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# Heterogeneous catalysts for the transformation of fatty acid triglycerides and their derivatives to fuel hydrocarbons

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## Contents


| | | |
|---|---|---|
| I. | Introduction | 911 |
| II. | Catalytic transesterification of triglycerides and their derivatives | 913 |
| III. | Catalytic cracking of fatty acid triglycerides and their derivatives | 917 |
| IV. | Hydrocracking of fatty acid triglycerides and their derivatives | 919 |
| V. | Decarboxylation of fatty acid triglycerides and their derivatives | 922 |
| VI. | Conclusion | 923 |


**Abstract. The results of studies devoted to the catalysts for transformation of fatty acid triglycerides and their derivatives to fuel hydrocarbons are presented and described systematically. Various approaches to the use of heterogeneous catalysts for the production of biofuel from these raw materials are considered. The bibliography includes 134 references.**

## I. Introduction

It is generally acknowledged that biomass, as a relatively fast accumulator of the solar energy, may be regarded as an alternative to traditional fossil fuels such as oil, natural gas, coal.[1–3] The biomass energy may be straightly used *via* combustion or mediately used *via* processing into higher grade fuels such as fuel biogas and synthesis gas,[4,5] oil fuels,[1,2,6] transport fuels[7,8] and more valuable products for the chemical industry.[3–6] Since any kind of energy used on the Earth (except for nuclear energy) has energy of the Sun as its origin, it seems reasonable to compare the solar energy being absorbed, the current biomass reserves and the global energy consumption. The experts estimates[1–4] are given in Table 1, the Table containing the data concerning up-to-date level of energy consumption and forecast for 2050. Not only the growth was estimated but also the technological level of biomass processing that would provide bioenergy resources of desired quality and ensure their competitive consumption on a free market. As a whole, even if the optimistic prognoses are taken into consideration, the contribution of bioenergy would not exceed 20% of the total production of energy by 2050.

The production of engine biofuels is regarded as an important trend in the bio-energy manufacture. The methods of their production can be conventially divided into chemical and biotechnological ones. The chemical approach involves the use of both homogeneous and heterogeneous catalysts traditional for chemical industry for the synthesis of biofuels. It also concerns non-catalytic methods such as the production of biodiesel fuel under subcritical and supercritical conditions.[9–13] The biotechnological approach is based on the use of microorganisms. The recent review by Varfolomeev and coworkers[12] and also the papers[14–16] deal with biotechnological approach to the production of various sorts of biofuel (bioethanol, biobutanol, biomethane, biohydrogen, biodiesel), so this is not considered in the present review.

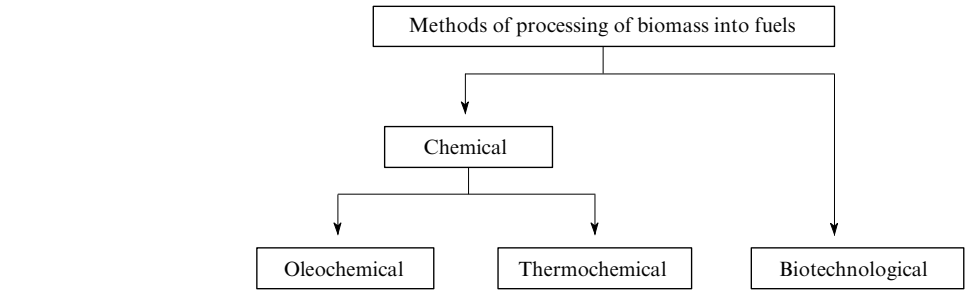
**Table 1**. Solar energy, the biomass reserves and global annual energy consumption.[1–4]

| Energy | Amount per year[a] | |
|---|---|---|
| | TW | EJ |
| The solar energy falling on the Earth | 178 000 | 5 500 000 |
| The part absorbed by the atmosphere | 120 000 | – |
| The part absorbed by the Earth as a whole | 53 000 | 3 700 000 |
| Land absorption | 16 000 | – |
| Photosynthesis on land ( < 1% of the irradiation absorbed by land) | 128 | ~4000 |
| Biomass available for processing | 46 | ~1426 |
| Up-to-date energy consumption | 14 | ~430 |
| Energy consumption by 2050 | > 30 | 600 – 1800 |
| The amount of biomass being processed by 2050 (estimated) | – | 100 – 350 |

[a] 1 TW = $10^{12}$ W; 1 EJ = $10^{18}$ J.

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| | | | |
|---|---|---|---|
| Raw materials | Food waste, animal fats, vegetable oils | Wood, agricultural waste, cellulose | Grain, sugarcane |
| Pretreatment | Purification, grinding, maceration | Gasification, pyrolysis | Metabolic synthesis |
| Intermediates | Suspensions, fats, vegetable oils | Synthesis gas, bio-oil | Simple sugars |
| Further treatment | Transesterification | Hydrotreating | Metabolic synthesis |
| Final products | Biodiesel | Gasoline and diesel fractions | Alcohols |

**Figure 1.** Key methods of processing of biomass into fuels.

The chemical approach includes a wide variety of chemical processing of vegetable raw materials into the fuel hydrocarbons. According to experts of the New Energy Finance company, such processes are classified into two trends, namely, thermochemical and oleochemical. As it is shown in Fig. 1, the initial stage of the thermochemical trend includes gasification and pyrolysis of lignocellulosic raw materials, which is the most widespread type of renewable raw materials and, hence, has been chosen to serve as an example. The obtained products of pyrolysis and gasification may then be processed into biofuel hydrocarbons by the Fischer–Tropsch process, catalytic cracking, hydrocracking, hydrodeoxygenation and isomerization. The oleochemical trend comprises processing of vegetable oils and animal fat such as transesterification, hydrocracking and decarboxylation. The separation of the oleochemical approach into an independent type is caused by the specificity of the starting raw materials (vegetable oils, animal fat) and of the processing product, namely, biodiesel. By their chemical composition, vegetable oils and animal fats correspond to a mixture of fatty acid triglycerides. The number of carbon atoms in fatty acids may vary in the range 6–24; the major part are saturated and unsaturated $C_{16}-C_{18}$ acids. The hydrocarbons obtained as a result of processing have a high energy content and their compositions are similar to those of hydrocarbons of traditional diesel fuels. This makes the development of such processes mostly attractive.

It is the processes of the oleochemical type that are the main target of the present review, namely, transesterification, hydrocracking, cracking and decarboxylation and first of all the catalysts to realize these processes.

The method of producing fatty acid esters from the corresponding triglycerides by transesterification has been known for long.[17–20] Since plant fatty acid esters were first regarded as fuel additives to the traditional diesel fuels, the investigations of this process became most intensive.[21–25] As a rule, until recently, homogeneous basic and acid catalysts were used as catalysts for transesterification. However, there are rather strict requirements to the fuel fatty acid esters (biodiesel), namely, neutral pH value, low content of alkali metals, soaps and other undesired side products. All this specifies the interest in the development of heterogeneous processes for the transesterification of the plant fatty acid triglycerides. Characteristic features of the homogeneous and heterogeneous catalysts for transesterification will be discussed below.

Yet another tendency of the oleochemical approach is ever increasing interest in the development of processes for the processing of the fatty acid triglycerides and their derivatives to the fuel products using heterogeneous catalysis as alternatives to the transesterification. An example is the catalytic cracking of oils and fats.[26] It is logical that the investigations concerning this trend were mostly oriented to the studies of zeolite catalyst of various nature. The disadvantage of this method is the rapid deactivation of the catalyst as a result of coking and also the formation of significant amounts of alkenes. In addition, the yield of target fuel hydrocarbons is lower as compared to the process of transesterification because of the formation of light hydrocarbons and carbon deposits on the catalyst surface. Thereby this approach has not found application in industry but it seems reasonable to discuss the catalysts of cracking in the present review in order to understand the processes of catalyst deactivation in other transformations of fatty acid derivatives.

The catalytic hydrocracking of vegetable oils is a more promising approach,[27] which makes it possible to increase

the yield of the target products, to decrease the content of alkenes in them and, due to the presence of hydrogen, to decrease coking. Until recently, the systems based on the transition,[29] including noble,[28] metals on various supports were used as catalysts in the investigation of this process. Linear alkanes with high cetane number that may by used as additives to the summer diesel fuels are formed as a result of the hydrocracking of fatty acid derivatives. Currently there are examples of the industrial use of the hydrocracking catalysts for this type of raw material, which will be discussed in detail in the corresponding Section.

The decarboxylation catalysts that allow one to carry out deoxygenation in the absence of hydrogen should be considered as a separate type of heterogeneous catalysts for the processing of vegetable oils and free fatty acids.[30] Out of the wide range of the catalysts considered below, Pd/C should be noted as most active.[31] It should also be mentioned that the problem of rapid deactivation of palladium catalysts in inert atmosphere has not been solved yet.

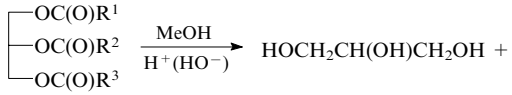
Besides the discussion of the existing catalysts for processing of fatty acid derivatives for the production of fuel hydrocarbons, the present review deals with the attempt to determine the main trends of further development of the catalytic methods of processing of plant oils to biofuel.

## II. Catalytic transesterification of triglycerides and their derivatives

Biodiesel along with bioethanol holds a leading position among different types of biofuels according to the volume of world output. Thus, in 2008 its world production was $>6.5$ million tonnes.[32] The EU countries (first of all Germany, France and Italy), the USA, Brazil and Argentina are the leaders of the production of biodiesel. The EU countries produce biodiesel mainly from rapeseed, while the USA and Argentina produce it from soya, Brazil uses castor oil, the ASEAN countries employ palm oil. Almost the whole amount of biodiesel is produced using homogeneous catalysts for transesterification.

### 1. Homogeneous transesterification

The traditional production process of biodiesel includes the transesterification of animal and plant fatty acid triglycerides by methanol under mild conditions (50–80 °C) with the use of either alkalis (NaOH or KOH)[32–35] or mineral acids ($H_2SO_4$, HCl, $H_3PO_4$)[36–38] as catalysts.



$$\left.\begin{matrix}\text{OC(O)R}^1\\ \text{OC(O)R}^2\\ \text{OC(O)R}^3\end{matrix}\right\} \xrightarrow[\text{H}^+(\text{HO}^-)]{\text{MeOH}} \text{HOCH}_2\text{CH(OH)CH}_2\text{OH} + \text{MeOC(O)R}^1 + \text{MeOC(O)R}^2 + \text{MeOC(O)R}^3.$$

There are also examples of the application of triglycerides of guanidine [$HNC(NH_2)_2$] and various amines[39,40] as the catalysts for homogeneous transesterification. This provides high degree of conversion (98%) in one step with minimum amount of waste water. Despite its simplicity, the homogeneous process of production of biodiesel has a number of disadvantages caused by the fact that the obtained mixture of products needs to be separated, neutralized, thoroughly washed and deprived of water. All this results in significant amounts of salts, soaps and waste water that should be disposed. In so doing, the catalyst is irreversibly lost. Besides, it should be taken into consideration that glycerol formed as a side product is contaminated by the solutions of salts and also requires additional purification.

