# Combined Conversion of Ethanol and Vegetable Oils to Hydrocarbons

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The present study presents combined ethanol and rapeseed oil conversion to $C_4$-$C_{12}$ hydrocarbons via a one-step hydrogen-free catalytic process. As a catalyst an industrial Pd-Zn/$Al_2O_3$/MFI sample was used. The novelty of the suggested process resides in the combined conversion of rapeseed oil and ethanol (fermentation mixtures) in an inert atmosphere without external molecular hydrogen that is usually used for vegetable oils conversion. Our previous study showed that ethanol conversion over the Pd-Zn/$Al_2O_3$/MFI catalyst led to the formation of a surplus amount of hydrogen (Chistyakov et al., 2013a) that may be used for hydrogenolysis of the C-O bonds of fatty acids triglycerides during the combined conversion.

In this work shown that the combined conversion produced significantly larger amounts of olefins and aromatics in comparison with conversion of pure ethanol. It is also shown that an initial concentration of 25-50 % of ethanol in the feed is optimal for the combined conversion. This amount of alcohol is sufficient to donate enough hydrogen to the system during conversion for a stable and smooth catalyst work while preventing coke formation. Fermentation mixtures and fusel oils were used for the combined conversion with rapeseed oil as well as ethanol.

## 1. Introduction

The search for economic routes for the production of petrochemicals and engine fuel components from primary biomass processing products is a topical challenge. In the recent years, researchers' attention has been drawn to the chemistry of alcohols obtained by fermentation of plant carbohydrates and lipids produced by diverse agricultural crops, fungi and micro algae (Demirbas, 2008).

The investigations were mainly focused on the production of the first generation biodiesel, which is methyl or ethyl esters of fatty acids. The transesterification process most effectively proceeds in the presence of homogeneous catalysts that made it less economical because of the very costly steps of catalyst recovery from the product mixture. Another significant disadvantage of this technology is the problem of utilization of significant amounts of 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 in 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). The main drawback of these methods is the necessity for additional external hydrogen. Since the absence of hydrogen is linked with a rapid deactivation of the catalysts by coking. Ethanol conversion over the Pd-Zn/$Al_2O_3$/MFI catalyst led to the formation of a surplus amount of hydrogen. The efficiency of this process was proposed to convert vegetable oils and ethanol (fermentation mixtures) together in an inert atmosphere without external molecular hydrogen addition.

## 2. Materials and Methods

For the catalytic experiments, the commercial Pd-Zn/MFI/γ-alumina catalyst was used. It contains 0.6 wt.% Pd and 1 wt.% Zn; Si/Al = 60 (Slivinskiy et al., 2003). Both gaseous and liquid organic products in the aqueous and organic phases were identified by GC-MS. The catalyst testing was performed in a PID Eng & Tech microcatalytic fixed-bed flow reactor unit, equipped with relevant instrumentation and control devices in order to keep the pressure 5 atm of Ar and the temperature in the 380–420 °C range, and substrates space velocity in the range of 0.6–2.4 $h^{-1}$. The starting material was rapeseed oil manufactured by the "Rossiiskie semena" containing triglycerides of following fatty acids (wt. %): $C_{17}H_{35}COOH$ (2.0-5.0), $C_{17}H_{33}COOH$ (50.0-55.0), $C_{19}H_{37}COOH$ (8.0-10.0), $C_{21}H_{41}COOH$ (30.0-35.0), pure ethanol and a mixture of alcohols that simulates biomass fermentation products (80 % ethanol , 5 % propanol , butanol, 5 %, 10 % isoamyl alcohol). Substrate composition was varied from 25 % rapeseed oil to 75 % of rapeseed oil.

## 3. Results and Discussion

### 3.1 Combined conversion of ethanol and rapeseed oil

Combined conversion of ethanol and rapeseed oils produced greater amount of olefins and aromatics in comparison with the composition of the products obtained from pure ethanol. The optimal conditions providing the maximal yield of the aim $C_3$-$C_{11}$ hydrocarbons fraction were found as T=350°C, VHSV=0.6, as well as T=420°C, VHSV=1.8, rapeseed oil to ethanol ratio 1:3 for pure ethanol and a mixture of ethanol and rape oil, respectively. The yield of light $C_1$-$C_2$ hydrocarbons did not exceed 5 wt.%. The carbon containing products composition obtained under the aforementioned conditions is presented in Table 1.

