

Article

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

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Abstract: The thermal and catalytic conversion processes of alternative feedstocks (e.g., waste and biomass) to different engine fuels can result in the formation of a significant amount of light hydrocarbons as by-products in the boiling range of gasoline. The properties of these C₅/C₆ hydrocarbons need to be improved due to many reasons, e.g., their benzene content, and/or poor oxidation stability (high olefin content) and low octane number (<60). The aim of the research work was to increase the octane number of benzene containing C₅/C₆ bioparaffin fractions by catalytic isomerization. These by-products were obtained from special hydrocracking of waste cooking oil to hydrocarbons in the boiling range of aviation turbine fuels (JET fuels)/diesel fuels. Experiments were carried out in a reactor system containing down-flow tubular reactors over Pt/Al₂O₃/Cl and Pt/H-Mordenite/Al₂O₃ catalysts at 115–145 °C and 230–270 °C, respectively. Based on the results obtained at different process parameter combinations, it was concluded that the hydrogenation of benzene was complete over both catalysts, and the liquid yields were higher (ca. 98% > ca. 93 %) in the case of Pt/Al₂O₃/Cl. In addition, the octane number was also enhanced (ca. 32 > ca. 27 unit) in the products compared to the feedstock. This was because a higher isoparaffin content can be obtained at a lower operating temperature. Moreover, cracking side reactions take place to a lesser extent. The utilization of these isomerized bio-origin light fractions can contribute to the competitiveness of second-generation biofuels.

Keywords: waste-originated feedstock; isomerization; biogasoline; benzene-free; increased octane number

1. Introduction

The energy demand of the world is continuously increasing due to new industrial developments and population growth [1]. Internal combustion engines with different operation principles will remain the main form of propulsion for terrestrial, air, and maritime transportation in the next 20–30 years. Accordingly, hydrocarbons as engine fuels for internal combustion engines will continue to play an important role as demonstrated in Figures 1 and 2a,b [2]. The proportion of gasoline will decrease slightly, but will still account for a one-third share in 2040. This decrease is due to the better fuel economy and the spread of electric vehicles [3] (Figure 3). However, contrary to forecasts, electric vehicles cannot spread as rapidly as expected, due to reasons such as availability of raw materials, recycling, sustainability, etc.

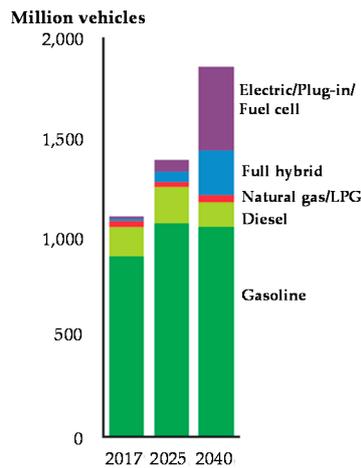


Figure 1. Light-duty vehicles by fleet type.

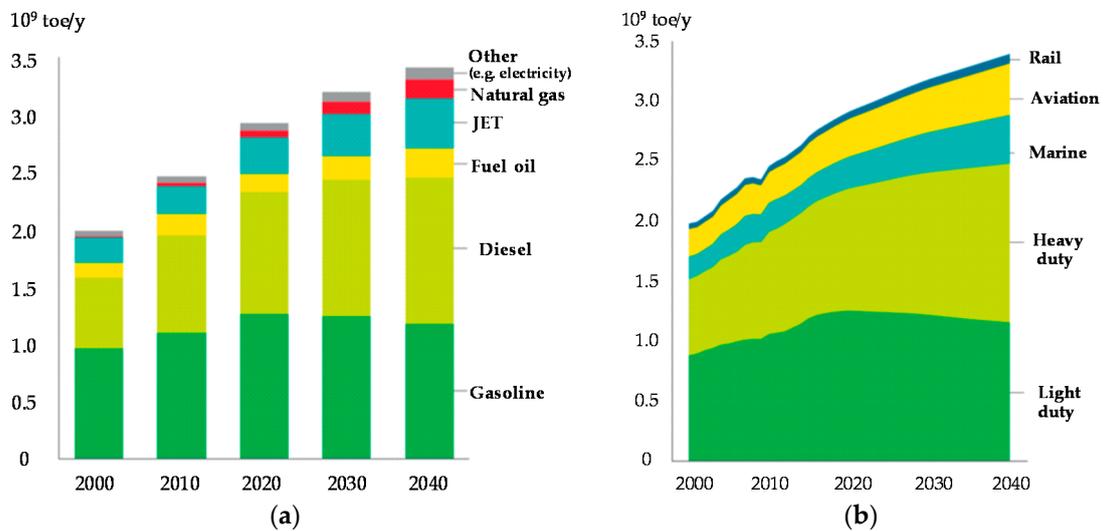


Figure 2. (a) Global energy mix by engine fuels. (b) Energy demand by type of transportation.

