activity (Yoon et al., 2006).

In hydrocarbon industry is well established and proven the use of acidic ion exchange resin as catalysts (for example in case of synthesis of ethers; such as MTBE: methyl tertiary-butyl ether, ETBE: ethyl tertiary-butyl ether). Nowadays the importance of the MTBE as gasoline blending component significantly decreased because of its environmental and health risks (Marchionna et al., 2001) and only part of the MTBE plants are converted to produce bio-ETBE. Therefore, the application of acidic cation exchange resin catalysts for oligomerization can be a good solution for the following challenges. The restriction on the use of MTBE contributed to form mostly unused ion-exchange resin catalysts producing capacities as well as free refinery capacities.

Based on the previous, the development of catalyst systems to be capable of oligomerization of feedstocks available in the refinery as a by-product is relevant and industry-supported research topic.

Over the last few decades the application of acidic ion exchange resin catalysts in the oligomerization reactions has been investigated. For oligomerization of isobutene the sulfonic acid groups containing catalysts were found to be the most suitable among the commercially available ion exchange resin catalysts (Bringué et al., 2012). Primarily the aim was to produce dimers (gasoline blending components) with the conversion of various C_4 model compounds. Golombok et al. (2001) examined Amberlyst XN1010 and Nafion catalysts compared with other solid catalysts to dimerize 1-butene with about 45 % and 75 % conversion. Marchionna et al. (2001) reported the oligomerization of C_3-C_5 olefins to gasoline components with 95-99 RON on Amberlyst catalyst. De Bruijn et al. (2001) determined that on Nafion catalysts propylene could be converted with 90-95 % olefin conversion. Ouni et al. (2006) dimerized isobutene in a miniplant scale reactor to isooctane in the presence of 2-methyl-2-propanol (TBA) which increasing the dimer selectivity on ion exchange resin catalyst. Honkela et al. (2005) achieved 100 % dimer selectivity with isobutene and TBA on Amberlyst catalysts. Some of the communications dealt with the possibility of the production of higher degree oligomers. Alcantara et al. (2000) investigated trimerization of isobutene and 90 (w/w) % triisobutylene was in the final oligomer mixture. Jhung et al. (2009) examined oligomerization of isobutene and achieved about 100 % conversion and higher than 70 % trimer selectivity on Amberlyst 35. But these experiments were always carried out with model compounds and not with the feedstocks available in the industry. In our earlier papers we reported our results achieved with ion exchange resins and FCC naphtha feedstock and we achieved high olefin conversion (higher than 90 %) (Kriván et al., 2012) and we investigated their applicability in layered bed, too (Kriván et al., 2013).

Based on the abovementioned the main objective of our research was to study the oligomerization of real (industrial) feeds on ion exchange resin catalysts. In the scope of this work we studied the selectivity of the formation of oligomers with different carbon atom numbers, and thus with different boiling points especially.

2. Experimental

The aim of our experimental work was to produce such isoolefin-rich products from the olefin content of hydrocarbon fractions with different composition with oligomerization on an acidic ion exchange resin catalyst; which products can be used as blending components for different motor fuels after hydrogenation. We carried out our experiments not with individual model olefins, but a pre-fraction (light part) of light 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). Such preparation of the feedstock was necessary because we found in earlier experiments, that the heavier feedstock components, such as various aromatic and cyclic compounds adsorbed on the active sites of the catalyst so that the catalyst activity was reduced. The applied redistilled feedstock contained 34.2 % unsaturated components (mainly C_5-C_6 hydrocarbons), which were important from the point of view of oligomerization.

We performed further experiments feedstocks with different compositions on the ion exchange resin catalyst to determine its suitability for oligomerization. The feedstock A was the mixture of the products obtained in earlier experiments with ion exchange resin and distillated light FCC naphtha feedstock. Feedstock B was the 50-50 % mixture of the product mixture and distillated light FCC naphtha, in order to increase the proportion of reactive light olefins. Feedstock C was the mixture of heavier fraction of the products (oligomer product and some light fraction) and distillated light FCC naphtha in 50-50 weight ratio, and feedstock D was the lighter fraction of products with lower olefin content. So we had four feedstocks with different light olefin content and heavier (C_{8+}) hydrocarbon content. The composition and Engler distillation characteristics of the feedstocks are in Table 2.

