

Isomerization of n-C₅/C₆ Bioparaffins to Gasoline Components with High Octane Number

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The conversion processes of alternative feedstocks, e.g. biomass and waste, to different fuels result in the formation of light hydrocarbons such as C₅/C₆ fractions mainly as side products in boiling range of gasoline in a significant amount. The properties of the C₅/C₆ fractions need to be improved because of their low octane number (< 60) and poor oxidation stability (high olefin content), benzene content, etc. The most suitable process to increase the octane number of these fractions is the skeletal isomerization of the normal paraffins to branched alkanes. The aim of this work was the isomerization of C₅/C₆ bioparaffin fractions obtained as side-products from special hydrocracking of waste cooking oil to hydrocarbons in boiling range of JET/Diesel fuels. The C₅/C₆ mixture was isomerized over Pt/H-Mordenite catalyst in a down-flow tubular reactor in continuous operation mode. During the experiments, the process parameters were varied in different ranges, such as the temperature of 220 – 270 °C, the liquid hourly space velocity of 1.0 – 3.0 h⁻¹, pressure of 30 bar, H₂/hydrocarbon molar ratio of 1:1. The approach values of the thermodynamic equilibrium concentrations for individual iso-paraffin components in products obtained at favourable process conditions were > 69 – 92 %. The increase of research octane number of the products compared to the feedstocks was higher with > 26 units. By the separation of n-paraffins and single-branched i-paraffins of the products, the C₅/C₆ isoparaffin mixture could have a high-octane number (≥ 92). Parallel to the isomerization, the hydrogenation of benzene and oxygen-containing compounds was complete. Accordingly, the utilization of isomerized light fractions of alternative diesel fuel production from different biomass and waste-sources can contribute to the competitiveness of second generation bio-fuels.

1. Introduction

The use of engine fuels will continuously increase in the world by 2030-2040 (Ma et al., 2017), within this, the proportion of gasoline will be slightly decreased, but it will still reach the share of 1/3 in 2040 (ExxonMobil, 2017). Sustainable production of alternative engine fuels is a big challenge. The foreseen decreasing of fossil reserves, global protection of environment and sustainability are the main driving forces for the research of renewable alternative energy sources (Srivastava and Hancsók, 2014). The latest directive of the European Union requires the production of fuels from non-edible, renewable/waste feedstocks (European Parliament, 2018). Nowadays the main alternative component of gasoline is bioethanol (Mansouri et al., 2016); it is a molecular constituent in the ethyl-tert-butyl-eter (bio-ETBE) as well, which is important gasoline blending component (Abdellatif et al., 2017). Despite the numerous advantages of ethanol it has also many disadvantages, such as low energy content, good solubility in water, increases the vapour pressure in gasoline, etc. (Mansetti and Andersen, 2015). Moreover, it is produced mainly from food-based plants, e.g. corn. As a result of the persistent research and development in the last few years the construction of plants using lignocellulose as feedstock has already begun. However, their technological efficiency and reliability need to be proven. The conversion processes of alternative feedstocks, such as biomass and waste to different fuels result in the formation of light hydrocarbons, e.g. C₅-C₇ fractions, mainly as side products in boiling range of gasoline in a significant amount. The following processes can result in light hydrocarbons from alternative sources: (a) from waste or biomass-derived syngas by Fischer-Tropsch (F-T) synthesis via direct synthesis which result in C₅-C₇ fraction so called F-T. light gasoline (Sauciuc et al., 2012), or, eventually, via indirect route by F-T synthesis combined with the hydrocracking of heavy F-T

wax; the oligomerization and hydrogenation of light olefins (C_{2-3}) obtained from F-T synthesis can also give light hydrocarbons.

From (b) the oligomerization of fuel gas rich in light olefins such as ethylene, propylene or butylene obtained from bio-oil or other bio-originated feedstock, e.g. rice straw biomass (Wang et al., 2017). The obtained iso-olefins need to be hydrogenated to iso-alkanes. Another possibility (c) is the oligomerization and followed hydrogenation of light gasoline fraction having high olefin content obtained from thermal/catalytic cracking of waste polyolefins with different structures, such as polyethylene or polypropylene. Gasoline-range hydrocarbons can be produced (d) from sorbitol, a sugar-based compound from lignocellulosic biomass, via hydrodeoxygenation over Zr-phosphate-supported Pd-bimetallic (Pd+ Pt/Ru/Ni/W etc.) catalysts (Kwon et al., 2018). The product mixture contains a large number of individual components with a very different structure, e.g. corrosive acids, compounds in the aqueous phase, etc. The treating and separation of the products could require complex and expensive solutions. In the so-called power-to-paraffin process (e) hydrogen produced via water electrolysis can be used for the hydrogenation of carbon monoxide/carbon dioxide to get alkanes (Herz et al., 2017). Alkanes can be obtained (f) from bioethanol via dehydration, oligomerization and hydrogenation of olefinic double bonds (Mohsenzadeh et al., 2017). N-alkanes can be manufactured (g) through simple sugars from lignocellulose applying a very complex and expensive production process; products have very low octane number which should be increased by catalytic process (Huber et al., 2005).

