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# Catalytic Methods for the Manufacturing of High-Production Volume Chemicals from Vegetable Oils and Fats (Review)

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**Abstract**—Current status of catalytic chemistry and technology for the manufacturing of high production volume chemicals, such as biofuel, higher olefins, and higher fatty alcohols, from the renewable feedstocks-inedible oils and fats is discussed. Analysis of achievements in the area of fundamental research and industrial application of inedible oils and fats is presented. The dynamics of growth in the production of biodiesel and biokerosene over recent years is shown. Various types of feedstock and deoxygenation catalysts are described. Modern concepts of the mechanisms of this process based on the results of kinetic and quantum—chemical studies on model acids and catalytic sites are discussed. New ways of selective preparation of olefins from vegetable oils and fats via decarbonylation of higher fatty acids over Cu and Ni catalysts are discussed. Industrial processes and catalysts for hydrogenation of higher fatty acids and esters into corresponding alcohols are considered. Published data on the mechanisms of these reactions are surveyed.

**Keywords:** deoxygenation, stearic acid, higher fatty alcohols, higher olefins, catalysts, mechanisms of chemical reactions

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The prospects of use of renewable feedstock are undoubtedly associated with the value of proven world reserves of petroleum and its cost in the world market. Despite high volatility of its price which has been observed lately, attention to this feedstock not only does not subside but demonstrates stable growth [1].

Inedible vegetable oils and fats are one of the promising types of renewable feedstock. At present, it is already evident that valuable high production volume (HPV) chemicals, such as motor fuels (mainly diesel and aviation fuels), higher olefins (HOs), and higher fatty alcohols (HFALs), can be obtained via catalytic deoxygenation[1] of triglycerides (TGs) or their parent higher fatty acids (HFAs).

The aim of this review is the analysis of current achievements in this field to cover the latest results of fundamental studies and practical application of inedible oils and fats for the production of HPV chemicals.

## BIODIESEL AND BIOKEROSENE

This is one of the most rapidly growing lines of research and development [2–5]. According to the data of Scopus, the number of publications on the manufacturing of biofuels from fatty acids exceeded 600 in 2013. On the other hand, while there was almost no production of biodiesel from oils and fats in 1995, already 9.57 million tons of biodiesel, including second-generation biodiesel (with the hydrocarbon composition), was produced in 2010. In 2011, 254 plants were built in Europe only, the total capacity of which was 22.1 million tons per year. In 2012, the total capacity of these plants reached 23.5 million tons per year. Note that, nevertheless, existing production capacities exceed the volume of production of biodiesel almost twofold [6].

The decrease in the consumption of first-generation biodiesel (with the ester composition), mainly because of its low quality, resulted in the decrease in its production. At the same time, the production of second-generation biodiesel grows. The prognosis for the production in the EU for 2020 is about 20 million tons. Growth in the fraction of biofuels in transport fuels to 10% is expected. The world production of biodiesel was about 25 million tons in 2013 [7], and the prognosis for 2020 is about 57 million m$^3$ per year [8].

Inedible oils from oilplants such as algae, gold-of-pleasure (*Camelina sativa*), salad rocket (*Eruca sativa*

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[1] Hereinafter, deoxygenation means the removal of oxygen from fatty acids, their esters, and other derivatives in the form of CO (decarbonylation), $CO_2$ (decarboxylation), and $H_2O$ (decarbonylation, hydrodeoxygenation) with the formation of hydrocarbons. Hydrodeoxygenation leads to the removal of oxygen in the form of water only. Works on the oxidative decarboxylation of acid, e.g., with persulfate ion, are not included in this review.