Homogeneous transesterification of fatty acid triglycerides in the presence of mineral acids did not find such a wide use as the alkaline method due to lower rates of the process, the necessity of the use of more rigorous conditions (higher temperature, higher methanol : triglyceride ratio and larger amount of the catalyst), and also due to the formation of undesired products, namely, glycerol methyl ethers.[41] The disadvantages listed above increase the prime cost of the biodiesel obtained which limits the commercial application of this process on the competitive market.

Recently ethanol has been regarded as a more attractive reagent for transesterification than methanol due to its lower toxicity. However, the fatty acid ethyl esters posess greater viscosity and are characterized by lower cloud and setting points than the methyl esters,† which decreases the quality of the fuel obtained. In addition, the possibility of the use of ethanol is greatly limited by its higher cost in comparison with methanol.

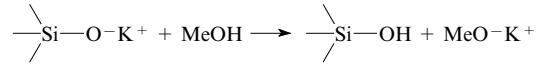
### 2. Heterogeneous transesterification

The disadvantages of the homogeneous method of transesterification listed above caused the research interest in the synthesis of biodiesel using heterogeneous catalysts. During the last five years the number of papers dealing with the more environment-friendly method of producing biodiesel using heterogeneous basic[42–47] and acid[37,43,48–52] catalysts increased greatly. The advantages of this process are not only the possibility of repeated use but also the quality of the biodiesel obtained, which is higher than in the case of homogeneous method of production. The removal of the step of oil pretreatment, the minimization of the formation of liquid wastes, the elimination of the formation of salts and soaps are also advantages of the method using heterogeneous catalysts. As far as the mechanisms of transesterification involving acid and basic sites are different, it seems reasonable to consider these two classes of catalysts separately.

### 3. The basic catalysts of transesterification

If the homogeneous Brønsted basic catalysts (NaOH, KOH, $Na_2CO_3$) are mixed with alcohol, the active alkali metal alkoxide is formed and it attacks the carboxyl carbon atom of triglyceride.[53] That is why alkoxides (NaOMe, KOMe) are often directly used as catalysts.

Such mechanism is also realized in the case of heterogeneous Brønsted basic catalysts, for example, in the case of basic zeolites:[54]

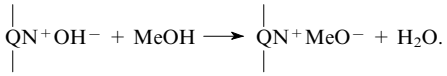


$$\equiv\text{Si—O}^-\text{K}^+ + \text{MeOH} \longrightarrow \equiv\text{Si—OH} + \text{MeO}^-\text{K}^+.$$

At the same time the homogeneous alkoxide is also formed. In case of Brønsted basic catalysts of resin type modified by quaternary ammonium bases ($QN^+OH^-$), the quaternary ammonium cation is bound to the surface of the catalyst and, correspondingly, the catalytically active

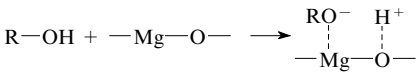
† See, *e.g.*, N N A N Yusuf, S K Kamarudin, Z Yaakub *Energy Convers. Manage*. **52** 2741 (2011).

anions also stay on the surface of the heterogeneous catalyst.[53]



In this case, the transesterification occurs by the Eley–Rideal type mechanism between the methoxide ion adsorbed by the cation and the ester groups.

In the case of heterogeneous Lewis catalysts, the formation of alkoxide species is also a key point. Thus, it has been shown[55] in the course of the investigation of transesterification of ethyl acetate on MgO that the reaction proceeds between the molecule of alcohol adsorbed on the surface of magnesium oxide and the molecule of ethyl acetate from the liquid phase also by the Eley–Rideal type mechanism.



The testing of industrial $MgO/Al_2O_3$, hydrotalcites and MgO ($S_{sp}$ = 300 $m^2\ g^{-1}$) in the process of transesterification of the rapeseed oil at the methanol boiling point (65 °C) for 22 h is described.[50] It was shown that MgO is more active than hydrotalcites. The yield of biodiesel is 64% with the concentration of a catalyst being 10 mass %. At the same time it was reported[42] that the calcined hydrotalcites and MgO are successfully used for the production of biodiesel at higher temperatures. High yields (90%–92%) were obtained after 1 hour at the temperature of 180–200 °C. In this process, at least four different types of active basic sites were identified on the surface of magnesium oxide and calcined hydrotalcites. The strongest basic sites initiated the transesterification even at 100 °C. The weaker basic sites became active in the target reaction at higher temperatures. It has also been established that the activity of heterogeneous catalysts depends not only on the strength of the basic sites but also on the textural characteristics of the catalyst. In turn, these characteristics depend on the nature of catalyst precursor and the method of preparation. It has been shown[56] that the carrying out the transesterification of fatty acid triglycerides under supercritical conditions (300 °C, 8 MPa) makes the process more efficient and gives high yields of fatty acid esters (91%) in the presence of MgO after 10 min. It seems that under these conditions, the diffusion restrictions of the mass transfer of the products and reactants in the catalyst grain are withdrawn.

Since the starting vegetable oils, fats and methanol contain water, the stability of heterogeneous catalysts for the transesterification against water is an important requirement. The influence of water (10 000 ppm) on the activity of various catalysts at 180 °C was studied.[42] It turned out that the activity of both magnesium oxide and hydrotalcites does not change in the presence of the excess of water. However it was found out[57] that during a more continuous experiment Mg/Al-hydrotalcites loose their activity without showing high stability. Thus after 24 h at 180 °C the yield of biodiesel was 77 mass %, the concentration of Mg and Al ions in the reaction medium being 17 800 and 6900 ppm, respectively. This prejudices the prospects of the use of these catalysts on the industrial scale.

The activity of activated CaO as the catalyst for transesterification for the production of biodiesel was also studied.[58] Since the active sites of CaO are blocked by the molecules of $H_2O$ and $CO_2$ from the air, calcium oxide was calcined at 700 °C before the reaction. In the reuse and regeneration, no loss of the activity of CaO was observed; however, dissolution of calcium oxide took place. It was concluded that in this case, the overall process of transesterification was a combination of the homogeneous and heterogeneous reactions.

The catalyst based on ZnO with SrO additive obtained by calcination of a $ZnO-Sr(NO_3)_2$ mixture at 600 °C for 5 hours has shown a high activity in transesterification of soybean oil.[59] In the boiling methanol at the molar ratio methanol : oil = 12 and concentration of the catalyst being 5 mass %, the conversion of soybean oil was 94.7%. However, the catalyst deactivated rapidly and could not be reused. The authors considered that the main reason of the deactivation was the blockage of the active sites by the reaction products. though the effect of leaching of SrO, which may also be the reason of deactivation, was not investigated.

It has been established that sodium silicate may also be used as the catalyst for transesterification. Under the conditions of microwave irradiation at the temperatures of 60–120 °C, the high rates of the process are provided.[60] Unfortunately, the catalyst cannot be reused due to its destruction under the action of irradiation.

Basic catalysts supported on oxides, usually $Al_2O_3$, were investigated.[48,61–63] NaOH, $K_2CO_3$, $KNO_3$, KF were supported on aluminium oxide by means of impregnation. Then the samples were calcined at 500–600 °C. The catalysts thus obtained demonstrated high activity at 65 °C, the catalyst concentrations being 3 mass %–6 mass %. However, no data concerning the leaching of the alkali metals from the support or the data on the stability of the systems were reported in the papers cited. Meanwhile, it was shown[53] that the high conversion of rapeseed oil that may be achieved in the presence of $K_2CO_3$ supported on MgO and $Al_2O_3$ is accompanied by the transfer of a part of calcium carbonate into the solution.

The basic zeolites of NaX type showed low activity in the transesterification of fatty acid triglycerides at 60–65 °C.[64,65] The conversion of soybean oil does not exceed 10% even if the process is conducted for 24 hours and the catalyst concentration is up to 10 mass %. It seems that the low effectiveness of zeolite catalysts can be attributed to the small size of pores of zeolite, which complicates the transport of large molecules of fatty acid triglycerides in them. The deposition of NaOH or KOH on the zeolites with the subsequent calcination at 500 °C resulted in the yield of fatty acid methyl esters being increased up to 82%–85% under the same conditions. However, for such systems, the effect of leaching of the active component was also observed along with the decrease in the yield of biodiesel from 85% to 49% on the reuse of the catalyst.[65]

The attempts of application of microporous titanium-containing zeolites ETS-10 and ETS-4 having high activity at low temperatures (100 °C) and at low methanol : oil ratios (6 : 1) as catalysts for transesterification should be mentioned.[64,66] Quite a good yield of biodiesel (up to 92%) was achieved after 3 h at the concentration of catalyst of 10 mass %. The ETS-10 zeolite was more active than NaX,

obviously, due to the basic properties of the surface. However if reused, the activity of ETS-10 in the target process significantly decreased.

Ion exchange resins produced by Mitsubishi Chemical (PA308, PA306, PA306s, HPA25) showed high activity in the process of transesterification of trioleate by ethanol at 60–100 °C.[67] However, the activity noticeably decreased during the experiment due to the presence of oleic acid, which is formed as a result of direct ion exchange reaction of hydroxide ion with the oleic acid moiety in the glyceride. At the same time, the ion exchange resins may be easily regenerated by a three-stage method that includes washing by a 5% solution of citric acid in ethanol for the removal of organic compounds, regeneration by 1 M solution of NaOH and washing by ethanol. The stability of ion exchange resins may be increased by the preliminary washing by methanol. In this process, most of $HO^-$ groups are replaced by $MeO^-$ groups; hence, carboxylic acids are not formed and the deactivation of the catalyst is prevented.[68]

In patent,[69] the results of testing of a series of basic mixed oxides M–Al–O (M = Sr, Ba), M–Mg–O (M = Y, La) and M–La–O (M = Sr, Ba) in transesterification of rapeseed oil in a flow type reactor at a temperature of 200 °C, pressure of 2 MPa and molar excess of methanol of 9 : 1 are given. It is shown that the conversion of rapeseed oil depends on the nature of the catalyst and under other conditions being the same, it decreases from 100% to 35% in the series

$$\text{Sr–La–O} > \text{Ba–La–O} > \text{La–Mg–O} \geqslant \text{Y–Mg–O} > > \text{Ba–Al–O} > \text{Sr–Al–O}.$$

At the same time the conversion of rapeseed oil on these samples stayed approximately constant for 9 hours of operation. Thus, on using the systems Sr–La–O and Ba–La–O under the mentioned conditions of the reaction, a practically complete conversion of rapeseed oil was achieved. The achieved result corresponds to the data[70] according to which the La-containing catalysts demonstrate high activity in the transesterification of sunflower seed oil at 200 °C. However, the oil : methanol ratio was significantly higher and was 1 : 30 (instead of 1 : 9). In addition, as it was shown in a patent,[69] in the case of Ba–Al–O and Sr–Al–O aluminates, the temperature of calcination of the samples does not affect their activity in the target process over a broad interval. Moreover, the increase in the calcination temperature from 700 to 1200 °C led to the decrease both in the specific surface area and pore space. For example, a Ba–Al–O sample calcined at 700 °C is characterized by bimodal pore size distribution (with maxima corresponding to the diameters of ~200 and 750 Å); at the same time, the specific surface area was 112 $m^2\ g^{-1}$, the pore space and effective pore diameter being 1.0 $cm^3\ g^{-1}$ and 302 Å respectively. A Ba–Al–O sample calcined at 1200 °C was characterized by significantly lesser pore space and effective diameter, being 0.05 $cm^3\ g^{-1}$ and 181 Å respectively, which is explained by a more intensive volume sintering process. This gives rise to fine pores with diameters of 30–50 Å in which the process of transesterification does not occur. As a whole, the decrease in the pore space of the M–Al–O samples with the increase of the calcination temperature occurs due to the sharp decrease in the content of mesopores with diameter of 100–400 Å without the significant change of the macropores with diameter of 400–1000 Å. Taking into the consideration the fact that the activity of the samples in this case changes insignificantly, it may be assumed that the main contribution to the activity of the catalysts listed above for the three-phase process of transesterification of fatty acid triglycerides is made by the active sites in micropores where the diffusion restrictions to the mass transfer of the reactants and products of the reaction are minimized. Despite the relatively low activity of alkali earth metal aluminates, it may be supposed that these catalytic systems are promising for the production of biodiesel because they have high chemical and thermal stability.

