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Nowadays, production of biofuels is a rather hot topic due to depleting of conventional fossil fuel feedstocks and a number of other factors. Plant lipid-based feedstocks are very important for production of diesel-, kerosene-, and gasoline-like hydrocarbons. Usually, (hydro)deoxygenation processes are aimed at obtaining of linear hydrocarbons known to have poor fuel characteristics compared to the branched ones. Thus, further hydroisomerization is required to improve their properties as motor fuel components. This review article is focused on conversion of lipid-based feedstocks and model compounds into high-quality fuel components for a single step – direct cracking into aromatics and merged hydrodeoxygenation-hydroisomerization to obtain isoparaffins. The second process is quite novel and a number of the research articles presented in the literature is relatively low. As auxiliary subsections, hydroisomerization of straight hydrocarbons and techno-economic analysis of renewable diesel-like fuel production are briefly reviewed as well.
1. Introduction

According to the forecasts, world energy consumption from 2015 to 2040 can increase by 35% [1], although the 2019–20 coronavirus pandemic is now drastically affecting the world economy and, correspondingly, the world energetic and transport sectors [2,3]. One of the main consumers of fossil energy in the form of fuels is the transport sector: it holds up to 45% of the global demand for crude oil [1], and is ultimately one of the main causes of CO2 emissions [4]. The expected increase in the needs in motor fuels to 2040 [1] resulted in the increased attention to biofuels being produced from biomass, which are considered as a sustained alternative to fossil fuels. They are known to be more friendly to the environment; also, some regions have focused on biofuels to minimize vehicle emissions. It is also considered that the utilization of biofuels, along with electric vehicles will provide sustainability of the transport sector [6].

Liquid transport biofuels have been used since the early days of the automobile industry. Peanut oil was used by R. Diesel to demonstrate the working of the compression ignition engine at the World’s Exhibition in Paris (1898). Vegetable oils had been used for diesel engines up to 1920th when the engines were upgraded in order to utilize residues of petroleum instead [7]. However, although the possibility of direct using vegetable oils as a fuel is still considered today, [8–10] they possess some features (e.g. higher viscosity, low volatility, high reactivity of unsaturated bonds), which cause problems arising at a long-term operation of internal combustion engines [11]. This problem was recognized in the early twentieth century: many researchers admitted that high viscosity of vegetable oils could lead to the operational problems. One of the first patented approaches suggested the use of palm oil ethyl esters, obtained by transesterification of the oil with ethanol (Belgian patent 422,877 issued in 1937) [12].

Today, the first generation biodiesel, representing fatty acid methyl esters (FAME), is obtained by the transesterification from vegetable oils or animal fats in the presence of heterogeneous catalysts [5]. The name “biodiesel” itself was introduced in the United States in 1992 due to the National Soy diesel board [13]. Biodiesel derived from vegetable oils and animal fats is an alternative to diesel fuel. Although this is a fairly advanced technology suitable for commercial use, this type of fuel contains a high amount of oxygenated compounds and, as a result, has a lower calorific value, higher viscosity and relatively poor performance at low temperatures compared to petroleum diesel fuel [5]. To overcome some of the typical biodiesel disadvantages caused by the higher oxygen content, it is necessary to carry out deoxygenation of the first generation biodiesel [5] and/or vegetable oils directly [14] to produce hydrocarbons – second generation of biodiesel (green diesel).

Oxygen from compounds with ester group (triglycerides, monoaalkyl ethers of fatty acids), can be removed from the feedstock via three routes:

1. decarboxylation (DCX), when oxygen is removed in the form of CO2;
2. decarbonylation (DCN), when oxygen is removed in the form of CO;
3. hydrodeoxygenation (HDO), when it is necessary to use hydrogen, and oxygen is removed in the form of water.

The mechanisms of deoxygenation (DO) are described in more detail in numerous reviews focused on this subject (e.g. in [5,15–17] and many others).

Currently, the need for better biofuels from consumers raises interest to development of approaches to production of hydroprocessed esters and fatty acids (HEFA), which by their properties are very close to traditional fuels derived from the fossil feedstocks [18]. Thus, the fatty acids included in the composition of vegetable oils act as attractive compounds that can be used to produce diesel-like hydrocarbon fuels [15]. The yield and composition of HEFA-jet and HEFA-diesel (or so-called green diesel) produced in one process, as well as other products, mainly depend on the process conditions, a feedstock type and catalyst capabilities [16]. However, it should be noted that the products of DO of vegetable oils mainly consist of C15–C18 alkanes. Despite the relatively high cetane index, the mixtures obtained through the processing of vegetable oils have relatively low fuel characteristics, namely – cold flow properties. A further processing of vegetable oils into isomerized alkanes is considered as the next possible step [19]. However, the merger of the separate hydrodeoxygenation and hydroisomerization into a single step (HDO-HI) would significantly simplify the conversion of lipidic feedstocks to obtain isomerized paraffins.

Another attractive way of a single-step conversion of the lipids into high-valuable fuel components is their direct cracking over acidic catalysts to obtain aromatics enriched with benzene-toluene-xylene (BTX) fraction. Thus, in this paper, one-step catalytic processing of fatty oxygenates of lipid nature into isomerized alkanes and aromatics are considered. As auxiliary subsection – a partition focused on main aspects of hydroisomerization of hydrocarbons is presented in brief. In addition, a concise review of techno economic analyses of fuels via hyd roprocessing and other ways from vegetable oils and their deriva tives are provided as well.

2. Aromatics and isoalkanes as motor fuel components

As commonly known, hydrocarbon liquid fuels represent mixtures of hydrocarbons that should meet certain requirements to be able to be used as motor fuels. Such hydrocarbons are mostly alkanes, naphthenes, olefins and aromatics. Their properties and peculiarities of composition/structure define, ultimately, a set of properties of a certain fuel. In Tables 1–3 requirements to gasoline, jet fuel and diesel fuel are provided. As can be seen, the main part of all the fuels is represented by paraffins and naphthenes (being the rest of their composition), while contents of aromatics and olefins are limited, at least in the case of gasoline and jet fuel. However, aromatics is also a significant part of all the fuels, especially of diesel one, where content of aromatic hydrocarbons can achieve or even exceed 30 vol% [20].

Therefore, both saturated and aromatic hydrocarbons are important components of motor fuels defining their main properties in significant degree. Branched alkanes, due to many attractive properties take a special place among saturated hydrocarbons. In the following subsections, properties of aromatics and isomerized alkanes as fuel components are highlighted briefly.

2.1. Properties of aromatics

The content of aromatic compounds as well as isomerized and straight alkanes in different fuels has a different effect on their performance. In the case of gasoline, aromatics and isoparaffins both have high octane numbers (ON) (Table 4) [24], but because of ecological reasons aromatics content should be limited (at a level of 35%, benzene – 0.8%) [25].

A stronger limitation on aromatics content (25%) is established for jet fuel (Table 2). This is caused by the following factors: 1) poor combustion quality due to the tendency to generate more carbonaceous particles in combustion (especially fuels with high naphthalenes content); 2) poor low-temperature flow properties. However, aromatic hydrocarbons are characterized by the best volumetric energy contents compared to others [26].

In diesel fuels, under limitation is only PAHs content at a level of 8 wt% (Table 3), while content of monoaromatic compounds is not limited by the EN 590 standard. Nevertheless, an increase in the content of aromatic compounds leads to an increase in NOX emissions; aromatics and polyaromatic compounds are the reason of particulate matter emissions and soot [24]. In addition, low cetane numbers of aromatic hydrocarbons (Table 4) cause the necessity of their limited content in diesel fuel as well.

Nonetheless, taking into account the existing restrictions, aromatics anyway are an important component of liquid hydrocarbon fuels.
2.2. Properties of branched alkanes

Unlike aromatics, branched (isomerized) alkanes have much higher potential as motor fuel components. There are no established limitations on their content in the above fuels, in contradistinction to aromatics and olefins. In the case of gasoline, isoalkanes are known to distinguish by a very high octane number compared to straight ones, which is necessary to ensure a high quality gasoline required for modern internal combustion engines. For example, n-heptane has a research octane number (RON) rating of 0, 2-methylhexane – 53, and 2,3-dimethylpentane – 93.\(^2\)

Due to the molecular shape of isoparaffins (as well as naphthenes and substituted aromatics) inappropriate to fitting more easily into a crystal structure, they have substantially lower melting (freezing) points than linear paraffins and unsubstituted aromatics.\(^3\) This property of isoalkanes makes them one of the key components in jet fuel and diesel fuel, which have limitations on freezing point and cold filter plugging points (diesel) (Tables 2 and 3). In the case of arctic sorts of fuels:

| Property | Units | Minimum limit | Maximum limit | Test method |
|----------|-------|---------------|---------------|-------------|
| Density at 15 °C | kg/m\(^3\) | 720 | 775 | EN ISO 3675 |
| Vapour Pressure (Summer – Class A) | kPa | 45 | 60* | EN ISO 13016-1 |

