

The Direct Conversion of Rapeseed Oil Towards Hydrocarbons over Industrial Catalysts

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The current study presents rapeseed oil conversion investigation over industrial Pt/ γ -Al₂O₃ and Pd-Zn/MFI/ γ -Al₂O₃ catalysts. During reductive pre-treatment of Pt/ γ -Al₂O₃ catalyst got new properties that results in the direct hydrogenative treatment of rape seed oil towards alkanes with total yield reached up to 90 wt.% and conversion about 100%. Via temperature varying one may adjust process selectivity towards hydrocarbons either gasoline or diesel fractions. It's noteworthy that initial oil contained acids with carbon number not exceeds 22, but products composition contained alkanes C₂₃₊. The total yield of extra heavy alkanes C₂₃₊ was 0.5-5 wt.% depending on process conditions. Obtained data suggested the possibility of intermolecular cross-coupling reaction of glycerol fragments with acid fragments took place.

1. Introduction

Searching of cost-effective ways allowing to obtain petrochemical products and components of motor fuels from primary products of biomass processing is a global problem, the relevance of which is defined both the limited oil resources and the requirements of the environment protection. Development of motor fuel production processes on the basis of promising types of plant oils is being a subject of intensive research nowadays (Demirbas, 2008). The investigations focus on the production of first generation biodiesel, which is methyl or ethyl esters of the fatty acids present in vegetable oils. The transesterification process most effectively proceeds in the presence of homogeneous catalysts and, as such, is less economical because of the very costly steps of catalyst recovery from the product mixture and its utilization. Another significant disadvantage of this technology is the problem of utilization of significant amounts of the byproduct glycerol containing esterifying agents (methanol, ethanol) as impurities. The problem of isolation of glycerol free of the impurities of the esterifying alcohols can be solved with the use of a three stage process, according to which oils are saponified at the first stage to yield watered glycerol and salts of the corresponding fatty acids, after which the acids are converted into the H-form and subjected to hydrogenation (Mäki-Arvela et al., 2011).

2. Materials and Methods

For catalytic experiments the commercial Pd-Zn/MFI/ γ -alumina catalyst was used containing 0.6 wt% Pd and 1 wt% Zn; Si/Al = 60 (Slivinskiy et al., 2003) and the AP-64 commercial alumina–platinum catalyst (~0.6 wt % Pt/ γ -Al₂O₃; specific surface area, ~200 m²/g; pore volume, 0.65 cm³) was used as well. Both gaseous and liquid organic products in aqueous and organic phases were identified by GC-MS. Catalyst testing was performed in a PID Eng & Tech microcatalytic fixed-bed flow reactor unit, equipped with relevant instrumentation and control devices, in a hydrogen stream providing a molar excess of 10:1 relative to the substrate introduced at a temperature of 360–420 °C, a pressure of 50 atm, and a rape oil space velocity in the range of 0.6–2.4 h⁻¹. The starting material was rapeseed oil manufactured by the “ORELRASMASLO” containing triglycerides of next fatty acids (wt. %): C₁₇H₃₅COOH (2.0-5.0), C₁₇H₃₃COOH (50.0-55.0), C₁₉H₃₇COOH (8.0-10.0), C₂₁H₄₁COOH (30.0-35.0) (oil 1) manufactured by the “Rossiiskie semena” containing triglycerides of next fatty acids (wt. %): C₁₇H₃₅COOH (2.0-5.0), C₁₇H₃₃COOH (90.0-95.0), C₁₉H₃₇COOH (1.0-2.0), C₂₁H₄₁COOH (~0.2) (oil 2).

3. Results and Discussion

3.1. Rapeseed oil conversion over PdZn/MFI/Al₂O₃

The experimental data showed that rape oil in the presence of the PdZn/MFI/Al₂O₃ catalytic system exhaustively transforms into an alkane–aromatic hydrocarbon fraction up to C₁₂ containing an insignificant amount of olefins; the products composition obtained under found optimal conditions providing the maximal yield of aim fraction of hydrocarbons C₃–C₁₂ is presented in Table 1.

