FUTURE REFINING CATALYSIS – INTRODUCTION OF BIOMASS FEEDSTOCKS

David KUBIČKA

Department of Refinery and Petrochemical Research, Research Institute of Inorganic Chemistry, Záluží 1, 436 70 Litvínov, Czech Republic; e-mail: david.kubicka@vuanch.cz

Refining catalysis has been developing over many years to satisfy the demand for high-quality and environmentally-acceptable automotive fuels. Biomass-derived feedstocks have been recently introduced into refineries posing thus new challenges for refining processes and catalysis. The manuscript focuses on three prominent biomass-derived feedstocks: triglycerides, bio-oils and Fischer–Tropsch products from gasified biomass. Due to high oxygen content in biomass feedstocks, deoxygenation processes play an important role in upgrading of these feedstocks. Thus, first peculiarities of deoxygenation are discussed in detail in the context of hydrotreatment processes. Different possibilities of triglycerides and bio-oils deoxygenation including their coprocessing with crude-oil-derived fractions are described. Since biomass-to-liquid processes are very important for the conversion of general biomass into liquid products, the second part deals with the aspects of biomass conversion to synthesis gas, Fischer–Tropsch synthesis and introduction of new co-catalysts.
Keywords: Refining catalysis; Biomass feedstocks; Triglycerides; Bio-oils; Hydrodeoxygenation; Fischer–Tropsch synthesis.

Crude-oil refining is one of the most important industries of our time. It supplies the society mainly with automotive fuels covering thus one third of its energy consumption[1]. At the same time it is an exclusive supplier of feedstocks for the petrochemical industry which produces a wide variety of base chemicals (ethene, propene, benzene, ammonia, sulfuric acid) which are essential for the production of polymers and other products. Since the crude-oil reserves are finite and decreasing, new resources for the production of fuels and chemicals have to be sought.

As far as transportation fuels and base chemicals are concerned, our economy is almost completely carbon-based (hydrocarbon-based), i.e. the transportation fuels and base chemicals have a carbon chain backbone. The only sustainable (renewable) source of organic carbon is currently the plant biomass[2]. Consequently, the efficient use of this source is the only feasible way

forward in order to decrease the impact of human activities on the environment (climate) on the one hand, and to facilitate a transition from crude-oil-dependent society (i.e. an unsustainable one) to a renewable-energy-dependent society on the other. The estimated worldwide biomass energy potential in 2050 is[3] between 150–450 EJ/year. For comparison, the current annual worldwide total energy consumption is about 470 EJ and has been predicted[4] to rise to 740 EJ/year in 2030.

The crude-oil refining relies completely on catalysis. The fractional composition of crude oil deviates substantially from the desired product slate and catalytic processes, such as fluid catalytic cracking (FCC) and hydrocracking have to be used to satisfy the demand for gasoline and diesel. Additionally, the composition of the primary gasoline and diesel fractions is altered by subsequent catalytic processes to optimize their properties (e.g. by catalytic reforming, isomerization) and to minimize their environmental impacts (e.g. hydrodesulfurization). Despite the maturity of these technologies, they continue to develop intensively. Apart from the economics the main development drivers in the refining catalysis are environmental and social issues, development of refinery processes and feedstock changes. The mutual interactions between these drivers are schematically depicted in Fig. 1.

Environmental concerns and growing public awareness have successfully contributed to a substantial decrease in pollutants emitted due to combus-
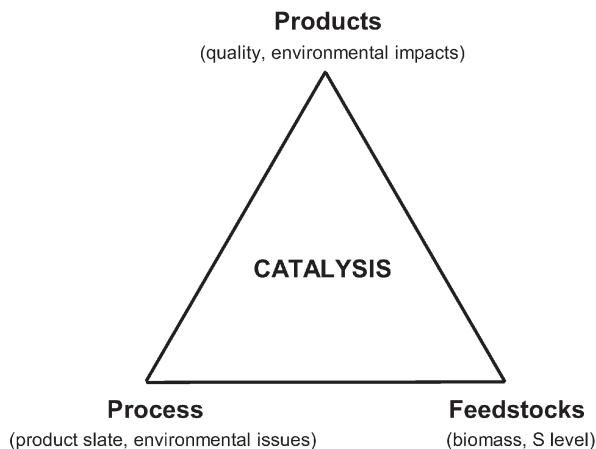
Products
(quality, environmental impacts)

CATALYSIS

Process
(product slate, environmental issues)

Feedstocks
(biomass, S level)