**Distillation**

| Property | % v/v | Minimum limit | Maximum limit | Test method |
|----------|-------|---------------|---------------|-------------|
| Evaporated at 70 °C (E70) | – | 20 | 48 | EN ISO 3405 |
| Evaporated at 100 °C (E100) | – | 46 | 71 | – |
| Evaporated at 150 °C (E150) | – | 75 | – | – |
| Final Boiling Point (FBP) | °C | – | 210 | – |
| Distillation Residue (DR) | % v/v | – | 2 | – |

**Hydrocarbon type content**

| Property | % v/v | Minimum limit | Maximum limit | Test method |
|----------|-------|---------------|---------------|-------------|
| Olefins | – | – | 18 | EN 14517, EN 15553 |
| Aromatics | – | – | 35 | – |
| Benzene | – | – | 1 | UNE EN 238 |

**Oxygen and Oxygenates content**

| Property | % w/w | Minimum limit | Maximum limit | Test method |
|----------|-------|---------------|---------------|-------------|
| Oxygen content | – | – | 2.7 | UNE EN 13132 |
| Ethanol | % v/v | – | 5 | EN 13132 |

**Sulfur and Copper content**

| Property | mg/kg | Minimum limit | Maximum limit | Test method |
|----------|-------|---------------|---------------|-------------|
| Sulfur content | – | – | 10 | EN ISO 20846 |

**Copper strip corrosion (3 h at 50 °C)**

| Property | Rating | Minimum limit | Maximum limit | Test method |
|----------|--------|---------------|---------------|-------------|
| Copper strip corrosion | – | – | Class 1 | EN ISO 2160 |

* – Extra vapour pressure is permitted depending on EtOH content.

### Table 2

Jet fuel specifications. Adopted from [22].

| Property | ASTM D1655-04a | IATA | Def Stan 91-91 | ASTM D7566 | MIL-DTL-83133E specification* |
|----------|----------------|------|----------------|------------|-----------------|
| **Composition** | | | | | |
| Acidity, total (mg KOH/g) | 0.1, max | 0.015, max | 0.012, max | 0.1, max | 0.015, max |
| Aromatics (vol%) | 25, max | 25, max | 25, max | 25, max (8, min) | 25, max |
| Sulfur, total (wt%) | 0.3, max | 0.3, max | 0.3, max | 0.3, max | 0.3, max |
| **Volatility** | | | | | |
| 10% Recovery (°C) | 205, max | 205, max | 205, max | 205, max | 205, max |
| 20% Recovery (°C) | – | – | – | – | – |
| 50% Recovery (°C) | – | – | – | (15, min) | – |
| 90% Recovery (°C) | – | – | – | (40, min) | – |
| Final BP (°C) | 300, max | 300, max | 300, max | 300, max | 300, max |
| Flash point (°C) | 38, min | 38, min | 38, min | 38, min | 38, min |
| Density @ 15 °C (kg/m\(^3\)) | 775–840 | 775–840 | 775–840 | 775–840 | 775–840 |
| **Fluidity** | | | | | |
| Freezing point (°C) | – | – | – | – | – |
| Viscosity @ –20 °C (cSt) | 8, max | 8, max | 8, max | 8, max | 8, max |
| **Combustion** | | | | | |
| Net heat of comb. (MJ/kg) | 42.8, min | 42.8, min | 42.8, min | 42.8, min | 42.8, min |
| Smoke point (mm) | 25, min | 25, min | 25, min | 25, min | 25, min |
| Smoke point (mm) and naphthalenes (vol%) | 19 (min), 3 (max) | 19 (min), 3 (max) | 19 (min), 3 (max) | 18 (min), 3 (max) | 19 (min), 3 (max) |
| **Thermal stability** | | | | | |
| JFTOT Delta P @ 260 °C (mm Hg) | 25, max | 25, max | 25, max | 25, max | 25, max |
| Tube deposit Rating (Visual) | < 3 | < 3 | < 3 | < 3 | < 3 |
| **Conductivity** | | | | | |
| Conductivity (pS/m) | 50–450 | 50–450 | 50–600 | – | – |
| **Lubricity** | | | | | |
| BOCLE wear scar diameter (mm) | – | 0.85, max | 0.85, max | 0.85, max | – |

* – MIL-DTL-83133E is the standard specifically for JP-8 fuel
In Table 5, cetane numbers (CN) as well as boiling and melting points of selected diesel range hydrocarbons are presented. As can be seen from this table, melting points of isomerized paraffins are lower than points of selected diesel range alkanes are presented. As can be seen thus increasing importance of isoparaffins [31]. According to EN 590. Adapted from [23].

### Table 3

| Property                                      | Units   | Limits | Test method* |
|-----------------------------------------------|---------|--------|--------------|
| Density @15 °C                                | kg/m³   | 820.0  | EN ISO 3675/EN |
| Flash Point                                   | °C      | 55     | EN ISO 2719  |
| Cetane Number                                 | –       | EN ISO 5165/EN |
| Cetane Index                                  | –       | EN ISO 4264  |
| Cold Filter Plugging Point                    | –       | EN116  |
| Winter                                        | –       | –      |
| Summer                                        | –       | –      |
| Viscosity at 40 °C                            | mm²/s   | 2.000  | EN ISO 3104  |
| Polycyclic Aromatic                           | % (m/m) | 8.0    | EN 12916    |
| Hydrcarbons                                   | –       |       |
| Sulfur Content                                | mg/kg   | 10.0   | EN ISO 20846/ |
| Copper Strip Corrosion (3hr @ 50 °C Carbon Residue) | –       | –      |
| (on 10% Distillation Residue)                 | % (m/m) | 0.30   | EN ISO 10370 |
| Ash Content                                   | % (m/m) | 0.01   | EN ISO 6245  |
| Total Contamination                           | mg/kg   | 24     | EN 12662    |
| Water Content                                 | mg/kg   | 200    | EN ISO 12937 |
| Manganese Content                             | mg/l    | 2.0    | prEN 16576  |
| Distillation                                  | –       | –      |
| % (V/V) Recovered at 250 °C                   | % (V/V) | < 65   | EN ISO 3924  |
| % (V/V) Recovered at 350 °C                   | % (V/V) | 85     | EN ISO 3924  |
| % (V/V) Recovered at 95% (% V/V) Recovered at 350 °C | % (V/V) | 360    | EN ISO 3924  |
| Oxidation Stability                           | g/m³    | 25     | EN 12205    |
| Scar Diameter                                 | h       | 20     | EN 15751    |
| Lubricity, Corrected Wear                     | –       | –      |
| (WSD 1,4) at 60 °C                            | μm      | 460    | EN ISO 12156-1 |
| Fatty Acid Methyl Ester (FAME)***              | % (V/V) | 7.0    | EN 14078    |
| Filter blocking tendency                      | –       | 2.52   | IP 387, procedure B only |

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### Table 4

Predicted fuel property values according to [24] and Tboiling/Tmelting (°C) according to [27,28].

| Aromatics                      | CN* | RON* | MON* | Tboiling, °C | Tmelting, °C |
|--------------------------------|-----|------|------|--------------|--------------|
| Toluene                        | 4   | 111  | 101  | –95          | 111          |
| Styrene                        | 0   | 107  | 94   | –31          | 145          |
| ortho-Xylene                   | 10  | 109  | 99   | –25          | 144          |
| Ethylbenzene                   | 7   | 112  | 99   | –95          | 136          |
| 1,2,3-Trimethylbenzene         | 8   | 108  | 98   | –25          | 176          |
| 1,3-Diethylbenzene             | 4   | 113  | 99   | –84          | 181          |
| 1-Methyl-3-n-propylbenzene     | 12  | 110  | 96   | –82.5        | 182          |
| Isopropyl benzene (Cumene)     | 6   | 112  | 102  | –96          | 152          |
| tert-Butylbenzene              | 2   | 112  | 107  | –58          | 169          |
| Cycloparaffins                 | 1,1,2-Trimethylcyclohexane | 29  | 96   | 91   | –29          | 145.2         |
| 1,1,2-Trimethylcyclop propane  | 13  | 105  | 88   | –21.6        | 114          |
| Cycloptane                     | 26  | 98   | 79   | –93.8        | 49.3          |
| 1, trans-2-Dimethylcyclohexane | 29  | 77   | 75   | –90          | 123.5         |
| Methylcyclohexane              | 30  | 70   | 70   | –127         | 109.9         |
| Methylcyclopentane             | 24  | 80   | 74   | –143         | 71.8          |
| tert-Butylcyclohexane          | 31  | 96   | 85   | –41.2        | 171.5         |
| 1,3-Dimethylcyclohexane        | 31  | 65   | 64   | n.d.         | 122.5         |
| 1-Methyl-1-ethylcyclohexane    | 39  | 67   | 76   | n.d.         | 152.2         |

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### Table 5

Cetane number, boiling and melting points of some diesel range hydrocarbons based on data from [32] and [33].