Table 1: Composition of products of rape oil conversion under optimal conditions

| Rape oil conversion products | Product composition, wt % | |
|--|-----------------------------|----------------------------|
| | 360°C , 1.2 h ⁻¹ | 420°C, 2.4 h ⁻¹ |
| C1 | 0.54 | 1.04 |
| C2 | 4.89 | 4.83 |
| C2= | 0.18 | 0.32 |
| C3 | 11.71 | 10.79 |
| C3= | 0.37 | 0.75 |
| iso-C4 | 9.50 | 5.88 |
| n-C4 | 5.30 | 2.19 |
| C4= | 1.49 | 1.81 |
| iso-C5 | 9.91 | 4.52 |
| n-C5 | 2.60 | 1.46 |
| C5= | 0.66 | 1.12 |
| 2,3-Me-C4 | 1.09 | 0.45 |
| iso-C6 | 2.04 | 0.94 |
| n-C6 | 3.40 | 0.72 |
| Benzene | 7.04 | 6.56 |
| Toluene | 16.92 | 18.42 |
| Ethylbenzene | 3.79 | 4.81 |
| <i>o,p</i> -Xylene | 9.24 | 13.06 |
| <i>m</i> -Xylene | 2.23 | 3.15 |
| Propylbenzene | 0.00 | 0.94 |
| Methylethylbenzene | 4.16 | 5.93 |
| 1,2,3-Trimethylbenzene | 0.80 | 1.40 |
| Methylphenylethylene | 0.61 | 1.01 |
| 1,2-Diethylbenzene | 0.00 | 1.61 |
| α -Phenyl- β -ethylethylene | 0.00 | 0.96 |
| Naphthalene | 0.00 | 1.16 |
| α -Methylnaphthalene | 0.63 | 1.40 |
| CO | 0.58 | 2.55 |
| CO ₂ | 0.33 | 0.21 |
| Σ | 100.00 | 100.00 |

It is interesting that during the oil conversion process, no aliphatic hydrocarbons with the carbon number greater than 6 are formed, a peculiarity that seems to be due to the specific structure of the test zeolite. The main products of the reaction are C₄–C₈ hydrocarbons, and their total content is 62 wt %, which is

most likely caused by the specific structural features of the zeolite (Table 1). The presence of heavier aromatic compounds suggests defectiveness of the zeolite pore structure (Minachev et al, 1966). At the same time, an almost complete lack of sensitivity to the impact of heat on the formation of aromatic hydrocarbons with the increasing temperature allows for the assumption that the cyclization reaction occurs via the so called "hydrocarbon pool" mechanism described previously by the example of production of an identical alkane–aromatic fraction from methanol and ethanol (Seiler et al., 2003).

To determine the contribution of the processes of decarbonylation and decarboxylation of the acid moieties of rape oil fatty acid triglycerides and to reveal what is the conversion product the RO glycerol residue, we performed comparative analysis of the amount of carbon (mole of C atoms) and oxygen (mole of O atoms) introduced into the reaction and obtained as a result of catalysis. Tables 2 and 3 present the results in terms of millimoles of C and O atoms in the ester moiety of FATG and in the products of the catalytic reaction. From the data in Table 2, it is seen that during the course of conversion of fatty acid triglycerides (FATG), the decarboxylation of the acid residue at 360 °C is not intense, since the yield in number of moles of C atoms in carbon monoxide and dioxide is less than one tenth of the theoretical yield. The elevation of temperature to 420 °C significantly intensifies the formation of CO; its yield in moles of C atoms is approximately one third of the theoretically value. Table 3 shows that oxygen contained in the FATG molecule mainly transforms into water, thereby suggesting a high contribution of the C–O bond hydrogenation reaction.

At the initial steps of FATG conversion, the decarbonylation and decarboxylation of the acid residues are likely to proceed, being followed by reduction of the forming carbon oxides to methane; however the total yield of methane and carbon oxides is 20 mol % of the theoretically value at 360°C and 50 mol% at 420°C. The amount of propane obtained in both of the cases is in two times the amount that can form from glycerol introduced into the system. The whole variety of these findings allows for the conclusion that the reduction (hydrogenation) of C–O bonds and the subsequent cracking of the forming carbon fragments are the most intense processes in the presence of PdZn/MFI/Al₂O₃ and the contribution of the decarbonylation and decarboxylation reactions increases with the increasing temperature.

The service life tests of the PdZn/MFI/Al₂O₃ catalyst showed that the exhaustive conversion of rape oil is achieved within 50 h and the selectivity for the target alkane–aromatic fraction is conserved. Such operation stability of the catalytic system can be explained by its structural peculiarities and hydrogenating activity of Pd-containing active components, which impede the formation of condensation products on the catalyst surface.

