

INVESTIGATION OF THE OLIGOMERIZATION OF LIGHT OLEFINS ON ION EXCHANGE RESIN CATALYST

E. KRIVÁN, G. MARSI, J. HANCSÓK✉

Department of MOL Hydrocarbon and Coal Processing, University of Pannonia
Egyetem street 10, H-8201 Veszprém, P.O. Box 158., HUNGARY
✉E-mail: hancsojk@almos.uni-pannon.hu

The requirements against the quality of motor fuels were rendered more rigorous in the past decade; the most important ones were the major reductions of the sulphur and aromatic content. Besides the changing of the regulation of the motor fuels, the harmful material emission of the Otto- and Diesel-engine built vehicles was also limited significantly. These effects make necessary the greater use of the environmentally friendly, relatively “clean burning”, technically heteroatom- and aromatic free, great n- and i-paraffinic containing blending components in the case of gasoline and diesel gas oils. During our experimental work we studied the possibilities of producing motor fuel blending components like these blending components with the oligomerization of the olefin content of light FCC-naphtha – assuming later industrial application – on Amberlyst-15 acidic ion exchange resin type catalyst. This topic is very important in a modern oil refinery, because different isoparaffin-rich motor fuel blending components can be produced (depending on the catalyst and the process parameters), and this technology can grow considerably the gasoline- and diesel gas oil flexibility of the oil refinery, too. The aim of our experiments was to produce motor fuel blending components with the oligomerization of C₄-C₆ olefins in light FCC-naphtha matrix. Working on the acidic ion exchange resin catalyst under different process parameters (T: 80–130 °C, P: 15–30 bar, LHSV: 0.5–3.0 h⁻¹) we determined that in the studied process parameter range in preferable case (T: 100–110°C, P: 25–30 bar, LHSV 0.5–1.0 h⁻¹) the liquid product yield was: greater than 95%, the conversion of olefins: 90–92%, the selectivity of C₈-C₁₁: 70–76%, while the selectivity of C₁₂₊: 24–30%.

Keywords: oligomerization, ion exchange resin, light olefin, FCC naphtha

Introduction

During the fluid catalytic cracking (FCC) of heavy distillates and other thermal technologies light olefins (carbon number: 3-6) are formed as side products. Due to the more rigorous regulations the blending of the FCC-naphtha to motor fuel is limited, because it has great olefin content and vapour pressure, therefore it is necessary to convert these olefins. The growing demands for motor fuels in the world make it necessary to develop new technologies or make technologies perfect that would be suitable for producing different motor fuels (gasoline, JET, diesel gas oil). Therefore against the conventional solutions (alkylation, producing of ethers) the oligomerization technologies have a greater importance, because they have greater flexibility from the aspect of product composition. During the oligomerization, olefins can be produced with different boiling point range (components are formed with gasoline, JET, diesel gas oil boiling point range depending on the grade of oligomerization), which can be convert to isoparaffins after hydrogenation. Until now the oligomerization was studied with the application of different catalysts, like zeolits [1, 2], ionic liquids [3], metal-oxides [4, 5], and sulphated metal-oxide catalysts [6].

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 [7, 8]. 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 unused product capacity with the ion exchange catalyst, of which only a part will be converted to bio-ETBE (ethyl-tercier-buthyl-ether) plant.

The ion exchange resins are catalysts that are regenerative and applied in different hydrocarbon processes. The acidic ion exchange resins, which are available commercial, have different acidic strength, depending on the type of the contained acidic group (e.g.: -SO₃H, -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%) [8]. 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 [9, 10], but there are some papers which worked on the possibilities of producing trimers, too [8, 11]. But these experiments were carried out with model compounds (isobutene), not with the materials available in the industry.

Experimental

The aim of our experimental work was to produce isoolefin-rich products with great yield from 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.

Apparatus

We carried out the experiments in a great laboratory, high pressure reactor system. The effective volume of the fixed bed reactor was 100 cm³. This equipment included the main apparatus and machines which can be found in an industrial plant also. The simplified theoretical process system is shown in *Fig. 1*.