| Alkane                          | CN  | Tboiling, °C | Tmelting, °C |
|--------------------------------|-----|--------------|--------------|
| Tridecane, n-C13                | 90.0/90.8 | 235          | –6           |
| 2-Methyldecanec                | –68.2 | 229          | –5.3         |
| 2,5-Dimethyldecanec            | 58.0/58.0 | 214          | –70          |
| Tetradecane, n-C14              | 96.1/94.6 | 235          | –5.5         |
| 2,6,10-Trimethyldecanec         | –75.0 | 253          | –           |
| 4,5-Dipropylcyclohexane        | –    | –            | < –80        |
| Pentadecane, n-C15              | 98.0/98.1 | 270          | +9.8         |
| 2-Methyltetradecanec           | –75.2 | 265          | –8.3         |
| Hexadecane, n-C16              | 100.0/101.4 | 287          | +18.1        |
| 3-Methylpentadecanec           | –71.3 | 267          | –22.3        |
| 7,8-Dimethyltetradecanec       | –    | –            | –70          |
| Heptadecane, n-C17              | 105/104.5 | 302          | +21.7        |
| 7-Bulyldecanec                 | –    | –            | –79          |
| Octadecane, n-C18              | 108.3/107.4 | 317.5        | +28.1        |
| 8-Propylpentadecanec           | –    | –            | –70          |
| 2-Methylheptadecanec           | –83.9 | 313          | +5           |
| 9-Methylheptadecanec           | 66.0/62.1 | –          | –8           |
| Nonadecane, n-C19               | 110.0/110.2 | 331.7        | +32          |
| 2-Methylododecanec             | –86.4 | 327          | –            |
| Eicosane, n-C20                 | 112.0/112.9 | 245          | +36          |

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### vegetable oils

- experimental/computational CN values.

As compared to other pathways, catalytic cracking is simple: in this case no any additional reagents (e.g. hydrogen) as well as catalysts having a sophisticated composition are necessary. In addition, many literature sources indicate on the cracking of vegetable oils can be carried out using FCC units, either in a mixture with petroleum fractions (vacuum gas oils, etc.), or separately [36–50]. Since catalytic cracking of lipidic feedstocks is aimed at production of hydrocarbons in the hydrogen-free atmosphere, temperatures of the process are high enough – 250–550 °C, in order to ensure high rates of decomposition of the oxygen containing compounds (triglycerides, esters, free fatty acids (FFA)). Such conditions favor to dehydrogenation and dehydrocyclization reactions to form olefins and aromatics. In addition, catalytic cracking of the feedstocks is usually characterized by a relatively high yields of gaseous products and coke (10 wt% or more), and liquid hydrocarbon products are usually enriched with high content of unsaturate.
of gasoline fractions. In general, mechanism of thermal decomposition of triglycerides can be represented as follows [35,51]:

Decomposition of a triglyceride:

\[
\text{CH}_2\text{OCOR'} \quad \text{CH}_2 \\
| \\
\text{CHOCOCR}_2' \to \text{CH} + \text{R'}\text{COOH} + \text{R'}\text{COOH} + \text{R'}\text{CH} = \text{CO} \\
| \\
\text{CH}_2\text{OCOR}'' \quad \text{CHO}
\]

Decomposition of fatty acids:

\[
\text{RCOOH} \to \text{CO}_2 + \text{RH} \\
\text{2RCOOH} \to \text{CO}_2 + \text{H}_2\text{O} + \text{RCOR}
\]

Decomposition of ketenes and acrolein:

\[
\text{2R''CH} = \text{CO} \to \text{2CO} + \text{RHC} = \text{CHR} \\
\text{CH}_2 = \text{CHCHO} \to \text{CO} + \text{C}_2\text{H}_4
\]

Decomposition of hydrocarbons into elements (coking):

\[
\text{C}_n\text{H}_y \to \text{xC} + (\text{y}/2)\text{H}_2 \\
\text{Dehydrogenation of paraffins:} \\
\text{C}_n\text{H}_{2n} + 2 \to \text{C}_n\text{H}_{2n} + \text{H}_2 \\
\text{Splitting decomposition of paraffins:} \\
\text{C}_n\text{H}_{2n} + 2 \to \text{C}_{n-m}\text{H}_{2n-2m} + 2 + \text{C}_m\text{H}_{2m} \\
\text{Alkylation of paraffins, the reverse of (6)} \\
\text{Isomerization of paraffins:} \\
\text{n}-\text{C}_n\text{H}_{2n} + 2 \to \text{i}-\text{C}_n\text{H}_{2n} + 2 \\
\text{Dehydrocyclization of paraffins} \\
\text{Polymerization of olefins} \\
\text{Depolymerization of olefins, reverse (10)} \\
\text{Decomposition of olefins into diolefins} \\
\text{Decomposition of olefins into acetylenic hydrocarbon} \\
\text{Aromatization or cyclization of olefins} \\
\text{Hydrogenation of olefins} \\
\text{Isomerization of olefins (16)}
\]

The main valuable products of lipid feedstock catalytic cracking are gasoline-like hydrocarbons enriched with BTX fraction forming via dehydrocyclization of paraffins and olefins according to reactions (9) and (14). Catalysts used for the cracking are mainly acidic and based on zeolites (ZSM-5, USY etc.); in addition, some other catalysts are used, which are also acidic or basic.

### 3.1. Cracking over zeolite-based catalysts

Firstly, catalytic cracking of vegetable oils has been carried out by Mobil Corp. using HZSM-5 (Zeolite Socony Mobil-5) zeolite as a catalyst [52]. It was found that the use of this catalyst enables obtaining high quality gasoline components – BTX from several vegetable oils due to its pronounced shape selectivity caused by specific structure (Figs. 1 and 2). Later, the high performance of HZSM-5 was confirmed by Prasad et al. [53,54], Katikaneni et al. [55] as well by many other researchers. Furthermore, zeolite HZSM-5 is used to produce aromatic hydrocarbons from bio-oil and vegetable biomass based feedstocks [56–62].

Nowadays, research studies aimed at catalytic cracking of lipid-based feedstocks in the presence of zeolite-based catalysts can be divided into four groups. Although ZSM-5 was firstly tested for vegetable oils cracking many years ago, interest to ZSM-5-based catalysts is still remained at a high level, that causes the fact that the first three groups are based on ZSM-5: ZSM-5 itself, which can be in H- or Na-form, ZSM-5 promoted with transition metal oxides and ZSM-5-based composites with other porous materials. The fourth group of the catalysts is mainly represented by industrial FCC catalysts, which are based usually on ultrastable Y zeolite.

The use of non-modified ZSM-5 in continuous flow-fixed bed reactor for the cracking was shown to result in a high yield of gaseous products (ca. 40–70%) and biogasoline (10–36%) at 450 °C [64,65]. The obtained biogasoline was found to be enriched with aromatic hydrocarbons. It is interesting to note, that the use of the refined vegetable oil gives rise to elevated yield of gaseous products compared to the unrefined one, when higher yields of kerosene and diesel fractions were observed. This effect is explained by the fact that admixtures contained in the unrefined oil partially deactivate the catalyst through its poisoning by sulfur and phosphorus of proteins and lipids usually contained in unrefined oils, thus decreasing its cracking ability. The use of hydrogen led to higher yields of liquid products than in the case of nitrogen atmosphere (Tables 6 and 7).

Zandonai et al. showed that ZSM-5 in Na-form can have a worse durability in the cracking than that in H-form. Furthermore, coke deposits were higher by 2.5 times for the Na-form [65]. When using ZSM-5 in H-form for cracking of lipid-based feedstocks at milder conditions (T = 350–440 °C) in a batch reactor, yields of OLP can reach 85–90% and blends of the OLPs with diesel fuel can be compliant with the EN 590 standard and thus such OLP can be used as a components of motor fuels [66].

Modification of ZSM-5, as a rule, positively affects activity and selectivity to hydrocarbons in cracking of vegetable oils [67–72]. Zhao et al. [67] showed that modification of the zeolite with Zn for cracking of camelina oil did not affect its structure but lowered specific surface area and pore volume accompanied by mesopore share increasing i.e. micropores were blocked by ZnO. Zinc oxide appeared to promote decarbonylation, decarboxylation and dehydrogenation reactions. Li et al. promoted ZSM-5 with CuO (5–30 wt%) that was found to give rise to increase in concentration of Lewis acid sites of the catalysts at 5 and 10% of Cu content enhancing catalytic properties of the initial zeolite, in terms of yield of hydrocarbons [69]. Modification of ZSM-5 by nanodispersed iron, zinc and copper oxides (Fe-Zn-ZSM-5, Fe-Zn-Cu-ZSM-5, Fe-Zn-Cu-Ni-ZSM-5) led to significant enhancement of the catalytic activity compared to pure ZSM-5 in the terms of yield of biogasoline in the cracking of palm oil in a batch reactor [68]. The yield of biogasoline was maximal (59 wt%) when the catalyst promoted with the maximal number of metals was used – due to ability of the metal oxides to suppress coke formation.