*Table 1: Composition of carbon containing products obtained using respective optimal conditions*

| Conversion products | Product composition, wt.% | |
|---|---|---|
| | Ethanol | Mixture of ethanol and rapeseed oil |
| Aliphatic components | | |
| C1 | 0.19 | 0.21 |
| C2 | 3.95 | 0.82 |
| C2= | 0.42 | 4.55 |
| C3 | 13.71 | 4.59 |
| C3= | 0.56 | 6.35 |
| C4 | 21.37 | 5.79 |
| C4= | 0.74 | 7.24 |
| C5 | 12.98 | 2.49 |
| C5= | 0.00 | 2.14 |
| C6 | 3.44 | 0.00 |
| C7 | 1.34 | 0.00 |
| Aromatic components | | |
| C6 | 1.11 | 4.16 |
| C7 | 9.01 | 19.71 |
| C8 | 14.15 | 29.73 |
| C9 | 11.47 | 4.84 |
| C10 | 5.26 | 3.20 |
| α-Methylnaphthalene | 0.00 | 1.84 |
| CO | 0.00 | 2.08 |
| CO2 | 0.30 | 2.41 |
| Σ | 100.00 | 100.00 |

It is interesting to note that during the oil conversion process, no aliphatic hydrocarbons with carbon numbers largerer than 5 were formed. This particularity seems to be due to the specific structure of the

tested zeolite. The main products of the reaction are $C_4$–$C_8$ hydrocarbons, and their total content is 62 wt.%, which is most likely caused by the specific structural features of the zeolite (Table 1). Importantly, the yield of light hydrocarbons $C_1$-$C_2$ did not exceed 5 wt. %. When the temperature was increased of from 330 to 420 °C during the pure ethanol conversion process, the $C_1$-$C_2$ hydrocarbons fraction yield was increased up to 20 wt.%. The phenomenon of decrease in gaseous alkanes yield by adding to ethanol co-reagent with largerer molecular weight was previously observed in cross-coupling reaction of glycerol and ethanol in the presence of Re-W, Re-Ta - containing catalytic systems. It can be assumed that the higher molecular weight intermediates formed during the conversion of oil are competitively chemisorbed on the active catalyst sites and react with an alcohol molecule, involving its in carbon chain growth. Absence of aliphatic hydrocarbons $C_6$ and $C_7$, which have been found for the conversion of pure ethanol confirm this as well.

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 an increase of temperature on the formation of aromatic hydrocarbons allows doing the assumption that the cyclization reaction occurs via the so called "hydrocarbon pool" mechanism previously described for the example for the production of an identical alkane–aromatic fraction from methanol and ethanol (Seiler et al., 2003).

As in the case of rapeseed oil conversion (Chistyakov et al, 2013b) among aromatic products dominated toluene, xylenes, that indicates a vigorous reaction takes place according to the mechanism of hydrocarbon pool in the pores of the zeolite. A small amount of methylnaphthalene, as noted earlier, probably formed by the defects of the zeolite structure.

Except hydrocarbons, carbon oxides were also detected in the reaction products. Carbon oxides may be both issued from aliphatic alcohols transformation products and in this case, they are a source of additional hydrogen, or produce by decarbonylation/decarboxylation of rapeseed oil triglycerides and in this case consumption of the hydrogen is reduced.

Tests made varying the content of oil in the mixture show that, with increasing the oil content from 25 to 75 vol.% the aromatics content in the reaction products is increased from 40 to 60 wt.%. The olefins content is also increased from 7 to 22 wt.%. Eventually, for a mixture containing 75 vol.% of rapeseed oil alkanes content is 5 wt.%. It is important to note that molecular hydrogen content decreases either.

Thus optimum is for less than 50 vol.% of rapeseed oil in the feed. When increasing the content of rapeseed oil rapid coking of the catalyst is possible.

Long-terms run on the PdZn/MFI/Al$_2$O$_3$ catalyst were carried out for a mixture of ethanol and oil at optimum conditions. It was showed that the exhaustive conversion of the substrates was achieved during 50 h and the selectivity to the aim alkane–aromatic fraction was constant. Such operation stability of the catalytic system can be explained by its structural particularities and by the hydrogenating activity of Pd-containing active components, which impede the formation of condensation products on the catalyst surface (Chistyakov et al, 2013b).