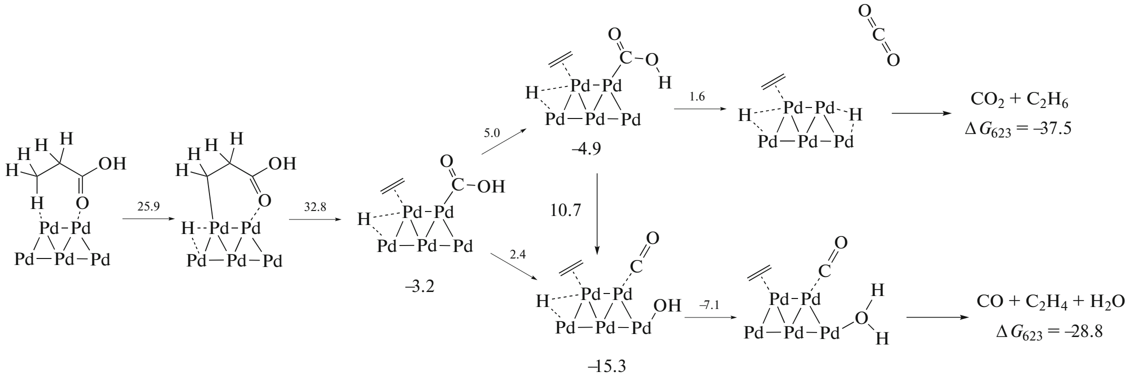
Mill), and jatropha, as well as wood waste (derosined tall oil) are the most promising for industrial application. Waste yellow grease, brown grease, and rendered animal fats are preferable as fat waste for recycling [3]. Currently, the main industrial process for the production of hydrocarbon biofuels is the hydrodeoxygenation of esters (mainly fatty acid TGs) [3, 9] which proceeds according to the following main reaction equation without taking into account hydrogen consumed for the hydrogenation of the double bonds in the acid radicals of the initial TG molecules:

$$C_3H_5O_3(RCO_2)_3 + 15H_2 = 3RCH_3 + C_3H_8 + 9H_2O.$$

Catalysts and processes used in the industry are discussed in reviews [2–4]. It is assumed that catalysts for decarbonylation and decarboxylation are mostly Group VIII metals of periodic table, while hydrodeoxygenation catalysts are transition metal sulfides [5].

Two-step technology for the production of biofuels discussed in literature, which includes the hydrolysis of oils and fats to fatty acids with their subsequent deoxygenation into hydrocarbons with the fuel composition, is very attractive [3]. The advantage of this method is the preparation of not only the fuel but also glycerol as a valuable byproduct in the process, as well as a sharp decrease in the consumption of hydrogen when compared to the traditional hydrodeoxygenation technology.

Lately, certain success has been achieved in studying the kinetics and understanding the mechanism of deoxygenation, without which it is hard to imagine the creation of a modern process technology and new highly efficient catalysts. Relatively recently, a cycle of works has emerged, in which this reaction was studied using methods of quantum–chemical and kinetic simulation via an example of propanoic and stearic (St) acids, respectively, in the presence of alumina-supported palladium catalysts [3, 10]. The choice of fatty acids as the models of oils and fats is concerned with the fact that the deoxygenation of the latter proceeds via the intermediate formation of these acids [5]. The mechanism of deoxygenation of propanoic acid based on quantum–chemical calculations (Priroda program [11], DFT–PBE method [12], L11 basis sets [13], the calculation procedure is given in [14]) can be represented as Scheme 1.



**Scheme 1.** Propanoic acid deoxygenation over the $Pd_{15}$ cluster (it is depicted as a pentanuclear cluster fragment). Values of $\Delta G^{\neq}_{623}$ of activated complexes are indicated over arrows, while values of $\Delta G_{623}$ of intermediates, below structures (they are given relative to independent $C_2H_5COOH$ and $Pd_{15}$).

The rate-determining step of the reaction is the R–COOH bond cleavage ($\Delta G^{\neq}_{623}$ = 32.8 kcal/mol). There are no thermodynamic limitations for the routes of decarboxylation and decarbonylation ($\Delta G_{623}$ = –37.5 and $\Delta G_{623}$ = –28.8 kcal/mol, respectively). However, decarbonylation is faster for kinetic reasons ($\Delta G^{\neq}$ = 5.6 versus $\Delta G^{\neq}$ = 8.2 kcal/mol for decarboxylation).

The results of the experimental study of the kinetics of the St deoxygenation reaction over palladium catalysts are in full agreement with quantum–chemical calculations. Thus, methyl formate was experimentally detected among the reaction products (the reaction products were subjected to methylation for chromatographic analysis, as a result of which formic acid formed transformed into the ester). Apparently, formic acid is formed as a result of insertion of a hydrogen atom in the Pd–COOH bond. In addition, as is shown in a series of works, the reaction indeed predominantly proceeds via the decarbonylation route not only over palladium but also over other metals [14–16].

The detailed study of the kinetics of this reaction based on the quantitative analysis of ten reactants using various instrumental methods (chromatography and UV, IR, and $^1$H NMR spectroscopy) made it possible to obtain a mathematical model describing the transformations of St to almost its 100% conversion within the accuracy of the experimental error. It is based on the Langmuir–Hinshelwood theory; however, as opposed to its classic version, it involves adsorption of not only reagents and products but also of other reactants present in the system including intermediates. In addition, the model involves the formation of complexes containing more than one adsorbed molecule per active site on the catalyst surface [10]. These transformations amount to 17 routes, of which the main four are St decarbonylation, heptadecene hydrogenation, St decarboxylation, and St hydrodeoxygenation.