Some research studies are focused on mixed zeolite systems as well as composite materials for vegetable oil cracking. Application of mesoporous MCM-41 based materials to synthesize composites with ZSM-5 allows obtaining materials with multiporous structure, which improves mass transfer of the large feedstock molecules (triglycerides of fatty acids) to active sites of microporous zeolites [70,71]. Ramya et al. synthesized composite materials of AlMCM-41 (5–20%)/ZSM-5 composite with a core–shell structure for jatropha oil cracking [71]. They showed that compared to individual HZSM-5 and AlMCM-41, the use of the composite catalyst increased conversion of the feedstock from 62 to 65 to 99% in the same conditions (T = 400 °C, WHSV = 4.6 h⁻¹, t = 1 h). Yield of biofuel was 70%, selectivity to gasoline – 61%. A possible mechanism of jatropha oil triglycerides cracking in this process is presented in Fig. 3.

However, mixing ZSM-5 with other zeolites can decrease its
performance. For example, Twaiq et al. tested blends of USY and β zeolites with HZSM-5 in palm oil cracking [73]. They found that addition of HZSM-5 (10–30 wt%) improves performance of the USY due to a synergetic effect of the pore size of the two zeolites. In the case of mixture β + HZSM-5 – the reverse trend was observed. Meanwhile, the highest was efficiency of pristine HZSM-5.

In order to approach the conditions of petroleum refining industry, some researchers utilize FCC catalysts for lipid-based feedstock cracking that are usually based on USY zeolite, and study the cracking of vegetable oils and other similar substrates in the conditions close to industrial ones [72,74–76]. Lovás et al. studied cracking of rapeseed oil and its mixture with hydrogenated vacuum gas oil under simulated fluid catalytic cracking conditions that were maximally close to those of industrial FCC (T = 525 °C) [72]. They used FCC catalysts of the following types: 1) based on zeolite Y – FCC-ECAT (ECAT is a standard fluid catalytic cracking equilibrium catalyst based on ultra-stable zeolite Y); 2) based on ZSM-5 – FCC-ZSM-5; 3) their mixture (90 wt% of FCC-ECAT and 10 wt% of FCC-ZSM-5). According to the results of the testing, for cracking rapeseed oil it was found that the catalyst mixture was the most effective: this resulted in the most preferable yield of propylene and C4 gaseous products, as well as gasoline fraction.

Li et al. optimized cottonseed oil cracking via non-catalytic and catalytic pyrolysis in fixed-fluidized bed reactor using two FCC catalysts (CHZ-4 and LANK-98 – both from Shanghai Oil Refinery) and amorphous silica [74]. It was shown, that the use of the catalysts gives rise to a shifting of organic liquid product (OLP) composition towards increase in gasoline fractions, decline of diesel and residual fractions as well as to the coke yield growth. Optimization of palm oil cracking was done by Tamunaidu et al. in [75] using a transport riser reactor over a REY catalyst. The optimal process variables were found to be the following: T = 450 °C, catalyst/oil ratio = 5 and residence time in the reactor was 20 s. At such conditions palm oil conversion was 75.8%, yield of OLPs was 53.5 wt%, they contained 33.5 wt% of biogasoline. Yield of gaseous products was 14.2 wt%. The obtained liquid products were enriched with aromatic hydrocarbons (Table 8).

Shimada et al. studied cracking of waxes extracted from Euglena gracilis algae over RFCC E-Cat catalyst [76]. The main component of the used feedstock is myristyl myristate. It is interestingly, that deoxygenation of the wax esters (WEs) was distinguished to occur with a
higher rate and a selectivity towards water formation, than in the case of saturated triglycerides. This observation can be explained by the fact that the first stage of transformation of wax esters is their cleavage to saturated fatty acids and higher olefins (Fig. 4). The above transformations of olefins through cracking, cyclization and aromatization results in formation of active hydrogen accelerating HDO of saturated fatty acids. Furthermore, cracking of the waxes produces significant quantities of olefins and alkanes instead of aromatics, that makes such feedstock perspective for hydrocarbon biofuels production.

Thus, application of zeolites for conversion of lipid-based feedstocks

Fig. 3. Possible mechanism of a triglyceride cracking over the composite catalyst. A – Propane or propene, B – CO or CO$_2$, C – long chain hydrocarbons, X – C$_4$ – C$_7$ hydrocarbons, Y – both straight chain and branched hydrocarbons (C$_n$H$_{2n+2}$) and aromatics. Adopted from [71].

Table 8
Aromatics content in OLP (wt%) of crude palm oil cracking over REY catalyst. Adapted from [75].

| Aromatics | Crude palm oil |
|-----------|----------------|
|           | 400 °C | 450 °C |
| Benzene   | 2.8    | 4.1    |
| Toluene   | 13.0   | 17.0   |
| Xylene    | 14.9   | 19.5   |

Fig. 4. Schematic diagram of the deoxygenation reaction mechanism during catalytic cracking of WEs. Red arrows represent the hydrogen-transfer reaction pathway. Hydrogen species released from R8 are consumed preferentially in the hydrodeoxygenation reaction (red solid arrows) rather than the olefin hydrogenation (red dashed arrows). Adapted from [76]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
is characterized by a high depth of the feed cracking with a high yield of light fractions, especially gasoline one, enriched with aromatics representing mainly valuable RTX fraction. Of the highest interest are catalysts based on ZSM-5, the performance of which in the cracking process can be enhanced through promotion with transition metal oxides or via synthesis of composites with mesoporous materials, like MCM-41.

3.2. Cracking in the presence of other types of catalysts

A relatively high yields of coke and gaseous products when using zeolite catalysts, stimulate research studies, in which catalysts with milder acidity or, even, basic ones are investigated. As less acidic catalysts, such materials are used as MCM-41, γ-Al2O3, ZrO2, NbOPO4 [77–80]. In all the cases, unlike zeolites, OLPs being produced in the cracking over these catalytic materials include mainly straight hydrocarbons (both alkanes and alkenes) instead of aromatics, as they do not possess the specific shape selectivity like zeolites, especially ZSM-5. Furthermore, yields of coke and gaseous products are considerably lower (as a rule – < 10% in the both cases). Investigation of cracking of palm kernel oil and palm olein oil over a series of MCM-41 mesoporous materials showed that they are selective to linear alkanes C13 and C17 correspondingly [77]. It was also found, that yields of liquid products decreased with simultaneous growth of specific surface area (from 550 to 1200 m²g⁻¹). Maximal yield of OLPs (fractions gasoline-kerosene-deiesel) could exceed 86 wt% in the case of the first feedstock, and 73% – in the case of the second one. Using ZrO2 as a catalyst for WCO cracking resulted in attaining a yield of OLPs of 83 wt% [79]. The main components of the OLPs, with concentration more 1% were alkenes and oxygenates (alcohols, ketones and others). Scaldaferri et al. compared cracking of soybean oil over niobium phosphate catalyst (NbOPO₄) with conventional catalytic systems (FCC, HBeta, ZSM-5, Pd/C) [80]. NbOPO₄ exhibited the highest yield of the OLPs; the highest hydrocarbons content in the OLPs was found in the case of Pd/C (99 wt%) and NbOPO₄ (86 wt%) catalysts. It was also discovered that niobium phosphate catalyst generated less gaseous products and coke as well as OLPs obtained over this catalyst had lower content of aromatics.

Several works are devoted to study of cracking/pyrolysis of lipidic feedstocks in the presence of alkaline catalysts. Silva Almeida and Mancio et al. used sodium carbonate as a promising catalyst for cracking of several types of fats wastes – fats, oils, and grease (FOG) from grease traps in two laboratory reactors (143 ml, 1.5 l) and a pilot-scale slurry reactor of 143 l in volume equipped with a stirring device [81–83]. Yield of OLPs was 60–67 wt%, they consisted of hydrocarbons (mostly linear alkanes and alkenes) by ca. 80%. Mancio et al. evaluated an influence of concentration of sodium carbonate for palm oil cracking in the pilot-scale reactor of 143 l in volume in a batch mode [83]. They found that optimal concentration of the catalyst is 15 wt%, at which the maximal rate of conversion of the feedstock into the products was observed as well as acid value of the OLPs was minimal. Due to the high content of hydrocarbons (mainly of diesel fraction) in the OLPs (92.8%), their properties met to ANP No 65 (Diesel S10 specification).

Chang et al. [84] received bio-gasoline and bio-diesel through fast pyrolysis of WCOs over a series of catalysts representing pellets made of bentonite, as a binder, mixed with the such active components (25 wt %) as Na₂CO₃, NaOH, CaO and Al₂(SO₄)₃, using a continuous flow fixed catalyst bed reactor equipped with feedstock evaporator. It was found, that the best is CaO-based catalyst, optimal temperature – 500 °C, WHSV – 1.04 h⁻¹. Acid value of the pyrolysis oil in the case of CaO was the lowest and close to zero. Yield of OLPs was ~63% (~35% bio-gasoline and ~26% bio-diesel consisting mainly of linear paraffins). It should be noted that in this case yield of coke was high enough – 18.9%. The CaO-based catalyst maintained activity up to seven cycles “experiment-regeneration”.