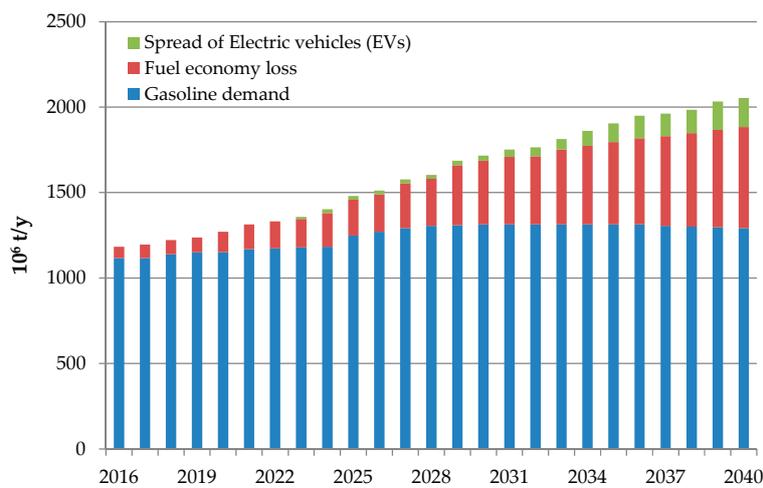


Figure 3. Expected gasoline demand taking into account to better fuel economy and the spread of electric vehicles.

Sustainable production of alternative engine fuels is a big challenge. Accordingly, different biofuels presently play a significant role for many countries in the world. The foreseen decrease of fossil reserves, global protection of the environment, and sustainability of mobility are the main driving forces for the research into renewable alternative energy sources [4]. The latest directive of the European Union requires the production of fuels from non-edible, renewable, or waste feedstocks [5]. Currently, the main bio-component of gasoline is bioethanol [6], which is also a molecular constituent in ethyl-tert-butyl-eter (bio-ETBE), an important gasoline blending component [7]. Despite the numerous advantages of ethanol, it has also many disadvantages, such as high solubility in water, increase of vapor pressure in gasoline, lower energy content, corrosion effects, high ozone producing potential, and high atmospheric reactivity [8]. Moreover, it is mainly produced from food-based plants, e.g., corn. As a result of persistent research and development in the last few years, the construction of plants using lignocellulose as feedstock has already begun [9]. However, their technological efficiency and reliability need to be proven [10].

The conversion processes of alternative feedstocks, such as biomass and waste, to different fuels result in the formation of a significant amount of light hydrocarbons (e.g., C₅-C₇ fractions), mainly as by-products in the boiling range of gasoline. The following processes can result in light hydrocarbons from alternative sources:

- From waste or biomass-derived syngas by Fischer–Tropsch (F–T) synthesis via direct synthesis, which results in the so-called C₅-C₇ fraction, F–T light gasoline [11], or, eventually, via indirect route by F–T synthesis combined with the hydrocracking of heavy F–T wax [12]. The oligomerization and hydrogenation of light olefins (C₂=–C₃=) obtained from F–T synthesis can also yield light hydrocarbons [13].
- From 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 [14]. The obtained iso-olefins need to be hydrogenated to iso-alkanes.
- Another possibility is the oligomerization and subsequent hydrogenation of light gasoline fractions having a high olefin content obtained from thermal/catalytic cracking of waste polyolefins with different structures, such as polyethylene or polypropylene [15].
- Gasoline-range hydrocarbons can be produced from sorbitol, a sugar-based compound from lignocellulosic biomass, via hydrodeoxygenation over Zr-phosphate-supported Pd-bimetallic (Pd+ Pt/Ru/Ni/W etc.) catalysts [16]. The product mixture contains a large number of individual components with very different structures, e.g., corrosive acids and compounds in the aqueous phase. The treating and separation of the products could require complex and expensive solutions.
- In the so-called renewable power-to-paraffin hydrocarbons process, hydrogen produced via water electrolysis can be used for the hydrogenation of carbon monoxide/carbon dioxide to get alkanes [17,18].
- Alkanes can be obtained from bioethanol via dehydration, oligomerization, and hydrogenation of olefinic double bounds [19].
- N-alkanes can be manufactured through simple sugars from lignocellulose applying a very complex and expensive production process: acid-catalyzed dehydration, Aldol condensation (base catalyst), hydrogenation on metal catalyst, dehydration, and hydrogenation (acid and metal catalysts). Such products have very a low octane number, which should be increased by the catalytic process [20].
- Paraffins can be obtained from long-chain fatty aldehydes by oxidative deformylation [21].
- Liquid alkanes ($\leq C_{13}$) can be produced from CO₂ and H₂O on Co/TiO₂ catalyst by the Solar Photothermochemical Alkane Reverse Combustion (SPARC) method [22].
- Alkanes can be obtained from C₅-C₆ sugars through hydroxymethylfurfural, levulinic acid, and gamma-valerolactone.

- The simplest reaction pathway for the production of C₅-C₇ 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 [23] or waste lards [24] from protein processing industry [25].

Based on the results of the presented publications it was concluded that by-products containing mainly C₅-C₇ paraffins can be obtained from different alternative sources. These by-products have very low octane numbers (<55–65) and contain undesirable components, such as olefins, aromatics, oxygenates, and other corrosive compounds; therefore, they are not suitable as gasoline blending components (“drop in fuel”). Isomerization and dehydrocyclization (aromatization) are the main chemical processes for the quality improvement of n-paraffins to enhance their octane number. Via isomerization the products are iso-paraffins, and via the dehydrocyclization process the obtained products are aromatics. Aromatics, including benzene, have very high octane numbers, e.g., the research octane number (RON) of benzene is 101. However, they are carcinogenic, therefore their concentration in gasoline must be reduced. Gasoline standards strictly limit the concentration of benzene, e.g., in California, USA, the limit is 0.62 v/v%, and in the EU this value is 1.0 v/v% [4].