Kinetic and quantum–chemical simulation of this reaction has shown that the decarbonylation proceeds predominantly over active sites containing hydrogen adsorbed on the palladium site, while decarboxylation, over the sites containing an adsorbed water molecule. Therefore, the decarbonylation product (water) promotes the St decarboxylation reaction. Indeed, introducing water into the reaction mixture leads to a sharp increase in the contribution from the decarboxylation reaction [10]. Equations describing the kinetics of this complex reaction are presented in [3, 10]. The nature of the metal and acidity of the support used play an important role in the ratio of reaction rates by different routes [14].

## HIGHER OLEFINS

As opposed to the use of oils and fats for the preparation of biodiesel and HFALs, the reaction of selective preparation of HOs is studied insufficiently. From our viewpoint, there are at least two reasons for it. The first reason is relative complexity of this reaction associated with the high reactivity of the products which readily undergo various transformations at elevated temperatures, so that the selectivity for HOs drops substantially. The second reason is economical and political. Due to the fact that in the European Union, a goal to achieve the 20% satisfaction of the need in energy from renewable sources by 2020 has been established, corresponding requirements on the use of renewable types of feedstock for the production of transport biofuel, which are obligatory and keeping with them is financially encouraged, were issued to the EU member states (Renewable Energy Directive and the ETS Directive). This, in turn, leads to the decrease in the availability of biological resources for industrial processes for the manufacturing of chemicals. At the same time, it is declared that the development of renewable energy sources should not result in conflicts between various ways of use of renewable feedstock [17]. Preparing HOs from oils and fats would be a very important and economically advisable way of using renewable feedstock for the industrial production of detergents [18], synthetic lubricating oils [19, 20] and their additives [21], etc. Currently, HOs are obtained from petrochemical products as a result of complex and multistep processes.

As already mentioned above, deoxygenation of acids and esters proceeds predominantly via decarbonylation, and one of the main tasks of selective preparation of olefins is to prevent them from hydrogenation into paraffins. Thus, catalysts based on nickel (loading of 20–30%) [22] or platinum (about 1%) [23] and doped with conventional additives, such as tin, zinc, and germanium salts and sulfur derivatives, that suppress the activity of the metal in the hydrogenation of olefins were studied in a few works devoted to this topic. Note that paraffins are predominantly formed over such catalysts (nickel loading of 10–30%) without the addition of these promoting agents [24, 25].

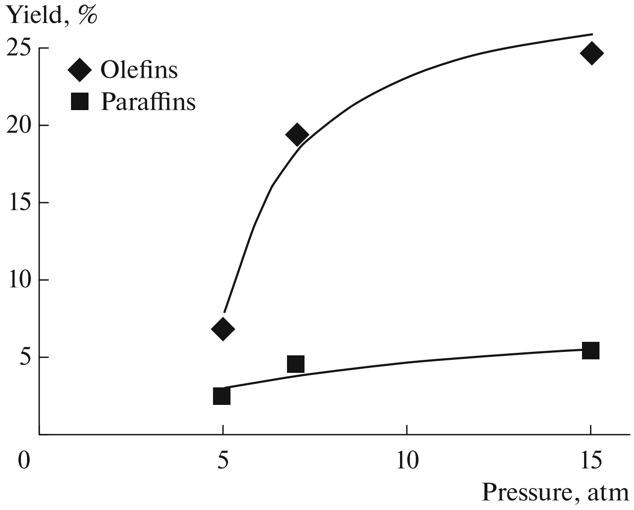
To increase the selectivity, the decarbonylation reaction over nickel and platinum catalysts was also conducted in an inert gas, not a hydrogen atmosphere [22, 23]. Likewise, the application of Ru catalysts makes it possible to conduct hydrogen-free deoxygenation of oleic acid to olefins, not paraffins [26]. The researchers [26] assume that the reaction proceeds via the positional isomerization of the initial acid with its subsequent deoxygenation to the olefin. The conversion over 4 h is low (29%).

