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Studies on the Direct Hydrocracking of Fatty Acid Triglycerides on Ni–Cu/CeO_2–ZrO_2 Catalyst

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Abstract

The reaction of catalytic hydrocracking the triglycerides of fatty acids from rapeseed oil with obtaining a mixture of C_{12}–C_{19} alkanes on Ni–Cu/CeO_2–ZrO_2 catalyst under mild conditions (0.5 MPa H_2, 300–380 °C) was studied. Basing on the distribution of hydrocracking products at different contact time and temperature values, a scheme is proposed for stepwise hydrocracking the triglycerides of fatty acids that takes into account the formation of oxygen-containing intermediate products (fatty acids, esters, alcohols, and waxes).

Key words: catalyst, hydrocracking, green diesel, hydrocarbon species

INTRODUCTION

Owing to the fact that the world oil and gas resources are exhaustible the production of motor fuel from renewable phytogenous raw material becomes increasingly important. According to the forecasts, the global energy consumption will increase, including the production of biofuel. [1] Currently, the widest application is found by two types of biofuel such as biodiesel and bioethanol.

Bioethanol is produced mainly from sugar cane and corn, as well as other crops with high starch or sugar, cassava, potatoes, sugar beets, sweet potatoes, sorghum and barley. The production of fuel purpose bioethanol in 2005 reached 36.3 billion litres [1]. Moreover, when the bioethanol is used as a supplement to traditional gasoline, biodiesel is added to diesel fuel.

Biodiesel is a mixture of fatty acid methyl esters obtained by re-esterification of vegetable and animal fats with methanol. The range of raw materials used to produce biodiesel, is permanently expanding. So, biodiesel is produced from rapeseed in Europe, from soy in the USA, from canola (rapeseed variety) in Canada, from palm oil in Indonesia and the Philippines, from castor oil in Brazil, from jatropha in India; waste oil, animal fat, fish oil are widely used. Biodiesel production in the EU countries in 2008 amounted to about 16 million ton [1].

It should be noted that vegetable oil could not be used directly as a fuel due to a high viscosity and an increased tendency to carbon deposition.

Apart from the fact of producing the biodiesel from vegetable oils (triglycerides of fatty acids) one could obtain another type of biofuel such as green diesel via hydrocracking fatty acid triglycerides. Green diesel represents a mixture of several isomers of C_{12}–C_{18} alkanes with a high cetane number; it is used as an additive to common diesel fuel. The first mention concerning the process of hydrocracking vegetable oil species with obtaining carboxylic acids, propyl esters and alkanes was described by the authors of [2] in 1989.

The authors of [2] used an 8.3 % Ni/SiO_2 catalyst for the hydrocracking of soybean oil.

The process was carried out at 450 °C and at the pressure of H_2 amounting to 1.5 and 3.0 MPa. The main products of hydrocracking were carboxylic acids (47.9 mass %), C_5–C_{18} saturated and unsaturated hydrocarbon species (16.0 mass %), CH_4 (33.5 mass %). It is obvious that the formation of methane in significant amounts represents an undesirable process, and the yield of alkanes was low.

The authors of [3] investigated the process of rapeseed oil catalytic cracking within the temperature range of 485–585 °C and atmospheric pressure on the catalyst E_{cat}/ZSM-5 (E_{cat} is a commercial catalyst, E_{cat} mass fraction – 80 %, ZSM-5 – 20 %) using a flow-through reactor.

The cracking products included gasoline fraction (C_5, b. p. 215 °C), light cyclic oil species (215–325 °C), and heavy cyclic oil (>325 °C). Heavy cyclic oil species were fractionated into four components: 1) b. p. = 325–360 °C, 2) fatty acids (360–400 °C), 3) intermediate components (400–520 °C), and 4) triglycerides (>520 °C). The gasoline fraction consisted of *n*-paraffins, isoparaffins, naphthenes, *n*-olefins, isoolefins as well as aromatic compounds with boiling point amounting up to 200 °C. Yield of gasoline fraction was equal to about 60 mass %, whereas that of isoparaffins (C_5–C_{11}) was of about 30 mass %.

In addition, for the hydrocracking of rapeseed oil one can use sulphided catalysts Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 traditional for oil industry [4–6]. When vegetable oil with low sulphur content is used as a source raw material the sulphided catalysts rapidly lose sulphur to be reduced and deactivated. Consequently, the efficient hydrocracking vegetable oils requires for non-sulphide catalysts to use.