### 3.2 Combined conversion of rapeseed oil and a fermentation mixture

The conversion of an alcohols mixture simulating biomass fermentation products with rapeseed oil was studied in the presence of the Pd-Zn/MFI/γ-alumina catalyst as well. The optimal conditions providing the maximal yield of the aim $C_3$-$C_{12}$ hydrocarbons fraction were T = 330°C and VHSV = 1.2 (for aliphatic hydrocarbons production), as well as T = 420°C and VHSV = 1.2 (for aromatics production) for a rapeseed oil to alcohols ratio of 1:3. The products composition obtained via fermentation mixture conversion under optimal conditions is presented in Figure 1. Aromatic components yields are shown separately in Table 2. The composition of hydrocarbon products of combined conversion of the alcohols mixture and rapeseed oil obtained under optimal conditions is presented in Figure 2. The aromatic components yields are shown separately in Table 3.

In the case of the alcohols mixture conversion, the alkane-aromatic fraction yield reached 90 wt.%. Wherein the main component of the initial mixture is ethanol, which includes only two carbon atoms, among alkane predominant products, butanes are found, and the yield of $C_1$ and $C_2$ alkane is approximately 5 wt.%. The obtained data suggest the possibility of inter molecular cross-coupling reaction of alcohols fragments.

Among the aromatic products, toluene and xylenes are the main products, which indicates that a vigorous reaction takes place according to the hydrocarbon pool mechanism in the pores of the zeolite.

Changes occurring during the combined conversion of fermentation products and rapeseed oil are similar to those observed in the case of ethanol and rapeseed oil combined conversion. Namely, in the products the amount of olefins increases, and aliphatic hydrocarbons $C_7$ are not detected at all. The yield of light hydrocarbons is also significantly reduced despite the elevated temperature. The obtained data suggest the possibility of inter molecular cross-coupling reaction between alcohols fragments and acid fragments.

Stability tests of the PdZn/MFI/Al$_2$O$_3$ catalyst were carried out for a fermentation mixture and the rapeseed oil under optimal conditions. It was found that full conversion of the substrates is achieved during 50 h and that the selectivity to the target alkane–aromatic fraction is kept constant.
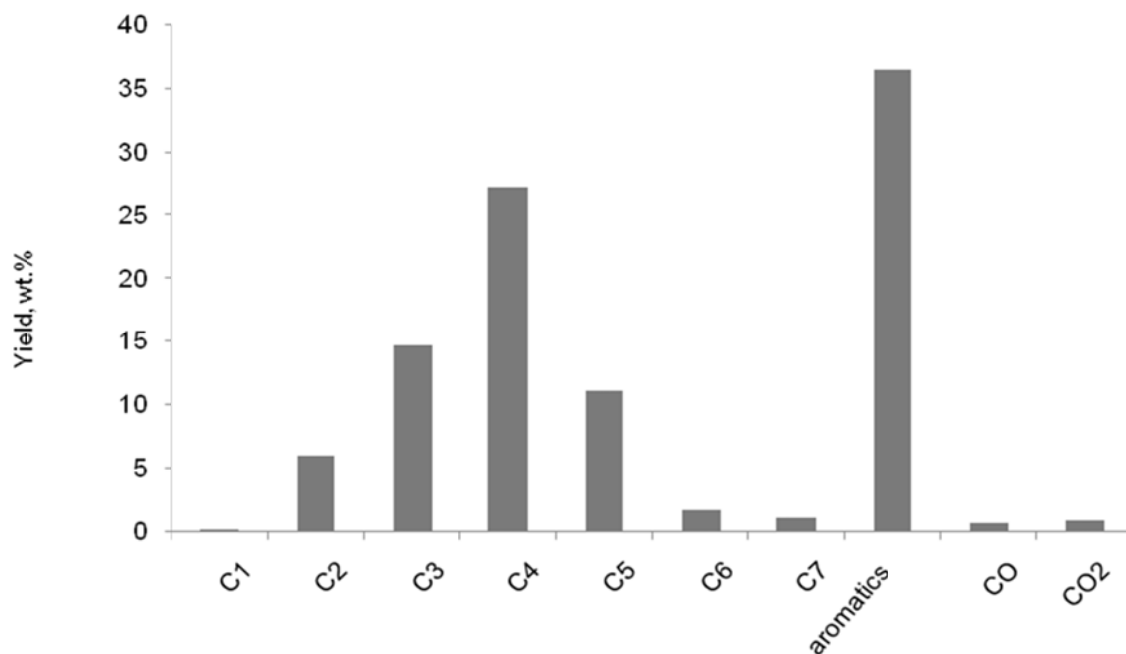