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

2. Experimental Part

The aim of the research work was the investigation of quality improvement, mainly the octane number increasing possibilities of C₅/C₆ bioparaffin fractions by isomerization and the hydrogenation of benzene and oxygenates (e.g., methyl-/ethyl-formate, methyl-acetate, and 2-butanone) in one catalytic step. These light hydrocarbons were obtained as side products by the special hydrocracking of waste cooking oil to hydrocarbons in the boiling range of JET fuels/diesel fuels. The aim of the study was also the determination of favorable process parameters, such as temperature, liquid hourly space velocity, pressure, and hydrogen/feedstock ratio, for the conversion of C₅/C₆ fractions to hydrocarbons with a high octane number in different catalytic systems. In addition, the activity and selectivity of the two applied catalysts with different composition were compared during the experiments.

2.1. Apparatus

The catalytic experiments were carried out in an experimental apparatus (Figure 4) containing all the important equipment that can be found in the reactor system of a modern industrial hydrogenation/isomerization plant, e.g., dryer, compressor, pumps, feed vessel, pre-heater, reactor, cooler, separator, and flow meters, etc.. The composition of the products can be measured by gas chromatograph connected to the reactor system. It is important to emphasize that the reactors can be operated in parallel or serial. The length and diameter of the fixed bed reactors are 470 and 25 mm, respectively.

2.2.2. Catalysts and Adsorbents

Based on the preliminary experimental results with various kinds of catalysts, Pt/Al₂O₃/Cl and Pt/H-Mordenite/Al₂O₃ catalysts were selected for quality improvement of feedstock “A” and “B”, respectively. The main properties of the catalysts are summarized in Table 2.

Table 2. The main properties of catalysts used in the experiments.

Properties	Pt/Al ₂ O ₃ /Cl	Pt/H-Mordenite/Al ₂ O ₃
Pt-content, %	0.28	0.38
Pt-dispersion, %	84	89
Specific surface area (BET), m ² /g	426	448
Si/Al molar ratio	-	19.5
Chlorine content, % (Reactor I/Reactor II)	3.1/7.6	-
Length/diameter of catalyst extrudates (average, mm)	3.9/1.8	4.8/2.4

During the pre-selection of the catalysts, Pt/Al₂O₃/Cl showed the highest isomerization activity at favorably low temperatures. However, this catalyst is very sensitive to the water and sulfur content of the feedstock; thus, these impurities were removed from feedstock “B” to obtain feedstock “A” by commercial Molecular Sieves 4A and 13X purchased from Sigma-Aldrich. Hydrogenation and isomerization of feedstock “A” over the Pt/Al₂O₃/Cl catalyst were carried out in the reactor system where both reactors were operated in serial. Halogen content of the Pt/Al₂O₃/Cl in case of Reactor I was lower than that of Reactor II to ensure sufficiently available active sites for the hydrogenation of benzene and for the isomerization reactions. The catalyst volume in Reactor I (40 cm³) was half of the volume used in Reactor II (80 cm³) to avoid significant increases in temperature in Reactor I. This heat releases during the fast hydrogenation reaction of benzene to cyclohexane, and during isomerization reactions, which are also exothermic.

The catalytic isomerization of feedstock “B” over Pt/H-Mordenite/Al₂O₃ was carried out on one side of the same catalytic test apparatus. Compared to the commercial light gasoline 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. Higher platinum content increases the number of available active metal sites of the catalyst for the hydrogenation of benzene, as well as the other hydrogenation/dehydrogenation reactions. A volume of 80 cm³ of catalyst was placed in the middle of the reactor and treated before the experiments as follows: dried at 150 °C for 2 h in nitrogen, heated to 300 °C at 25–30 °C/h in hydrogen atmosphere (40 dm³/h), temperature was held for 3 h, and then increased to 400 °C and held for 1 h.

2.2.3. Process Parameters

The process parameters of the systematic technological experiments over two different catalysts were varied in different ranges (Table 3).

Table 3. The process parameters of the experiments.

Process Parameters	Pt/Al ₂ O ₃ /Cl	Pt/H-Mordenite/Al ₂ O ₃
Temperature, °C	115–145	220–270
LHSV ¹ , h ⁻¹	1.0–3.0 ²	1.0–3.0
Pressure, bar	30	30
H ₂ /feedstock molar ratio	0.15:1.0	1.0:1.0

¹ Liquid hourly space velocity. ² for the total catalyst volume.

2.2.4. Analytical and Calculation Methods

Hydrocarbon composition of the feedstock 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 by blending octane numbers of the individual components. In order to evaluate the efficiency of isomerization and the yields of iso- and cyclo-paraffins, the thermodynamic equilibrium concentration (ATEC_T) was calculated according to Equation (1).