It is well known that deoxygenation catalysts, which are active at 300–400°C, become rapidly deactivated in the absence of hydrogen [10, 27–29]. It is now apparent that this effect is associated with the presence of unsaturated compounds (reactants and/or products) in the reaction mixture. Hollak et al. [30] confirmed that there is strong but reversible adsorption of unsaturated compounds over a catalyst, e.g., a palladium catalyst, which had been demonstrated earlier using kinetic methods [10]. The catalyst deactivation accelerates with an increase in the degree of unsaturation of reactants, which is what causes the decrease in the activity of the catalyst during the initial period of deactivation. Under the deoxygenation conditions, unsaturated compounds can form oligomers which are precursors of coke generated over long time on stream of the catalyst.

Hollak et al. [31] also demonstrated the feasibility of decarbonylation of glycerol tristearate and trioleate in the presence of a Pd/C catalyst without special introduction of hydrogen. Water that hydrolyzed initial TGs to acids and glycerol under the experimental conditions (250°C, time on stream of 20 h) was added to the reaction mixture. The cited authors suggested that glycerol, moreover, underwent steam reforming to CO. Carbon monoxide gave hydrogen via the water-gas shift reaction.

Conducting deoxygenation with the simultaneous removal of the product from the reaction mixture by distillation is another traditional technique offered for improving the yield of olefins [23].

Relatively recently, it was shown for the first time [32] that copper-based monometal catalysts obtained



Dependence of the yield of olefins and paraffins on the hydrogen pressure (catalyst 3.24% Ni on $Al_2O_3$; 350°C; 1 h).

from Cu(II) salts, in the absence of additives, are capable of transforming St into the corresponding olefin in a hydrogen atmosphere. The choice of copper was determined by its low activity in olefin hydrogenation.

Quantum–chemical simulation of this reaction was performed for the case of a copper catalyst [32, 33]. The obtained data (active site model was a $Cu_{15}$ cluster and the reactant was propanoic acid) showed that in its main characteristic features, the reaction mechanism was similar to that over palladium (R–COOH bond cleavage is the limiting step, decarbonylation is more preferable as opposed to decarboxylation from the kinetic viewpoint, etc.) [10, 32]. For copper at 350°C, it is more energetically favorable to interact with atomic hydrogen, thus forming the Cu–H–Cu species, rather than to adsorb molecular $H_2$ (Gibbs free energy of adsorption of molecular hydrogen with copper is 9.3 kcal/mol, while it decreases to 2.4 kcal/mol in the case of dissociation of $H_2$).

It was found that the reduction of the olefin hydrogenating activity and, hence, the enhancement of the selectivity for HOs can be achieved not only in the presence of monometal catalysts that are relatively inactive in hydrogenation, such as copper, but also in the presence of more active catalysts, e.g., nickel [34].

The authors supposed that the effect of reduction of the activity in the hydrogenation of olefins can be achieved by decreasing the metal loading on the support (γ-aluminum oxide) to 2–4% (generally, as noted above, 10–30% Ni contacts are used in deoxygenation). Indeed, in the presence of 3.24% nickel catalyst on aluminum oxide at 350°C and a hydrogen pressure of 15 atm, the conversion of St was 78.5% over 2 h, while the selectivity for heptadecenes was 42.6%. Introducing silver into the nickel catalyst (to an Ag : Ni molar ratio of 0.87) leads to an increase in selectivity to 54.8% at a 85.6% conversion (reaction time 2 h). This effect is not observed when a mechanical mixture of nickel and silver catalysts in the same ratio is used instead of the aforementioned catalyst.

It is interesting to note that the dependence of the yield of olefins and paraffins on the hydrogen pressure in the presence of a nickel–silver catalyst is similar to the dependence observed for the nickel contact, i.e., the yield of olefins grows with an increase in the hydrogen pressure (figure).

The results of the quantum-chemical simulation of St deoxygenation over a nickel catalyst are important for understanding the mechanism of deoxygenation [33]. A $Ni_{15}$ nickel cluster similar to $Cu_{15}$ in structure was used as the active site model [32]. As noted above, the acid deoxygenation mechanism includes the adsorption of a substrate over a $Pd_{15}$ or $Cu_{15}$ active site, cleavage of the C–H bond, and insertion of palladium in the R–COOH C–C bond to form an M–COOH fragment. Its further decomposition can proceed mainly by two routes. The first route is associated with the formation of $CO_2$ as a result of cleavage of the OCO–H bond, while the second route, with the formation of CO as a result of cleavage of the OC–OH bond.