Fɪɢ. 1
Schematic representation of development drivers in the refining catalysis (for details, see the text)

tion of automotive fuels; e.g. Pb-based octane boosters were completely abandoned in the developed countries[5], the sulfur level in transportation fuels has been drastically reduced, ultralow sulfur fuels (10 ppm S) have been introduced in the developed countries[5–7] and the concentration of aromatics has been cut as well[5,6,8]. The role of catalysis in the achieved environmental benefits is indispensable, as will be shown later using the example of hydrodesulfurization. Catalysis plays a vital role in development of refining processes as well; let the prime objective be the product-slate modification or the environmental aspects. New catalytic processes have been developed (e.g. production of octane boosters, such as methyl or ethyl *tert*-butyl ethers[9]) or are being developed (e.g. alkylation using heterogeneous catalysts)[10]. Processes have been (and are being) modified to satisfy the changing demands: the increasing demands for middle distillates (diesel fuel) and propene have given rise to new hydrocracking[11] and FCC catalysts[12,13], respectively.

Finally, catalysis has to deal with the challenge of new and ever-changing feedstocks. On the one hand, the crude oils are getting heavier and more sour (i.e. have higher density and sulfur content)[14] and, at the same time, lighter products with ultralow sulfur contents are demanded[15]. On the other hand, the limited reserves of fossil fuels and the increasing concentrations of atmospheric CO_2 that is generally accepted to be caused by combustion of fossil fuels and to contribute to global warming have led to introduction of biomass, a renewable source of carbon, into the liquid fuels production scheme[16,17].

The biomass-based fuels may help diminish the impact of human activities on the environment, provided that they are produced in a sustainable way (based on their life cycle analysis). Other possible benefits are decreasing the dependence of fuel production on crude oil and development of rural areas. As the price of crude oil is predicted to continue growing (the crude-oil price will climb to a record average price above 90 \$/barrel and possibly even above 100 \$/barrel in 2011)[18], biomass-derived fuels (biofuels) may even become price-competitive. (The crude-oil prices predicted for 2011 have become reality already in February 2008.) The gasoline and diesel engines will remain the dominating powertrains[16,19] until 2030 and biofuels should thus be compatible with these engine technologies as well as with the corresponding fuels. Moreover, the compatibility of biofuels with fossil automotive fuels is important also from the distribution point of view. Processing of biomass feedstocks in crude-oil refineries to produce biofuels offers a wide range of advantages from both technological and economical point of view – availability of up- and down-stream processes for automo-

tive fuels, experience in catalytic processes for fuel production, existing technologies to be used for coprocessing biomass and crude-oil feedstocks, availability of utilities and possibility of synergies.

Besides biofuels there are other alternatives to conventional transportation fuels such as methane (compressed or liquefied), hydrogen and fuel cells. Nevertheless, the state-of-art of these alternatives indicates that they will cover only a small share of the energy demand in the transport sector[16,19] by 2030 and therefore they cannot be, in contrast to biofuels, used immediately. In the short term, biofuels are thus the only alternative to reduce the impact of fossil fuels on the environment. In the long term, the energy efficiency, distribution infrastructure and sustainability of the individual alternatives will determine which will predominate beyond 2030. The perspective of biofuels is in the use of the abundant lignocellulosic biomass, which can be converted by (i) pyrolysis into a mixture of oxygen-containing compounds (bio-oil) or by (ii) gasification into synthesis gas (a mixture of H_2 and CO). The main advantages of lignocellulosic biomass are its availability and independence on food-supply chain; the main disadvantages being the high degree of complexity and variability of composition, which make its use technologically and energetically demanding.

The objective of this contribution is to address the possibilities of processing or coprocessing biomass-derived feedstocks in existing oil refineries. Two principal catalytic approaches will be discussed – deoxygenation of liquid biomass feedstocks, such as vegetable oils and bio-oils, and synthesis of fuels and chemicals from gasified biomass.

FROM HYDRODESULFURIZATION (HDS) TO HYDRODEOXYGENATION (HDO) – GOING BEYOND BIODIESEL

A typical feature of biomass is that it contains large quantities of heteroatoms, mainly oxygen. The elimination of heteroatoms is vital for the quality of the final fuels, as these should contain only hydrocarbons in the optimal case. The presence of heteroatom-containing compounds is usually a source of problems – combustion of sulfur-containing compounds contributes significantly to air pollution, oxygenates lower the higher heating value (HHV) of the fuel, may be miscible with water and suffer from decreased oxidation stability as compared with hydrocarbons. In spite of these drawbacks, ethers and lower alcohols have found their use in gasoline and methyl esters of fatty acids (FAME, also called biodiesel) are blended in diesel.

Sulfur is the main heteroatom present in fossil fuels and is removed by hydrodesulfurization (HDS), which is the prominent reaction in hydro-treatment, hydroprocessing and hydrocracking. Analogously, oxygen can be removed from fuels by hydrodeoxygenation (HDO) using, e.g., hydro-treatment or hydrocracking processes. Biomass feedstocks that are rich in oxygen could be thus upgraded by HDO to obtain high-quality automotive fuels. Obviously, HDO would challenge the existing production of biodiesel as both technologies would compete for the same feedstocks, namely tri-glycerides.