Earlier [7, 8] it was demonstrated that Ni–Cu/CeO_2–ZrO_2 catalyst is active in the process of biodiesel hydrodeoxygenation under mild conditions (1.0 MPa H_2, 360 °C). It seemed appropriate to investigate the direct hydrocracking of fatty acid triglycerides (FATG) by the example of rapeseed oil in the presence of a catalyst to produce green diesel.

The present work was aimed at studying the basic laws of mild FATG (for example, rapeseed oil) hydrocracking depending on the process conditions. These studies are necessary for further optimizing the process of obtaining green diesel and determining the major kinetic parameters of the hydrocracking. Furthermore, an additional objective of our work consisted in obtaining data concerning the formation of intermediate products resulted from partial reduction (for example, fatty alcohols) those are more valuable chemical products than the alkanes of combustion purposes.

EXPERIMENTAL

We used rapeseed oil (Altai Territory) that represents a mixture of FATG (Table 1).

Hydrocracking of rapeseed oil was carried out in a flow-through reactor with the volume capacity equal to 10 mL and internal diameter of 13 mm. We used Ni–Cu/CeO_2–ZrO_2 catalyst with the following composition, mass %: Cu 10.4, Ni 30.3, Ce 17.5, Zr 28.0, O 13.8; S_{sp} = 141 m^2/g. The use of Ni–Cu/CeO_2–ZrO_2 catalyst was caused by several reasons: 1) Ni is traditionally used in hydrogenation and hydrocracking processes, 2) the addition of copper allows increasing the temperature of nickel reduction on average by 100 °C, and 3) mixed CeO_2–ZrO_2 carrier has active centers with mobile oxygen, where on an additional activation of oxygen-containing organic compounds could occur. The catalyst was prepared *via* co-precipitating a mixture of nickel, cop-

TABLE 1

Rapeseed oil composition

Fatty acid residue	Empirical formula	Number of C/Number of double bonds	Content,%
Oleic acid	$C_{17}H_{33}COOH$	18/1	63.3
Stearic acid	$C_{17}H_{35}COOH$	18/0	5.6
Linoleic acid	$C_{17}H_{31}COOH$	18/2	18.8
Linolenic acid	$C_{17}H_{29}COOH$	18/3	12.3
Erucic acid	$C_{21}H_{41}COOH$	22/1	<1

per, cerium and zirconium nitrate solutions by means of NaOH solution. A detailed preparation technique is presented in [7]. The system was fed with hydrogen and argon at a volume flow rate of 10 L/h. The total system pressure was equal to 1.0 MPa. Rapeseed oil was supplied directly into the reactor at flow rate values amounting to 13.3, 25.4, 34.5 and 49.4 mL/h (LHSV = 2.66, 5.08, 6.89 and 9.87 h^{-1}, respectively).

For each value of LHSV (this parameter of the process is defined as the ratio of the rapeseed oil volumetric flow rate to the amount of catalyst loaded), we determined the distribution hydrocracking products at different temperature values (300, 320, 340, 360 and 380 °C). Specimens were gathered in a separator to be sampled under steady-state conditions, their composition was determined by means of gas chromatography in an on-line mode. The accumulation of liquid sample in the separator began at certain parameters (T, P, τ_{cont}) began when a constant composition of the gas phase was reached.

The analysis of liquid products was performed using a Chromos GC-1000 chromatograph, equipped with a flame ionization detector and Zebron ZB-1 capillary column (stationary phase 100 % dimethylpolysiloxane, column length 30 m, internal diameter 0.32 mm, the thickness of the stationary phase 0.25 μm). The analysis of gaseous rapeseed oil hydrocracking products (H_2, CH_4) was performed in 15–20 min, in the on-line mode of Chromos GC-1000 chromatograph (thermal conductivity detector, Chromosorb-160 column, 4 m long). Additionally, the analysis of the liquid phase products was carried out using ^1H and ^{13}C NMR spectroscopy. The NMR spectra were registered with the use of a Bruker Avance 400 spectrometer at 400.13 (^1H) and 100.61 MHz (^{13}C) frequencies.