Thus, the use of catalysts having less acidity and without the specific shape selectivity typical for zeolites, or basic ones, gives rise to reduction of cracking intensity and to decrease in yields of gaseous products, coke and light fractions as well as aromatics with the shifting of hydrocarbon fraction distribution towards diesel fraction represented mainly by linear alkanes and olefins.

4. Production of hydrocarbon fractions enriched with isomerized alkanes via merged hydrodeoxygenation-hydroisomerization of lipidic feedstocks

In order to obtain hydrocarbon fractions enriched with isomerized alkanes from vegetable oils or other lipid-based feedstocks for one stage, bifunctional catalysts active in the both deoxygenation and isomerization are necessary. The combination of the deoxygenation and isomerization steps into the one enables to simplify production of light hydrocarbon fractions of fuel purposes having improved fuel properties. Isomerized alkanes are known to have better anti-knocking index (in the case of gasoline) and lower freezing point (diesel) etc. In order to make possible such combination, it is necessary that a used catalyst had the appropriate bifunctionality.

In the most of research studies, catalysts used to produce isomerized alkanes from lipidic feedstocks as well as conditions are the same or very similar to those used for hydroisomerization of alkanes. Thus, some aspects of catalytic hydrocarbon hydroisomerization are necessary to be reviewed briefly.

4.1. Catalytic hydroisomerization of hydrocarbons

Isomerization of straight alkanes is a very important process in petroleum industry. This process is usually carried out in the presence of hydrogen to prevent deactivation of catalysts and formation of unsaturated hydrocarbons. HI of C₇-C₁₀ alkanes is performed to produce high octane number gasoline, and C₁₁-C₁₉ – to obtain diesel fuel with high cetane index and good cold flow properties due to reduction of viscosity as well as freezing point. For this process, bifunctional catalysts based on metallic active component and acid supports are generally applied. Metallic sites catalyze hydrogenation/dehydrogenation and acid sites – skeletal isomerization through carbeneium ions formation [29,85]. The hydroisomerization mechanism of n-paraffins over the bifunctional catalysts can be presented in the of the following consecutive steps [85]:

1. dehydrogenation on the metal;
2. protonation of olefins on the Brønsted acid sites with formation of a secondary alkylcarbenium;
3. rearrangement of the alkylcarbenium ion via formation of cyclic alkylcarbenium type transition state;
4. deprotonation;
5. hydrogenation.

A scheme of pathways of hydroisomerization and cracking of n-alkanes over the bifunctional catalysts is well-established in literature (Fig. 5) [86].

Typical acidic supports used in HI catalysts can be divided into the following groups [85,87–90]:

1. amorphous oxides or mixture of oxides (i.e. chlorinated Al₂O₃, HF-treated Al₂O₃, SiO₂-Al₂O₃, (Al-)ZrO₂/SO₄²⁻, WO₃/ZrO₂, WO₃/Al-ZrO₂);
2. zeolites (Y, Beta, Mordenite, ZSM-5, ZSM-22, ZSM-23);
3. silicoaluminophosphates (SAPO-5, SAPO-11, SAPO-31, SAPO-34, SAPO-41);
4. mesoporous materials (MCM-41, AlMCM-41 etc.).

The most active in isomerization due to very high acidity are chlorinated alumina and sulfated zirconia, which enable to reduce HI temperatures to 120–180 °C [29]. Such low temperatures are
thermodynamically favorable for the multibranched alkanes formation (Fig. 6).

However, gradual leaching of chlorine and sulfate groups into HI products gives rise to their contamination and gradual deactivation of the catalysts. Zeolites and SAPOs are less acidic, but more tolerant of admixtures and regenerable. However, zeolite- and SAPO-supported catalysts are used at higher operating temperatures (typically 200–360 °C) [88,92–95]. Mesoporous SiO2-based materials have the lowest acidity, but due to their unique structure they usually used in the form of composites with zeolites and SAPOs having mostly microporous structure [92,96].

Active component responsible for hydrogenation/dehydrogenation can be a noble metal (mainly Pt) [85,86,95,97,98] or bicomponent systems like Ni(Co)Mo(W) in both sulfided [85] and non-sulfided [99] forms. Recently, active components based on phosphides and carbides of transition metals are considered as promising as they exhibit plausible hydrogen transfer reactions (including hydrodesulfurization and hydrodenitrogenation) [93,94,100–106]. From the other hand, they are stable to poisoning by sulfur unlike Pt [107].

The best catalysts for isomerization of n-paraffins should have a relatively high hydrogenation activity and a low acidity to achieve maximal hydroisomerization versus (hydro)cracking, which always accompanies hydroisomerization. The hydrocracking reaction causes the degradation of the n-paraffins to less valuable and lighter products [85]. Thus, catalysts based on zeolites, SAPOs, other moderate acidic materials and their composites with various mesoporous materials are the most suitable for the hydroisomerization.

4.2. Application of zeolite- and silicoaluminophosphate-supported catalysts for HDO-HI of lipidic feedstocks and model compounds

Since isomerization of paraffins is favored at low temperatures (ca. 200–300 °C) and deoxygenation – at higher ones (ca. 300–400 °C), a certain balance in the operating temperatures should be maintained to ensure a sufficient depth of HDO and isomerization.

Zeolite- and SAPO-supported catalysts used in the HDO-HI of the lipidic feedstocks are mostly based on two types of active components: noble metal based (Pt, Pd – i.e. typical catalysis of hydrocarbon hydroisomerization) [108–116] and Ni-based (with metallic Ni or Ni-containing) [117–123]. The main results obtained in the experiments on HDO-HI of various oils, esters or fatty acids in the presence of zeolite- and silicoaluminophosphate-supported catalysts are summarized in Table 9.

In the most of presented research studies, application of Pt-based catalysts in the HDO-HI resulted in conversion of lipid-based feedstocks or their model compounds close or equal 100% with a high share of isomerized paraffins in the OLPs. Wang et al. achieved 100% conversion of soybean oil at 357 °C and hydrogen pressure of 4 MPa using 1% Pt/SAPO-11 or 1% Pt/ZSM-22 having a moderate acidity and straight ten-membered-ring channels that are appropriate for isomerization of long paraffins [108]. Maximal achieved yield of isomerized paraffins was 63%. Herskovitz et al. and Rabaev et al. also processed soybean oil via HDO-HI under similar conditions over Pt/SAPO-11–Al2O3 catalyst in a trickle-bed reactor [109,110]. As SAPO-11 gradually deactivated because of presence of water in the reaction mixture, they tried to improve its durability through addition of a surfactant hexadecylamine (HDA) to the crystallization gel of SAPO-11 at a ratio of HDA/Al2O3 ~0.6. This modification resulted in increase in the relative content of Si (nAl (4-n) Si) tetrahedra with n = 3–4 in the structure of the resulting silicoaluminophosphate that enhanced the stability and activity of these catalysts in the isomerization of hydrocarbons. As a result, in long-term testing (up to 1000 h of TOS) they showed that a certain stability of the catalysts has been achieved despite their activity decreased during the first 200 h of testing [110]. Ahmad et al. obtained dodecylbenzene and heptadecane as the main products of HDO-HI of oleic acid over Pt/SAPO-11 catalyst under hydrogen and CO2 media [111]. Chen et al. investigated catalysts Pt/ZSM-22@SiO2 in HDO-HI of methyl palmitate.

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**Fig. 5.** Scheme of pathways of hydroisomerization and cracking of a n-alkane. Adopted from [86] A: Hydrogenation-dehydrogenation on metallic sites; B: Protonation-deprotonation on acid sites; C: Addition of proton to form alkylcarbonium ion on acid sites; D: Dehydrogenation to form alkylcarbenium ion; E: Competitive adsorption-desorption of alkene and carbenium on acid sites; F: Rearrangement of alkylcarbenium ion; G: Cracking of alkylcarbenium ion.