Table 2: Amount of carbon atoms (mmole) in acid and glycerol moieties passed through the catalyst bed during experiment

| Fed | 360°C, 1.2 h ⁻¹ | 420°C, 2.4 h ⁻¹ |
|--|----------------------------|----------------------------|
| mmoles of C atoms from glycerol | 35.03 | 67.61 |
| mmoles of carboxylic C atoms | 35.03 | 67.61 |
| Σ | 70.06 | 135.22 |
| Obtained | | |
| mmoles of C atoms from CH ₄ | 3.09 | 12.40 |
| mmoles of C atoms from C ₂ H ₆ | 29.92 | 61.39 |
| mmoles of C atoms from C ₃ H ₈ | 73.22 | 140.40 |
| mmoles of C atoms from CO | 1.91 | 17.40 |
| mmoles of C atoms from CO ₂ | 0.69 | 0.91 |
| Σ | 108.83 | 232.5 |

Glycerol residue of FATG is supposed to be completely transformed into the propane fraction. The increased amount of C₃ hydrocarbons in comparison with the theoretically predicted yield of their formation from glycerol suggests the occurrence of the secondary cracking of alkanes, since an increase in the propane yield at an elevated temperature (420 °C) is accompanied by a decrease in the amount of aliphatic hydrocarbons. The FATG transformation products primarily contain alkylaromatic compounds, which can be products of condensation of the carbon compounds formed as a result of cracking of the initial aliphatic chains of fatty acids. Zinc containing active components are known to display high activity in transformation of alkanes (Seiler et al., 2003) and olefins (Slater, 1964) into alkylaromatic compounds. It

can be assumed that it is on the zinc containing active components that the condensation of the carbon products of cracking proceeds via the hydrocarbon pool mechanism. The sieving effect of the zeolite support is manifested in the formation of the principal C₄–C₈ fraction. The composition of alkanes in the liquid fraction is limited to C₆, and the proportion of branched paraffins in them reaches 80%. Such a high concentration of branched alkanes is due to the superacidic properties of the zeolite support (A. Corma, 1997). The composition and yield of the aromatic compounds is almost independent of the process temperature, thereby indicating that the stage of their formation is fast. This conclusion is also confirmed by the increase in their yield with the decreasing space time. It is quite likely that as the space velocity increases and, hence, the space time decreases, the contribution of the secondary cracking and hydrogenation processes of the saturated carbon chains decreases, leading to an increase in the yield of mainly aromatic hydrocarbons. The high hydrogenating ability and close location of the hydrogenation and cyclization sites on the surface ensure stable operation of the catalyst in time as a result of effective hydrogen transfer hindering the build-up of condensation products.

Table 3: Amount of oxygen atoms (mmole) in ester groups passed through the catalyst bed during experiment

| Fed | 360°C, 1.2 h ⁻¹ | 420°C, 2.4 h ⁻¹ |
|---|----------------------------|----------------------------|
| mmoles of O atoms | 70.06 | 135.23 |
| Obtained | | |
| mmoles of O atoms from H ₂ O | 66.68 | 115.38 |
| mmoles of O atoms from CO | 1.91 | 17.40 |
| mmoles of O atoms from CO ₂ | 1.38 | 1.81 |
| Σ | 69.97 | 134.59 |

3.2. Rapeseed oil conversion over Pt/Al₂O₃

In the present work revealed that the industrial platinum alumina catalyst Pt/Al₂O₃ after exposure (12-14 h.) in a hydrogen atmosphere at 450 °C completely changes the selectivity of the reaction of reductive fatty acids triglycerides (FATG) deoxygenation, leading to the formation of a narrow fraction of alkanes.

In the presence of the pretreated in hydrogen sample of Pt/Al₂O₃ under 420 °C and flow rate 0.6 h⁻¹ oil 1 and oil 2 completely converted to alkanes C₁–C₂₃₊ with the release of a stoichiometric amount of water - 6-7 % by weight. The content of gaseous hydrocarbons C₁–C₃ is 4-7 wt.%. Figure 1 shows that the oil 1 converts mainly into C₁₇, the yield of which reaches up to 64 wt.%. And the conversion of oil 2 leads to the predominant formation of C₁₇ and C₂₁, the total output of which is 48 wt.%. Figure 1 also shows that in addition to the main components of the original oil forms high-alkanes with carbon atoms number up to C₂₈ (oil 1) to C₃₁ (oil 2) in quantity of 3.0-5.0 wt.%. Alkanes fraction C₂₃₊, apparently formed by embedding the carbon skeleton of glycerol fragment in one of the forming hydrocarbons.