We have determined the process parameters based on literature data and our earlier experiments. The examined temperature range was: 80–130 °C, pressure range: 15–30 bar, liquid hour space velocity: 0.5–3.0 h⁻¹. Thereinafter we show the results of the measurements with two different feedstocks.

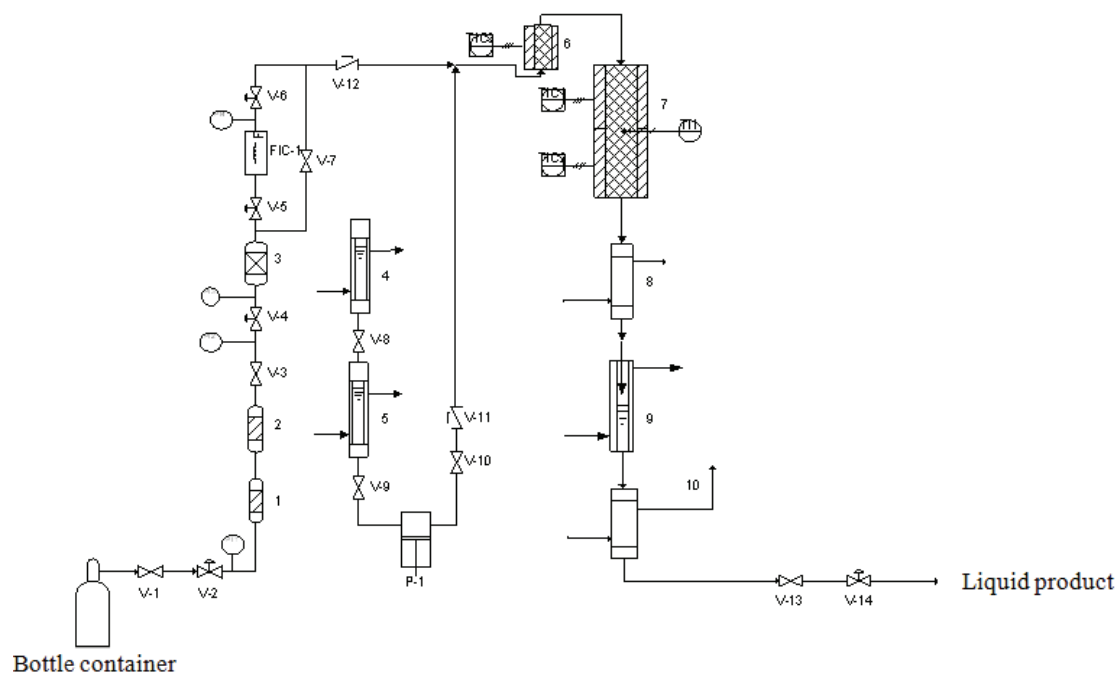


Figure 1: Simplified scheme of the test apparatus

(1 oxygen converter; 2 gas dryer; 3, 11 gas filter; 4, 5 burettes for liquid feed; 6 pre-heater; 7 reactor; 8, 10 heat exchange; 9 separator; V-1, V-3, V-7, V-8, V-9, V-10, V-15, V-16, V-18 closing valve; V-2, V-4, V-5, V-6, V-13, V-14, V-17, V-19 control valve; V-11, V-12 back valve; PI1, PI2, PI3, PI4 manometer; P-1 pump; FIC-1 gas flow meter/ controller; PIR-1 pressure register; FI-1 gas flow meter; PIC-1 pressure meter/ controller)

Materials

Assuming a later industrial application we carried out our experiments not with individual olefins, but with light FCC-naphtha from a refinery, and with the part of the FCC-naphtha, distilled to 60°C (*Table 1*). The applied redistilled feedstock contained 34% unsaturated components (mainly C₅-C₆ hydrocarbons), which were important from the point of view of oligomerization.

We carried out the experiments on an Amberlyst-15 type catalyst (*Table 2*). We loaded 80 cm³ catalyst into the reactor.