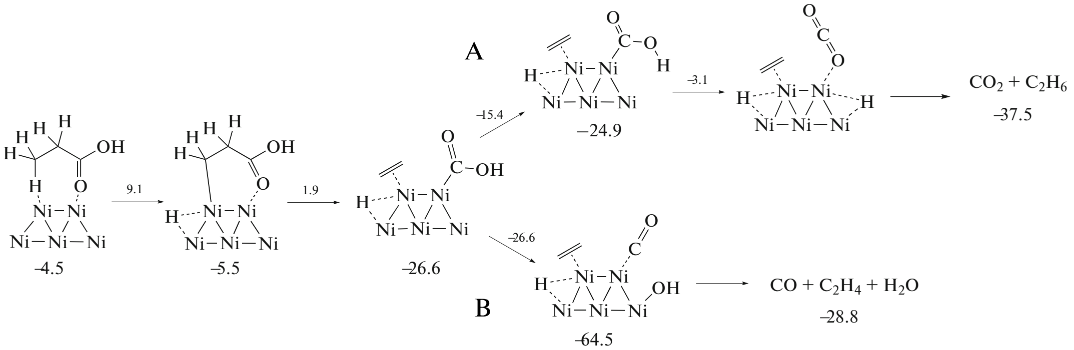
The simulation of the decarbonylation and decarboxylation reaction over $Ni_{15}$ showed that, in general, the sequence and set of steps (Scheme 2) remained the same as over the other metals examined [33]. The main difference is the barrier-free (0.0 kcal/mol) decomposition of the COOH particle via the decarbonylation route (B, Scheme 2). At the same time, the decarboxylation route is characterized by high barriers. For example, for the step of H atom migration from the COOH particle onto nickel, this quantity that is determined by the difference in the energies of the activated complex and intermediate is 21.8 kcal/mol. Therefore, the contributions from decarbonylation and decarboxylation reactions stronger differ from each other as compared to palladium or copper sites. Because of kinetic reasons, the reaction predominantly proceeds towards decarbonylation over nickel, i.e., olefin is the primary product, as in the case of palladium or copper.

In addition, the degradation of the COOH particle via route B (Scheme 2) yields an intermediate, the relative energy of which is substantially lower than the thermodynamic effect of the reaction (–64.5 versus –28.8 kcal/mol). Therefore, the known "energy gap" method was used for the correct evaluation of the free energy of activation of the reaction [33]. According to the results of application of this method, the free energy of activation of decarbonylation over the $Ni_{15}$ cluster is 44.8 kcal/mol.

**Table 1.** Relative Gibbs energies $\Delta G_{623}$ for adsorption and free energies of activation $\Delta G^{\neq}_{623}$ for the H atom addition and propanoic acid decarbonylation (kcal/mol) [33]

| Model | Propanoic acid decarbonylation | | Propene hydrogenation | | Isopropenyl radical hydrogenation | |
|---|---|---|---|---|---|---|
| | adsorption of $C_2H_5COOH$ | decarbonylation | adsorption of $C_3H_6$ | H atom addition | adsorption of $(CH_3)CH^{\bullet}$ | H atom addition |
| $Pd_{15}$ | −1.1 | 32.8 | – | – | – | – |
| $Pd_{15}(H)_2$ | – | 32.3 | −4.5 | 18.7 | −12.4 | 11.4 |
| $Cu_{15}$ | −2.7 | 40.2 | – | – | – | – |
| $Cu_{15}(H)_2$ | – | 41.5 | −6.4 | 22.3 | −7.0 | 9.7 |
| $Ni_{15}$ | −4.6 | 44.8 | – | – | – | – |
| $Ni_{15}(H)_2$ | – | 42.8 | −10.9 | 18.0 | −9.8 | 8.8 |

In the presence of a nickel catalyst, the St decarbonylation with the formation of olefins proceeds even in the presence of hydrogen, moreover, as noted above, the selectivity of the reaction over nickel has an unusual dependence on its pressure: with the growth in $P_{H2}$ (from 5 to 15 atm), the selectivity and, hence, the yield of olefins does not drop as it was to be expected but increases. Here, the yield of paraffins grows unsubstantially (from ~3 to ~5%). A similar dependence is observed in the presence of a copper catalyst as well [32]. Therefore, hydrogen plays a more complex role in this process other than only olefin hydrogenation.



**Scheme 2.** Propanoic acid deoxygenation over the $Ni_{15}$ cluster (it is depicted as a pentanuclear cluster fragment). Values of $\Delta G^{\neq}_{623}$ of activated complexes are indicated over arrows, while values of $\Delta G_{623}$ of intermediates, below structures (they are given relative to independent $C_2H_5COOH$ and $Ni_{15}$).