The FATG content was determined by means of the technique of high performance liquid chromatography using a MiliChrom A-02 liquid chromatograph equipped with ProntoSIL-120-5-C18 AQ (75 × 2 mm) microcolumn and a UV detector.

RESULTS AND DISCUSSION

In the course of NMR and GC analyzing the products of rapeseed oil hydrocracking in the presence of Ni–Cu/CeO_2–ZrO_2 catalyst, the following compounds were found: alkanes (mainly $C_{17}H_{36}$), 1,3- and 1,2-diglycerides, free fatty acids and other oxygen-containing compounds (methyl esters of fatty acids RCOOMe, alcohols RCH_2OH, aldehydes RC(O)H, ketones RC(O)R and RC(O)Me, waxes RCOOR). The yields of rapeseed oil hydrocracking products in the presence of a catalyst Ni–Cu/CeO_2–ZrO_2 were plotted against the temperature at different contact times (τ_{cont}) and P_{H_2} = 5 bar (Fig. 1).

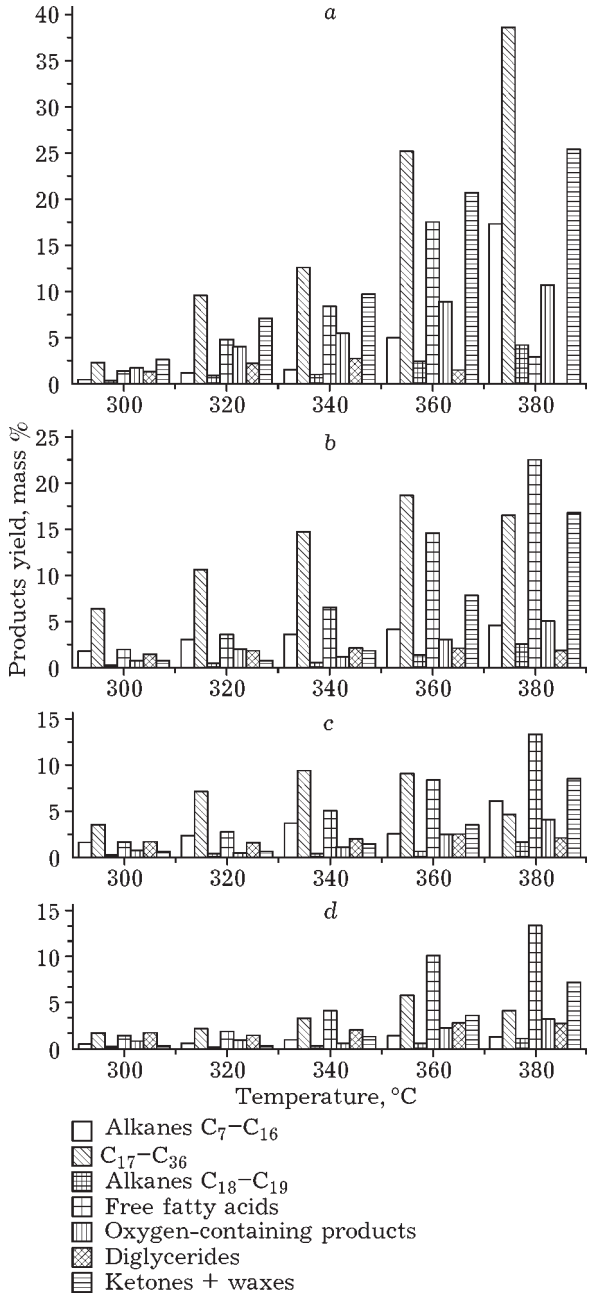

Fig. 1. Yield of rapeseed oil hydrocracking products depending temperature. LHSV, h^{-1}: 2.66 (*a*), 5.08 (*b*), 6.89 (*c*) 9.87 (*d*).

It should be noted that the complete conversion of FATG was observed only at $T = 380$ °C and LHSV = 2.66 h^{-1}; the yield of alkanes was equal to about 60 mol. %. The yield of the main product heptadecane $C_{17}H_{36}$ was equal to 37.8 mol. %. There was also a high yield of the partial reduction products of fatty acids observed (alcohols RCOH, aldehydes RC(O)H, ketones RC(O)R and RC(O)Me, waxes RCOOR). It should be noted that in this case, a dimerization products of fatty acid such as ketone $C_{17}C(O)C_{17}$ prevailed among them. In all the other cases, the main oxygen-containing products of FATG hydrocracking represented free acids. Basing on the analysis of experimental data we assumed that all the other oxygen compounds observed represent the products of their partial reduction. In general, the main products of triglyceride conversion are presented by alkanes, fatty acids, ketones and waxes. It should be also noted that when the temperature changed from 300 to 380 °C, we observed an increase in the yield due increasing the conversion level of triglycerides. A similar trend is also observed with increasing the contact time.