Thus, a wide variety of catalysts of basic nature that exhibit significant activity in the transesterification of fatty acid triglycerides under relatively mild conditions has been described in the literature. However, it should be mentioned that testing of the catalysts was mainly carried out in the batch reactors. On the one hand, this allowed decreasing the diffusion restrictions of mass transfer of the reactants and products of the transesterification reaction. On the other hand, this cannot be recommended for the industrial application. This problem could be solved by carrying out the process in a flow type reactor, but in this case, it is necessary to use increased temperature and methanol vapour pressure in order to increase the rate of the reaction. It was shown that the rate of transesterification in the three-phase process is in direct proportion to the pressure of methanol. The increase in the pressure, in turn, increases the solubility of methanol in fatty acid triglycerides which partially withdraws the restrictions on the mass transfer of methanol to the active sites of heterogeneous catalyst. Another problem for this type of catalysts is their low stability due to the leaching of the active component into the solution. There are few investigations of the stability of basic catalysts for transesterification. Undoubtedly, more attention should be paid to this problem in the future.

## 4. The acid catalysts of transesterification

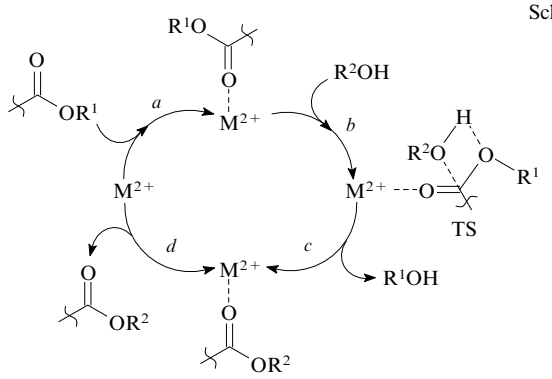
The acid catalysts are widely used in the reactions of producing of biodiesel, both Brønsted ($H_2SO_4$, *p*-toluenesulfonic acid) [37,53] and Lewis (metal acetates, metal complexes) [53,71–73] homogeneous acids being used.

In the case of Brønsted acid catalysts, the mechanism of transesterification (esterification) involves the protonation of C=O unit to increase its electrophilicity, which in turn facilitates the nucleophilic attack of the alcohol.[74]

It was shown[75] that the mechanism of esterification on the heterogeneous catalysts with Brønsted acidity is similar to that of the reaction with homogeneous analogues. For instance, it was found out that the polymeric material Nafion SAC-13 supported on $SiO_2$ has the same specific activity (TOF) as $H_2SO_4$ in the esterification of acetic acid by methanol. The reaction is realized by the Eley–Rideal type mechanism *via* the nucleophilic attack of methanol from the liquid phase on the adsorbed molecule of carboxylic acid.[76] The same mechanism is realized for transesterification (Scheme 1).[75,77]

It is assumed that at the first step (*a*) electrophilic particles are formed as a result of interaction with homogeneous or heterogeneous Lewis acids. Then the formed Lewis complex is subjected to the nucleophilic attack by alcohol (step *b*) with the formation of corresponding four-centred transition state (TS), which decomposes to give a new alcohol at step *c*. At step *d* the ester formed is desorbed

Scheme 1




from the Lewis acid site and the reaction cycle closes up. It was shown that there exists the optimal strength of acid sites. Very strong Lewis acids do not reveal significant activity in transesterification of fatty acid triglycerides due to the fact that the desorption of products does not take place.[75–78]

Since the acid catalysts may simultaneously initiate both esterification and transesterification they may be used in the processing of low-quality raw materials with high content of free fatty acids.[39, 53, 79] A series of acid catalysts has been tested[80] for transesterification of glycerol triacetate (triacetin) with methanol at 60 °C. As a result, the catalysts were arranged in the following series according to the decrease in the activity:

> $H_2SO_4$ > Amberlyst-15 (polystyrenesulfonic resin) > sulfated $ZrO_2$ (SZ) > Nafion NR50 (perfluorated alkanesulfonic resin) > $ZrO_2$ modified by an anion $WO_4^{2-}$ (WZ) > supported $H_3PO_4$ (SPA) > zeolite β > zeolite ETS-10 (H).

Zeolites possess low activity due to the space restrictions accompanying the mass transfer of voluminous triglycerides inside the pores. At the same time, ETS-10 zeolite has a weak acid site. Catalysts Amberlyst-15, SZ and WZ significantly lost their activity after the fifth cycle of the reaction due to the blockage of active sites by intermediates and products of the reaction. On the contrary, the activity of catalyst Nafion NR50 was increased after the first cycle due to swelling. The activity of Nafion NR50 remained constant during subsequent cycles. It should be mentioned that usually at low temperatures the activity of acid catalysts is low and it is necessary to carry out transesterification at temperatures higher than 170 °C in order to achieve high rates of the process. But ion exchange resins could not be used at higher temperatures because of their thermodestruction.

A stable and highly active catalyst for esterification may be obtained by the partial carbonization of natural materials (sugars, starch, cellulose) with subsequent sulfation.[51, 81] Due to the higher concentration of acid sites on the surface, such catalysts show higher activity in esterification of oleic acid than other acid catalysts. Besides that, the decrease in the activity of carbon catalysts after 50 cycles was only 7%. These catalysts may be used at higher temperature (up to 275 °C) than ion exchange resins (up to 120 °C), which allows one to decrease the time needed to attain high yields of biodiesel.[81]

A comparative study of a series of heterogeneous catalysts for transesterification of soybean oil by methanol at 200–300 °C and for esterification of octoic acid at 175–200 °C was carried out.[82] $ZrO_2-Al_2O_3$ modified by $WO_4^{2-}$ ions (WZA), sulfated $ZrO_2-Al_2O_3$ (SZA) and sulfated tin oxide (STO) were used as catalysts. The WZA catalyst showed the highest activity in transesterification (Table 2), while in the case of esterification of octoic acid, the sequence of activities was changed to a reverse one: STO ⩾ SZA > WZA.

**Table 2**. Activity of catalysts for transesterification of soybean oil and esterification of octoic acid by methanol (the process was carried out in a flow type reactor at atmospheric pressure).

| Catalyst | Conversion (%) | |
|---|---|---|
| | transesterification | esterification |
| WZA | 90 | 95 |
| $ZrO_2-Al_2O_3$ | 80 | 100 |
| SZA | 75 | 100 |
| STO | 15 | 100 |

Nevertheless, $ZrO_2-Al_2O_3$ modified by $WO_4^{2-}$ ions is the most attractive catalyst for both transesterification and esterification due to its high activity and stability.[82] Besides, $TiO_2-ZrO_2$ (11 mass % Ti) and $Al_2O_3-ZrO_2$ (2.6 mass % Al) also showed high activities in both reactions.[83]

High activity of sulfated tin oxide was confirmed.[84] While investigating the transesterification of palm and coconut oils by methanol, it was revealed that acid catalysts can be arranged in the following sequence according to their activities: sulfated zirconium oxide ⩾ sulfated tin oxide > ZnO > $ZrO_2$ (Fig. 2).

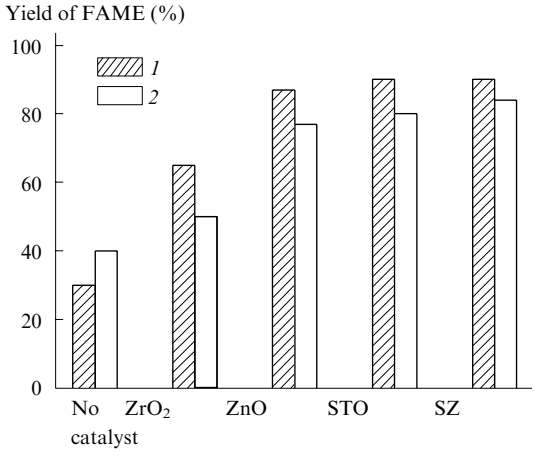



**Figure 2.** Yields of fatty acid methyl esters (FAME) in transesterification of palm (*1*) and coconut (*2*) oils at 200 °C, time of reaction being 4 h and molar ratio methanol : oil = 6.[84]

A higher content of water and free fatty acids in coconut oil compared to palm oil led to the decrease in the activities of all catalysts, which indicates a high sensitivity of this type of catalysts to the impurities. In addition, it was shown that the most active catalyst, namely, sulfated $ZrO_2$, is completely deactivated. Nevertheless, the repeated sulfation and calcination led to its complete regeneration.[84]

Zinc-containing catalysts found wide application in the investigations of heterogeneous transesterification processes

**Table 3**. Activity of catalysts based on ZnO in the transesterification of vegetable oils.

| Catalyst | Oil | Ratio methanol : oil | Mass or content of catalyst | $T$/°C | Time of reaction /h | Yield of FAME (%) | Ref. |
|---|---|---|---|---|---|---|---|
| ZnO | rapeseed | 1 : 3 (by mass) | 1.8 g | 170 | 4 | 64 | 18 |
| ZnO | rapeseed | 1 : 1 (by mass) | 1.2 g | 225 – 230 | 6 | 93 | 18 |
| ZnO | rapeseed | – | – | 235 | 1 | 91 | 18 |
| $Sr(NO_3)_2$ – ZnO | soybean | 12 : 1 (mol.) | 5 mass % | 65 | 5 | 94 | 59 |
| KF – ZnO | soybean | 10 : 1 (mol.) | 3 mass % | 65 | 9 | 87 | 59 |
| KOH – ZnO | soybean | 10 : 1 (mol.) | 3 mass % | 65 | 9 | 82 | 59 |
| $La_2O_3$ – ZnO | soybean | 10 : 7 (by mass) | 3 g | 200 | 3 | 95 | 85 |

(Table 3). The use of such catalysts was first mentioned in patent,[18] which describes the application of zinc silicate as a catalyst for transesterification of coconut oil at 250 – 280 °C.