The simplest reaction pathway for the production of C_5 - C_7 paraffins is the special hydrocracking of natural/waste fatty acids as a by-product and/or natural/waste fatty acid esters, e.g. waste cooking oil (Bezergianni et al., 2009) or waste lards from protein processing industry (Baladincz and Hancsók, 2015).

Based on the results of the presented publications it was concluded that side-products containing mainly C_5 - C_7 paraffins could be obtained from different alternative sources. These side-products have very low octane number (<50 – 60) and contain undesirable components, such as olefins, aromatics, oxygen-containing compounds and other corrosive compounds; therefore they are not suitable as gasoline blending components. Isomerization and dehydrocyclization are the main chemical processes for the quality improvement of n-paraffins to enhance their octane number. Via isomerization, the products are iso-paraffins, via dehydrocyclization process the obtained products are aromatics. Aromatics, including benzene, have very high octane number, e.g. RON of benzene is 108, however, they are carcinogenic and their concentration in gasoline must be reduced. The gasoline standards are strictly limit the concentration of benzene, e.g., in California, USA the limit is 0.62 v/v %, in the EU this value is 1.0 v/v %.

No experimental results were given about the quality improvement, e.g. increasing the octane number of light gasoline fraction obtained from alternative sources in the publications. Based on the aforesaid reasons the main research target was to investigate the quality improvement of light hydrocarbons rich in n-paraffins, containing benzene, oxygenates from alternative source via hydroisomerization. The main goal was also to convert the n-paraffins to branched paraffins with higher octane number and the hydrogenation, i.e. saturation of benzene to cyclo-hexane and its isomerization to methyl-cyclo-pentane.

2. Experimental part

In this study, the quality improvement, mainly the octane number increasing possibilities of C_5/C_6 bioparaffin fractions by isomerization and the hydrogenation of benzene and oxygenates (e.g., methyl- ethyl-formate, methyl-propionate, methyl-acetate, 2-butanone, butyl-formate, etc.) was investigated in one step. These light hydrocarbons (Table 1) were obtained as side products by the special hydrocracking of waste cooking oil to hydrocarbons in the boiling range of JET/Diesel fuels. The aim of the study was also the determination of favourable process parameters (temperature, liquid hourly space velocity, pressure, hydrogen/feedstock ratio) for the conversion possibilities of C_5/C_6 fraction to hydrocarbons with high octane number.

2.1 Catalyst

Platinum/H-Mordenite/ Al_2O_3 catalyst was applied in the isomerization experiments. Compared to the commercial isomerization catalysts (Pt-content: 0.30 – 0.34 %) used in industry, platinum content was slightly increased to 0.38 %, this value was determined in previous experiments. It increased the number of the available active metal sites of the catalyst for the hydrogenation of benzene and oxygen-containing compounds, beside the other hydrogenation/dehydrogenation reactions. The main characteristics of the catalyst were as follows, Si:Al molar ratio of 19:5, Pt dispersion of 89 %, BET specific area of 448 m^2/g , acidity of 0.82 meq NH_3/g . The average length and diameter of catalyst particles were 4.8 and 2.4 μm , respectively. 100 cm^3 of catalyst placed in the middle of the reactor was dried at 150 $^\circ C$ for 2 h in nitrogen. After that it was heated to 300 $^\circ C$ at 25 – 30 $^\circ C/h$ in a hydrogen atmosphere (40 dm^3/h) and it was treated for 3 h at that temperature, then at 400 $^\circ C$ for 1 h.