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

where $(c_{i-Cx})_T$ is the concentration of the isomer at the actual temperature in the C₆ fraction of product, and $(C_{i-Cx})_{ThT}$ is the equilibrium concentration of the isomer.

The Pt content of the catalysts was determined by the inductively coupled plasma (ICP) method; the platinum dispersion of catalysts was determined by CO pulse chemisorption, and CO consumption was detected by a thermal conductivity detector. The Al and Si contents of H-Mordenite were also determined by the ICP method. The specific surface areas were determined by the Brunauer–Emmett–Teller (BET) method from the corresponding nitrogen adsorption isotherm. The chlorine content of catalysts was measured by the Volhard method [26]; the sample was dissolved in concentrated sulfuric acid and Cl ions were precipitated with silver nitrate solution. Excess silver solution was back titrated with a thiocyanate solution to give the amount of chlorine in the original sample. The chlorine contents of products were determined according to the ASTM D4929–19 (Standard Test Method for Determination of Organic Chloride Content in Crude Oil). The oxygen-containing compounds were detected by GC-MS. The water contents of the feedstock and products were determined by Coulometric Karl Fischer titration.

3. Results and Discussion

Catalysts and the optimal process parameter combinations for the quality improvement of biogasoline fractions were determined based on preliminary experimental results to obtain the most favorable experimental results.

The yield of gas and liquid product mixtures obtained from the two different catalysts differed in the function of process parameters. The yield of the gas products obtained in Reactor I from feedstock “A” over the Pt/Al₂O₃/Cl catalyst was higher than 99.3% in every case. This was due to the low chlorine content of the catalyst, the high liquid hourly space velocity (LHSV), and the low experimental temperature applied in Reactor I. The low chlorine content of the catalyst results in lower acidity, and thus lower cracking activity. The yields of products obtained from Reactor II decreased up to 2.1%, which was higher than in the case of Reactor I. This was due to the higher chlorine content, and thus higher acidity and cracking activity of the catalyst.

According to the above, the yields of the liquid products varied from 97.2% to 99.4% in the function of process parameters, as shown in Table 4. These yield values are high even from an industrial perspective. The lowest acceptable yield value for a light naphtha isomerization unit is 92%. Data in Table 4 illustrate well that the gas production was low (0.6–2.8 %), due to the reasons mentioned above.

The yield of gas phase products (C₁–C₄) obtained from feedstock “B” on the Pt/H-Mordenite/Al₂O₃ catalyst was below 5% up to 250 °C at every LHSV. At higher temperatures and lower LHSV the yield of gas products sharply increased because the cracking reactions took place to a greater extent (Table 5). About 45% of the gas phase product was i-butane, which can be utilized for alkylate production or as an LPG (propane-butane gas) blending component.

Table 4. Yield of the liquid products in the function of process parameters (catalyst: Pt/Al₂O₃/Cl, feedstock: "A").

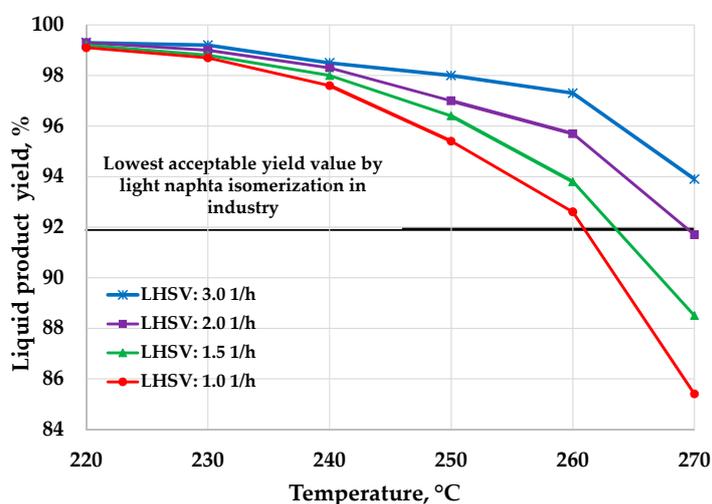
Liquid Hourly Space Velocity ¹ , h ⁻¹	Yield of Liquid Products, %			
	115 °C	125 °C	135 °C	145 °C
1.0	98.6	98.1	97.6	97.2
1.33	98.8	98.3	97.9	97.4
1.66	99.1	98.6	98.2	97.7
2.0	99.4	98.9	98.5	98.0

¹ LHSV values for the total catalyst volume of Reactor I and II.

Table 5. Yield of the gas products as a function of process parameters (catalyst: Pt/H-Mordenite/Al₂O₃, feedstock: "B").

LHSV, h ⁻¹	Yield of Gas Products, %					
	220 °C	230 °C	240 °C	250 °C	260 °C	270 °C
1.0	0.9	1.3	2.4	4.6	7.4	14.6
1.5	0.8	1.2	2.0	3.6	6.2	11.5
2.0	0.7	1.0	1.7	3.0	4.3	8.3
3.0	0.7	0.8	1.5	2.0	2.7	6.1

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 (Figure 5). The yield of liquid products changed between 85.4% and 99.3%. 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. Curves in Figure 5 illustrate well that iso-paraffins can be obtained with high yield from high n-paraffin containing biogasoline fractions for a wide range of process parameters.