Table 1: The composition of the applied feedstocks

Hydrocarbons	Composition, %	
	Total FCC naphtha	Light FCC naphtha distillate
butenes	2.1	2.7
i-pentane	25.6	36.7
pentene	3.7	4.6
n-pentane	3.4	4.2
dimethyl-butene	18.8	20.6
2-methyl-pentene	1	1
methyl-pentane	14.2	16.8
hexene	1.6	2.2
hexane	1.3	1.7
methyl-cyclopentene	1.3	1.7
methyl-cyclopentane	2.1	2.7
cyclohexene	0.6	0.8
cyclohexane	0.4	0.7
other hydrocarbon	22.9	3.6
Total olefin	29.1	33.6

Table 2: Main parameters of the Amberlyst-15 ion exchange resin

Properties	Amberlyst-15
Acidity, meq H ⁺ /g (dry)	4.75
Humidity content, %	53.1
Apparent density, g/cm ³	0.77
Specific surface area, m ² /g	45
Particle size (95%-os volume), mm	0.63–1.25
Porosity, cm ³ /g	0.3

Testing and calculating methods

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. At first for the dehydration of the catalyst, we increased the temperature to 105 °C with nitrogen flow, and we held this temperature for 2 hours, after that we set the temperature to the temperature of the first experimental point. After that we increased the pressure to the adequate value. We started the experiment when the system was in steady-state.

We examined 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 achieved results we determined the value of the transformation of the olefin content of the feedstock (conversion), and the quantity of the C₈-C₁₂, and the C₁₂₊ fraction (selectivity).

Results and discussion

At the first experiment we carried out our measurements with light FCC-naphtha feedstock, in a temperature range of 80–130 °C, the pressure was 15 and 30 bar, and with a liquid hourly space velocity range of 0.5–3.0 h⁻¹. Based on the results we determined that at all measure points the liquid product yield was greater than 95%. The value of the olefin conversion changed between 5 and 16.5%. In Fig. 2 and 3 we show the values of the olefin conversion, measured at constant pressure, 20 and 30 bar.

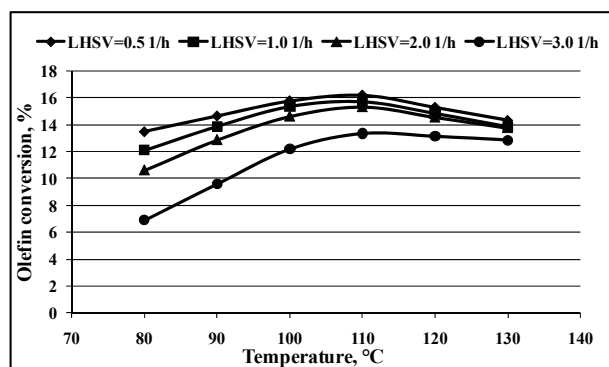


Figure 2: Conversion of olefins as a function of the temperature and pressure (P = 20 bar, light FCC-naphtha)

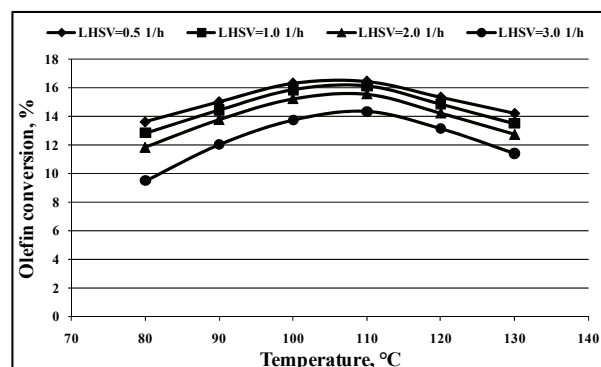


Figure 3: Conversion of olefins as a function the temperature and pressure (P = 20 bar, light FCC-naphtha)

We found that with the changing of the temperature, the conversion of olefin had a maximum value at 100–110 °C, while with the reduction of the liquid hourly space velocity the value got greater. At 30 bar pressure the measured conversion was greater than the measured conversion at 20 bar.