In spite of the revealed effect of leaching of zinc with the formation of zinc soap at high temperatures, a similar conclusion about the perspectives of the application of ZnO as the catalyst for transesterification was made.[86] Besides zinc oxide, two samples of $ZnO-Al_2O_3$ catalyst (29% ZnO) were tested. They were prepared by treatment of $Al_2O_3$ with a solution of $Zn(NO_3)_2$ with subsequent calcination at 500 °C or by mixing of the aluminium oxide gel with ZnO with subsequent calcination at 600 °C. These zinc aluminates demonstrated approximately similar activities and higher stability in comparison with commercial spherical ZnO (see Table 3). In this case, the maximum content of zinc in the final product (biodiesel) did not exceed 5 ppm. Since the compounds of aluminium are unstable against hydrothermal treatment, it is noted that in order to achieve the high yields of biodiesel ( > 99%), it is necessary that the content of water in reaction medium should not exceed 1500 ppm.[87] It was also found [88] that zinc aluminate $ZnAl_2O_4$ is active not only in transesterification but also in esterification of free fatty acids contained in fatty acid triglycerides. However, at the same time, there are no data in this patent concerning the stability of zinc aluminate in the case of its application in the conversion of oil with high content of free fatty acids though it is known [86] that free fatty acids are able to leach the zinc catalyst with the formation of zinc soaps.

High yields (96%) of biodiesel were reported [89] for transesterification of soybean oil for 26 hours at the methanol boiling point with metallic zinc and iodine used as a catalytic system. However, no data is given on the possibility of reuse of the catalyst or on the nature of active sites.

The application of binary system based on zinc and iron cyanides gave promising results.[90, 91] These catalysts are Lewis acids, they have hydrophobic nature and they are insoluble under the conditions of the process (170 °C). Due to their hydrophobic nature, these catalysts may be used even for the transesterification of the oils with high content of free fatty acids and water. It is noted that Zn – Fe catalyst is active in esterification of free fatty acids, reducing the iodine value of the reaction products. It should be pointed out that the addition of water does not affect the activity of catalyst but leads to the formation of significant amounts of free fatty acids.

Thus, investigations of heterogeneous acid catalysts of transesterifcation revealed the same trends as investigations of basic catalysts. In most cases, the target process is studied in static mode and in spite of the observed effect of leaching of the active component, insufficient attention is paid to the problems of stability and regeneration of catalysts.

Consequently, though according to the estimates of the F.O.Licht consulting company, the world output of biodiesel is growing and in 2009 it amounted to 14.5 million tonnes, the process of its production is based on the application of homogeneous catalysts and the process is accompanied by the formation of large amounts of waste products. These problems encourage the investigation and development of heterogeneous method of producing biodiesel. Industrial companies of different countries apply significant efforts to the search for efficient catalysts. Now there are examples of commercial implementation of the processes of production of biodiesel based on heterogeneous catalysts.[92] Nevertheless, the investigations in this area are continued because there is yet a number of problems to be solved. One of the most difficult problems is the development of the catalyst with reasonable activity under milder conditions than the traditional heterogeneous process of transesterification (220 – 240 °C, 4.0 – 6.0 MPa).[18]

The catalysts for transesterification described above are prospective candidates for the development of industrial process. But at the same time it should be recognized that industrial catalysts should be stable against poisoning and leaching of the active component. As it has already been mentioned, no due attention has been paid to this aspect in most of the papers. It should also be noted that consistent data on the stability and leaching of active component may be obtained only by using flow type fixed catalyst bed reactors, while most researchers have used perfect-mixing static autoclaves. In this case, the data obtained can only be considered as tentative.[58, 80, 93] Nevertheless, even from the results of these works it is clear that the problem of increasing of stability of catalysts in the presence of water at high temperatures ( > 170 °C) is the most topical due to the fact that the activity mainly decreases because of leaching of the active component from the catalyst.

## III. Catalytic cracking of fatty acid triglycerides and their derivatives

Catalytic cracking may be regarded as an alternative to the process of transesterification of fatty acid triglycerides and their derivatives for the production of liquid fuels. As a result of cracking of esters and fatty acid triglycerides, the hydrocarbons of diesel, gasoline and kerosene fractions as well as light hydrocarbons, solid carbon residue and water are formed. The process is carried out in inert atmosphere at 300 – 400 °C,[94] zeolites are usually used as catalysts [*e.g.*, HZSM and β,[95] MCM-41,[96] SBA-15 (Ref. 97)], the activity and selectivity of such catalysts in the process of cracking of fatty acid triglycerides depending on acidic properties, sizes

and shapes of pores and other characteristics of zeolite. The authors of a study[96] carried out cracking of palm and coconut oils at 450 °C, atmospheric pressure and WHSV‡ 2.5 $h^{-1}$ on mesoporous aluminosilicate MCM-41 at the ratio Al : Si = 50. Depending on the dimensions of pores of the used zeolite, the yield of diesel fraction was 10% to 44% in the case of cracking of palm kernel oil and 10% – 32% in the case of cracking of palm oil. The yield of gasoline fraction was 17% – 51% and 12% – 43%, respectively. The investigation of the dependence of zeolite activity on its acid properties has revealed that on the increase of the content of Al in the sample (with the increase of its acidity), the activity increases. The cracking of palm oil was carried[98] out under similar conditions: on the MCM-41 zeolite, the yield of gasoline fraction reached 30.3%, and on the H-β zeolite, it was 16.1%. The MCM-41 zeolite was more active in the cracking to light hydrocarbons. It was also shown that on H-β the selectivities of formation of gasoline and kerosene fractions are approximately equal, the amount of the diesel fraction being twice smaller, while on MCM-41 the selectivities of formation of these fractions relate as 40 : 10 : 5. A higher yield of gasoline fraction (59.1%) upon the cracking of palm oil was achieved[99] at the same temperature on the REY zeolite (Albemarle Co., Singapore). One of the disadvantages of this process is a relatively high yield of gaseous products comprising a mixture of carbon oxides and light hydrocarbons. As a result, the yield of target liquid hydrocarbons decreases. From Table 4 it is clear that the minimum yield of gaseous hydrocarbons was achieved when mesoporous zeolites MCM-41 were used.

The composition of the gaseous phase (in %) of the products of cracking of palm oil at 450 °C, atmospheric pressure and WHSV = 2.5 $h^{-1}$ on the MCM-41 zeolite was as follows:[98]

| CO | $CO_2$ | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $C_{4+}$ | $C_{5+}$ |
|---|---|---|---|---|---|---|---|---|
| 4.4 | 1.6 | 4.7 | 3.9 | 7.1 | 12.1 | 20.8 | 27.7 | 17.7 |

‡ WHSV is Weight Hourly Space Velocity, hourly average space velocity of reactant feeding (into the reactor with a fixed catalyst bed) per mass unit of catalyst.

Despite high thermal stability, the MCM-41 zeolite is unstable in the presence of water at high temperatures, which limits its application in the cracking reactions where water is one of the products. Mesoporous zeolite SBA-15 is more stable under the conditions of hydrothermal treatment.[104] However, due to the absence of aluminium in the structure it does not posess sufficient acidity. The authors of paper[105] synthesized aluminium-containing zeolite AlSBA and investigated its stability under the conditions of hydrothermal treatment and also the activity in the cracking reaction of a mixture of fatty acids (waste products of the production of palm oil). The stability testing was carried out by passing steam through a zeolite bed in a flow reactor at 800 °C, resulting in the decrease of the specific surface area of AlMCM-41 by 88% (in the process the pore space decreased from 1.00 to 0.32 $cm^3\ g^{-1}$) and the decrease of the specific surface area of SBA-15 and AlSBA by 43.7% and 46.2%, respectively, which indicates the instability of AlMCM-41 under these conditions. Experiments on the investigation of zeolite activity were carried out in a flow type reactor at atmospheric pressure, a temperature of 450 °C, WHSV = 2.5 $h^{-1}$ and the ratio reactant : catalyst = 8. The results are presented in Figure 3. It is clear that the activity of aluminium-containing zeolite AlSBA, which is more stable than AlMCM-41 under the conditions of hydrothermal treatment, approximately equals the activity of AlMCM-41. The conversion of fatty acids is a bit higher though the yield of gaseous phase is also higher in the case of AlSBA. At the same time, its activity significantly exceeds the activity of aluminium-free (and less acidic) SBA-15.

The influence of the reaction conditions (temperature, catalyst : reactant ratio, time of contact) on the catalyst activity and selectivity in cottonseed oil cracking was studied.[103] The catalyst used was a mixture of LK-98 and CHZ-4 zeolites. It was shown that on increasing the temperature of the reaction from 400 to 500 °C the yield of gaseous products significantly increases (from 7.5% to 24%), the yield of gasoline and diesel fractions of hydrocarbons (m.p. $\leqslant$360 °C) being insignificantly decreased (from 64% to 52.1%).

**Table 4**. Activity of zeolite catalysts in the cracking of vegetable oils.

| Oil | Catalyst | Reaction conditions | Conversion (%) | Yield (%) | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | | | gas | liquid hydrocarbons | solid residue | |
| Palm | MCM-41 (1)[a] | $p$ = 0.1 MPa, $T$ = 450 °C, | 78 | 6 | 55 | 9 | 100 |
| | MCM-41 (2)[a] | WHSV = 2.5 $h^{-1}$ | 86 | 9 | 59 | 9 | 100 |
| | MCM-41 (3)[a] | | 89 | 13 | 64 | 8 | 100 |
| | MCM-41 (4)[a] | | 87 | 9 | 61 | 9 | 100 |
| Palm | zeolite REY | $p$ = 0.1 MPa, $T$ = 450 °C, | 73 | 16 | 48 | – | 101 |
| | zeolite β | cat. : oil = 5 (by mass) | 84 | 20 | 56 | – | 101 |
| | zeolite SBA-15 | | 78 | 16 | 54 | – | 101 |
| Rapeseed | HZSM-5 (1)[b] | $T$ = 370 °C, WHSV = 3 $h^{-1}$ | 98 | 32 | 55 | 2 | 102 |
| | HZSM-5 (2)[b] | | 73 | 10 | 56 | 3 | 102 |
| Cottonseed | mixture of zeolites LK-98 and CHZ-4 | $p$ = 0.1 MPa, $T$ = 450 °C, cat. : oil = 7 (by mass) | – | 17 | 56 | – | 103 |

[a] Catalysts are mesoporous aluminosilicates differing by the method of preparation; [b] catalysts differ by temperature and time of calcination: 24 h at 400 °C (1) and 4 h at 1000 °C (2).

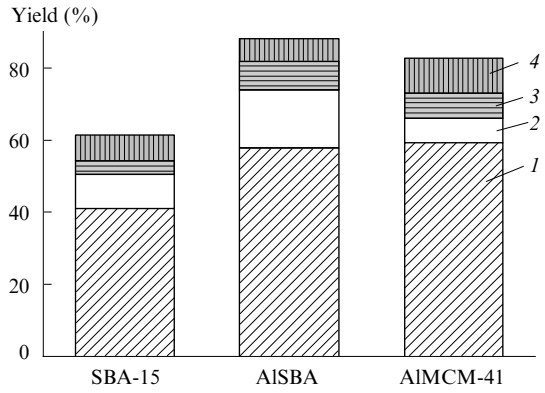



**Figure 3.** Composition of products of cracking of a mixture of fatty acids (wastes of the production of palm oil) on SBA-15, AlSBA and AlMCM-41 zeolites.[105]
(*1*) Liquid hydrocarbons, (*2*) gas, (*3*) water, (*4*) carbon.