Table 1: The main characteristics of light biogasoline side products (fractions)

Characteristics	Feedstocks	
	„A”	„B”
Composition, %		
C ₁ -C ₄	0.2	0.1
i-C ₅ / n-C ₅	4.0 / 47.9	2.5 / 37.7
2,2- / 2,3-DMB	<0.01 / 0.3	0.2 / 0.4
2- / 3-MP	4.0 / 2.6	4.8 / 3.4
n-C ₆	37.4	43.5
m-CP / c-C ₆	0.2 / 1.1	1.1 / 1.4
Benzene / ΣC ₇	1.4 / 0.9	3.3 / 1.6
Oxygen-containing compounds	0.8	2.0
Sulphur content, mg/kg	2.5	4.0
Water content, mg/kg	14	15
C ₅ paraffin hydrocarbons in feedstock, %	51.9	40.2
Research octane number (RON) / Motor octane number (MON)	48.8 / 47.5	45.9 / 44.7
Sensibility (RON-MON) of feedstocks	1.3	1.2
Paraffin hydrocarbons, %	97.8	94.7
Total liquid i-, c-paraffin content, %	35.3	35.2

2.2 Analytical and calculation methods

Hydrocarbon composition of the feedstocks and products was determined according to ASTM D 5134-13(2017) standard. Octane numbers of the feeds and products were calculated from their hydrocarbon composition and blending octane numbers of the individual components. In order to evaluate the efficiency of isomerization besides the yields of iso- and cycloparaffins the approach to the thermodynamic equilibrium concentration (ATEC_T) was calculated according to Eq(1).

$$\text{ATEC}_T = \frac{(C_{i-Cx})_T}{(C_{i-Cx})_{THT}} * 100 \quad (1)$$

Where,

ATEC_T: approach of thermodynamic equilibrium concentration at the actual temperature

(C_{i-Cx})_T: concentration of the isomer on the actual temperature in the C₆ fraction of product

(C_{i-Cx})_{THT}: equilibrium concentration of the isomer

The platinum dispersion of catalyst was determined by CO pulse chemisorption, CO consumption was detected by a thermal conductivity detector. The Al and Si contents of H-Mordenite and Pt content were determined by inductively coupled plasma (ICP), the specific surface areas were determined by Brunauer –Emmett-Teller (BET) method from the corresponding nitrogen adsorption isotherm. The acidity of the catalyst was determined by temperature programmed desorption (TPD) of NH₃.

2.3 Catalytic test apparatus

The experiments were carried out in an apparatus containing a tubular down-flow reactor with an effective volume of 100 cm³. The length and diameter of the fixed bed reactors were 470 and 25 mm, respectively. It contains all the equipment and devices such as oxygen converter, gas dryer, flow meters, pumps, cooler, separator, valves, etc. which are applied in the reactor system of an industrial heterogeneous catalytic plant (Hancsó et al., 2007). The experiments were carried out in continuous operation with steady-state catalyst activity.

3. Results and discussion

The yield of gas phase products (C₄-) was below 5 % up to 250 °C in case of both “A” and “B” feedstocks at every liquid hourly space velocity (LHSV), at higher temperatures and at lower LHSV the yield of gas products sharply increased, because the cracking reactions have taken place in a higher extent (Figure 1.). The yield of gas products obtained from feedstock “B” was slightly higher than in the case of feedstock “A”, mainly at higher temperatures and at longer residence time. It can be explained by the fact that the feedstock “B” had higher C₆ hydrocarbon content, which has lower thermal stability than C₅ hydrocarbons. In addition, the stability of C₆ iso-carbenium ions produced as intermediate products from isomerization is lower than that of iso-pentyl carbenium ion (Holló et al., 2002). About 45 % of the gas phase product was i-butane which can be utilized for alkylate production or as LPG (propane-butane gas) blending component.

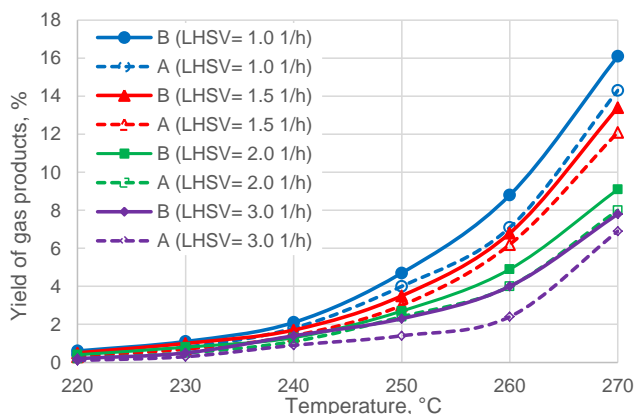


Figure 1: Yields of gas products as a function of temperature and LHSV ($P=30$ bar, H_2 /feedstock ratio 1:1)

According to the yield data of gas products, the yield value of the liquid products changed in opposite tendency due to the above mentioned cracking reactions (Table 2). The yield of liquid products changed between 79 and 99.9 %. The lowest values were obtained under the strictest process parameters, at high temperature ($T: 270$ °C) and high residence time (LHSV: 1.0 h^{-1}) in the catalytic system.