**Fig. 6.** Thermodynamic distribution of C5, C6, and C7. Adopted from [91].
| Catalyst | Feedstock(s)          | Conditions                        | Type of reactor       | Effect                                                                 | Reference |
|----------|-----------------------|-----------------------------------|-----------------------|----------------------------------------------------------------------|-----------|
| 1% Pt/SAPO-11 | Soybean oil | T = 310–420 °C, P = 4 MPa, t = 0.5–4 h | Continuous-flow       | 100% substrate conversion was achieved at 357 °C, and P(H2) = 4 MPa. The yield of OLPs was about 80%, the yield of isoolpanes reached 63% | [108]    |
| 1% Pt/ZSM-22 |                   |                                   |                       |                                                                      |           |
| Pr/SAPO-11-Al2O3 | Soybean oil | T = 375–380 °C, P = 30 atm, WHSV = 5–40 h⁻¹, H2/feed = 800 | Trickle-bed reactor   | The blend of OLPs of soybean oil HT for 560 h was a mixture of diesel hydrocarbons, which included branched alkanes, naphtenenes, and aromatics. The ratio of isomerized alkanes to linear ones exceeded 2. The product met all the EN-590 standard requirements to diesel fuels and can be used in mixtures with them | [109]    |
| Pr/SAPO-11-SiO2 | Methyl palmitate    | T = 300–360 °C, P = 30 bar, WHSV = 5–40 h⁻¹, H2/feed = 800 | Continuous-flow       | Increasing in the yield of monoioimerized alkanes from 71 to 95 wt% (300 °C). The optimal SiO2 content was 20 wt%. A further increase in SiO2 content on outer surface of the zeolite particles led to a decrease in catalytic activity of the catalyst, both by gradually changing the Pt faces from (1 1 1) to (1 0 0) and by reducing the number of external acid sites on the zeolite surface, which also are adsorption centers. A decline of the SiO2/Al2O3 ratio in the zeolite led to an improvement of the catalysts activity both by reducing the size of platinum particles and increasing the number of Pt faces (1 1 1), and by increasing in the number of acid sites in the support | [110]    |
| Pt/SiO2/SAPO-11 | Methyl palmitate    | T = 370–375 °C, P = 3 MPa, H2/feed = 800, WHSV = 5 h⁻¹ | Continuous-flow       | Proportion of isomerized C15-C18 alkanes and cracking products increased with an increase in the platinum content from 0.5 to 2.0 wt%. Deactivation of catalysts in both HDO and HI | [111]    |
| Ni/H-β-zeolite | Sunflower oil       | T = 300 °C, P = 3.0 MPa, WHSV = 2 h⁻¹, H2 flow rate = 160 ml·min⁻¹ | Continuous-flow       | Feedstock conversion 98–99%, yield of lighter products < 1.2%, the OLPs are mainly straight alkanes C12-C15 | [112]    |
| Ni/ZSM-5 (Si/Al: 38) |              |                                   | Down-flow reactor     | The content of straight and isomerized alkanes C12 and C14 in OLPs at T = 320–350 °C was close to 100%. Ratio of isoolpanes to the linear ones was up to 10 and more. The freezing point of the average OLPs obtained at 340 °C (WHSV = 0.9–1.6 h⁻¹) and TOS = 0–22 h was below ~50 °C. The catalyst was unstable under process conditions due to the sintering of Pd particles | [113]    |
| Ni/ZSM-5 (Si/Al: 50) |              |                                   |                       |                                                                      |           |
| Ni/β-zeolite | Castor oil          | T = 300 °C, P = 3.0 MPa, WHSV = 2 h⁻¹, H2 flow rate = 160 ml·min⁻¹ | Continuous-flow       | The OLPs are mainly straight alkanes C14-C19 | [114]    |
| Ni/USY | N/SiO2/SAPO-11 |                                   |                       |                                                                      |           |
| Ni/C30 | Ni/ZSM-5 (Si/Al: 100) |                                   |                       |                                                                      |           |
| Ni/SiO2/SAPO-11 | Ni/β-zeolite |                                   |                       |                                                                      |           |
| Ni/MCM-41-AFTE-USA | Soybean oil | T = 300–380 °C, P = 4.0 MPa, WHSV = 1–30 h⁻¹, H2 flow rate = 300 ml·min⁻¹ | Continuous-flow       | The best results were obtained when using 8 wt% Ni/SiO2/SAPO-11 catalyst. At 370 °C, 4 MPa, 1 h⁻¹ 100% conversion of the feed was achieved, OLPs yield was 74.8%. Selectivity to alkanes was 100%, 86.5% from which were isomerized ones | [115]    |
| Ni/H-ZSM-22 | Palmitic acid       | T = 150–260 °C, P = 4 MPa, t = 0.5–4 h | Batch                 | Catalysts obtained by impregnating the support with a melt of nickel nitrate crystallohydrate were characterized by a higher dispersion of nickel and effectiveness (iso/ n up to 0.8). Testing the catalysts for their durability in the process at 260 °C, 4 h, P(H2) = 4 MPa for five testing cycles showed that the substrate conversion maintained at 100%, but the molar ratio of C14/C12 alkanes and the yield of isoolpanes alkanes was decreasing. | [116]    |
The zeolite component was partially covered with silica to passivate acidic sites on the external surface of the support and directing the pathway of isomerization towards monobranched alkanes formation [112]. Monobranched diesel alkanes are known to have a higher cetane number (> 85, multibranched < 60).

Also, they investigated an effect of modification of Pt-based catalyst by tin in the composition of PtSn/SAPO-11 system in HDO-HI of the same substrate [113]. Addition of Sn to the Pt/SAPO-11 system followed by partial reduction with hydrogen resulted in redistribution of tin to two tin-containing phases: SnO2-x (0 < x < 2) and PtSn alloys. The presence of the both phases improved catalyst activity in the both HDO and HI due to the following factors. SnO2-x appeared to have a weak Lewis acid sites that increased total acidity of the catalysts, which was confirmed by FT-IR spectra of pyridine adsorption (Fig. 7). From the IR bands at 1455 and 1545 cm−1 relating to the coordinated and ionized pyridine correspondingly, it can be seen that the increase in Sn content leads to content of weak Lewis acid sites (i.e., after evacuation point < −47 °C). The most effective catalyst has the composition of 40% Ni,P/HZSM-22. In this case conversion of palmitic acid reached 99.6% with a hydrocarbon yield of 42.9%. Aldehydes and ketones were detected as intermediates. Their further HDO led to formation of the corresponding hydrocarbons. The study of catalysts by a series of techniques showed that the Ni,P phase is involved in DCN/DCX, while Brönsted acidic sites of the zeolite support corresponded hydrocarbons. The study of catalysts by a series of techniques showed that the Ni,P phase is involved in DCN/DCX, while Brönsted acidic sites of the zeolite support were found to depend mainly on acidity of a support (Fig. 9). The use of non-modified zeolites with elevated acidity (ZSM-5, USY and H-Beta) led to formation of C5-C7 fraction of alkanes and elevated ratio of isomerized alkanes to the linear ones. Application of supports having a low concentration of acidic sites (SAPO-11, modified USY) gave rise predominantly to formation of long alkanes C14-C18. Wang et al. studied HDO-HI of soybean oil over Ni supported by SAPO-11 and a series of zeolites: ZSM-5, ZSM-22, ZSM-23 and β [118]. The best result was obtained in the case of 8% Ni/SAPO-11 at 370 °C, pressure of 4 MPa and WHSV of 1 h−1. 100% conversion of soybean oil achieved with selectivity to isoalkanes of 85%. They concluded that a good catalyst should be enough mesoporous with one-dimensional micropore channels having appropriate size as well as moderate mesoporosity.

Liu et al. reported on HDO-HI of castor oil over Ni-based catalysts supported by ZSM-5, H-Beta, USY and SAPO-11. Active components were both metallic nickel and nickel phosphides [117]. The conversion of the feedstock was 98–99% in all the cases. Pathways of substrate transformations and ratio of isomerized alkanes to the non-isomerized were found to depend mainly on acidity of a support (Fig. 9). The use of non-modified zeolites with elevated acidity (ZSM-5, USY and H-Beta) led to formation of C5-C7 fraction of alkanes and elevated ratio of isomerized alkanes to the linear ones. Application of supports having a low concentration of acidic sites (SAPO-11, modified USY) gave rise predominantly to formation of long alkanes C14-C18. Wang et al. studied HDO-HI of soybean oil over Ni supported by SAPO-11 and a series of zeolites: ZSM-5, ZSM-22, ZSM-23 and β [118]. The best result was obtained in the case of 8% Ni/SAPO-11 at 370 °C, pressure of 4 MPa and WHSV of 1 h−1. 100% conversion of soybean oil was achieved with selectivity to isoalkanes of 85%. They concluded that a good catalyst should be enough mesoporous with one-dimensional micropore channels having appropriate size as well as moderate mesoporosity.

Cao et al. synthesized Ni/H-ZSM-22 catalysts for HDO-HI of palmitic acid via impregnation of the support either by aqueous solution of Ni(NO3)2·6H2O or by its infiltration with the melt of this nickel salt at 65 °C (Tmelt = 56.7 °C) [119]. H2-TPR study (Fig. 10) revealed that in the case of the sample prepared via the melt infiltration (Ni/HZ-1, black TPR-curve a) NiO phase was reduced easier to metallic Ni due to lower reduction temperature (317 °C instead of 344 and 348 °C). Furthermore, NiO of different crystal sizes had a higher ability to reduce. Thus,
the Ni/HZ-1 sample obtained through melt infiltration has exhibited a better distribution of Ni over HZSM-22 and stronger metal-support interactions (second peak). In addition, the authors found that Ni/HZ-1 catalyst had higher dispersity and, thence, was more effective due to elevated activity in both HDO and HI.