Conventional Biodiesel

Biodiesel is currently the most important biofuel for diesel engines. Unlike vegetable oils it has a suitable viscosity and boiling point range. Depending on the local climate, rapeseed, soybean and palm oils are used for biodiesel production in Europe, U.S.A. and South Asia, respectively. Biodiesel production is based on the reaction of triglycerides of fatty acids with methanol in the presence of basic catalysts that yield methyl esters of the fatty acids (biodiesel) and glycerol (Fig. 2). Several detailed reviews can be found in the literature[20–22] and, thus, only the aspects of biodiesel production that are pertinent to this review will be briefly highlighted.

Glycerol is a byproduct of biodiesel production and its production corresponds to roughly 10 wt.% of the starting vegetable oil. Consequently, its utilization for making value-added chemicals is essential for the economics of biodiesel manufacture. Due to a sharp increase in biodiesel production in recent years[23], there is an excess of glycerol[24] on the market pushing down its prices and decreasing the profitability of biodiesel units. New applications of glycerol are, thus, required and developed[24]. The profitability is
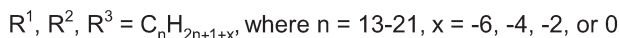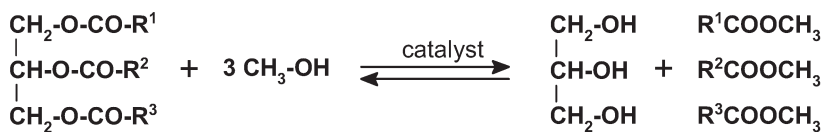
$$
\begin{array}{ccc}
CH_2\text{-O-CO-R}^1 & & CH_2\text{-OH} \quad R^1COOCH_3 \\
| & & | \\
CH\text{-O-CO-R}^2 \;+\; 3\,CH_3\text{-OH} \xrightarrow{\;catalyst\;} & CH\text{-OH} \;+\; R^2COOCH_3 \\
| & & | \\
CH_2\text{-O-CO-R}^3 & & CH_2\text{-OH} \quad R^3COOCH_3
\end{array}
$$

$R^1, R^2, R^3 = C_nH_{2n+1+x}$, where $n = 13\text{-}21$, $x = -6, -4, -2,$ or 0

Fig. 2

Simplified scheme of transesterificatition of vegetable oils with methanol. Typical reaction conditions: 60 °C, 101 kPa, CH_3OH/oil = 5–6 mol/mol

further affected by high prices of the raw materials, and new suitable feed-stocks are intensively sought[25,26]. In order to meet the biodiesel legislative specifications, the starting vegetable oils have to be of high quality and the feedstock flexibility is, thus, rather low. The main limiting quality factor from the production point of view is the content of free fatty acids, which, if present at high concentrations (>2%), prevent the use of the conventional process[20,21].

The industrial processes rely on homogenous catalysts (NaOH, KOH, or the corresponding methoxides) and are one of the few large-scale processes using homogeneous catalysts. The homogeneous catalyst exhibits high activity, but its inherent drawback is separation from products. Consequently, large quantities of waste waters need to be treated and, moreover, the produced glycerol contains impurities and water (its concentration is usually >20%). This severely limits glycerol application in synthesis of value-added chemicals and hence has a negative impact on the whole process economy. Recently, Axens has developed a heterogeneously-catalyzed process that is claimed to have higher yields of biodiesel and, more importantly, a glycerol purity >98% without need for its separation[27] making it suitable for the production of specialty chemicals. Nevertheless, the homogenous process still predominates.

Biodiesel can be easily blended into crude-oil-derived diesel. In Europe, it is allowed to sell diesel fuel containing up to 5% (v/v) of biodiesel as a conventional diesel[6]. The mixtures containing a higher percentage of biodiesel have to be distributed separately because they do not meet the specifications of diesel engine manufacturers. Due to the stricter CO_2/km emission requirements[28] set for the modern vehicles, the lower oxidation stability of biodiesel (as compared with diesel) becomes a liability. To achieve the CO_2 emission standards, higher injection pressures and, consequently, temperatures are used. Under these conditions, biodiesel is prone to polymerization reactions which form deposits in the injection nozzles and lead ultimately to engine failure[29]. The long-term storage of biodiesel is problematic as well since oxidation and biodegradation (by microorganisms) can take place. The cold-flow properties of biodiesel are acceptable for mild climate regions, but not for the cold climate ones.