Figure 1: Composition of carbon containing products obtained via a fermentation mixture conversion under optimal conditions
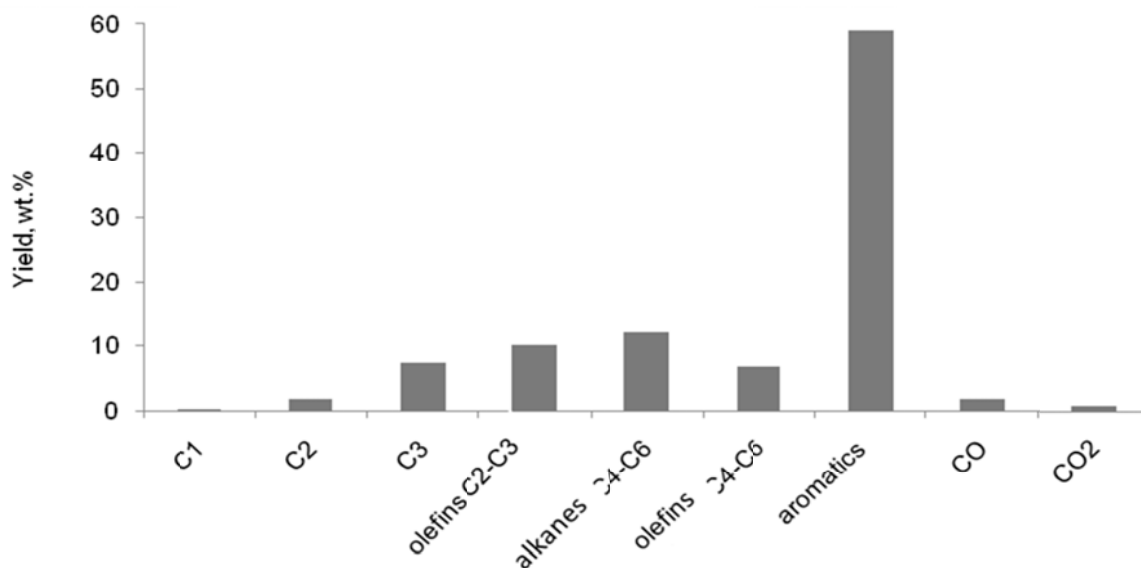


Figure 2: Composition of carbon containing products obtained via the combined conversion of rapeseed oil and a fermentation mixture

*Table 2: Aromatic products yields of an alcohols mixture conversion obtained under optimal conditions*

| Component | Yield, wt.% |
|---|---|
| Benzene | 0.42 |
| Toluene | 7.98 |
| m-Xylene | 2.93 |
| o,p-Xylene | 8.83 |
| **ΣBTX** | **20.17** |
| ethylbenzene | 2.10 |
| methylethylbenzene | 7.75 |
| trimethylbenzene | 2.90 |
| diethylbenzene | 2.29 |
| dimethylethylbenzene | 1.19 |
| **Σ** | **36.4** |

*Table 3: Aromatic products yields obtained from the combined conversion of rapeseed oil and a fermentation mixture under optimal conditions*

| Component | Yield,% wt. |
|---|---|
| Benzene | 6.41 |
| Toluene | 18 |
| m-Xylene | 3.08 |
| o,p-Xylene | 12.77 |
| **ΣBTX** | **40.26** |
| ethylbenzene | 4.7 |
| propylbenzene | 0.92 |
| methylethylbenzene | 5.8 |
| trimethylbenzene | 1.37 |
| methylstyrene | 0.99 |
| diethylbenzene | 1.58 |
| Ethylstyrene | 0.94 |
| Naphthalene | 1.13 |
| methylnaphthalene | 1.37 |
| **Σ** | **59.06** |