Chen et al. promoted Ni-based catalyst supported by SAPO-11 by MoO$_{3-x}$ phase HDO-HI of methyl laurate [120]. They found that in the case of the lowest reduction temperature (400 °C) the obtaining catalysts had the highest acidity (that was revealed in NH$_3$-TPD study, Fig. 11) and thus were maximally selective to isomerized alkanes. The NH$_3$-TPD study of the catalysts revealed that new acid sites, including strong ones, were generated after reduction at 400–500 °C, that exhibited in the form of peak emerged at 550 °C in the TPD profiles not observed for the support, oxidized catalyst or catalyst reduced at 550 °C. Catalyst having the optimal balance between activity and selectivity in HDO and HI was reduced at 450 °C due to synergetic effect between Ni and Mo$^{4+}$.

Although vegetable oils do not contain sulfur, sulfided NiMoS/ NiWS-based catalysts were found to be applicable in the HDO-HI of the feedstocks. Qian et al. investigated an effect of porous structure of support in sulfided catalysts of NiMo/SAPO-11 and NiMo/AlSBA-15 composition in HDO-HI of methylsteaerate [121]. They concluded that porous structure of the used support has a significant effect: SAPO-11-supported catalyst generated mainly monobranched alkanes (pore size = 0.6 nm). In the case of NiMo/AlSBA-15 (pore size 3.3 nm) yields of cracking products and multibranched alkanes were found to be significantly higher due to higher acidity and wider pores of the support. Verma et al. obtained OLPs ~40% of green diesel, ~40% biokerosene and ~20% biogasoline via HDO-HI of Jatropha oil over NiMo/SAPO-11 and NiWS/SAPO-11 catalysts [122]. The catalysts were stable in the testing for at least six days, when sulfur content in the OLPs was relatively low.

Furthermore, nickel phosphides based systems are also found to be applicable for the HDO-HI of lipid-based feedstocks that has been demonstrated by Liu et al. in [117] and [123].

In addition, Sousa et al. investigated HDO-HI of palm kernel oil and palm olein as well as their hydrolysates using thermally activated β-Zeolite in H-form without any additional active component. [124]. Content of hydrocarbons in the OLPs varied from 24 to 98 wt% and dependent on a substrate and time of the process. The hydrocarbon fraction contained a significant content of isomerization and aromatization products, the presence of which led to a decline of freezing point to −18 to −30 °C. The catalyst exhibited stability for four cycles of testing without any notable deactivation.

4.3. Application of HDO-HI catalysts supported by other porous materials

To obtain isomerized alkanes through one-stage hydrodeoxygenation-hydroisomerization from lipidic feedstocks many researchers use catalysts supported also by other supports: aluminosilicates, SiO$_2$ based mesoporous material SBA-15 doped and non-doped by alumina, γ-Al$_2$O$_3$ (including WO$_3$ modified) and porous carbon materials (CNTs, activated carbons). Active components are mainly represented by metallic Ni or Co, as well as sulfide or partially reduced Ni-based systems promoted with Mo. The main results of HDO-HI of various feedstocks in the presence of such catalysts are summarized in Table 10. In general, it is important to note that the number of examples describing the use of catalysts with other supports is significantly lower than those in which catalysts supported by zeolites and SAPOs are utilized. This most probably is connected with their lower performance in terms of yield of isomerized paraffins.

Kulikov et al. reported on rapeseed oil conversion over Pt-Pd-Al-
HMS system [134] in which the support represented mesoporous aluminosilicate mixed with boehmite (30 wt%). They found that at 275 °C HDO occurs completely and gasoline content in OLPs is 9%. Temperature increase results in a growth of cracking contribution accompanied by increase in yields of gasoline and gaseous products. Optimal conditions with maximal yield of diesel fraction (~94%) including isomerized paraffins (20%) were found to be the following: T = 300 °C, LHSV = 1 h⁻¹. Veriansyah et al. carried out a screening of catalysts in HDO-HI of soybean oil at 400 °C, and initial hydrogen pressure of 9.2 MPa [135]. They found that conversion of the feedstock declines in the range: NiMoS/γ-Al₂O₃ (92.9%) > 4.29 wt% Pd/γ-Al₂O₃ (91.9%) > CoMoS/γ-Al₂O₃ (78.9%) > 57.6 wt% Ni/SiO₂-Al₂O₃ (60.8%) > 4.95 wt% Pt/γ-Al₂O₃ (50.8%) > 3.06 wt% Ru/Al₂O₃ (39.7%). Ni and Pd-based catalysts were found to generate OLPs composed mainly of linear C₁₇ and C₁₅ alkanes, while in the case of CoMoS/γ-Al₂O₃ catalyst an elevated yield of isomerized alkanes and lighter cracking products were detected. Phimsen et al. investigated HDO-HI of oil extracted from spent coffee grounds over Pd/C and sulfided NiMo/γ-Al₂O₃ catalysts and in a batch reactor equipped with shaker [136]. Such oil contains FFA (6.14 wt%). Contents of isoalkanes and olefins in OLPs were 10.3 and 4.8 wt%, correspondingly, in the case of the sulfided catalyst, and 1.7 and 22.3 wt% correspondingly in the case of Pd-based catalyst.

Nepomnyashchiiy et al. carried out HDO-HI of sunflower oil over NiMoS/WO₃-Al₂O₃ catalytic systems at 380 °C, 4.0 MPa and WHSV of 1 h⁻¹ [137]. They found that increase in WO₃ content leads to a growth

Fig. 9. Scheme of the conversion of castor oil with H₂ catalyzed by nickel-based bifunctional catalyst. Adopted from [117].
of concentration of acid sites in the support, mainly at the expense of weak and medium ones. OLPs yield was 81–83 wt% and increase in WO3 was found to enable higher yields of isomerized alkanes. However, the used catalyst was not stable enough and gradually deactivated in all cases.

Ochoa-Hernández et al. [138] studied HDO of mixture of esters the main of which was methyl oleate (about 70%) [141], over Ni- and Co-based catalysts supported by both pure SBA-15 and modified by Al2O3 (Al-SBA-15). It was found that doping of SBA-15 by alumina resulted in appearing of acid sites in the support and as a result – conversion of the ester mixture was becoming close to 100% and content of isomerized paraffins was increasing in several times.

Liu et al. carried out HDO-HI of Jatropha oil containing FFA using trifunctional catalysts combining functions of hydrogenation, HDO and isomerization/ cracking [139]. The catalysts were represented by sulfided systems of NiMo/SiO2, NiMo/γ-Al2O3 and NiMo/SiO2-Al2O3 compositions. Application of catalyst with the mixed support enabled to obtain a mixture of alkanes including of 10% C8−C10 and 25% of isoalkanes. Freezing point of the OLPs was –10 °C.

Han et al. [140] used Mo2C/CNTs catalysts for HDO-HI of several types of vegetable oils and model compounds (decanal, stearic acid and methyl palmitate) at 220–260 °C and hydrogen pressure of 2.0 MPa in a batch reactor. Catalytic activity of catalysts based on molybdenum carbide was compared to that of Pd- and Pt catalysts. The Mo2C-based catalysts were found to be stable to leaching unlike the noble metal-based systems in the process conditions. In HDO-HI of various vegetable oils (Fig. 12) over 20%Mo2C/CNTs catalyst maximal yield of alkanes was 87%, in which proportion of isomerized alkanes was 55%.

4.4. Concluding remarks on HDO-HI of lipidic feedstocks

Thus, HDO-HI over zeolite- or SAPO-based catalysts with active components based on noble metals (which are typical HI catalysts) or even nickel, in the exemplary conditions of the hydrotreatment enables to obtain OLPs composed mainly of hydrocarbons, which can contain up to 90% or even more of isomerized paraffins. Yields of hydrocarbons can be close to the maximal possible. The pathways of transformations of triglycerides or model compounds can be easily controlled by acidity and geometric characteristics of the used zeolites or SAPOs. When increasing the HDO-HI temperature, fractional composition of the hydrocarbons is shifting towards lighter – biojet fuel or biogasoline fractions.

However, there is a potential challenge when applying zeolite- and SAPOs-supported catalysts: the both this supports are known to be not enough stable in hydrothermal conditions [110,142,143]. A probable solution of this issue can be their preservation with special agents (e.g. silanes) to prevent their dealumination [142] and development of porous acidic materials as alternative supports (e.g. mixed TiO2-ZrO2 [144] or the like).

The use of catalysts supported by other supports (γ-alumina, CNTs etc.) with similar active components generally results in conversion of lipidic feedstocks into OLPs with less content of isomerized alkanes. Thus, such catalytic systems need further development.

5. Techno-economic analysis of renewable diesel and jet fuel production from renewable feedstocks

One of the main limitations of a widespread use of bio-jet and second generation of biodiesel fuel is the relatively high cost of their production in comparison with fuels obtained from fossil feedstocks. Thus, the price of biojet fuel largely depends on many factors, in addition to the catalysts and process used for the processing of vegetable oils. Nowadays, many authors focused on estimation of biofuel prices produced mainly from different vegetable oils.