The use of vegetable oils for production of biodiesel (fatty acid methyl esters (FAME)) is associated with the socio-economic and technical problems discussed above. Some of them could be tackled by converting triglycerides, in particular those not suitable for food production, to hydrocarbons in the diesel fuel range, so-called green or renewable diesel. This can be achieved

by selectively removing oxygen atoms while keeping the carbon–carbon bonds intact, i.e. by hydrodeoxygenation (HDO).

Apart from the technical problems discussed above, the use of triglycerides is connected with the fundamental questions of the sustainability of their production and of the competition with food production. To address these issues, non-food triglyceride sources such as algae oils, trap greases, waste vegetable oils and animal fats, non-edible oils from marginal lands should be primarily used for production of fuels from triglycerides. Some of these feedstocks are not suitable for conventional biodiesel production (trap greases, animal fats); nevertheless they could be conveniently upgraded to transportation fuels by deoxygenation.

Lessons from Hydrodesulfurization (HDS)

Hydrodesulfurization (HDS) is a mature and wide-spread process and the reaction itself has been studied in meticulous detail, due to its industrial significance, for several decades[7,15,30–32]. It can thus provide useful insights into the considerably less investigated hydrodeoxygenation (HDO) which is in principle an analogous reaction. In addition, the competition between HDO and HDS during hydroprocessing mixtures containing both organic sulfur and oxygen compounds may be detrimental for common hydrotreatment of crude-oil- and biomass-derived feedstocks.

Hydrotreatment is an indispensable refinery process and the hydrotreatment catalysts are, together with the cracking and three-way exhaust gas catalysts, the most important industrial catalysts[7]. The Mo and W transition metal sulfides promoted with Co and/or Ni metal sulfides have been the active components of hydrotreatment catalysts from the very beginning of the process. They are usually supported on γ-Al_2O_3 doped sometimes with SiO_2, phosphorus and boron[7]. Despite the fact that the active components of the hydrotreatment catalysts have not really changed over the years, they have undergone substantial development and innovations in order to cope with the ever-growing requirements for their performance. The main development drivers have been the need to process sourer and heavier crude oils including new synthetic crude oils produced from tar sands, the increasing demand for transportation fuels and the changing product slate demand, the production of ultralow sulfur transportation fuels (environmental concerns), the innovations in the engine and automotive industry and the efforts to increase the refinery throughput[15].

In order to increase the performance of hydrotreatment catalysts it is essential to understand in detail the hydrotreatment chemistry, particularly

the inhibition effects involved, and the active sites. The inhibition in hydrotreatment originates from the competitive adsorption of possible reactants (S-, N- and O-containing organics and aromatics) and from hydrogen availability at the active sites, i.e. from hydrogen diffusion limitations. It has been observed that trace concentrations of organic nitrogen compounds (<30 ppm) deteriorate the HDS activity by strong adsorption on active sites and their inhibition[31,33–38]. While there is an agreement on the inhibition by N-containing species, the inhibition by aromatics has been a matter of disputes[33,39–41]. Recently, Choudhary et al.[39] have reported that in hydrotreatment of heavy oils the extent of sulfur removal is determined by the content of aromatics having three or more rings and not by the nature and content of sulfur species. The inhibition effect of aromatics seems to depend on their adsorption strength as compared with that of sulfur species. Due to the strong adsorption of the aromatics containing three and more rings, they inhibit the HDS reactions[39,40] while the effect of aromatics having one or two rings on HDS is negligible[33,40]. Using model feedstocks, Egorova et al.[37] have observed inhibition of HDS by naphthalene, but not by toluene. Hence, HDS of heavy oils is more demanding than HDS of naphtha and middle distillates due to higher concentrations of polyaromatic hydrocarbons in heavy oils. However, only little is known about the effects of oxygenates on HDS and of S- and N-species and aromatics on HDO. Organic nitrogen compounds, in particular the basic ones, and H_2S cause strong to moderate inhibition of HDO[31]. It has been reported that the efficiency of a typical HDS process can be expected to decrease when S- and O-containing compounds are present simultaneously[42].