**Figure 5.** Change of liquid product yields as a function of temperature and LHSV (catalyst: Pt/H-Mordenite, feedstock: "B").

Based on the gas and liquid product yields obtained from the different catalysts, it was concluded that the liquid yield obtained from Pt/Al₂O₃/Cl was significantly higher than in the case of Pt/H-Mordenite/Al₂O₃. The reason for this was because the cracking reactions took place to a lesser extent due to the lower isomerization temperature.

In order to evaluate the isomerization reaction results, the thermodynamic equilibrium concentration (ATEC) was determined for the individual components in the C₅ and C₆ 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 C₅ fraction) and 2,2-dimethyl-butane (2,2-DMB in C₆ fraction). Only 2-MB can be formed from n-pentane during isomerization; 2,2-dimethyl-propane (2,2-DMP) cannot be formed due to the steric and reaction mechanism reasons. The 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 [27].

Figure 6a,b demonstrate the ATEC values of 2-MB and 2,2-DMB in the liquid products obtained from feedstock “A” on the Pt/Al₂O₃/Cl catalyst as a function of process parameters.

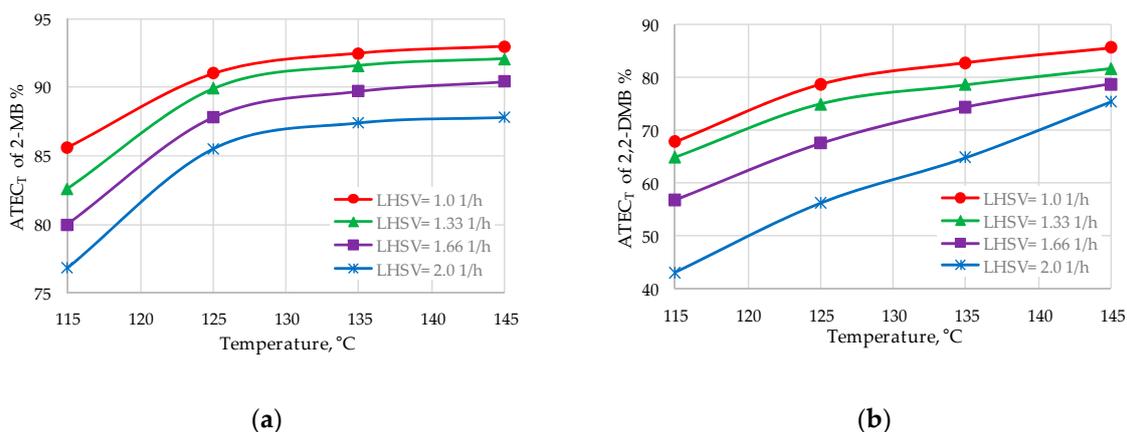


Figure 6. ATEC of 2-MB (a) and 2,2-DMB (b) as a function of temperature and LHSV (catalyst: Pt/Al₂O₃/Cl, feedstock: “A”).

As a comparison, ATEC values of 2-MB and 2,2-DMB in the liquid products obtained from feedstock “B” on the Pt/H-Mordenite/Al₂O₃ catalyst as a function of process parameters are shown in Figure 7a,b.

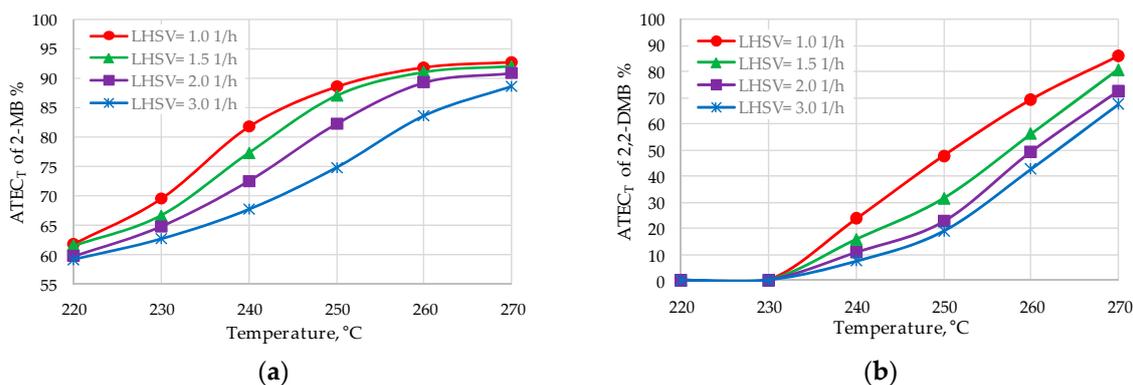


Figure 7. ATEC of 2-MB (a) and 2,2-DMB (b) as a function of temperature and LHSV (catalyst: Pt/H-Mordenite/Al₂O₃, feedstock: “B”).