Apparently, at least two side reactions occurring during decarbonylation (temperature of 250–350°C) may lower its selectivity in the formation of olefins. These are abovementioned hydrogenation of olefins and oligomerization of heptadecenes into heavier olefins:

$$C_{17}H_{34} + H_2 \rightarrow C_{17}H_{36} \text{ hydrogenation}$$

$$nC_{17}H_{34} \rightarrow (C_{17}H_{34})_n \text{ oligomerization.}$$

Decreasing the rate of olefin hydrogenation by using catalysts that have low activity in this reaction has been discussed above. As for the oligomerization reaction, the obtained data gave the authors grounds to assume (see below) that metal hydrides formed during the interaction of metal catalysts and molecular hydrogen may play an important role in the inhibition of oligomerization [32, 35]: $2M + 1/2\,H_2 \rightarrow M{-}H{-}M$ (a fragment of the structure).

According to Bullock [36], hydrides are capable of terminating the chains of radical reactions including, apparently, thermal radical oligomerization:

$$R^{\bullet} + M{-}H{-}M \rightarrow RH + M{-}M, \text{ where } M = \text{Cu and Ni.}$$

If these two reactions are summed, we eventually obtain hydrogenation of radicals with molecular hydrogen in the presence of metals which play the role of “negative” catalysts for the radical olefin oligomerization reaction:

$$R^{\bullet} + 1/2\,H_2 \rightarrow RH.$$

**Table 2.** Examples of industrial hydrogenation processes used for the production of higher fatty alcohols

| Country and company | Capacity with respect to alcohols, t/y | Feedstock | Catalyst | Main catalyst components | Temperature, °C | Hydrogen pressure, MPa |
|---|---|---|---|---|---|---|
| United States, Procter And Gamble | 90000 | Methyl esters of acids of coconut and palm oils | Suspended | Cu and Cr | 330–340 | 23–25 |
| Great Britain, Marchon Products | 20000 | Methyl esters of acids of coconut, palm, and tall oils | Suspended | Cu and Cr | 280–330 | 30 |
| France, Sinnova | 7000 | Triglycerides and esters of natural acids | Suspended | Cu and Cr | 300 | 30–35<br>(25% $N_2$) |
| Japan, Kao Soap | 15000 | – | Suspended | Cu and Cr | – | – |
| Germany, Deutsche Hydrierwerke | 10000 | Synthetic fatty acids | Fixed-bed | Cu and Zn | 250–300 | 22–30 |

**Table 3.** Worldwide capacities of production plants for HFALs in 2010 [42]

| Continent/country | HFALs production capacity, thousand tons per year | | |
|---|---|---|---|
| | from natural feedstock $>C_{10}$ | from synthetic feedstock $>C_{11}$ | Total |
| America/United States | 250 | 500 | 750 |
| Europe/South Africa | 525 | 525 | 1050 |
| Asia | 1550 | 5 | 1555 |
| Total | 2325 | 1030 | 3355 |

Therefore, the available literature data allow the conclusion that in the presence of metal catalysts, hydrogen can terminate the radical oligomerization chain, thus enhancing the selectivity of the decarbonylation reaction in the formation of olefins. The decrease in the selectivity with a decrease in $P_{H_2}$ found for copper and nickel metal catalysts [32, 34] is probably due to a decrease in the concentration of metal hydrides inhibiting oligomerization and is consistent with the abovementioned scheme.

Data of quantum-chemical simulation performed for the reaction in the presence of palladium, copper, and nickel support the proposed mechanism [33]. The calculation data obtained in [33] and summarized in Table 1 suggest that palladium and nickel are the most active in olefin hydrogenation, while palladium is less active in propenyl radical hydrogenation (suppression of oligomerization reaction). Copper hydrogenates olefins at a lower rate as compared to palladium, but it terminates oligomerization at a higher rate than does Pd. Nickel is almost as active in the hydrogenation of propene as palladium, but it is the most active in the termination of oligomerization. This apparently is what explains the observed experimental facts [10, 32, 34] that, in the Pd, Cu, and Ni triad, the latter metal is characterized by the highest selectivity in the formation of olefins, while palladium, by the lowest.