The importance of the inhibition effects has grown significantly with the advent of ultralow sulfur fuels in the recent years, as even the most refractory S-containing species (e.g. dimethyldibenzothiophenes) have to be eliminated to achieve <10 ppm S in the final product. Any loss of HDS activity is thus detrimental. As a result, much attention has been focused on revealing the reaction pathways of HDS[31,32,43–48]. Out of a great variety of organic S-containing species, benzothiophenes and dibenzothiophenes (DBT) are the most difficult to desulfurize. Generally, it is agreed that their desulfurization follows two parallel reaction pathways: hydrogenolysis (direct elimination of S) and hydrogenation followed by extraction of sulfur in the form of hydrogen sulfide[32,46,47] (Fig. 3). In desulfurization of DBT, the direct elimination of sulfur by hydrogenolysis is preferred[32]. The rate of direct sulfur elimination, however, decreases significantly, when alkyl- or dialkylbenzothiophenes (in particular those substituted at the carbon atoms adjacent to the sulfur atom) have to be desulfurized, whereas the

hydrogenation pathway is practically unaffected[32,46]. Consequently, CoMoS/Al$_2$O$_3$ is outperformed in HDS of 4,6-dimethyldibenzothiophene (DMDBT) by NiMoS/Al$_2$O$_3$, which is a superior hydrogenation and HDN catalyst as compared with CoMoS/Al$_2$O$_3$ (ref.[46]). However, the sulfur removal via the hydrogenation pathway is accompanied by a significant increase in hydrogen consumption due to aromatics hydrogenation and, thus, the isomerization of DMDBT to facilitate the direct HDS (hydrogenolysis) to save hydrogen has been proposed and investigated[43,44,48–50] (Fig. 3).

The fundamental knowledge of the desulfurization reaction pathways, their inhibition mechanisms and the active sites involved is therefore of paramount importance for the selection of the most efficient catalyst and of the optimum operating conditions. As biomass-derived raw materials (oxygenated feedstocks) are close to being introduced into refinery streams for hydroprocessing, deoxygenation (hydrodeoxygenation) has to be taken into account. Particularly, the plausible inhibition effects have to be studied in detail together with HDS, HDN and hydrogenation reactions to optimize the performance of the current hydrotreatment catalysts with respect to the new, oxygen-containing, refinery feedstocks.

Removing Oxygen – Hydrodeoxygenation (HDO) and Hydrodecarboxylation (HDC)

A wide variety of raw materials suitable for the production of fuels can be derived from biomass – synthesis gas or hydrogen (by gasification), ethanol
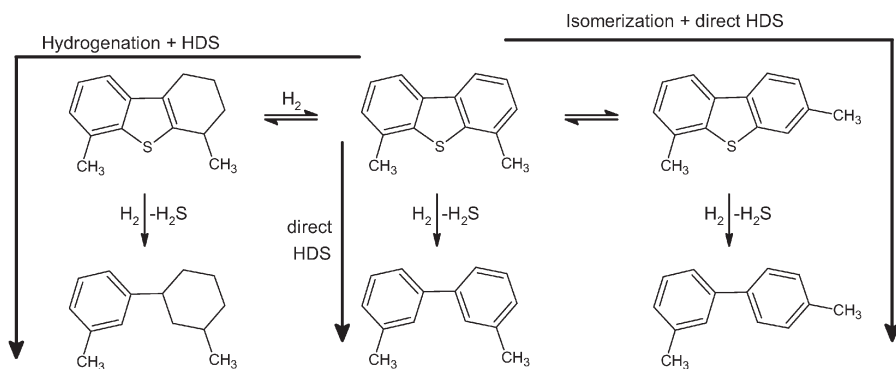

FIG. 3
A general scheme of 4,6-dimethyldibenzothiophene hydrodesulfurization[43–45]

or butanol (by fermentation), sugars (by hydrolysis), bio-oil (by pyrolysis) and triglycerides (by extraction and/or pressing). The production and use of alcohols and sugars for fuels fall outside the scope of this paper and will not be discussed here; the use of synthesis gas will be discussed in a separate chapter. This chapter will be devoted to deoxygenation of biomass-derived liquid feedstocks, i.e. to elimination of oxygen from vegetable oils and bio-oils.

Vegetable oils (i.e. triglycerides of fatty acids) obtained from suitable plants are currently used as food and raw material for biodiesel production (see above). In contrast to biodiesel production, low quality oils (e.g. used frying oils), yellow and trap greases, tallow and lard, i.e. resources that can not be used for food production, can be used as a starting material for production of fuels by deoxygenation as well. Typical oxygen content is about 10 wt.%.

Bio-oils, on the other hand, are manufactured from non-food biomass (wood, straw, etc.) by pyrolysis (usually without a catalyst) in the absence of oxygen or by high pressure liquefaction. Although the high pressure liquefaction yields better-quality bio-oil product (lower content of moisture and oxygen, Table I), the lower yield of bio-oil and higher price, in comparison with pyrolysis, favor the biomass pyrolysis processes for industrial

TABLE I
Elemental composition (in wt.%), moisture content (in wt.%) and properties of biomass- and crude-oil-derived feedstocks[2,59]