Curves in Figure 6a,b and Figure 7a,b demonstrate well that the concentrations of the two emphasized isomers increasingly approach the thermodynamic equilibrium concentrations by increasing the reaction temperatures and decreasing the LHSV. However, the extent of the increase in ATEC values lessened by increasing the temperature, especially at 125–145 °C and 250–270 °C, respectively, 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 in case of the Pt/Al₂O₃/Cl catalyst, the ATEC values of 2-MB at the temperature of 125–145 °C and LHSV

of 1.0–1.66 h⁻¹ were 87.8–93.0%, with an absolute difference of 5.2%, while, in the case of 2,2-DMB, these values changed between 67.5% and 85.6%, with an absolute difference of 18.1%. However, in the case of the Pt/H-Mordenite/Al₂O₃ catalyst, the ATEC values of 2-MB at a temperature of 250–270 °C and LHSV of 1.0–1.5 h⁻¹ were 87.0–92.8%, with an absolute difference of 5.8%, while, in the case of 2,2-DMB, these values changed between 32.1% and 86.8%, with an absolute difference of 54.7%.

Based on the results of a previous publication [28] it was shown that among the C₆ i-paraffins obtained, the ATEC value of 2,3-dimethylbutane (2,3-DMB), 2-methylpropane (2-MP), and 3-methylpropane (3-MP) were significantly higher than in the case of 2,2-DMB. To prove this phenomenon in the present study, ATEC values of 2-MP obtained from both feedstocks on the applied catalysts are illustrated in Figure 8a,b.

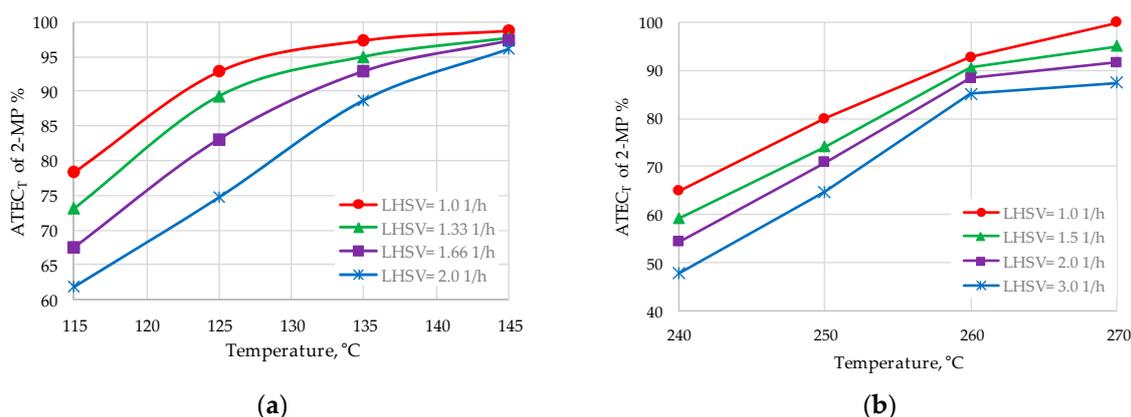


Figure 8. ATEC values of 2-MP (a) (catalyst: Pt/Al₂O₃/Cl, feedstock: "A"); and 2-MP (b) (catalyst: Pt/H-Mordenite/Al₂O₃, feedstock: "B") as a function of temperature and LHSV.

The highest ATEC values of the individual i-paraffins presented in the figures were obtained at 145 °C (Pt/Al₂O₃/Cl) and at 270 °C (Pt/H-Mordenite/Al₂O₃) at LHSV of 1.0 h⁻¹. However, the liquid yields were the lowest due to the high hydrocracking activity of catalysts at these process parameters. It is also important to emphasize that the highest possible equilibrium concentrations of 2-MB and 2,2-DMB at the highest experimental temperature are the lowest, because these values are decreasing approximately exponentially with increasing temperature due to the exothermic skeletal isomerization reactions [4].

Based on the results obtained from the two different catalysts, the most favorable process parameter combinations for the isomerization of benzene containing bio-originated C₅–C₆ fractions are the following: temperature, 125–135 °C; LHSV, 1.0–1.33 h⁻¹ (Pt/Al₂O₃/Cl); and: temperature, 260 °C; LHSV, 1.0–1.5 h⁻¹ (Pt/H-Mordenite/Al₂O₃). The benzene content of the target products was <0.05 mg/kg, and oxygenate content was not detected, thus the hydrogenation was complete. The main properties of the liquid products obtained over both catalysts at favorable process parameter combinations are summarized in Table 6. From the results, it was concluded that in the case of the Pt/Al₂O₃/Cl catalyst the yield of the liquid products and their research octane number was higher with ca. 5% and 4–5 units, respectively, compared to the results obtained on Pt/H-Mordenite/Al₂O₃. When the n-paraffins and the mono-methyl pentanes having low octane number were recirculated with 95%, the RON of the products could reach 92. This is a good result taking into account that the feedstock was benzene free. It is noted that benzene has a high research octane number (101), and its hydrogenation to cyclohexane results in a lower octane number (84). This decrease in octane should be compensated for by the production of isomers having a very high RON. These i-paraffins are free of sulfur and aromatics; consequently, during their application in internal combustion engines compared to current engine fuels, the pollutant emission is lower and contains less harmful pollutants.

Table 6. Main characteristics of liquid products obtained over Pt/Al₂O₃/Cl and Pt/H-Mordenite catalysts at favorable process parameters (respectively: temperature, 125–135 °C; LHSV, 1.0–1.33 h⁻¹; and temperature, 260 °C; LHSV, 1.0–1.5 h⁻¹).