At the very low contact time (τ_{cont} = 365, LHSV = 9.87 h^{-1}), fatty acids were the main observed product, whereas at a higher value of contact time (τ_{cont} = 1353 s, LHSV = 2.66 h^{-1}) the main products were presented by alkanes (mainly $C_{17}H_{36}$).

A more detailed analysis of the experimental data resulted in the following conclusions:

1. When LHSV = 2.66 h^{-1}, an increase in temperature results in increasing the yield of alkanes (60 mol. % at 380 °C), the content of free fatty acids increases up to 18 mol. % at 360 °C and then decreases to 4 mol. % at 380 °C (*i. e.*, at the temperature higher than 360 °C, fatty acids begin to turn into other products). The yield of other oxygen-containing products also increases with temperature amounting to about 35 mol. % at the maximum temperature.

2. When LHSV = 5.08 and 6.89 h^{-1}, similar trends can be traced: at 360 °C the content of alkanes increases to amount to 27 and 15 mol. %, respectively, whereas at the temperature of 380 °C it is reduced. The yield of fatty acids and oxygen-containing products increases with temperature to amount to 23 and 20 mol. %, respectively, at LHSV = 5.08 h^{-1}; 15 and 10 mol. %, respectively, at LHSV = 6.89 h^{-1}. The situation is similar at LHSV = 9.87 h^{-1}: the maximum content of alkanes is attained at $T = 360$ °C (about 8 mol. %), whereas the yield of fatty acids and other oxygen-containing products increases gradually with increasing the temperature to reach a maximum (14 and 10 mol. %, respectively) at 380 °C.

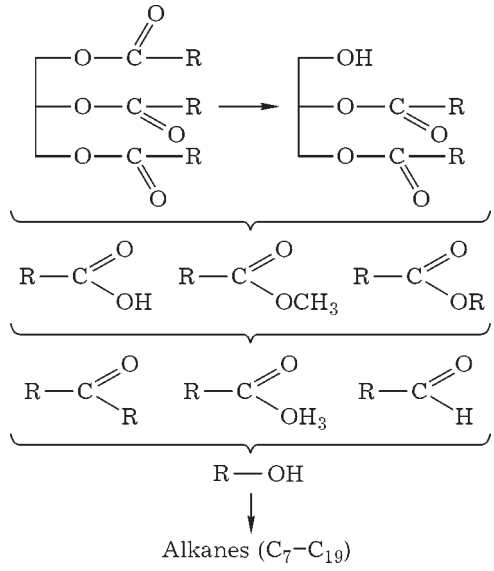

Fig. 2. Reaction route for hydrocracking the triglycerides of fatty acids.

Basing on the obtained hydrocracking products distribution for FATG rapeseed oil we proposed a scheme of initial conversion and intermediate species (Fig. 2). At the initial stage of the hydrocracking the triglycerides are converted into diglycerides of *via* removing the fatty acid residue which is reduced to form fatty acid.

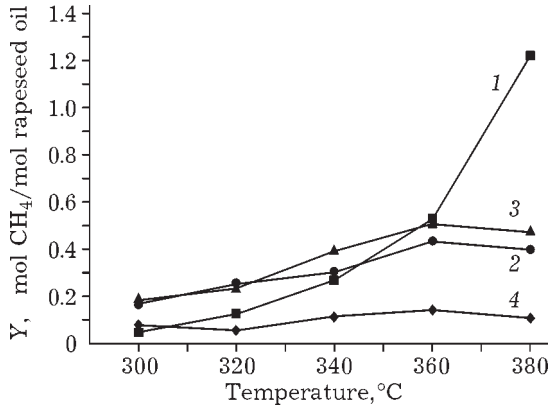

Fig. 3. Methanation level for the fatty acid triglyceride of rapeseed oil (*Y*) depending on the reaction temperature. LHSV, h^{-1}: 2.66 (*1*), 5.08 (*2*), 6.89 (*3*), 9.87 (*4*).