Thus, despite their tendency to coke formation, zeolites are sufficiently active and effective catalysts for cracking of vegetable oil triglycerides with the production of hydrocarbons of gasoline, kerosene and diesel fractions, the properties of zeolite (such as acidity, pore size and specific surface area) significantly affecting the selectivity of reaction. The use of mesoporous MCM-41 zeolites results in lower yields of undesired products, namely, light hydrocarbons, though these zeolites do not possess sufficient stability under the conditions of hydrothermal treatment. As a whole, in spite of the simplicity of catalytic cracking as a method for production of fuel hydrocarbons from plant fatty acid triglycerides, the low yield of target liquid products, significant formation of gaseous products and rapid deactivation of the catalyst as a result of coking should be mentioned. Undoubtedly, the problem of regeneration of catalysts for cracking can be solved much easier than that for the catalysts for transesterification. However, hydrocracking seems a more promising approach to the processing of fatty acid derivatives. The products saturated with hydrogen are formed, and this has a positive impact on their technical characteristics and fuel performance.

## IV. Hydrocracking of fatty acid triglycerides and their derivatives

Hydrocracking of fatty acid triglycerides in the presence of catalysts based on transition metals may give hydrocarbons that are formed in the processes of hydrodeoxygenation, decarboxylation and decarbonylation of triglycerides (Fig. 4). Also the hydrogenation of double bonds of unsaturated acid residues and the formation of the products of cyclization and aromatization may take place under the conditions of hydrocraking.[106] The products of deoxygenation (n-alkanes) have the same carbon chain length as the initial fatty acids constituent in triglycerides. In the process, oxygen is removed as water and the glycerol residue transforms into propane.

In the case of decarboxylation in the presence of hydrogen, the chain of the alkanes obtained is one atom shorter than that of the starting acids because in this case, the terminal C–C bond is cleaved and oxygen is removed mainly in the form of CO and $CO_2$, the glycerol residue

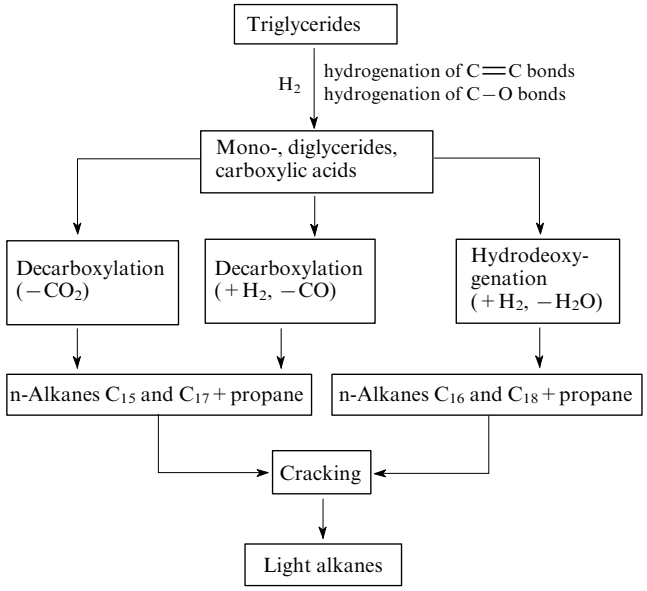



**Figure 4.** Scheme of transformation of triglycerides into hydrocarbons by cracking of vegetable oils.

also being transformed into propane.[107] Thus, the main products of hydrocracking of triglycerides are $C_{15}-C_{17}$ n-alkanes; this mixture is known as Green diesel or Supercetane.[108]

One of the advantages of hydrocracking over transesterification is the possibility of implementing this process in the standard existing oil refining equipment. As regards their composition and properties, the products of hydrocracking are similar to hydrocarbons of diesel and gasoline oil fractions and may be used with them jointly in internal combustion engine. Moreover, the mixture of hydrocarbons obtained upon cracking (Green diesel) has a higher cetane number than biodiesel and diesel fuel (Table 5) and also possesses a higher stability due to the absence of oxygen-containing functional groups. Thereby this process now attracts more attention of researches than the producing of biodiesel. In May 2007, the Neste Oil company started up the plant for processing vegetable and animal fats and also their derivatives in the forms of free fatty acids and esters into Green diesel in Porvo (Finland). The plant capacity is 170 000 tons per year.[26, 114]

**Table 5**. Cetane ratings of various fuels and oils.

| Type of fuel | Cetane rating | Ref. |
|---|---|---|
| Diesel fuel | 47 | 109 |
| Sunflower-seed oil | 37.1 | 109 |
| Biodiesel from sunflower-seed oil | 45.5 | 109 |
| Green diesel from sunflower-seed oil | > 80 | 110 |
| Palm oil | 42 | 111 |
| Biodiesel from palm oil | 71.4 | 112 |
| Green diesel from palm oil | > 92 | 113 |

For hydrocracking of vegetable oils and fatty acids, industrial sulfided catalysts for hydrodesulfurization are used most often, namely, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$.[106, 115, 116] The hydrocracking of rapeseed oil on the

$NiMo/Al_2O_3$ catalyst in a flow type reactor at temperatures of 310 and 360 °C and hydrogen pressures of 7 and 15 MPa was repoted.[117] The main reaction products were n-octadecane (depending on the conditions the selectivity of its formation was from 51.8 mass % to 78.2 mass %) and n-heptadecane (from 10.5 mass% to 24.9 mass %), the increase of the temperature causing the increase of the yield of heptadecane and the decrease of the yield of octadecane. The overall selectivity of formation of lighter alkanes was on average 5% – 6%. The cetane number of the mixtures obtained was 103, the content of sulfur in the products being 9 – 10 ppm.

In another study,[118] two catalyst beds were used for hydrocracking of rapeseed oil, namely, sulfided $NiMo/Al_2O_3$ and reduced $Ni/Al_2O_3$. The process was carried out in a flow type reactor in the temperature range of 240 – 360 °C, hydrogen pressure being 0.5 – 8 MPa, at WHSV = 1 $h^{-1}$ and molar ratio hydrogen : rapeseed oil = 100. As a result of reaction, rapeseed oil transformed mainly into heptadecane and octadecane. At the same time, similarly to the investigation,[117] the rise of temperature led to the increase in the yield of heptadecane and its isomers (from 10% to 23% upon the temperature rise from 270 to 350 °C), the selectivity of formation of octadecane and its isomers being decreased from 90% to 76%.

The transformations of vegetable oils and stearic acid on the reduced $Ni/SiO_2$ catalyst and sulfided $NiMo/\gamma\text{-}Al_2O_3$ catalyst (Procatalyse company) in a batch reactor were studied.[115] The $Ni/SiO_2$ catalyst, which is widely used in industry for the hydrogenation of vegetable oils, was prepared by wet impregnation and contained 8.3 mass % of Ni. In the presence of this catalyst under the starting hydrogen pressure of 4 MPa and temperature of 395 °C, stearic acid was decarboxylated and decarbonylated, and the resulting CO was converted to methane due to the high methanizing activity of reduced $Ni/SiO_2$. In the case of hydrocracking of soybean oil on the same catalyst but under different conditions (at 370 °C and hydrogen pressure of 11 MPa), the reaction mixture formed after the process consisted of 12 mol.% of carboxylic acids and of 88 mol.% of hydrocarbons (n-$C_{15}H_{32}$, n-$C_{16}H_{34}$, n-$C_{17}H_{36}$ and n-$C_{18}H_{38}$). The process of hydrocracking of vegetable oils (soybean oil, passionfruit oil, babassu oil) on sulfided $NiMo/\gamma\text{-}Al_2O_3$ catalyst was also studied.[116] The yield of n-alkanes after 2 hours of reaction at 360 °C and under $H_2$ pressure of 14 MPa was 66 mass % – 76 mass %, the yield of gaseous phase (the major gaseous products were $CO_2$ with selectivity of formation of 80 mass %, CO and light $C_1 - C_4$ hydrocarbons) and water was 9 mass % – 13 mass % and 5 mass %, respectively. Besides n-alkanes, the reaction gave a significant amount of cycloalkanes (up to 13 mass %) and aromatic compounds (up to 14 mass %), formed as a result of cyclization of polyunsaturated fatty acids.

The selectivity of the formation of products of hydrocracking of rapeseed oil on sulfided catalyst $NiMo/\gamma\text{-}Al_2O_3$ has been studied[119] in a flow type reactor with static bed under the hydrogen pressure of 7 MPa in the temperature range of 260 – 340 °C. Rapeseed oil was diluted by octane (which had been shown to remain unchanged under reaction conditions and thus it was suitable as an inert solvent) in volume ratio of 1 : 1, the WHSV was 1 $h^{-1}$, the reaction was carried out in the excess of hydrogen (1000 : 1 by volume). The hydrocarbons present in gaseous products included only propane (0.8 vol.% – 2.5 vol.%) and methane (trace). The composition of liquid hydrocarbon products depended on the reaction temperature. At low temperatures (260 – 300 °C) a turbid suspension of white crystals in a liquid was obtained. It could probably be a mixture of intermediates, namely, hydrogenated triglycerides, stearic acid, waxes and higher paraffins. At higher temperatures, a transparent colourless liquid formed. The content of starting reactants and intemediates was reduced with the increase of temperature. Above 310 °C the reaction mixture did not contain triglycerides or free fatty acids. n-Octadecane was the major product of the reaction. At 300 °C its concentration in liquid hydrocarbon fraction was ~70 mass %, the concentration of n-heptane being 13 mass %. With temperature rise, the yield of octadecane decreased, while the yield of heptadecane increased. Also, temperature rise induced an increase in the selectivity of the formation of isoalkanes. When the temperature of the reaction changed from 275 to 340 °C, their concentration in the organic products of cracking increased from 5 mass % to 40 mass %.

As a whole, the sulfided catalysts for hydrorefining showed high activity in hydrocracking of vegetable oils during initial period of time but then the activity fell because of the coking of the catalyst. The main reason of rapid deactivation of silfided catalysts is the loss of sulfur and the reduction of transition metals to their metallic state. The reactivation of catalysts does not take place due to the low content of sulfur in the starting vegetable raw material. This problem may be solved either by the application of sulfide-free catalysts or by the use of mixtures of vegetable oil with high-sulfur petroleum products as the feedstock. In the latter case, the sulfided catalysts act as catalysts of not only desulfurization but also hydrodeoxygenation.

A patent[120] describes the dependence of the degree of conversion and selectivity of formation of the products of hydrocracking of rapeseed oil on non-sulfided catalyst $NiCu/CeO_2 - ZrO_2$ on the temperature at a reduced hydrogen pressure. The process was carried out in a flow type reactor with a fixed catalyst bed under the hydrogen pressure of 0.5 MPa in the temperature range of 300 – 380 °C. Analysis of the products of hydrocracking by $^1H$, $^{13}C$ NMR and gas chromatography detected the following compounds (Fig. 5): alkanes (mainly, $C_{17}H_{36}$), 1,3- and 1,2-diglycerides, free fatty acids and other oxygen-containing compounds (fatty acid methyl esters, alcohols, aldehydes, ketones, waxes).

The complete conversion of fatty acid triglycerides at LHSV§ = 2.66 $h^{-1}$ was observed only at 380 °C, the yield of alkanes was ~60 mass %; the yield of the major product, namely, heptadecane, being 37.8 mass %. The high yield of oxygen-containing products of partial reduction of fatty acids (alcohols, aldehydes, ketones, waxes) was also mentioned, the product of decarboxylation of fatty acid, namely, ketone $(C_{17}H_{35})_2CO$, prevailing among them. The complete conversion of triglycerides and intermediate oxygen-containing products was achieved on increasing the hydrogen pressure up to 6.0 – 7.0 MPa.