## HIGHER FATTY ALCOHOLS

Saturated and unsaturated monatomic $C_6$–$C_{22}$ alcohols are usually referred to as HFALs. The area of their application is quite wide, namely, $C_6$–$C_8$ alcohols are flotation reagents, selective agents for the extraction of metal salts from aqueous solutions, solvents for paint-and-lacquer materials and synthetic resins, and feedstock for the manufacturing of various esters and ethers; $C_{10}$–$C_{18}$ and $C_{12}$–$C_{18}$ alcohols are mainly used in the production of anionic and nonionic surfactants; $C_{10}$–$C_{20}$ alcohols are retardants of water evaporation from the surface of water bodies, components of antifoaming agents in the processes of evaporation and fermentation, vulcanization accelerators, and feedstock in the production of plasticizers, tertiary amine oxides, and corrosion inhibitors; and $C_{12}$–$C_{20}$ secondary alcohols are the base of nonionic surfactants [37].

HFALs are produced from various kinds of feedstock including renewable feedstock. Coconut and palm kernel oils are used for the production of $C_{12}$–$C_{14}$ alcohols. Palm and soya been oils, as well as rendered animal fat are the main sources of $C_{16}$–$C_{18}$ alcohols. Rapeseed oil reach in erucic acid mainly gives HFALs with 20 or 22 carbon atoms [38].

In most industrially developed countries, HFAL production plants were constructed quite long ago, including production from oils and fats or acids obtained thereof. It is interesting to note that the first unit for catalytic hydrogenation of saturated fatty acids under high pressure was came into operation in 1930. The so called Adkins catalyst ($CuOl \cdot Cr_2O_3$), where CuOl is copper oleate, was employed in it [39].

Examples of large-scale industrial hydrogenation processes of production plants engineered in the last century are presented in Table 2 [40].

As opposed to the first half of the 20th century when HFALs were produced exclusively from natural feedstock, they were produced worldwide from natural and synthetic feedstock in about equal parts by the end of the century, although this ratio was about 3 : 1 in Asia [38]. In recent decades, new HFAL production plants have been created in Asian countries (Malaysia, Indonesia, Philippines, etc.) using in most part already natural TGs and their derivatives as feedstock [41]. It is seen from the data of Table 3 that about 70% of global HFALs production capacities were based on renewable feedstock already in 2010. Note that 67% of these capacities are concentrated in Asia [42].

It was expected that the capacity of HFAL production in Asia could grow by more than 30% in 2013 (Table 4). Five projects which were located mainly in the industrial centers of South East Asia could enhance the total capacity of Asia with respect to HFALs by more than 500000 tons per year.

Note that the share of the $C_{12}$–$C_{14}$ fraction is 60–70% of the total global production of HFALs. Lurgi GmbH, Frankfurt, announced about receiving an order for technology and license transfer to a HFAL production plant in Jubail, Saudi Arabia, in the SABIC affiliate, Saudi Kayan. The oil-to-chemical complex will have a capacity of about 83 thousand tons per year of purified HFALs with various compositions with respect to the number of carbon atoms for use in the production of household care products. The feedstock of the plant for HFALs production is renewable natural oils such as palm oil [44].

The preparation of HFALs from natural feedstock includes the following steps. Preliminarily purified TGs are hydrolyzed or transesterified to give obtaining HFAs or their esters (FAEs), respectively, which are further subjected to hydrogenation. Generally, fats and oils themselves are not used for hydrogenation because the glycerol moiety is hydrogenated to less valuable propylene glycol and propanol in this case and, in addition, the consumption of hydrogen and catalyst increases. Some esters are obtained via the esterification of HFAs with an excess of methanol at 200–250°C and a relatively low pressure.

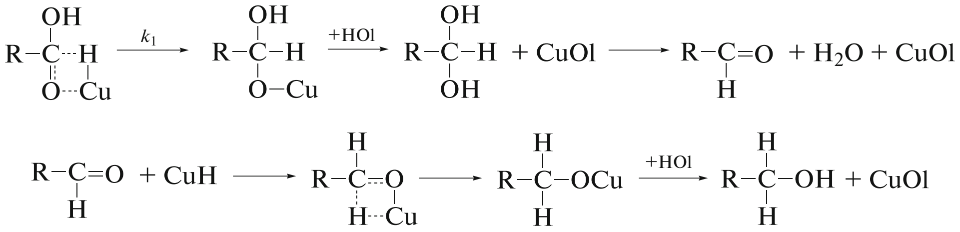
**Table 4.** Pilot HFAL production plants [43]

| Company | Capacity, thousand tons per year | Location |
|---|---|---|
| Musim Mas | 100 | Medan, Indonesia |
| Wilmar | 144 | Gresik, Indonesia |
| China Sanjiang Fine Chemicals | 135 | Zhapu, Zhejiang province, China |
| Kuala Lumpur Kepong | 100 | Klang, Malaysia |
| Pilipinas Kao | 40 | Jasaan, Philippines |
| Total | 519 | |