Composition, %	Heavy fuel oil	Vegetable oil[a]	Bio-oil	
			pyrolysed[b]	liquefied
Carbon	85.2	77.5	45.3	74.8
Hydrogen	12.8	11.6	7.5	8.0
Sulfur	1.8	<0.1	<0.1	<0.1
Nitrogen	0.1	<0.1	<0.1	<0.1
Oxygen	0.1	10.9	46.9	16.6
Moisture	<0.1	<0.1	44.8	5.1
HHV[c], MJ/kg	41.2	39.7	22.6	35.7
Viscosity, cP	12 (40 °C)	38 (40 °C)	59 (40 °C)	15000 (61 °C)

[a] Rape-seed oil. [b] Flash pyrolysis of wood. [c] Higher heating value.

application[51]. The highest yields of bio-oil (up to 70% on dry basis) are obtained by flash pyrolysis which is typically carried out at 500 °C, at very high heating rates and short contact times (typically <1 s)[52,53]. The main benefits of bio-oil in comparison with raw biomass are high energy density and easy transportability[53]. Consequently, pyrolysis processes are studied intensively[52–58] and several demonstration units using different concepts of pyrolysis (fluid bed, rotating cone, twin screw) have been constructed[54].

The composition of both discussed feedstocks differs enormously and will undoubtedly affect the mechanism of their deoxygenation. Whereas bio-oils are formed by very complex mixtures of oxygenates (phenols, ketones, aldehydes, carboxylic acids, esters, alcohols and ethers)[59], vegetable oils are formed almost exclusively by triglycerides of fatty acids, i.e. esters, accompanied in some cases by free fatty acids. Moreover, the high content of moisture in bio-oil, its immiscibility with crude-oil fractions and chemical instability pose a further challenge to their processing. Therefore, both the direct conversion to fuels by deoxygenation and gasification (steam reforming) to synthesis gas has been proposed for bio-oil upgrading[2,54,57,58,60,61]. On the other hand, direct deoxygenation of vegetable oils to fuels is the preferred upgrading technology in addition to their transesterification yielding biodiesel (see above).

Mechanistic Aspects of HDO

Deoxygenation of biomass-derived feedstocks can be achieved by several reactions – hydrodeoxygenation, decarboxylation, decarbonylation and dehydration[59]. Various combinations of these reactions can take place, depending on the feedstock composition, catalyst choice and reaction conditions. The most common and universal is hydrodeoxygenation (HDO), in which oxygen-containing materials are reduced with hydrogen, and hydrocarbons and water are formed. Decarboxylation is restricted only to carboxylic acids and their esters; the formation of hydrocarbons is accompanied by the release of CO_2. In the presence of hydrogen, the alkene resulting from CO_2 elimination is hydrogenated to the corresponding alkane and the reaction is then called hydrodecarboxylation (HDC). Decarbonylation and dehydration are reactions of ketones or aldehydes and alcohols, respectively. In line with the composition of biomass-derived feedstocks, hydrodeoxygenation is the most important deoxygenation reaction.

The catalytic hydrodeoxygenation has been reviewed by Furimsky[59] and the following order of reactivity of O-containing groups has been put forward: alcohols > ketones > alkyl ethers > carboxylic acids ≈ *m*- and

p-alkyl-substituted phenols ≈ naphthol > phenol > diaryl ethers ≈ *o*-alkyl-substituted phenols ≈ alkylfurans > benzofurans > dibenzo-furans[59,62,63]. In view of biomass feedstocks available, the reactivities of phenols, acids and esters are the most relevant. Phenols, which may account for up to 25% of liquids obtained by pyrolysis of lignocellulosic materials[59], are refractory oxygenates. Moreover, HDO of phenols depends on the position and type of other substituents; e.g., the reactivity of methylphenol (MP) decreases in the order *m*-MP > *p*-MP > *o*-MP [59,64]. HDO of phenols and furans (including benzo- and dibenzofurans) follows two parallel reaction pathways – direct (through hydrogenolysis) and indirect which proceeds by hydrogenation of aromatic ring[59,62,65].

On the other hand, carboxylic acids and their esters are more reactive than phenols[66,67]; carboxylic acids are less reactive than their esters[66]. Furthermore, there are two reaction pathways responsible for the conversion of carboxylic acids and their esters to hydrocarbons – hydrogenation of the carboxylic group and decarboxylation[66–69]. The origin of the decarboxylation activity of the sulfidized metal catalysts (NiMo, CoMo) has not been yet satisfactorily explained. It was, however, reported by Weisser and Landa[70] that sulfides of the promoters, i.e. Ni and Co, are more active in decarboxylation than molybdenum sulfide.