We used for the experiments an acidic cation exchange resin type catalyst (Table 3). We loaded 80 cm^3 catalysts into the reactor. 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 determined the process parameters based on literature data and our earlier experiments. The investigated temperature range was: 80-130 °C, pressure range: 30 bar, liquid hour space velocity (LHSV): 1.0-3.0 h^{-1}. At higher temperatures considering of recommendation of ion exchange resin manufacturers and our own experience, we did not perform experiments to avoid the thermal degradation of the resin.

We cooled the feedstock at nearly 0-5 °C in the storing and feeding burettes for all of the experiments. The experiments were carried out in nitrogen atmosphere, at each process parameters, when the catalytic system was in steady-state.

Table 1: The composition of the light FCC feedstock

Hydrocarbons	Composition, w/w%
C_4 hydrocarbon	0.7
n-pentane	4.6
Isopentane	36.2
C_5-olefins	24.6
Cyclopentane	0.6
n-hexane	1.2
Hexane-isomers	15.9
C_6-olefins	8.0
C_6-naphthenes	2.6
Benzene	1.2
C_7 and heavier hydrocarbons	4.4
Total olefin content	34.2
Sulphur content, mg/kg	0.9
Water content, mg/kg	52
Nitrogen content, mg/kg	9.0

Table 2: The main properties of feedstock A, B, C and D

Feedstock sign	A	B	C	D
Density (15.6°C), g/cm^3	0.6831	0.6707	0.7016	0.6497
Concentration of components, %				
C_4-C_7 paraffins	60.7	60.7	43.2	75.9
from this isopentane	33.2	32.8	18.3	46.1
C_4-C_7 naphthene	4.3	4.2	5.2	3.4
Benzene	1.5	1.5	1.7	1.3
C_4-C_7 olefins	15.4	24.9	21.1	19.2
C_8-C_{11} fraction	16.0	7.9	24.4	0.2
C_{12+} fraction	2.2	0.7	4.5	-
Engler distillation, °C				
Initial boiling point	33.6	32.0	36.8	31.8
50 ftf%	49.7	45.8	65.2	40.6
End boiling point	246.6	213.1	258.7	81.9

Table 3: Main properties of the ion exchange catalyst

Properties	Catalyst IE
Concentration of acidic sites, eq/kg	>4.7
Water content, %	<1.6
Density, g/l	610
Surface area, m^2/g	53
Average pore diameter, Å	300
Pore volume, cm^3/g	0.40

We determined the composition of the liquid hydrocarbon products with gas chromatography method (Shimadzu GC-2010), which contained a PONA column (ZB-1; 100 m × 0.25 mm × 0.5 mm). Based on the

gas chromatogram of the product we calculated the olefin conversion for the olefin content of the feedstock, the quantity of the heavier products in the 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 data characterized the oligomerization reactions that took place.

3. Results and discussion

Studying ion-exchange resin catalyst and different feedstocks the liquid product yield was over 98 %, which means that the cracking processes were relatively small in the studied temperature range. The reason for this was the relatively low experimental temperature range.

In case of light FCC feedstock the olefin conversion became larger by increasing the temperature. The maximum olefin conversion (88.4 %) was achieved at 120 °C, 30 bar and 1.0 h^{-1}.

The oligomerization process is exothermic, for which favors increasing temperature until achieving thermodynamic inhibition. However, at higher temperatures come to the front cracking reactions, and the structure of ion exchange resin catalyst and thus its properties also change.

Conversion achieved in these experiments was lower than values obtained in the experiments with model compounds. It is because of high inert - in terms of oligomerization - hydrocarbon content (about 66 %) of the feedstock, to which partly contributed the inactive hydrocarbon temporary occupation of the active sites of the catalyst as well.

The C_{12+} selectivity varied between 4.3 % (T= 120 °C, P= 30 bar, LHSV= 3.0 h^{-1}) and 10.6 % (T= 100 °C, P= 30 bar, LHSV= 1.0 h^{-1}) (Figure 2). By increasing LHSV at given temperature the C_{12+} selectivity decreased, as by increasing temperature at given LHSV too. The reason for this could be that at higher temperature in greater quantity forming heavier oligomeric products were left the pores of the catalyst more difficult (slower), which resulted the decreasing of C_{12+} selectivity.