Other papers of the same authors dealt with the investigation of a number of catalysts based on nickel ($Ni - Cu/CeO_2 - ZrO_2$, $Ni - Cu/ZrO_2$, $Ni - Cu/CeO_2$, $Ni/ZrO_2$)[121] and noble metals (Ru, Rh, Ir, Pt, Pd deposited on

§ A value similar to WHSV that characterizes the velocity of liquid feeding.

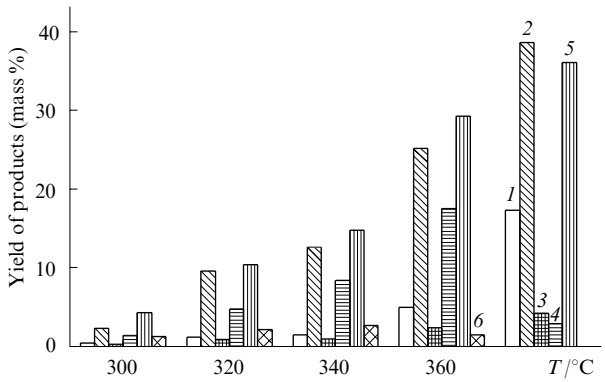



**Figure 5.** Dependence of the yield of products of hydrocraking of rapeseed oil on the reduced catalyst $NiCu/CeO_2-ZrO_2$ under hydrogen pressure of 0.5 MPa and LHSV = 2.66 $h^{-1}$ on the reaction temperature.
(*1*) Alkanes $C_7-C_{16}$, (*2*) $C_{17}H_{36}$, (*3*) alkanes $C_{18}-C_{19}$, (*4*) free fatty acids, (*5*) oxygen-containing products, (*6*) diglycerides.

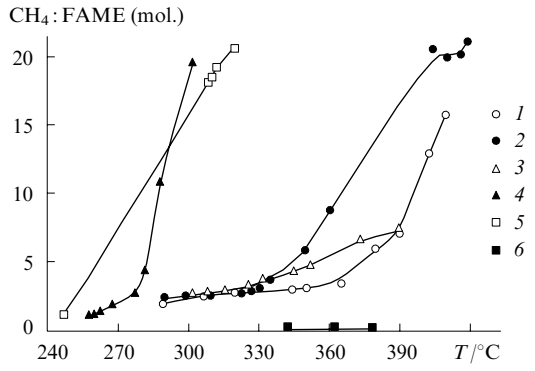



**Figure 7.** Dependences of the molar ratio $CH_4$ : FAME on the temperature of the process under a hydrogen pressure of 1.0 MPa at LHSV = 2 $h^{-1}$ (weight-average molecular weight of biodiesel is 297.7 g $mol^{-1}$).[121]
Catalysts: $Ni-Cu/CeO_2-ZrO_2$ (*1*), $Ni-Cu/ZrO_2$ (*2*), $Ni-Cu/CeO_2$ (*3*), $Ni/ZrO_2$ (*4*), $Ni/CeO_2$ (*5*), $CeO_2-ZrO_2$ (*6*).

$CeO_2-ZrO_2$)[122] in order to search for an effective catalyst for hydrocracking (hydrodeoxygenation) of fatty acid triglyceride derivatives. Out of the investigated systems, the highest activity in hydrodeoxygenation of fatty acid esters (biodiesel) was shown by nickel – copper catalysts (Fig. 6). In all of the cases, the major reaction products were $C_{15}-C_{17}$ hydrocarbons. In the presence of the $Ni/ZrO_2$ catalyst, the yield of alkanes drops even at relatively low temperatures (300 °C). The methanation of alkanes is the main reason for the decrease in their yields. The insertion of copper into the nickel catalyst provides high yields of alkanes at higher temperatures (up to 380 °C). In the case of $Ni-Cu/CeO_2-ZrO_2$, the yield of alkanes is close to the theoretically possible one (80 mass %).

It should be mentioned that copper itself is inactive in the hydrodeoxygenation of biediesel. Nevertheless, its presence in the nickel catalyst greatly influences the process of methanation of alkanes. From Fig. 7 it is clear that on nickel catalysts the methanation process goes intensively even at low temperatures (300 °C). In the presence of nickel–copper catalysts biodiesel quantitatively transforms into alkanes over a wider temperature range (300–360 °C).

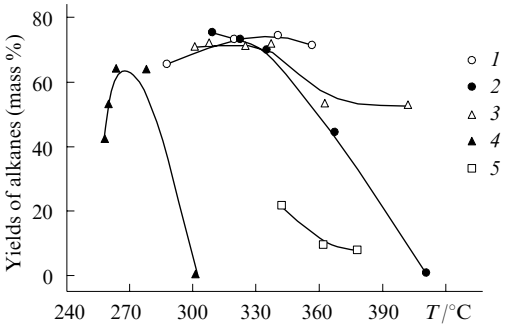



**Figure 6.** Dependences of the yield of alkanes on the temperature of hydrodeoxygenation of fatty acid esters in the presence of nickel catalysts under $H_2$ pressure of 1 MPa at LHSV = 2 $h^{-1}$ (Ref. 121).
Catalysts: $Ni-Cu/CeO_2-ZrO_2$ (*1*), $Ni-Cu/ZrO_2$ (*2*), $Ni-Cu/CeO_2$ (*3*), $Ni/ZrO_2$ (*4*), $Ni/CeO_2$ (*5*).

An essential disadvantage of Green diesel as engine fuel is its unsatisfactory low-temperature properties (relatively high viscosity and pour point), which are caused by the high concentration of normal alkanes; therefore it is advisable for the product of hydrocracking of triglycerides to undergo isomerization. Another paper[110] reports the isomerization of preliminarily hydrogenated sunflower-seed oil on the $Pt/HZSM\text{-}22/Al_2O_3$ catalyst, which contained 0.25 mass % – 1.1 mass % of Pt, in the range of temperature 280–370 °C, under the hydrogen pressure of 0.35–0.8 MPa, at LHSV = 1–4 $h^{-1}$ and the volumetric ratio $H_2$ : oil = 250–400 $nm^3\ m^{-3}$. The obtained liquid product (yield from 80% up to 90%) was a mixture of normal alkanes and isoalkanes (Table 6). As can be seen from Table 6, this catalyst provides a mixture of hydrocarbons with high concentration of isoalkanes (up to 82.5%), and at the same time the selectivity of their formation depends greatly on the temperature of the reaction.

Another example of application of zeolite catalysts for hydrocracking of fatty acid triglycerides[29] suggests the single-stage process of production, from sunflower-seed oil, of diesel fractions with improved performance characteristics due to the higher content of isomerization products of saturated alkanes. In the presence of bifunctional Pd/SAPO-31 catalyst (0.94% Pd; SAPO-31 being a mixed silicon, aluminium and phosphorus oxide) at 310–360 °C, WHSV = 0.9–1.6 $h^{-1}$ and $H_2$ pressure of 2.0 Mpa, it was

**Table 6**. Composition and properties of the products of isomerization of pre-hydrogenated sunflower-seed oil in the presence of the $Pt/HZSM\text{-}22/Al_2O_3$ catalyst under the hydrogen pressure of 5–6 MPa and LHSV = 2–3 $h^{-1}$ (Ref. 110).

| *T*/°C | Total yield of hydrocarbons (%) | Selectivity of formation (%) | | Cetane number |
|---|---|---|---|---|
| | | n-alkanes | isoalkanes | |
| 300 | 94.1–95.3 | 69.5–76.5 | 23.5–30.5 | 88–91 |
| 320 | 90.4–92.2 | 23.5–30 | 70–76.5 | 82–84 |
| 330 | 87.4–90.9 | 17.5–21 | 79–82.5 | 81–83 |
| 350 | 80.7–85.4 | 24–30 | 70–76 | 78–81 |

possible to achieve the ratio isoalkanes : n-alkanes = 16 at 100% degree of conversion of sunflower-seed oil. However, unfortunately, this ratio decreases with time virtually to zero, indicating deactivation of the catalyst. It has been shown that the main reason of deactivation of Pd/SAPO-31 is the decrease of the degree of dispersion of palladium from 50% to 11% after the reaction. Nevertheless, this way of producing high-cetane hydrocarbons from fatty acid triglycerides with the application of bifunctional catalysts for hydrocracking is promising and requires a more detailed development.

As a whole, the analysis of literature data on the catalysts for hydrocracking for processing of the derivatives of plant fatty acids has revealed the applicability of sulfided catalysts for desulfurization but only in combination with oil fractions. Another promising trend is the application of non-sulfided catalysts for hydrocracking that make it possible to process vegetable lipidic raw materials directly into fuel hydrocarbons. However in both cases, it is necessary to continue the investigations towards increasing the stability of catalysts as long as the specificity of starting raw materials (increased acidity, high content of oxygen, namely, 11 mass % – 12 mass %) restricts the choice of catalyst and process parameters.

## V. Decarboxylation of fatty acid triglycerides and their derivatives

Decarboxylation takes place almost always during cracking and hydrodeoxygenation of vegetable oils.[30] Nevertheless, this reaction should be considered separately from other processes of hydrogenolysis due to the fact that according to certain literature, it may proceed without participation of molecular hydrogen which is undoubtedly an advantage for industrial processes. The compounds containing carboxyl, ester and other functional groups undergo decarboxylation and as a result oxygen is removed from them in the form of $CO_2$:

$$\left.\begin{array}{l}\mathrm{OC(O)R^1}\\ \mathrm{OC(O)R^2}\\ \mathrm{OC(O)R^3}\end{array}\right\} \longrightarrow \mathrm{C_3H_8 + R^1H + R^2H + R^3H + 3\,CO_2}.$$