Table 2. Change of liquid product yields as a function of temperature and LHSV (feedstock "A" / "B")

LHSV, h^{-1}	Liquid yield, %					
	Temperature, °C					
	220	230	240	250	260	270
1.0	99.6 / 99.4	99.2 / 98.9	98.2 / 97.9	96.0 / 95.3	92.9 / 92.2	85.7 / 83.9
1.5	99.7 / 99.5	99.3 / 99.0	98.6 / 98.3	97.0 / 96.5	93.8 / 93.2	87.9 / 86.6
2.0	99.8 / 99.6	99.5 / 99.2	98.9 / 98.7	97.6 / 97.3	96.0 / 95.1	92.0 / 90.9
3.0	99.8 / 99.8	99.7 / 99.5	99.1 / 98.6	98.6 / 97.7	97.6 / 96.0	93.1 / 92.2

In order to evaluate the isomerization reaction results the approach of thermodynamic equilibrium concentration (ATEC) was determined for the individual components in the C_5 and C_6 fractions as a function of process parameters. The isomerization activity of the catalyst was monitored by the concentration of 2-methyl-butane (2-MB in C_5 fraction) and 2,2-dimethyl-butane (2,2-DMB). Only 2-MB can be formed from n-pentane during isomerization, 2,2-DMB cannot be formed due to the steric and reaction mechanism reasons. 2,2-DMB component has the lowest reaction rate among the hexane isomers, its formation is the rate-determining step of the isomerization of n-hexane, and its equilibrium concentration depends mainly on the reaction temperature (Hancsók et al., 1999). The ATEC values of products (2-MB and 2,2-DMB) obtained from feedstock "A" as a function of temperature and LHSV is demonstrated in Figures 2a and 2b. The values of products obtained from feedstock "B" showed the same tendency, in order to reduce the length of the paper these results are not presented.

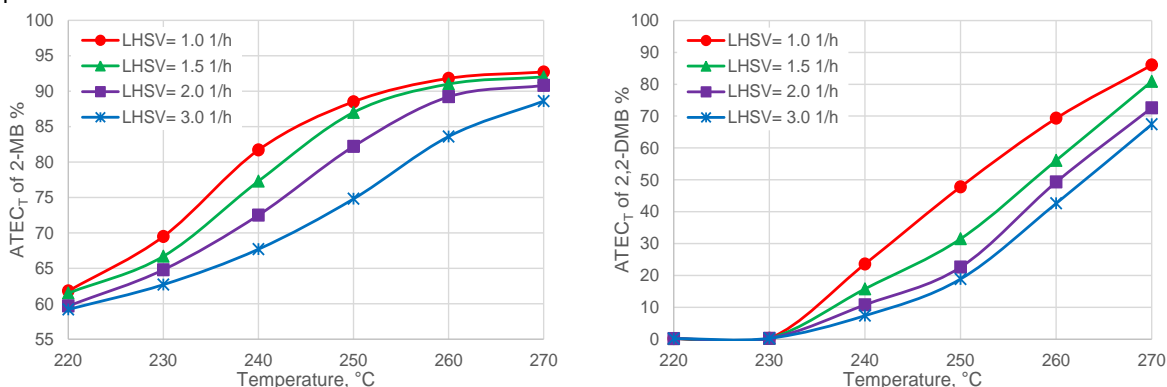


Figure 2: ATEC of 2-MB (Figure 2a) and 2,2-DMB (Figure 2b) as a function of temperature and LHSV ($P=30$ bar, H_2 /feedstock ratio 1:1; feedstock: "A")

Curves in Figures 2a and 2b demonstrate well that the concentrations of the two emphasized isomers approach the thermodynamic equilibrium concentrations increasingly by rising the reaction temperatures and decreasing the LHSV. However, the extent of increase in ATEC values decreased by increasing the temperature, especially between 250 and 270 °C at lower LHSV. The reason for this is that the process parameters have less impact on the reaction rate near to the equilibrium concentrations. This is also supported by the fact that the ATEC values of 2-MP at 250 – 270 °C and 1.0 – 1.5 h⁻¹ were 87.0 – 95.8 % with an absolute difference of 8.8 %, while in the case of 2,2-DMB these values changed between 56.1 and 88.8 % with an absolute difference of 32.7 %. ATEC data of other C₆ i-paraffins obtained from feedstock “A” is shown in Table 3. Data demonstrate well that those values of both tree hexane isomers were higher than in the case of 2,2-DMB.