We also found that during the experiments with light FCC-naphtha the conversion concerning to the olefin content of the feedstock is only 5–16.5%. The reason was that the heavier components of the feedstock, like the aromatic compounds and cyclic compounds, were adsorbed to the active spaces of the catalyst, so they reduced the activity of the catalyst. So, in case of the referred experiment we could not reach the expected conversion, therefore during the following experiments we cut the feedstock with distillation, so that the feedstock distilled to 60 °C should contain less compounds affecting the activity of the catalyst harmfully.

In case of the following experiment we studied the quantity of the olefin content of the narrower boiling point ranged feedstock under the process parameters applied earlier.

Based on the results, we found that in all points of the measurement, the yield of the liquid products was greater than 95%. The conversion of the olefin depended on the process parameters considerably. We compared the values of the conversion of olefin achieved at 20 and 30 bar pressure, in Fig. 4 and 5. Based on this we found that at constant pressure the conversion of olefins increased considerably, with the increase of the temperature, it was the greatest at 110 °C, and over 110 °C it reduced, while the reduction of the liquid hourly space velocity increased the conversion. The colour of the catalyst taken off from the reactor was darker than the colour of the new catalyst. The applied acidic ion exchange resin deactivated quickly at greater temperature, because it lost a part of its sulphonic groups [12].

The selectivity of C₈-C₁₁ (70–76%) and C₁₂₊ (24–30%) changed as a function of the temperature similarly to the conversion of olefins (Fig. 6). We reached the greatest selectivity of C₁₂₊ (29.8%) at temperature 110 °C, 30 bar pressure, and 1.0 h⁻¹ liquid hourly space velocity. Due to the relatively weak acidity of the acidic ion exchange resin tetramers formed in a little quantity, it is preferable from that aspect that the catalyst deactivates slower.

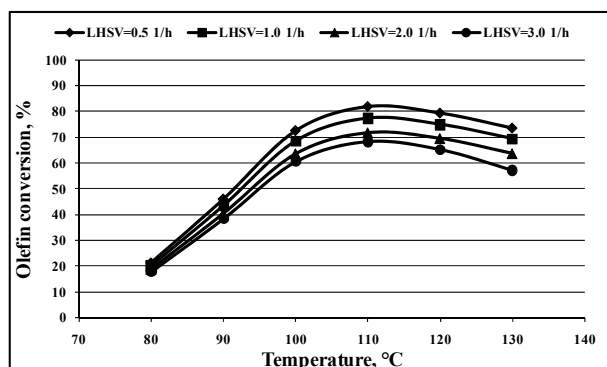


Figure 4: Conversion of olefins as a function of the temperature and pressure ($P = 20$ bar, feedstock: prefraction of light FCC-naphtha)

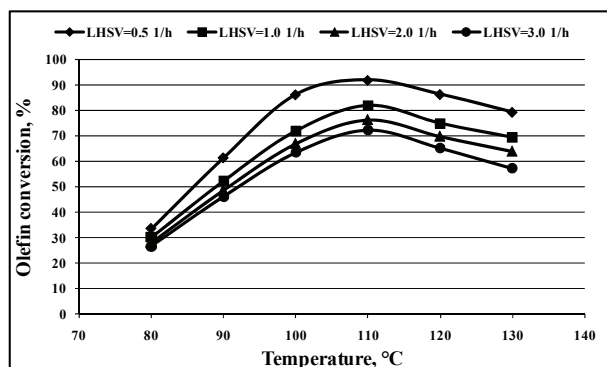


Figure 5: Conversion of olefins as a function of the temperature and pressure ($P = 30$ bar, feedstock: prefraction of light FCC-naphtha)