Studying the activity (performance) of applied ion exchange resin catalyst and assessment of the available product composition was conducted further experiments using four feedstocks with different compositions (Table 2). The olefin conversion was always referred to the olefin content of given feedstock. In case of feedstock A we gave the conversion values referred to the olefin content of distilled light FCC naphtha too (Figure 3). Feedstock A, as it was a mixture of several products, corresponded with a product obtained with approx. 55% olefin conversion, which could be increase in the second step to at least 80.0 % and at 130 °C to 95.8 %.

The olefin conversion and C_{12+} selectivity achieved applying different feedstocks and favourable process parameters are compared on Figure 4. The maximum olefin conversion we achieved during the experiments with feedstock B (91.5 %). This is due to feedstock B contained the most reactive component in terms of oligomerization. The minimum olefin conversion was observed in the case of feedstock C, which is caused by the higher concentration of the heavier hydrocarbons found in feedstock. During the experiments, these compounds are adsorbed stronger on the catalyst active sites than the light hydrocarbons; such occupy them in the front of reactive olefins, and also could clog the pores. The highest C_{12+} share was obtained during experiments conducted with feedstock C. This caused by the relatively
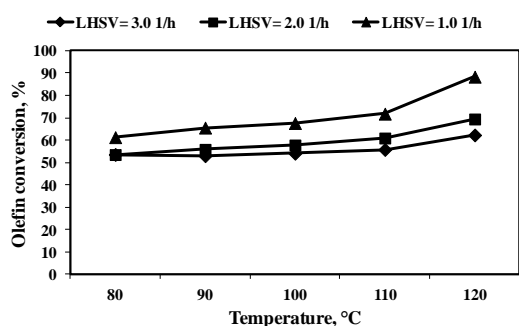

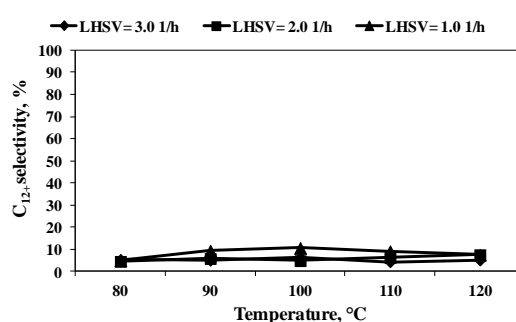Figure 1: The change of olefin conversion in function of temperature (P=30 bar)

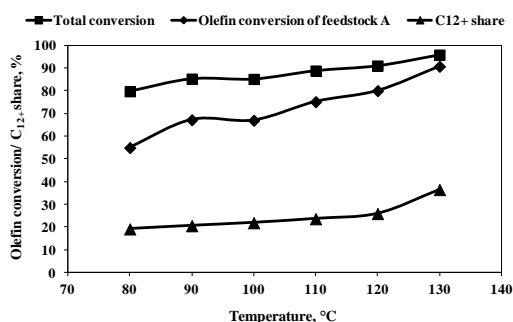Figure 2: The change of C_{12+} selectivity in function of temperature (P= 30 bar)

Figure 3 The changes of total conversion, olefin conversion of feedstock A and C_{12+} share in function of temperature (P= 30 bar, LHSV= $1.0 \, h^{-1}$)
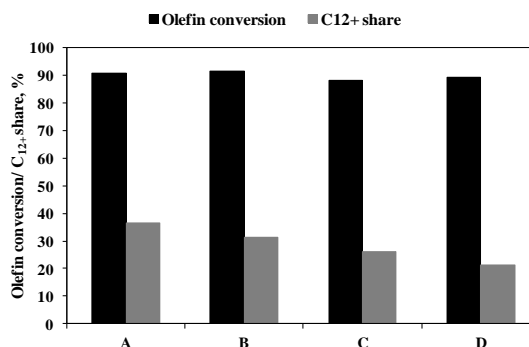
Figure 4 Comparison of olefin conversion and C_{12+} share in case of different feedstocks (T=130 °C, P= 30 bar, LHSV= $1.0 \, h^{-1}$)

high olefin content and so less inert component content of the feedstock, and its heavier hydrocarbon content too. The smallest C_{12+} share was achieved applying feedstock D, which resulted the small olefin and C_{8+} content of the feedstock.