Characteristics	Products	
	Pt/Al ₂ O ₃ /Cl	Pt/H-Mordenite
Liquid yield, % (0 % recirculation)	97.6–98.3	92.9–93.8
ATEC, %		
2-MB	89.9–92.5	90.5–91.8
2,2-DMB	75.0–82.8	57.6–70.4
2-MP	89.3–97.3	90.5–92.7
RON/MON (0 % recirculation)	79.4–80.9/78.1–79.5	74.9–76.4/73.9–75.4
Sensibility (RON-MON)	1.3–1.4	1.1–1.0
ΔRON/ΔMON (product-feedstock)	30.8–32.3/29.5–32.0	24.7–28.0/24.7–28.1
Liquid yield, % (95 % n-Cx recirculation)	75.4–78.1	68.1–69.3
RON/MON (95 % n-Cx recirculation)	87.1–88.8/85.3–86.7	84.1–85.3/83.0–84.3
Sensibility (RON-MON)	1.8–2.1	1.1–1.0
Liquid yield, % (95 % n-Cx, 2-MP, 3-MP recirculation)	57.6–60.4	52.7–54.8
RON/MON (95 % n-Cx, 2-MP, 3-MP recirculation)	91.7–92.3/90.0–90.7	88.7–90.0/87.5–88.9
Sensibility (RON-MON)	1.7–1.6	1.2–1.3

4. Conclusions

The catalytic isomerization process applying Pt/Al₂O₃/Cl and Pt/H-Mordenite/Al₂O₃ catalysts at favorable process parameters (respectively: temperature = 125–135 °C, LHSV = 1.0–1.33 h⁻¹; and temperature = 260 °C; LHSV = 1.0–1.5 h⁻¹; P = 30 bar; H₂/feedstock molar ratio = 0.15:1.0) is suitable to enhance the octane number of light biogasoline fractions containing benzene and oxygenates. The increase in octane number compared to the feedstock was ca. 32 and ca. 27 units, respectively. The yield of liquid products was high (ca. 98% and ca. 93%) and contained only paraffin hydrocarbons, primarily i-paraffins depending on the extent of recirculation of components having a low octane number. The thermodynamic equilibrium concentration values of these i-paraffins was around 75–95% and 56.1–92.7%. These light biogasoline blending components produced from renewable feedstocks by the presented catalytic hydroisomerization process with Pt/Al₂O₃/Cl and Pt/H-Mordenite/Al₂O₃ catalysts have lower pollutant emissions during their application. Unlike Pt/H-Mordenite/Al₂O₃, the Pt/Al₂O₃/Cl catalyst is very sensitive to water, sulfur, and oxygen-containing compounds; thus, feedstock needs to be pre-treated. However, the isomerization process at lower temperatures is energy and feedstock efficient (cracking reactions take place to a lesser extent). Moreover, the octane number of the products is higher by ca. 5 units. These factors more than compensate for the costs of the feedstock pre-treatment.