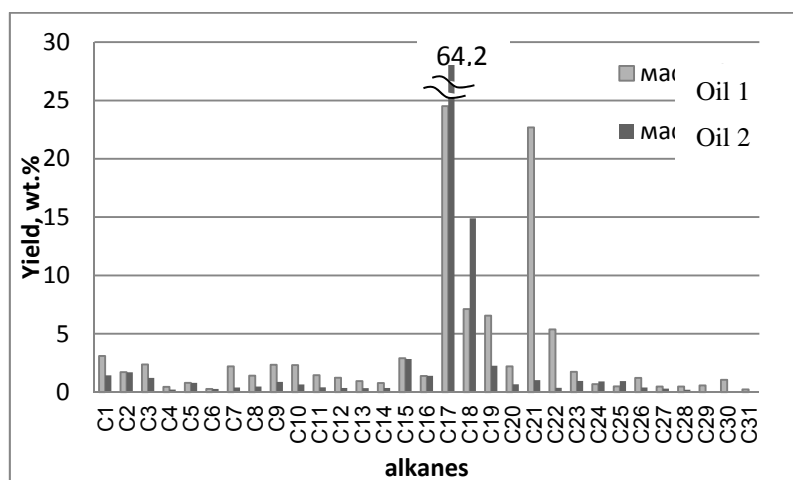


Figure 1: Alkanes composition obtained via rapeseed oil conversion over pretreated in hydrogen Pt/Al₂O₃ catalyst.

The absence in the IR spectra of the reaction products of the absorption bands belonging to groups of CO ($1,200\text{ cm}^{-1}$) and CO_2 ($1,750\text{ cm}^{-1}$) shows that both types of rapeseed oil in the deoxygenation in the presence of $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst completely converted into alkanes and water.

Besides the basic alkanes produced by reduction and decarboxylation of oil acyl fragments other products are formed, the composition of which is represented on continuous broad spectrum. These alkanes occur, probably as a result of hydrocracking of primary forming hydrocarbons.

The composition of the conversion products of both oils over pretreated catalyst $\text{Pt}/\text{Al}_2\text{O}_3$, changes little in the course of long experience over 40 h of continuous operation.

Figure 2 shows that, by varying the temperature, it is possible to obtain from rapeseed oil in one step primarily gasoline and diesel fractions. The results of long-term experience has shown that the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst without reductive pretreatment, as expected, in the first 28 h of operation at 420°C and 50 atm H_2 exhibits not only a high hydrogenation activity, but actively crack C-C bonds and isomerizes forming alkanes. The yield of light alkanes $\text{C}_1\text{-C}_3$ did not exceed 21.0 wt.% at first few hours of operating. However, the activity and selectivity of the catalyst for change, and after 28 hours of makeup goes to steady state, the same (in performance) is observed in the case of the catalyst subjected prolonged reduction treatment (Figure 3).

With exhaustive conversion of the initial FATG fraction $\text{C}_4\text{-C}_{23+}$ yield reaches up to 85.0-90.0 wt.% calculated on the weight of the carbon feedstock. Yield of gaseous hydrocarbons in the steady state does not exceed 5.0-6.0 wt.%. Among liquid products prevails alkane C_{17} , and among the gases - methane and ethane, the number of which (based on carbon) corresponds approximately to the expected mole quantity of the carboxy-groups in the feeding fatty acids. After the first 28 hours of work, the formation of heavy oil fraction alkanes $\text{C}_{23} - \text{C}_{28}$ took place that indicates a possible intramolecular condensation of the carbon skeleton of glycerol and acyl fragments of FATG.