Investigating the over time changes of catalytic activity and selectivity of ion exchange resin were performed long term experiments applying constant process parameters (110 °C and 130 °C temperature, 30 bar pressure, $1.0 \, h^{-1}$ LHSV), using light FCC naphtha feedstock (Table 1). Based on the obtained results (Figure 5 and 6), the olefin conversion at 110 °C decreased nearly 10 % over 192 hours (average from 78 % to 70 %), while the proportion of oligomers in the product reduced about 6 % (average from 25% to 19 %) (Figure 5). The C_8-C_{11} selectivity increased over measurement time, while the C_{12+} selectivity decreased. The reason for this could be that the pores of the ion exchange resin catalyst clogging by the formation of heavier oligomeric products and therefore reduced the achieved olefin conversion and the selectivity of greater degree oligomeric products as well.

During long term experiments carried out at 130 °C the olefin conversion decreased continuously (Figure 6). The rate of decreasing became significant after about 60 hours. Oligomer ratio decreased significantly after 36 hours and the C_{12+} selectivity too. However, after probably leaching heavier products these values became again slightly higher. The deactivation rate was higher than for experiments at 110 °C. The reason for this could be that - in addition to the above mentioned reasons - the catalyst degradation was occurring.

4. Conclusions

The potential feedstocks of oligomerization are produced in large quantities as a by-product in refineries and petrochemical technologies, mainly in case of fluid catalytic cracking of distillates (FCC) and other
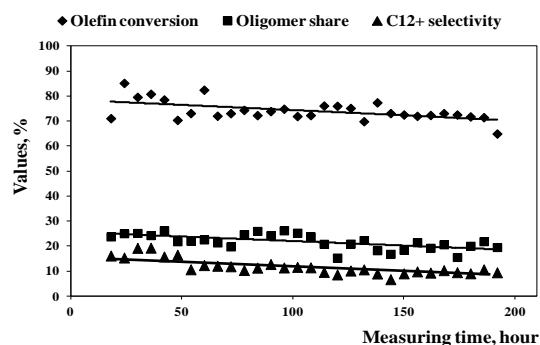

Figure 5 Olefin conversion, oligomer share and C_{12+} selectivity in function of measuring time (T=110 °C, P=30 bar, LHSV=$1.0 \, h^{-1}$)
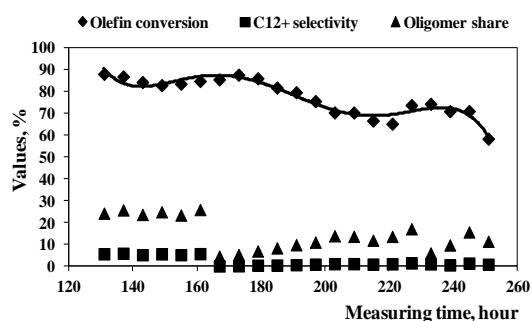
Figure 6 Olefin conversion, oligomer share and C_{12+} selectivity in function of measuring time (T=130 °C, P= 30 bar, LHSV= $1.0 \, h^{-1}$)

thermal technologies. With oligomerization from low-value light hydrocarbons (C_3-C_6 paraffins and olefins) "heavier" (with higher boiling point) and more valuable hydrocarbons can be produced.

In our experimental work we investigated the conversion possibilities with oligomerization of the C_4-C_6 olefin content of light FCC and more fractions with different composition on acidic ion exchange resin catalyst. The favourable application temperature of the ion exchange catalyst was 120-130 °C (P= 30 bar, LHSV= 1.0 h^{-1}). The available olefin conversion was also influenced by the composition of the feedstock. We achieved the best olefin conversion in the case of the feedstock with highest olefin content (olefin conversion: 91.5 %, C_{12+} selectivity: 31.2 %). So a feedstock with high olefin content such products of waste plastic cracking and steam reforming are preferably.

During the long term experiments carried out at 110 °C the activity of the resin catalyst decreased by approx. 10 % compared with the initial value (after 196 hours) but it was significantly reduced after 60 hours reaction time at 130 °C. The examined ion exchange resin - in the 100-120 °C temperature range - catalyzes the oligomerization reactions for a long time, but an in-situ regeneration should be necessary.

Acknowledgement

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