In industry, the hydrogenation process can be conducted in three ways: in a gas phase (esters containing 12–14 C atoms), over a trickle-bed catalyst (esters and acids), or with a catalyst slurry (esters or acids). The choice of the process depends on the hydrogenation technologies and feedstock used at the plant. In any case, copper-containing mixed oxide (chromium, cadmium, etc.) catalysts are used at temperatures of 200–300°C and hydrogen pressures of 20–30 MPa [42].

These catalysts have a number of disadvantages, first of all, low activity, metal leachability causing catalyst deactivation, and capability of contaminating the product [41]. There are reports about the appearance of new catalysts on the basis of platinum group metals (Pt, Ru, and Rh) on aluminum and titanium oxides which make it possible to decrease the temperature and hydrogen pressure, as well as, in some cases, preserve double bonds in obtained alcohols, e.g., $Pt/TiO_2$ [41, 45, 46]. For these catalysts, tin, germanium, and iron are used as promoting agents [41, 42].

The mechanism of catalytic hydrogenation of fatty acids and their derivatives to alcohols is discussed in the literature. Stouthamer [39] studied this reaction at temperatures of 245–270°C and hydrogen pressures of 100–175 atm in the presence of 0.5–5 mol % copper and/or cadmium oleates. It was found that the reaction started only after 5–10 passages, when the initial salts decomposed, thus forming a layer of copper and/or cadmium on the autoclave surface. In the work cited, a mechanism that includes the interaction of the copper hydride, produced under reaction conditions, with the acid molecule to form C–H and O–Cu bonds was proposed; as a result of subsequent transformations, the corresponding aldehyde is formed as an intermediate, which is reduced by copper hydride to the alcohol (presence of the aldehyde was not experimentally proven):



Adkins [47] shared the same point of view concerning the intermediate formation of an aldehyde from the acid residual of HFA in the reaction of alcohol formation. Interestingly, Donnis et al. at Haldor Topsoe [9] experimentally found that dodecan-1-ol and small quantities of dodecan-1-al are present among the products of methyl laurate hydrogenation (model of vegetable oils and animal fats) at 300°C and 50 bar over a sulfidized NiMo catalyst at low and medium degrees of conversion. This finding may lend evidence for the mechanism of formation of alcohols via aldehydes.

Another mechanism of this reaction is also possible. Based on data on the kinetics of hydrogenation over barium-modified copper chromite, Muttzall [48] concluded that the reaction proceeds according to the scheme:

$$RCOOCH_2R + H_2 \rightleftarrows 2RCH_2OH$$

without the formation of intermediate products. Although the cited studies [47, 48] were published quite long ago, no data disapproving these results have emerged in literature up to now.

## CONCLUSIONS

The analysis of the information presented above shows that catalytic chemistry based on the use of renewable feedstock, such as inedible oils and fats, has become an actively developing line of the fundamental science and industry. Initially only industrial facilities for the production of higher fatty alcohols alone from this kind of feedstock were actively created, but the 1990s are characterized by the rapid development of fuel industry (production of biodiesel and biokerosene), which has achieved impressive results by now. As opposed to these two lines, higher olefins are still produced only from petroleum feedstock despite obvious advantages of the use of oils and fats.

The progress in understanding the chemistry, kinetics, and mechanism of deoxygenation of fatty acids and their esters to fuel-grade alkanes provided intense development of the biofuel industry. Here, works on the creation of new highly efficient catalysts for the production of biofuels, which operate at lower temperatures (150–250°C), as well as the development of the technology for the production of biofuels via TG hydrolysis (similar to the technology used for HFALs) and deoxygenation of the formed acids to hydrocarbons with the fuel composition can be referred to as promising trends.

Developing new catalysts with reduced leachability, high activity, and enhanced durability is a relevant objective for the production of HFALs from natural feedstock. Regarding the production of HOs, this line is in its infancy and requires special attention. Developing efficient catalysts for the preparation of olefins with the selectivity of no less than 90% and studying the kinetics and mechanism of the relevant reactions are required, as well as creating mathematical models of the processes for the development of the technology for HO production from oils and fats.

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