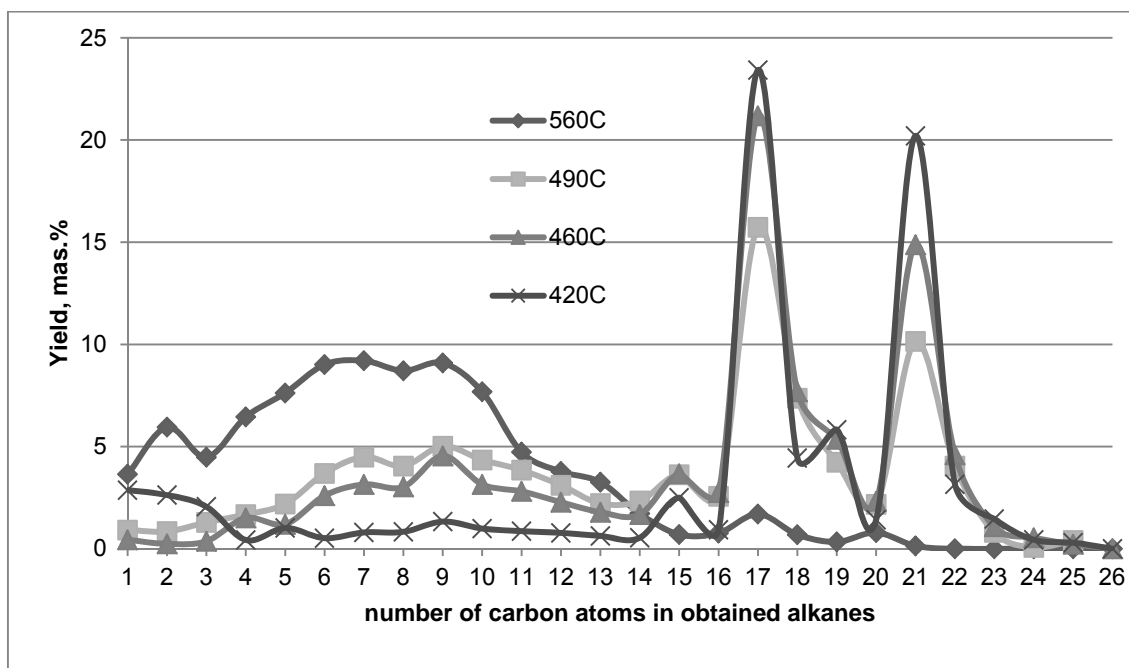


Figure 2: The dependence of alkanes composition obtained via rapeseed oil conversion over pre-treated in hydrogen $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst on process temperature.

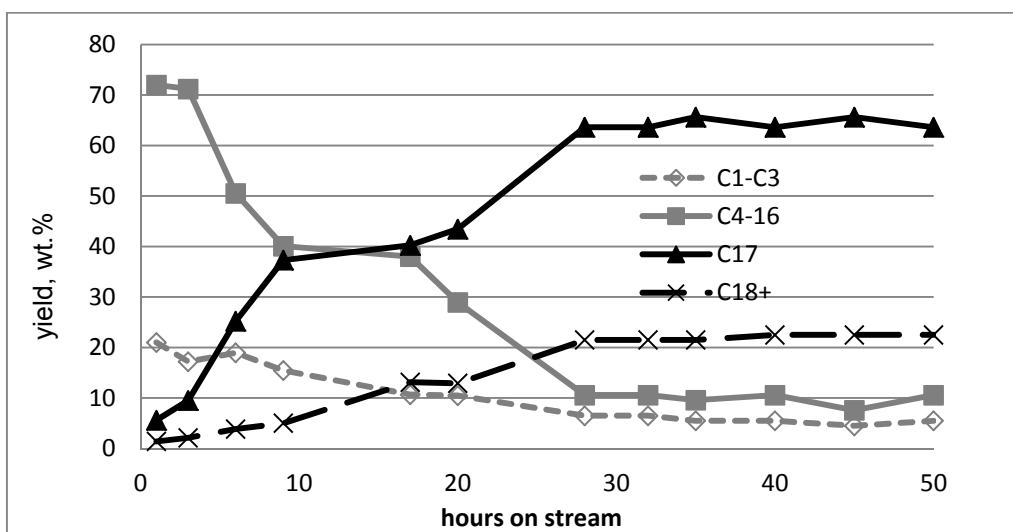


Figure 3: Evolution of main products fractions obtained via rapeseed oil conversion over initial Pt/Al_2O_3 catalyst during long-term experiment.

4. Conclusions

Obtained results show the new properties of well-known industrial Pt/Al_2O_3 and $PdZn/MFI/Al_2O_3$ catalysts. Application of Pt/Al_2O_3 allows to improve the efficiency of rape oil conversion towards valuable hydrocarbons in comparison with Ni containing catalysts described by Mikulec J. et al., 2009 and Kovács S. et al., 2010 due to realization of process in one step and also reducing the loss of valuable carbon mass via glycerol and acyl fragments condensation. Over $PdZn/MFI/Al_2O_3$ catalyst rape oil was converted into alkanes-aromatics fraction of hydrocarbons C_3-C_{11} that may be considered as high-octane additive to gasoline. Based on experimental data glycerol residue of FATG is supposed to be completely transformed into the propane fraction.

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