Though in this case the length of the carbon backbone chain of the reaction products is one carbon atom shorter than that of the reactants, this process seems to be a promising method of producing liquid hydrocarbons since it is carried out in inert atmosphere and it does not require significant consumption of hydrogen. Besides that the reaction of decarboxylation in contrast to, *e.g.*, hydrocracking, does not result in the formation of water, which has an unfavourable impact on the catalyst, especially if aluminium oxide is used as the suport. A number of works carried out in the laboratory of industrial chemistry of the chemical engineering centre of the Abo Academy (Finland) deals with the investigation of the production of hydrocarbons from fatty acids, their esters and triglycerides. Kubickova and coauthors[30] used pre-reduced industrial catalyst 5% Pd/C (Aldrich) for decarboxylation of stearic acid, ethyl stearate or tristearin. The reaction was carried out in the temperature range of 300 – 360 °C and total pressure of 1.7 – 4 MPa in inert atmosphere (He) in the presence of hydrogen. In all cases, n-heptadecane was the major product of the reaction, isomers of heptadecane and substituted undecylbenzenes being minor products. It has been shown that under low partial pressure of hydrogen, the formation of aromatic compounds is suppressed, the increase of hydrogen pressure causing a decrease of the degree of conversion of stearic acid. The kinetics of liquid-phase decarboxylation of ethyl stearate has been studied[123] on the same catalyst in the wide range of temperatures in a mixture of argon and hydrogen (5 mass % $H_2$ in Ar), the major reaction product being also n-heptadecane, including the case of reaction performed in inert atmosphere. Under similar conditions, the influence of solvent and substrates (oleic and linoleic acids, methyl linoleate) on the activity of the 5% Pd/C catalyst was studied.[124] Later, the same authors obtained a low-percentage catalyst containing 1 mass % of Pd supported on carbon, namely, Sibunit.[31, 125–127] This catalyst was tested in the reaction of decarboxylation of five different fatty acids ($C_{17}$, $C_{18}$, $C_{19}$, $C_{20}$ and $C_{22}$) in inert atmosphere at 300 °C under the pressure of 1.7 MPa, the ratio reactant : catalyst = 0.1 mol litre$^{-1}$ $g_{cat}^{-1}$ and demonstrated a relatively high activity. Thus, after 150 minutes of the process, the conversion of fatty acids was 83% to 93% except for the acid $C_{22}$ (conversion was 23%). The activity of palladium catalyst in the decarboxylation of stearic acid was also confirmed by a study[128] in which Pd (5%) supported on mesoporous silicon oxide was used. In inert atmosphere ($N_2$) at 300 °C in autoclave, the degree of conversion of stearic acid reached 85% – 90% after 6 hours, the selectivity of formation of n-heptadecane being ~100%. Under similar conditions in a flow reactor, the conversion of ethyl stearate was < 15%, the selectivity of formation of heptadecane being 87%, the second reaction product being stearic acid. At the same time, the authors noted the effect of deactivation of Pd/C-catalysts in the reaction performed in inert atmosphere. In order to increase the activity and stability of the catalyst, decarboxylation was carried out in the presence of $H_2$ in the mixture with the ratio Ar : $H_2$ = 19 and this led to good results. According to the stoichiometry of decarboxylation, no additional hydrogen is required. But if the formation of intermediate R – $CH_2$ – Z (Z being the active site of the catalyst) on the catalyst surface is assumed, then it becomes obvious that the presence of sufficient quantity of activated hydrogen on the surface is a necessary condition for the chemical act to be completed.

Basic oxides are also used for decarboxylation.[129, 130] They act not so much as catalysts but rather as reagents because they are able to bind organic acids and form salts with them and also participate in decarboxylation of acids with the formation of ketones, the oxides themselves being transformed into corresponding carbonates. On calcination in air, the latter may be easily regenerated to oxides. After such high-temperature treatment these oxides possess small specific surface area but in this case the yield of target products may be increased at the expence of the increase of the amount of oxide, which only slightly increases the process cost since the alkaline earth metal oxides such as MgO or CaO are relatively cheap reagents. Thus, for decarboxylation of fatty acids in the liquid phase to give ketones, the authors of patent[131] used mixed oxide MgO – $Al_2O_3$ (with ratio MgO : $Al_2O_3$ = 1 : 1). The reactant : catalyst ratio was 100 : 30, the reaction was carried out at 300 – 350 °C. In the first step, magnesium salts of organic acids were obtained. Then the decomposition of these salts resulted in ketones, which were removed from the reaction mixture by extraction. The yield of ketones was

from 82% to 89.2% depending on the conditions of reaction. A patent [132] describes the method of production of ketones from fatty acids on magnesium oxide in a flow type reactor at 360–370 °C and atmospheric pressure. Acetic and lauric acids were used as substrates. In order to avoid the formation of salts, MgO and reactants were preliminary heated up to 340 °C separately, the yield of ketones being 85%. A patent [133] describes the same process under similar conditions but with the application of brookite and without preliminary heating. In 2008, the Albemarle Catalysts Company B.V. patented [134] the process of producing ketones from carboxylic acids on hydrotalcite, which is stable against the action of acids and water, in the wide temperature (225–500 °C) and pressure (0.001–1 MPa) ranges.

One would expect the formation of symmetric ketone, *e.g.*, $(n\text{-}C_{17}H_{35})_2CO$, as a result of decarboxylation of fatty acid derivatives in the presence of basic catalysts. Such ketones may be used as lubricants but due to their high molecular weight they cannot be used as improving additives to traditional engine fuels.

The main characteristic feature and advantage of application of catalysts based on noble metals for decarboxylation is the fact that the main products of transformation of substrate (acid, ester, triglyceride) are hydrocarbons but not ketones as in the case of basic catalysts. However, the necessity of using hydrogen in the decarboxylation levels the main advantage of this method so it may be ranked similarly to the processes of hydrogenolysis.

## VI. Conclusion

When considering the processes of processing of vegetable oils and their derivatives as free fatty acids into fuel hydrocarbons applying heterogeneous catalysts, four trends should be marked out, namely, transesterification, cracking, hydrocracking and decarboxylation. Out of the processes listed above, transesterification providing biodiesel attracts the most attention. It may be explained, first, by significant world output of biodiesel, second, by the existence of unquestionable disadvantages of the homogeneous processes applied (low quality of biodiesel and glycerol, formation of significant amounts of waste water, high requirements to the starting raw materials). In spite of the obvious advantages of heterogeneous catalysts for transesterification and solitary examples of pilot testing, as a whole, the development of this trend is still at the laboratory level, the catalysts being studied in static autoclaves with intensive stirring. Only individual publications deal with the investigation of flow type processes of transesterification. The limitedness of use of heterogeneous catalysts for transesterification on industrial scale nowadays is caused by the fact that the catalysts being developed do not correspond to industrial requirements. In particular, they are unstable against the leaching of the active component in the presence of water, free fatty acids and glycerol at higher temperatures under continuous-flow conditions. Nevertheless the intensity of the investigations being carried out allows one to expect the development of stable catalysts for transesterification in the near future.

On developing the heterogeneous catalysts for transesterification of vegetable oils it is necessary to solve the set of problems traditional for heterogeneous catalysis: 1) search for most active systems, 2) stabilization of active component from leaching, 3) shaping of the catalyst. Now it may be considered that the first stage of the development of a catalyst for transesterification has been completed, because the active catalytic compositions were determined. In order to commercialize this technology, it is necessary to solve the remaining problems and to carry out durability tests.

The processes of processing of fatty acid triglycerides and their derivatives that are alternative to transesterification (catalytic cracking, hydrocracking and decarboxylation) are intensely developing despite of the relative limitedness of the range of applicable catalytic systems. As a matter of fact, the situation with catalysts for the mentioned processes is similar to the one with catalysts for transesterification. At the same time the first-priority requirement to catalysts is also their stability, to coking in this case, and their ability to multiple regeneration without the loss of activity. It should also be mentioned that nowadays not only the search for effective catalytic systems of processing of vegetable raw materials is in progress but also the range of processed renewable raw materials is constantly expanding. At the same time, the developers focus on the processing of microalgae with high contents of lipids and, undoubtedly, on the processing of lignocellulose as the most widespread renewable raw material.

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## References

1. A V Bridgwater, D Meier, D Radlein *Org. Geochem.* **30** 1479 (1999)
2. Z Sen *Prog. Energy Combust. Sci.* **30** 367 (2004)
3. T Searchinger, R Heimlich, R A Houghton, F Dong, A Elobeid, J Fabiosa, S Tokgoz, D Hayes, T-H Yu *Science* **319** 1238 (2008)
4. V Kirubakaran,V Sivaramakrishnan, R Nalini, T Sekar, M Premalatha, P Subramanian *Renew. Sustain. Energy Rev.* **13** 179 (2009)
5. R C Saxena, D Seal, S Kumar, H B Goyal *Renew. Sustain. Energy Rev.* **12** 1909 (2008)
6. D C Elliott *Energy Fuels* **21** 1792 (2007)
7. K W Lee, J X Yu, J H Mei, L Yan, Y W Kim, K W Chung *J. Ind. Eng. Chem.* **13** 799 (2007)
8. Y C Sharma, B Singh, S N Upadhyay *Fuel* **87** 2355 (2008)
9. S A Lermontov, L L Yurkova *Katal. Prom-ti* (2) 60 (2009) [a]
10. I Yu Popova *Sverkhkrit. Flyuidy: Teor. Prakt.* **2** (4) 85 (2007)
11. G Madras, C Kolluru, R Kumar *Fuel* **83** 2029 (2004)
12. S D Varfolomeev, E N Efremenko, L P Krylova *Russ. Chem. Rev.* **79** 491 (2010); *Usp. Khim.* **79** 544 (2010)
13. S A Lermontov, L L Ushakova *Izv. Akad. Nauk, Ser. Khim.* 102 (2008) [b]
14. A V Garabadzhiu, V A Galynkin, M M Karasev, G V Kozlov, T B Lisitskaya *Izv. St Peterb. Gos. Tekhnol. Iin-ta (Tekhn. Un-ta)* (7) 63 (2010)
15. A Yu Krylova, E A Kozyukov, A L Lapidus *Khim. Tv. Topliva* (6) 39 (2008)
16. V G Debabov *Biotekhnologiya* (1) 3 (2008)
17. GB P. 647174A (1950)
18. GB P. 795573A (1958)
19. GB P. 1334205A (1973)
20. US P. 4004041A (1977)
21. AT P. 235789A (1990)
22. US Appl. 20040231237 (2004)