Biofuels produced via different technology processes could possess principally different properties, but more advanced technology could result in higher prices of production of renewable fuels. Techno-economic analysis of waste vegetable oil conversion into green diesel via different ways was made in [145]. The authors analyze production of green diesel through catalytic HDO of vegetable oil, FAME biodiesel obtained via conventional homogeneous alkali catalysis (HACA) and supercritical processes (SCA). Annual total product cost was estimated for the plant capacity of 100,000 tons/year. Biodiesel price in both cases (HACA and SCA) was lower in comparison with green diesel produced via hydrogenation as with using stand-alone unit and incorporated in refinery as well (0.671 US$/kg; 0.727 US$/kg; 1.000 US$/kg and 0.808 US$/kg; respectively). Natelson et al. [146] estimated jet fuel break-even price production via hydrolysis, decarboxylation, and reforming using camellia oil as a feedstock. A refinery with annual nameplate capacity with 76,000 m3 of hydrocarbons was simulated. A break-even selling price was 0.80 US$/kg. Wang et al. estimated minimal jet fuel selling price of renewable jet producing via hydro-processing of jatropha oil [147]. Techno-economic analysis was made for a plant capacity of 2400 metric tons of feedstock per day. Two scenarios were estimated, the minimum jet fuel selling price (MUSP) value were 5.42 US$/gallon (1.43 US$/L) and 5.74 US$/gallon (1.51 US$/L) respectively for fruit and oil scenario.
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The minimal production cost was examined. The minimal production cost was assessed at 812 million L/year – $1.09/L for production costs. Influence of plant capacity (15–1161 million L/year) on hydrogenation-derived renewable diesel (HDRD) production cost was estimated using canola and camelina oils as feedstocks. In [152] hydrogenation-derived renewable diesel (HDRD) production from camelina oil was undertaken in [153]. A model investigates plant sizes of 112.5–675 million L/year and other.

Table 10
| Catalyst | Feedstock(s) | Conditions | Type of reactor | Effect |
|----------|--------------|------------|----------------|--------|
| Ni/Mo/γ-Al2O3 | Sunflower oil | T = 380 °C, P = 4.0 MPa, WHSV = 1 h⁻¹ | Continuous-flow | Maximal yield of diesel fraction alkanes (~94%) with isomerized alkanes content 20% at 300 °C and LHSV = 1 h⁻¹. |
| NiMo/WO3 | Methyl stearate | T = 300–375 °C, P = 3.0 MPa, LHSV = 10 h⁻¹, H2/feed = 2000 | Continuous-flow | Conversion of the feedstock decreases in the range: NiMo/γ-Al2O3 (92.9%) > 4.29 wt% Pd/γ-Al2O3 (91.9%) > CoMoS/γ-Al2O3 (78.9%) > 57.6 wt% Ni/SiO2-Al2O3 (60.8%) > 4.95 wt% Pt/γ-Al2O3 (50.8%) > 3.06 wt% Ru/Al2O3 (39.7%). |
| NiMo/γ-Al2O3 | Jatropha oil | T = 350 °C, P(H2) = 4 MPa, LHSV = 7.6 h⁻¹, H2/oil = 800 | Continuous-flow | The use of Ni and Pd-containing catalysts gives rise to obtaining mainly of straight alkanes C17 and C15. In the case of CoMoS/γ-Al2O3 a higher yield of isomerized alkanes as well as of lighter cracking products were found. |
| Pt/Pd-Al-HMS (30% Al2O3) | Rapeseed oil | T = 250–375 °C, P = 60 atm, LHSV = 0.5–2 h⁻¹, H2/oil = 1200 | Continuous-flow | Optimal conditions are the following: T = 400 °C, t = 2 h Activity of NiMo/γ-Al2O3 catalyst was found to be higher than that of Pt/C. |
| Pd/C | Oil extracted from spent coffee grounds | T = 375–450 °C, P(H2) = 0.5–2.5 MPa, t = 0.5–4 h, molar ratio H2/oil = 2 and 7 | Batch | Number of acid sites in the support increases along with tungsten oxide content growth mainly due to weak and medium acid sites. HDRD yield was 81–83 wt%, increasing in WO3 content enabled to increase of isomerized paraffins yield. Gradual deactivation of the catalyst. |
| NiMo/SiO2 | Mixture of esters | T = 300 and 340 °C, P = 30 bar, WHSV = 20.4 h⁻¹ | Continuous-flow | Promotion of the SBA-15 by Al2O3 led to the appearance of acidic properties of the support, as a result, the conversion of esters became close to 100%, the content of isomerized alkanes in the composition of the OLPs increased several times. The most effective catalyst was Co/SBA-15. |
| Ni/Al-SBA-15 | Decanal, stearic acid, methyl palmitate; several vegetable oils | T = 220–260 °C, P(H2) = 0.5–2.5 MPa, t = 1–3 h | Batch | When hydrotreating of various vegetable oils over the catalyst at T = 260 °C, P(H2) = 2.0 MPa, t = 3 h, the maximal yield of alkanes was 87%, the proportion of isomerized alkanes was 55%. |

Using different type of biomass was examined in many researches. For example, the technoeconomic analysis of aviation biofuels production cost from different sources were performed in [148]. It was shown that biojet fuels produced from palm oil via HEFA processes had a relatively low production cost as well as CO2 emissions (890 €/t and 52.0 g CO2 eq/MJ kerosene). Techno-economic comparison of biojet fuel. In [150] techno-economic assessment of HDRD (hydrogenated renewable diesel) production from palm fatty acid distillate (PFAD) was studied. The authors estimated that HDRD selling price of $2.74/L.

Fig. 12. Yield of alkanes and selectivity to isooalkanes for different oils according to data from [140]. Conditions: 20%Mo2C/CNTs, T = 260 °C, P (H2) = 2.0 MPa, t = 3 h. Republished with permission of Royal Society of Chemistry Copyright 2011; permission conveyed through Copyright Clearance Center, Inc.

HDDR from canola oil and $0.85–1.37/L for HDDR from camelina oil. Techno-economic analysis of hydprocesed renewable jet (HRJ) fuel production from camelina oil was undertaken in [153]. A model investigates plant sizes of 112.5–675 million L/year and other.
parameters. Minimum selling price of HRJ was US$ 1.06 l⁻¹ for a plant capacity 225 million L/year under the base case scenario.

Tao et al. performed TEO of HEFA production for five selected feedstocks [154]. Yield of products in case of biorefinery plant capacity 788 dry ton for different feedstocks was summarized in Table 11. It was shown that jet fuel yield was in the range 60–70%. Propane yield was within the range of 2–4%, and that strongly correlates with tri-, di- and mono-glycerides in feedstock.

Thus, different techno-economic estimations presented in the literature depend on a feedstock type as well as on a certain process of a biofuel production. Merging of several processes simplifies technology of a biofuel production and, therefore, could lead to decrease of operational and capital costs in the whole, making a biofuel to be more competitive with fossil feedstocks derived fuels. From this point of view, a further investigation of bifunctional catalysts enabling production of isomerized paraffins for one stage, represents a significant interest for the further development.

6. Conclusions and further perspective

Nowadays, conversion of lipid-based feedstocks into motor fuel components via/with oxygen removal, is studied very intensively due to the today’s considerable world ecological challenges. Processes of transformation of the feedstocks into oxygen-free motor fuel components can be divided to the few different directions. Direct cracking of vegetable oils over zeolite-based catalysts enabling production of mainly aromatics enriched with BTX fraction – a high-quality gasoline component (except benzene), looks attractive from the technological viewpoint. However, low yield of targeted products and high yields of coke and gaseous products as well as limitations on aromatics content in fuels cause the need to look for another approaches.

Deoxygenation of vegetable oils with or without hydrogen is aimed at production of linear paraffins. It can be performed in different media with different catalysts as well as with different selectivity to the products. However, hydrosomierization enables to produce isomerized alkanes having higher performance characteristics compared to the linear ones in all types of liquid motor hydrocarbon fuels. In the area of development of the catalysts, many research groups focus on oxygen removal from plant lipids and their derivatives to produce linear alkanes. Hydrosomierization, which is a deeper investigated process due to the larger number of research studies, primarily from the field of oil refining, is meant as an obvious step that does not require a separate study. This vision of the issue seems to cause a relatively low number of research studies focused on the direct conversion of lipid-based feedstocks into isoalkanes via merged HDO-HI. The analysis of the literature data showed the comparative similarity of active components of HDO and HI catalysts. Support acidity and process parameters could be key factors for development of new catalysts for production of isooalkanes and aromatics from vegetable lipids using a single catalytic system.

In the whole, successful development of the HDO-HI of lipid-based feedstocks needs an optimized hydrogen consumption as well as durable high-performance catalysts, the most perspective of which seemed are non-sulfided Ni-based systems supported by moderately acidic supports having appropriate porosity. The use of a one-step process is expected to improve the quality of the resulting fuel components and thereby reduce the relatively large difference in price between fuels obtained from fossil feedstocks and from the vegetable ones.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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