HDO is a reaction analogous to the other hydrotreatment reactions, namely hydrodesulfurization (HDS) and hydrodenitrogenation (HDN); the same types of catalysts, i.e. NiMo and CoMo sulfides, have been extensively studied[59,66–69]. HDO, HDS, HDN and hydrogenation of aromatics are competing reactions and this has to be kept in mind when studying real reaction systems. It has been established that the hydrotreatment rate decreases generally in the order HDS > HDO > HDN [59]. Nevertheless, deviations from the established order exist due to the complexities of a given feedstock, choice of catalyst and due to the inhibition of HDS, HDO and HDN by S-, O- and N-containing compounds and aromatics, including self-inhibition, i.e. inhibition by the reactant molecules[59].

Hydrogen sulfide, ammonia and water, i.e. the products of HDS, HDN and HDO, respectively, inhibit HDO of different O-containing compounds. For instance, in HDO of 4-ethylphenol the inhibition increases in the order H_2O << 2-ethylphenol < H_2S < NH_3 [65]. Ammonia inhibits the conversion of carboxylic esters and methoxy groups, but does not affect conversion of ketones[68]. H_2S, on the other hand, suppresses the conversion of ketones and phenols (by inhibiting their direct hydrogenolysis) and enhances the conversion of carboxylic esters by promoting their decarboxylation[63,67,68,71]. It was suggested[68,72] that the promotional effect is due to an increase in con-

centration of Bronsted acid sites in the sulfide phase caused by H_2S. Moreover, addition of H_2S to a feed containing oxygen compounds does not prevent the sulfidized catalyst deactivation[71,72]. In contrast to H_2S and NH_3, water has only a very weak inhibiting effect on the HDO reactions[68], but it dramatically lowers the overall catalyst activity[73,74]. The loss of the activity was ascribed to partial re-crystallization of the support γ-Al_2O_3 into the hydrated boehmite phase and partial oxidation of the NiS promoter; oxidation of the MoS_2 phase, however, was not observed[74]. Addition of H_2S was reported to compensate the loss of activity caused by water[73].

Apart from the inhibition by hydrotreatment products, heteroatoms-containing compounds can cause inhibition of hydrotreating reactions as well[42]. Interactions between sulfenyl and methoxy groups affecting the HDS and HDO rates have been observed. It has been suggested that the efficiency of a typical HDS process can be expected to decrease as a result of interactions between sulfenyl and methoxy groups[42].

HDO of Real Feeds – Conversion of Vegetable Oils

The experiments using probe compounds are undeniably crucial for revealing the underlying mechanisms of HDO, studying the inhibition effects and developing more active and selective catalysts. Nevertheless, experiments using real feedstocks under real conditions cannot be omitted as they provide invaluable information for process development. Cracking and hydrotreating approaches were suggested for upgrading vegetable oils (or, more generally, triglycerides) to hydrocarbons. Zeolites, mesoporous materials and composite materials have been studied extensively in the conversion of vegetable oils or fatty acids to hydrocarbon fuels[75–79]. Main products of catalytic cracking of vegetable oils are hydrocarbon gases and gasoline fraction; however, the yield of the most desired fuel fraction, i.e. diesel, is low[75–79]. Moreover, the liquid products contain rather high concentrations of aromatics[75–79] which are in conflict with the newest fuel specifications. Addition of vegetable oil to fluid-catalytic-cracking (FCC) feedstock led to an increased formation of coke[80]. Nonetheless, co-processing of vegetable oils with vacuum gas oil (VGO) has been proposed for production of gasoline and olefins[81–83] and has been planned for commercial demonstration[84].

The hydrogenation processes (hydrocracking, hydrotreatment), on the other hand, facilitate direct conversion of vegetable oils to hydrocarbons in the diesel fuel boiling range and seem thus to be more promising technologies even though they consume hydrogen[83–95]. Apart from academic re-

search activities, hydrodeoxygenation of triglycerides attracts attention of the industrial research as well[83,89–95]. The Finnish company Neste Oil has developed and commercialized a process, called NexBTL [89–91], for diesel production from vegetable oils and greases and other oil companies are developing their own solutions as well[92–95]. Diesel fuel obtained by HDO of vegetable oils (green diesel) is fully compatible with crude-oil based diesel. As it contains no aromatics and sulfur, it is even superior from the environmental point of view. The poor cold-flow properties of the primary HDO product have been solved by its mild isomerization[91]. Moreover, it has been demonstrated that NexBTL diesel, i.e. product of HDO of triglycerides, shows environmental benefits (in terms of emissions and energy consumption) over both conventional diesel and biodiesel (FAME)[96,97].