## 4. Conclusions

On the basis of the obtained results, it may be concluded that combined conversion of ethanol (fermentation mixtures) and rapeseed oil produced significantly greater amount of olefins and aromatics in comparison with the composition of the products obtained by conversion of pure ethanol. Such products may be considered as sulphur- and nitrogen-free additives to Euro-3 or Euro-4 gasoline. The yield of light $C_1$-$C_2$ hydrocarbons did not exceed 5-7 wt.%. The decrease in the gaseous alkanes yield by adding to the alcohol substrate a co-reagent with a greater molecular weight was previously observed in the cross-coupling reaction of glycerol and ethanol over Re-W- and Re-Ta-containing catalytic systems (Chistyakov et al., 2011). It can be assumed that the higher molecular weight intermediates formed during the conversion of oil is competitively chemisorbed on the active catalyst sites and react with an alcohol molecule, involving its carbon chain growth.

Among the conversion products, toluene, xylenes and trimethyl benzene are the main products, which indicates that a vigorous reaction takes place according to the hydrocarbon pool mechanism in the pores of the zeolite. A small amount of methylnaphthalene, as noted earlier, is probably formed on the defects of the zeolite structure.

An initial concentration of ethanol of 25-50 Vol.% is optimal for the combined conversion process. That amount of the alcohol donates enough hydrogen to the system during conversion for stable work , while preventing coke formation. If a fermentation mixture and fusel oil as a co-reagents with rapeseed oil ar used, then, optimal concentration of rapeseed oil in the feed decreased to 25 and 15 Vol.%, respectively.

Carbon oxide and dioxide yields did not exceed 5 wt.% in the considered catalytic experiments. This means that the reaction of C-O bonds hydrogenolysis is more intensive in comparison with the reaction of decarboxylation of rapeseed oil acidic fragments. So, the PdZn/MFI/Al$_2$O$_3$ catalyst may be considered as prospective for biomass products utilization towards hydrocarbons due to intensive hydrogen redistribution. Moreover, stability tests showed that the catalyst kept constant activity and selectivity during 50 h on stream in combined conversion process.

Application of PdZn/MFI/Al$_2$O$_3$ allows improving the efficiency of rapeseed 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 without additional hydrogen consumption.

## Acknowledgements

## References

Chistyakov A., Murzin V., Gubanov M., Tsodikov M., 2013, Pd-Zn Containing Catalysts for Ethanol Conversion Towards Hydrocarbons, Chemical Engineering Transactions, 32, 619-624**.**

Demirbas A., 2008. Biodiesel: A realistic fuel alternative for diesel engines, Springer-Verlad London Ltd., London, United Kingdom.

Mäki-Arvela P., Rozmyslowicz B., Lestari S., Simakova O., Eränen K., Salmi T., Murzin D.Yu., 2011, Catalytic Deoxygenation of Tall Oil Fatty Acid over Palladium Supported on Mesoporous Carbon, Energy and Fuels, 25, 2815-2825.

Patent RU 2248341, Catalyst, method of its creation and production of gasoline, Moscow, 2003 (in Russian)

Minachev Kh. M., Garanin V. I., Isakov Ya. I., 1966, The use of synthetic zeolites (molecular sieves) in catalysis (in Russian), Uspehi Khimii, 35, 2151-2177.

Seiler M., Wang W., Buchholz A., Hunger M., 2003, Direct evidence for the catalytically active role of the hydrocarbon pool formed on zeolite H-ZSM-5 during the methanol to olefin conversion, Catalysis Letters, 88, 187-191.

Chistyakov A., Gubanov M., Tsodikov M., 2013, The Direct Conversion of Rapeseed Oil Towards Hydrocarbons over Industrial Catalysts, Chemical Engineering Transactions, 32, 1093-1098.

Mikulec J., Cvengros J., Joríková L., Banic M., Kleinová A., 2009, Diesel production technology from renewable sources – second generation biofuels, Chemical Engineering Transactions, 18, 475-480.

Kovács S., Boda L., Leveles L., Thernesz A., Hancsók J., 2010, Catalytic Hydrogenating of Triglycerides for the Production of Bioparaffin Mixture, Chemical Engineering Transactions 21, 1321-1326.

Chistyakov A., Tsodikov M., Chudakova M., Gekhman A., Moiseev I., Luck F., 2011, New aspects of bioethanol one-step catalytic conversion into fuel components, Chemical engineering transactions, 24, 175-180.