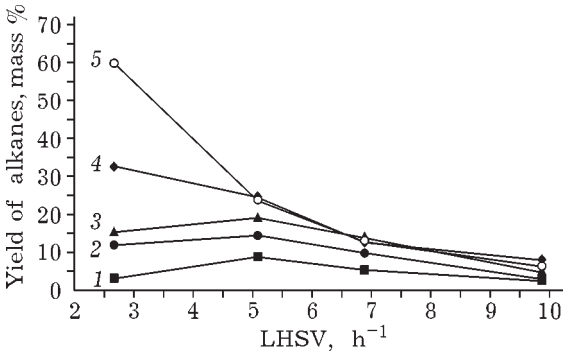

Fig. 4. Yield of alkanes depending on LHSV parameter at different temperature values, °C: 300 (*1*), 320 (*2*), 340 (*3*), 360 (*4*), 380 (*5*).

Methyl esters of fatty acids and waxes can be formed, too. In the course of the reaction, the compounds obtained are reduced to form ketones and aldehydes whose reduction results in obtaining corresponding alcohols. In the course of further catalytic hydrogenation the alcohols are converted into alkanes.

Figure 3 demonstrates the methanation level of rapeseed oil FATG (*Y*) depending on the temperature at different LHSV. In general, the parameter of *Y* did not exceed 0.4, except for the methanation level value obtained at 380 °C and LHSV = 2.66 h^{-1}, which value amounted to 1.3. This value of *Y* corresponds to a complete conversion of rapeseed oil FATG.

It should be noted that there is a slight upward trend of the methanation level with increasing the temperature at low contact time values. As a rule, the methanation level FATG at a low conversion level is insignificant, which indicates the possibility of targeted obtaining the products of partial reduction, with no significant loss of raw material.

Figures 4, 5 demonstrate data concerning the dependence of alkane yield and the conversion level of rapeseed oil FATG on the LHSV value in the course of the hydrocracking process.

One can see that with decreasing the contact time (by increasing the LHSV parameter) the conversion level of rapeseed oil FATG and the yield of alkanes exhibit a decrease. As the temperature increases from 300 to 380 °C the conversion level of FATG increases and, as a result, the yield of alkanes increases, too. The conversion level of FATG reached a maximum value (about 99 %) at the highest temperature (380 °C) and at the highest contact time (τ_{cont} = 0.38 h, LHSV = 2.66 h^{-1}). The yield of alkanes under these conditions was also the highest (about 60 %).

With the help of NMR technique we obtained information on the number of double bonds C=C in these products (Fig. 6). A general downward trend with increasing the contact time was established concerning the number of double bonds in the resulting product. In particular, when τ_{cont} = 0.1 h (LHSV = 9.87 h^{-1}) the average number of double bonds is approximately equal to one, which corresponds to the fatty acid residue of oleic acid, the hydrogenation of the double bonds under these conditions does not occur. With increasing the contact time the average number of double bonds in the fatty acid residues among the reaction

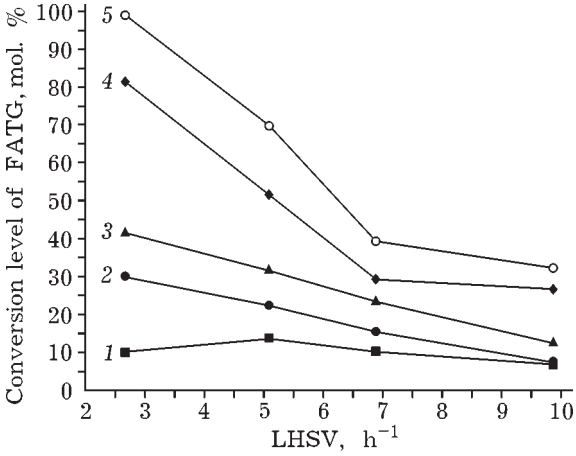

Fig. 5. Conversion level of fatty acid triglycerides depending on LHSV parameter at different temperature values, °C: 300 (*1*), 320 (*2*), 340 (*3*), 360 (*4*), 380 (*5*).