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References

1. BP Statistical Review of World Energy. Available online: <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf> (accessed on 9 March 2020).
2. ExxonMobil, Outlook for Energy 2019: A Perspective to 2040. Available online: https://corporate.exxonmobil.com/-/media/Global/Files/outlook-for-energy/2019-Outlook-for-Energy_v4.pdf (accessed on 5 March 2020).
3. Be Future Forward, Honeywell UOP. Available online: https://www.digitalrefining.com/article_1002373.pdf (accessed on 6 January 2020).
4. Srivastava, S.P.; Hancsók, J. *Fuels and Fuel-Additives*; John Wiley & Sons: Hoboken, NJ, USA, 2014; p. 374.
5. European Parliament, 2018, Directive of the European Parliament and of the Council cast, 2016/0382 (COD). Available online: <http://data.consilium.europa.eu/doc/document/PE-48-2018-INIT/en/pdf> (accessed on 5 February 2020).
6. Mansouri, A.; Rihani, R.; Laoufi, A.N.; Özkan, M. Production of bioethanol from a mixture of agricultural feedstocks: Biofuels characterization. *FUEL* **2016**, *185*, 612–621. [[CrossRef](#)]
7. Abdellatif, F.H.H.; Babin, J.; Arnal-Herault, C.; Nouvel, C.; Six, J.-L.; Jonquieres, A. Bio-based membranes for ethyl-tert-butyl-ether (ETBE) bio-fuel purification by pervaporation. *J. Membr. Sci.* **2017**, *524*, 449–459. [[CrossRef](#)]
8. Manzetti, S.; Andersen, O. A review of emission products from bioethanol and its blends with gasoline. Background for new guidelines for emission control. *FUEL* **2015**, *140*, 293–301. [[CrossRef](#)]
9. Toor, M.; Kumar, S.S.; Malyan, S.K.; Bishnoi, N.R.; Mathimani, T.; Rajendran, K.; Pugazhendhi, A. An overview on bioethanol production from lignocellulosic feedstocks. *Chemosphere* **2020**, *242*, 125080. [[CrossRef](#)] [[PubMed](#)]
10. Padella, M.; O'Connell, A.; Prussi, M. What is still Limiting the Deployment of Cellulosic Ethanol? Analysis of the Current Status of the Sector. *Appl. Sci.* **2019**, *9*, 4523. [[CrossRef](#)]
11. Sauciu, A.; Abosteif, Z.; Weber, G.; Potetz, A.; Rauch, R.; Hofbauer, H.; Schaub, G.; Dumitrescu, L. Influence of operating conditions on the performance of biomass-based Fischer-Tropsch synthesis. *Biomass. Convers. Bior.* **2012**, *2*, 253–263. [[CrossRef](#)]
12. Ershov, M.; Potanin, D.; Gueseva, A.; Abdellatif, T.M.M.; Kapustin, V. Novel strategy to develop the technology of high-octane alternative fuel based on low-octane gasoline Fischer-Tropsch process. *FUEL* **2020**, *261*, 116330. [[CrossRef](#)]
13. Atashi, H.; Dinarvandi, K. Determination of selectivity equations heavy and light product of petroleum on iron based catalysts in Fischer-Tropsch synthesis. *Petrol. Sci. Technol.* **2019**, *37*, 2035–2042. [[CrossRef](#)]
14. Wang, T.; Zhang, Q.; Ding, M.; Wang, C.; Li, Y.; Zhang, Q.; Ma, L. Bio-gasoline production by coupling of biomass catalytic pyrolysis and oligomerization. *Energy Proced.* **2017**, *105*, 858–863. [[CrossRef](#)]
15. Fehér, C.; Tomasek, S.; Hancsók, J.; Skoda-Földes, R. Oligomerization of light olefins in the presence of a supported Brønsted acidic ionic liquid catalyst. *Appl. Catal. B-Environ.* **2018**, *239*, 52–60. [[CrossRef](#)]
16. Kwon, E.E.; Kim, Y.T.; Kim, H.J.; Lin, K.Y.L.; Kim, K.H.; Lee, J.; Huber, G.W. Production of high-octane gasoline via hydrodeoxygenation of sorbitol over palladium-based bimetallic catalysts. *J. Environ. Manage.* **2018**, *227*, 329–334. [[CrossRef](#)] [[PubMed](#)]
17. Herz, G.; Reichelt, E.; Jahn, M. Design and evaluation of a Power-to-Liquid process for the production of valuable hydrocarbons from CO₂ and H₂O. *DGMK Tag.* **2017**, *2*, 181–186.
18. Mesfun, S.; Sanchez, D.L.; Leduc, S.; Wetterlund, E.; Lundgren, J.; Biberacher, M.; Kraxner, F. Power-to-gas and power-to-liquid for managing renewable electricity intermittency in the Alpine Region. *Renew Energy* **2017**, *107*, 361–372. [[CrossRef](#)]
19. Mohsenzadeh, A.; Zamani, A.; Taherzadeh, M.J. Bioethylene Production from Ethanol: A Review and Techno-economical Evaluation. *Chem. Bio. Eng. Rev.* **2017**, *4*, 75–91. [[CrossRef](#)]
20. Huber, G.W.; Chedda, J.N.; Barre, C.J.; Dumestic, J.A. Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* **2005**, *308*, 1446–1450. [[CrossRef](#)] [[PubMed](#)]
21. Shokri, D.; Que, L. Conversion of Aldehyde to Alkane by a Peroxoiron(III) Complex: A Functional Model for the Cyanobacterial Aldehyde-Deformylating Oxygenase. *J. Am. Chem. Soc.* **2015**, *137*, 7686–7691. [[CrossRef](#)]
22. Chanmanee, W.; Islam, M.F.; Dennis, B.H.; MacDonell, F.M. Solar photothermochemical alkane reverse combustion. *PNAS* **2016**, *113*, 2579–2584. [[CrossRef](#)]

23. Bezergianni, S.; Kalogianni, A. Hydrocracking of used cooking oil for biofuels production. *Bioresour. Technol.* **2009**, *100*, 3927–3932. [[CrossRef](#)]
24. Rosson, E.; Sgarbossa, P.; Pedrielli, F.; Mozzon, M.; Bertani, R. Bioliquids from raw waste animal fats: An alternative renewable energy source. *Biomass Conv. Bioref.* **2020**. [[CrossRef](#)]
25. Baladincz, P.; Hancsók, J. Fuel from waste animal fats. *Chem. Eng. J.* **2015**, *282*, 152–160. [[CrossRef](#)]
26. Jeffery, G.H.; Bassett, J.; Mendham, J.; Denney, R.C. *Vogel's Textbook of Quantitative Chemical Analysis*, 5th ed.; Longman Scientific & Technical: New York, NY, USA, 1989; pp. 355–356.
27. Hancsók, J.; Holló, A.; Debreczeni, É.; Perger, J.; Kalló, D. Benzene saturating isomerization. *Stud. Surf. Sci. Catal.* **1999**, *125*, 417–424.
28. Holló, A.; Hancsók, J.; Kalló, D. Kinetics of hydroisomerization of C₅-C₇ alkanes and their mixtures over platinum containing mordenite. *Appl. Catal. A-Gen.* **2002**, *229*, 93–102.



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