Table 3. The approach of the thermodynamic equilibrium concentration (ATEC) of 2,3-DMB, 2-MP, 3-MP, obtained from feedstock with 1.05 % benzene content as a function of temperature at different LHSV values (P= 30 bar, H₂/feedstock ratio 1:1)

Temperature, °C	ATEC								
	250	250	250	260	260	260	270	270	270
LHSV, h ⁻¹	1.0	1.5	2.0	1.0	1.5	2.0	1.0	1.5	2.0
Components									
2,3-DMB	65.5	52.4	44.8	79.4	75.7	74.3	93.9	88.3	84.1
2-MP	80.0	74.1	70.9	92.7	90.5	88.4	99.9	95.0	88.7
3-MP	78.0	69.2	64.3	86.8	83.1	82.3	99.1	93.9	86.2

Individual components with highest ATEC values were obtained at 270 °C. However, at this temperature at LHSV of 1.0 h⁻¹ the yield of liquid products was only 82.4 – 87.9 % due to the higher extent of hydrocracking reactions (see in Table 2). Taking these results into account, it has been found that the preferred conditions for the isomerization of C₅-C₆ fractions having benzene and oxygen-containing compounds are as follows: T: 250 – 260 °C, LHSV: 1.0 – 1.5 h⁻¹. This was confirmed by the fact that the benzene content of the products obtained at the mentioned process parameters was lower than 0.01 %; oxygen-content was not detectable, so the hydrogenation of components was complete.

The main properties of the products obtained from both feedstocks “A” and “B” at favourable process parameters are summarized in Table 4. From the results, it was concluded that the yield of the liquid products was > 92 %, research and motor octane numbers were higher with 26.2 – 27.6 and 26.6 – 27.9 units, respectively, compared to the feedstocks. The octane number of product mixtures can be enhanced by the separation and recirculation of n-paraffins, 2- and 3-methyl-pentane with low octane number (73 – 74). In this case, the product mixtures contain mainly i-paraffins with an octane number of ≥ 92. These i-paraffins are free of sulphur and aromatics, consequently, during their application in internal combustion engines compared to the current engine fuels, the pollutant emission is lower and contain less harmful pollutants.

Table 4: Main characteristics of liquid products obtained from both feedstock “A” and “B” at favourable process parameters (T= 260 °C; LHSV= 1.0 h⁻¹; P= 30 bar, H₂/feedstock ratio= 1:1)

Characteristics	Products	
	“A”	“B”
ATEC _T , %		
i-C ₅	91.8	91.4
2,3-DMB / 2-MP / 3-MP	69.3 / 79.4 / 92.7 / 86.8	69.1 / 78.9 / 91.8 / 85.7
Liquid yield, % (0 % recirculation)	92.9	92.2
RON / MON C ₅₊ (0 % recirculation)	76.4 / 75.4	72.1 / 71.3
Sensibility (RON-MON)	1.0	0.8
ΔRON / ΔMON (product-feedstock)	27.6 / 27.9	26.2 / 26.6
RON / MON (n-C _x recirculation)	86.8 / 85.9	85.2 / 84.4
RON / MON (n-C _x + 2- and 3-MP recirculation)	91.7 / 91.0	92.8 / 92.3
RON / MON: Feedstock “A”: 48.8/47.5; Feedstock “B”: 45.9/44.7		

4. Conclusions

Catalytic isomerization process applying Pt/H-Mordenite/Al₂O₃ catalyst with increased Pt content at favourable process parameters (T= 260 °C, LHSV= 1.0 h⁻¹, P= 30 bar, H₂/feedstock molar ratio= 1:1) is suitable to enhance the octane number of light gasoline fractions containing benzene and oxygenates obtained from waste cooking oil. The yield (> 92 %) and octane number (> 92 unit) of liquid products are high and containing only paraffin hydrocarbons, primarily i-paraffins depending on the extent of recirculation of components having low octane number. The approach of the thermodynamic equilibrium concentration values of these i-paraffins is around 69 – 92 %. These light gasoline blending components having lower pollutant emission during their application can be produced from renewable feedstocks by the presented catalytic hydroisomerization process.

Acknowledgments

The authors acknowledge the financial support of the project of the Economic Development and Innovation Operative Programme of Hungary, GINOP-2.3.2-15-2016-00053: Development of liquid fuels having high hydrogen content in the molecule (contribution to sustainable mobility) and the project of Széchenyi 2020 under the EFOP-3.6.1-16-2016-00015: University of Pannonia's comprehensive institutional development program to promote Smart Specialization Strategy. The Project is supported by the European Union and co-financed by Széchenyi 2020.

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