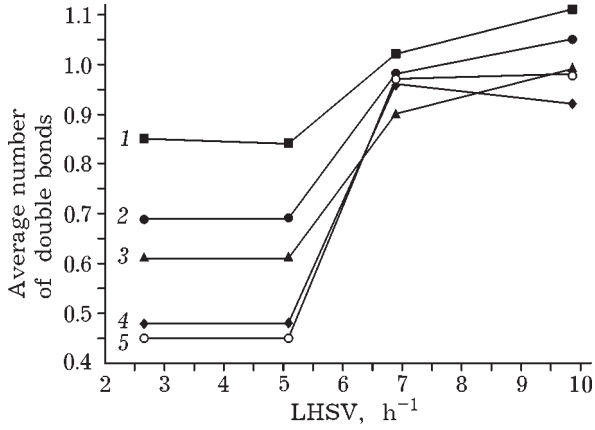

Fig. 6. Dependence of the average number of double bonds in the fatty acid residues of the parameter LHSV at different temperature value, °C: 300 (*1*), 320 (*2*), 340 (*3*), 360 (*4*), 380 (*5*).

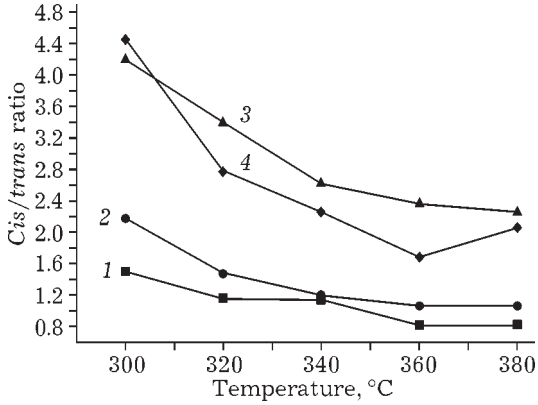

Fig. 7. Ratio *cis/trans* isomers depending on the temperature. LHSV, h^{-1}: 2.66 (*1*), 5.08 (*2*), 6.89 (*3*), 9.87 (*4*).

products is reduced, at τ_{cont} = 0.38 h (LHSV = 2.66 h^{-1}) and T = 360–380 °C, this value is equal to 0.5 (the ratio of saturated and unsaturated fatty acid residues is approximately equal to unity). In addition, at a maximum τ_{cont} value (0.38 h, LHSV = 2.66 h^{-1}) there was a distinct downward trend in the number of double bonds with increasing the temperature for the products of hydrocracking.

According to Figs. 5 and 6, increasing the contact time results not only in increasing the conversion level of FATG, but also in decreasing the number of double bonds in fatty acid residues, which indicates intensifying the process of hydrogenation. Thus, the dependences observed indicate that the process of FATG hydrocracking and the process of hydrogenating the double bonds of fatty acid residues are occurring in parallel, rather than in series, as it was suggested earlier by the authors of [9, 10].

In addition, using the method of NMR we obtained a *cis/trans* ratio between isomers depending on the temperature at different values of contact time (Fig. 7). It is seen that a general trend to decreasing the *cis/trans* ratio for isomers is observed with increasing the temperature, as well as with increasing the contact time.

The relationships obtained could be caused by a high reactivity power of the *cis* form with respect to hydrogenation (steric hindrance for the *trans* form), as well as by *cis/trans* isomerisation on the catalyst surface with no intermediate formation of hydrogenated products.

CONCLUSION

According to the results of the experiments, the following conclusion is drawn:

1. At low hydrogen pressure values (0.5 MPa), the Ni–Cu/CeO_2–ZrO_2 catalyst is active in the reaction of rapeseed oil FATG hydrocracking, thereby at LHSV = 2.66 h^{-1} and the temperature value equal to 380 °C the conversion of FATG reaches exhibits a maximum, whereas the content of alkanes amounts up to 60 mass %.

2. The number of double bonds in the products obtained with increasing the contact time exhibits a decrease, thereby the FATG conversion level increases, which indicates the process of hydrogenation to be intensified.

3. Under mild conditions one could obtain the products of partial FATG reduction the mixtures of alkanes, free fatty acids and their methyl esters, alcohols, waxes, ketones. With increasing the contact time and the temperature, the yield of various alkanes and oxygenated products (ketones, alcohols, waxes) increases, thereby there is a general trend to decreasing the *cis/trans* ratio for isomers.

4. A scheme is proposed for the sequence of FATG hydrocracking stages taking into account all the types of intermediates.

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