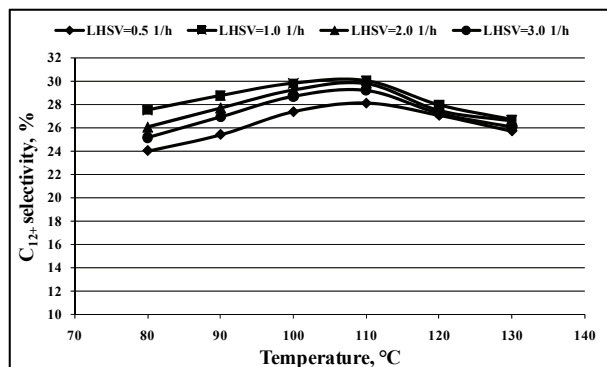


Figure 6: The changing of part of C_{12+} products as a function of the temperature and the liquid hour space velocity ($P = 30$ bar, prefraction of light FCC-naphtha)

With the increase of the liquid hourly space velocity the growing number of the olefin molecules increases the possibility of the forming of heavier oligomers, at the same time the greater volume flow „washes out” the intermedier products from the surface of the catalyst. The selectivity of C_{12+} changed as resultant of these effects as a function of the liquid hourly space velocity.

With the increase of the pressure the conversion of olefins increased in the examined ranges (Fig. 7). After reaching the liquid state (20.2 bar at 100 °C, 24.2 bar at 110 °C, determined with Soave-Redlich-Kwong (SRK) method), the following increase of the pressure had less

effect on the conversion of olefins. With the increase of the pressure the parts of the C_{12+} hydrocarbons got greater.

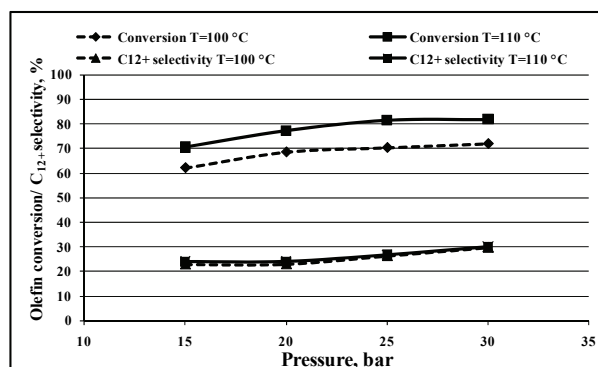


Figure 7: The effect of the pressure on the conversion of olefins and the selectivity of C_{12+} ($LHSV = 1.0$ h⁻¹, feedstock: prefraction of light FCC-naphtha)

We found that the conversion of olefins was lower than experienced by others in experiments with model compounds. The reason is that the industrial feedstock contained a relatively high quantity of inert materials from the aspect of oligomerization (66% paraffin and cyclic compounds), which obstructs the access to the active sites, or adsorbs to the active sites of the catalyst.

Summary

The growing degree of the use of motor fuels makes necessary the research and development of those new technologies that can produce adequate quality blending components from lower value feedstock. During our experimental work we studied the possibilities of converting the olefin content of light FCC-naphtha with oligomerization to greater carbon number isoolefin-rich products that can be applicable as blending components of motor fuels after hydrogenation. We studied the effect of the process parameters (temperature, pressure, liquid hourly space velocity) on the conversion of olefins and the selectivity of the products on Amberlyst-15 ion exchange resin catalyst.

In the course of the experiments carried out with acidic ion exchange resin, we successfully produced preferable products at 100–110 °C temperature, 25–30 bar pressure and 0.5–1.0 h⁻¹ liquid hourly space velocity (conversion of olefin was 90–92%, C_{12+} selectivity 24–30%). In all cases the selectivity of the C_{12+} products was lower than the selectivity of C_8 – C_{11} , the greatest value was 30%. We also found that the light FCC-naphtha applied as feedstock contained non-olefinic compounds that adsorbed to the active sites of the catalyst, therefore a distillation step is necessary to separate them and to increase the olefin content of the light FCC-naphtha, too.

The achieved products cannot be applied directly as motor fuel blending components, because of their great olefin content. But with catalytic hydrogenation isoparaffin-rich products can be produced with preferable quality. So with these two catalytic steps valuable products can

be produced from light olefin containing side products of an oil refinery.

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