23. WO P. 03004588 (2003)
24. JP P. 2000270886A (2000)
25. WO P. 2003032826A1 (2003)
26. M Snore, P Myaki-Arvela, I L Simakova, Yu Myullyuoia, D Yu Murzin *Sverkhkrit. Flyuidy: Teor. Prakt.* **4** (1) 3 (2009)
27. M Stumborg, D Soveran, W Craig , W Robinson, K Ha *Energy Biomass Waste* **16** 721 (1993)
28. K D Maher, D C Bressler *Bioresour. Technol.* **98** 2351 (2007)
29. O V Kikhtyanin, A E Rubanov, A B Ayupov, G V Echevsky *Fuel* **89** 3085 (2010)
30. I Kubičková, M Snåre, K Eränen, P Mäki-Arvela, D Yu Murzin *Catal. Today* **106** 197 (2005)
31. I Simakova, O Simakova, P Mäki-Arvela, D Yu Murzin *Catal. Today* **150** 28 (2010)
32. A Murugesan, C Umarani, T R Chinnusamy, M Krishnan, R Subramanian, N Neduzchezhain *Renew. Sustain. Energy Rev.* **13** 825 (2009)
33. G Vicente, M Martínez, J Aracil *Bioresour. Technol.* **92** 297 (2004)
34. M S A Moraes, L C Krause, M Espinosa da Cunha, C S Faccini, E Weber de Menezes, R C Veses, M R A Rodrigues, E B Caramão *Energy Fuels* **22** 1949 (2008)
35. M Balat, H Balat *Energy Convers. Manage.* **49** 2727 (2008)
36. S Zheng, M Kates, M A Dubé, D D McLean *Biomass Bioenergy* **30** 267 (2006)
37. E Lotero,Y Liu, D E Lopez, K Suwannakarn, D A Bruce, J G Goodwin Jr *Ind. Eng. Chem. Res.* **44** 5353 (2005)
38. A U Ishbaeva, L A Talipova, R N Shakhmaev, S S Vershinin, L V Spirikhin, V V Zorin *Bashkir. Khim. Zh.* **16** (2) 36 (2009)
39. U Schuchardt, R Sercheli, R M Vargas *J. Braz. Chem. Soc.* **9** 199 (1998)
40. T Čerče, S Peter, E Weidner *Ind. Eng. Chem. Res.* **44** 9535 (2005)
41. M Mittelbach, C Remschmidt *Biodiesel, the Comprehensive Handbook* (2nd Ed.) (Vienna: Börsedruck Ges. M.B.H., 2005)
42. M Di Serio, M Ledda, M Cozzolino, G Minutillo, R Tesser, E Santacesaria *Ind. Eng. Chem. Res.* **45** 3009 (2006)
43. M Di Serio, R Tesser, L Pengmei, E Santacesaria *Energy Fuels* **22** 207 (2008)
44. M Verziu, B Cojocaru, J Hu, R Richards, C Ciuculescu, P Filip, V I Parvulescu *Green Chem.* **10** 373 (2008)
45. D G Cantrell, L J Gillie, A F Lee, K Wilson *Appl. Catal., A* **287** 183 (2005)
46. H Chen, J-F Wang *Stud. Surf. Sci. Catal.* **159** 153 (2006)
47. G J Suppes, K Bockwinkel, S Lucas, J B Botts, M H Mason, J A Heppert *J. Am. Oil Chem. Soc.* **78** 139 (2001)
48. H-J Kim, B-S Kang, M-J Kim,Y M Park, D-K Kim, J-S Lee, K-Y Lee *Catal. Today* **93**–**95** 315 (2004)
49. H Ma, S Li, B Wang, R Wang, S Tian *J. Am. Oil Chem. Soc.* **85** 263 (2008)
50. E Leclercq, A Finiels, C Moreau *J. Am. Oil Chem. Soc.* **78** 1161 (2001)
51. M Toda, A Takagaki, M Okamura, J M Kondo, S Hayashi, K Domen, M Hara *Nature (London)* **438** 178 (2005)
52. C S MacLeod, A P Harvey, A F Lee, K Wilson *Chem. Eng. J.* **135** 63 (2008)
53. E Lotero, J G Goodwin, D A Bruce, K Suwannakarn, Y Liu, D E Lopez, in *Catalysis. A Specialist Periodical Report* Vol. 19 (Cambridge: Royal Society of Chemistry, 2006) p. 41
54. A Macario, G Giordano, B Onida, D Cocina, A Tagarelli, A M Giuffrè *Appl. Catal., A* **378** 160 (2010)
55. T F Dossin, M F Reyniers, G B Marin *Appl. Catal., B* **62** 35 (2006)
56. US P. 6818026 (2004)
57. WO P. 2005/021697 (2005)
58. M López Granados, M D Zafra Poves, D Marttn Alonso, R Mariscal, F Cabello Galisteo, R Moreno-Tost, J Santamaría, J L G Fierro *Appl. Catal., B* **73** 317 (2007)
59. Z Yang, W Xie *Fuel Process. Technol.* **88** 631 (2007)
60. WO P. 2006/002087 (2006)
61. T Ebiura, T Echizen, A Ishikawa, K Murai, T Baba *Appl. Catal., A* **283** 111 (2005)
62. W Xie, H Peng, L Chen *Appl. Catal., A* **300** 67 (2006)
63. W Xie, X Huang *Catal. Lett.* **107** 53 (2006)
64. G J Suppes, M A Dasari, E J Doskocil, P J Mankidy, M J Goff *Appl. Catal., A* **257** 213 (2004)
65. W Xie, X Huang, H Li *Bioresour. Technol.* **98** 936 (2007)
66. EP P. 0623581 (1999)
67. N Shibasaki-Kitakawa, H Honda, H Kuribayashi, T Toda, T Fukumura, T Yonemoto *Bioresour. Technol.* **98** 416 (2006)
68. Y Liu, E Lotero, J G Goodwin Jr, C Lu *J. Catal.* **246** 428 (2007)
69. RF P. 2366503 (2009); *Byull. Izobret.* (25) (2009)
70. H Sun, Y Ding, J Duan, Q Zhang, Z Wang, H Lou, X Zheng *Bioresour. Technol.* **101** 953 (2010)
71. F R Abreu, D G Lima, D G Hamú, S Einloft, J C Rubim, P A Z Suarez *J. Am. Oil Chem. Soc.* **80** 601 (2003)
72. M Di Serio, R Tesser, M Dimiccoli, F Cammarota, M Nastasi, E Santacesaria *J. Mol. Catal. A: Chem.* **239** 111 (2005)
73. US P. 5525126 (1996)
74. Y Liu, E Lotero, J G Goodwin Jr *J. Catal.* **243** 221 (2006)
75. Y Liu, E Lotero, J G Goodwin Jr *J. Catal.* **242** 278 (2006)
76. D E López, J G Goodwin Jr , D A Bruce *J. Catal.* **245** 381 (2007)
77. G W Parshall , S D Ittel *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes* (2nd Ed.) (New York: Wiley-Interscience, 1992)
78. B Bonelli, M Cozzolino, R Tesser, M Di Serio, M Piumetti, E Garrone, E Santacesaria *J. Catal.* **246** 293 (2007)
79. M G Kulkarni, A K Dalai *Ind. Eng. Chem. Res.* **45** 2901 (2006)
80. D E López, J G Goodwin Jr, D A Bruce, E Lotero *Appl. Catal., A* **295** 97 (2005)
81. M-H Zong, Z-Q Duan, W-Y Lou, T J Smith, H Wu *Green Chem.* **9** 434 (2007)
82. S Furuta, H Matsuhashi, K Arata *Catal. Commun.* **5** 721 (2004)
83. S Furuta, H Matsuhashi, K Arata *Biomass Bioenergy* **30** 870 (2006)
84. J Jitputti, B Kitiyanan, P Rangsunvigit, K Bunyakiat, L Attanatho, P Jenvanitpanjakul *Chem. Eng. J.* **116** 61 (2006)
85. S Yan, S O Salley, K Y S Ng *Appl. Catal., A* **353** 203 (2009)
86. US P. 5908946 (1999)
87. US P. 6878837 (2005)
88. US Appl. 2005/0113588 (2005)
89. H Li, W Xie *Catal. Lett.* **107** 25 (2006)
90. P S Sreeprasanth, R Srivastava, D Srinivas, P Ratnasamy *Appl. Catal., A* **314** 148 (2006)
91. WO P. 2007/043063 (2007)
92. L Bournay, D Casanave, B Delfort, G Hillion, J A Chodorge *Catal. Today* **106** 190 (2005)
93. J L Shumaker, C Crofcheck, S A Tackett, E Santillan-Jimenez, M Crocker *Catal. Lett.* **115** 56 (2007)
94. G Knothe *Prog. Energy Combust. Sci.* **36** 364 (2010)
95. G W Huber, A Corma *Angew. Chem., Int. Ed.* **46** 7184 (2007)
96. F A Twaiq, N A M Zabidi, A R Mohamed, S Bhatia *Fuel Process. Technol.* **84** 105 (2003)
97. Y-S Ooi, S Bhatia *Microporous Mesoporous Mater.* **102** 310 (2007)
98. Y-S Ooi, R Zakaria, A R Mohamed, S Bhatia *Appl. Catal., A* **274** 15 (2004)
99. P Tamunaidu, S Bhatia *Bioresour. Technol.* **98** 3593 (2007)
100. F A Twaiq, A R Mohamed, S Bhatia *Microporous Mesoporous Mater.* **64** 95 (2003)
101. T L Chew, S Bhatia *Bioresour. Technol.* **100** 2540 (2009)
102. Y S Prasad, N N Bakhshi *Appl. Catal.* **18** 71 (1985)
103. H Li, B Shen, J C Kabalu, M Nchare *Renew. Energy* **34** 1033 (2009)

104. D Zhao, J Feng, Q Huo, N Melosh, G H Fredrickson, B F Chmelka, G D Stucky *Science* **279** 548 (1998)
105. Y-S Ooi, R Zakaria, A R Mohamed, S Bhatia *Catal. Commun*. **5** 441 (2004)
106. G N da Rocha Filho, D Brodzki, G Djgga-Mariadassou *Fuel* **72** 543 (1993)
107. G W Huber, P O'Connor, A Corma *Appl. Catal., A* **329** 120 (2007)
108. T Kalnes, T Marker, D R Shonnard *Int. J. Chem. React. Eng*. **5** A48 (2007)
109. A S Ramadhas, S Jayaraj, C Muraleedharan *Renew. Energy* **29** 727 (2004)
110. J Hancsók, M Krár, S Magyar, L Boda, A Holló, D Kalló *Microporous Mesoporous Mater*. **101** 148 (2007)
111. C Tangsathitkulchai, Y Sittichaitaweekul, M Tangsathitkulchai *J. Am. Oil Chem. Soc*. **81** 401 (2004)
112. A S M A Haseeb, H H Masjuki, L J Ann, M A Fazal *Fuel Process. Technol*. **91** 329 (2010)
113. A Guzman, J E Torres, L P Prada, M L Nuñez *Catal. Today* **156** 38 (2010)
114. R Rapier, in *Biofuels, Solar and Wind as Renewable Energy Systems: Benefits and Risks* (Ed. D Pimentel) (Berlin: Springer, 2008) p. 153
115. J Gusmão, D Brodzki, G Djéga-Mariadassou, R Frety *Catal. Today* **5** 533 (1989)
116. G N da Rocha Filho, M H S Bentes, D Brodzki, G Djéga-Mariadassou *J. Am. Oil Chem. Soc*. **69** 266 (1992)
117. P Šimáček, D Kubička, G Šebor, M Pospíšil *Fuel* **89** 611 (2010)
118. Q Smejkal, L Smejkalová, D Kubička *Chem. Eng. J*. **146** 155 (2009)
119. P Šimáček, D Kubička, G Šebor, M Pospíšil *Fuel* **88** 456 (2009)
120. RF P. 2356629 (2009)
121. V A Yakovlev, S A Khromova, O V Sherstyuk, V O Dundich, D Yu Ermakov, V M Novopashina, M Yu Lebedev, O Bulavchenko, V N Parmon *Catal. Today* **144** 362 (2009)
122. V O Dundich, V A Yakovlev *Khim. Inter. Ustoich. Razv*. 527 (2009)
123. M Snåre, I Kubičková, P Mäki-Arvela, K Eränen, J Wärnå, D Yu Murzin *Chem. Eng. J*. **134** 29 (2007)
124. M Snåre, I Kubičková, P Mäki-Arvela, D Chichova, K Eränen, D Yu Murzin *Fuel* **87** 933 (2008)
125. I Simakova, O Simakova, P Mäki-Arvela, A Simakov, M Estrada, D Yu Murzin *Appl. Catal., A* **355** 100 (2009)
126. S Lestari, P Mäki-Arvela, I Simakova, J Beltramini, G Q Max Lu, D Yu Murzin *Catal. Lett*. **130** 48 (2009)
127. S Lestari, P Mäki-Arvela, H Bernas, O Simakova, R Sjöholm, J Beltramini, G Q Max Lu, J Myllyoja, I Simakova, D Yu Murzin *Energy Fuels* **23** 3842 (2009)
128. E W Ping, R Wallace, J Pierson, T F Fuller, C W Jones *Microporous Mesoporous Mater*. **132** 174 (2010)
129. US Appl. 2007244343A (2007)
130. G A H Mekhemer, S A Halawy, M A Mohamed, M I Zaki *J. Catal*. **230** 109 (2005)
131. US P. 3391191A1 (1968)
132. GB P. 834273A (1960)
133. GB P. 836205A (1960)
134. EP P. 1996536 (2008)

[a] — *Catal. Ind. (Engl. Transl.)*
[b] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[c] — *Chem. Sustain. Develop. (Engl. Transl.)*