The experimental results of hydrotreatment (hydrodeoxygenation) of rapeseed oil over sulfidized catalysts are in a good agreement with the results of HDO of relevant simpler probe compounds[66–69]; two main reaction pathways – direct hydrodeoxygenation (total hydrogenation, HDO) and decarboxylation (hydrodecarboxylation, HDC) – have been identified[87,88]. The extent of both reactions, at a complete conversion of rapeseed oil, is sensitive to the reaction temperature, pressure and choice of the catalyst. With increasing reaction temperature the yield of the HDC products rises at the expense of the HDO products[87,88]. On the other hand, augmenting hydrogen partial pressure results in the enhanced formation of HDO products[87,88] (Fig. 4). The extent of HDO and HDC reactions can be quite easily determined at complete conversion by using the concentration of hydrocarbons with an even and odd number of carbon atoms, respectively (see Fig. 4).

A simplified reaction network is depicted for triolein, a representative abundant triglyceride in vegetable oils, in Fig. 5. The initial reaction is the hydrogenation of double bonds which proceeds at milder conditions (<250 °C) than those needed for deoxygenation. Depending on the reaction conditions and catalyst choice, the saturated triglyceride undergoes direct hydrodecarboxylation or direct hydrodeoxygenation. Apart from propane, the main products are straight-chain alkanes with an even number of carbon atoms (n-octadecane for triolein) and water in the case of hydrodeoxygenation (HDO) and n-alkanes with an odd number of carbon atoms (n-heptadecane for triolein) and CO_2 in the case of hydrodecarboxylation (HDC). Alternatively, the triglycerides are hydrogenolyzed to the corresponding fatty acids (stearic acid for triolein) which can undergo either HDO or HDC or be hydrogenated to yield the corresponding fatty alcohols. As alcohols are deoxygenated more easily than acids and esters[59], they are

seldom found among the reaction products. However, fatty alcohol esters of fatty acids have been identified in the products as a result of esterification reactions[98]. The formation of alkyl esters of fatty acids under the hydrotreatment conditions has been reported by Landa et al.[99]. Besides
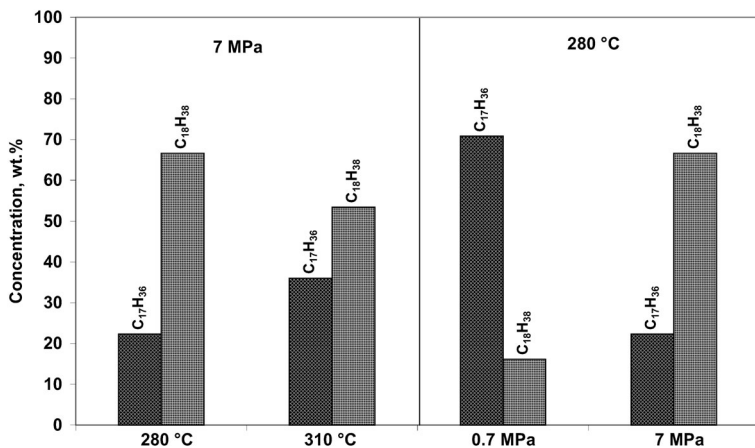

FIG. 4
Effect of temperature and pressure on the distribution of hydrodeoxygenation ($C_{18}H_{38}$) and hydrodecarboxylation ($C_{17}H_{36}$) products
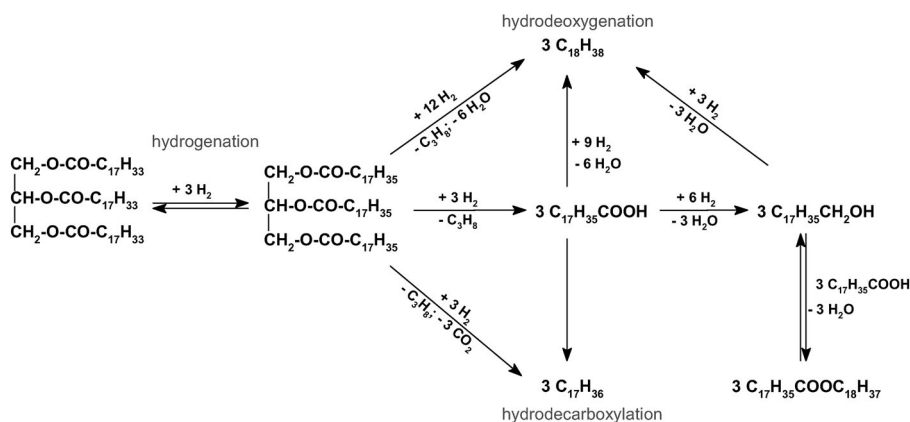

FIG. 5
Scheme of deoxygenation of triolein (the most abundant triglyceride in rapeseed oil)

HDO and HDC, decarbonylation has been proposed to take place as well[85,100]. Nevertheless, there is not enough conclusive evidence for the decarbonylation pathway as CO can originate from partial hydrogenation of CO_2.

The proportion of HDO and HDC at the total conversion of triglycerides to hydrocarbons is decisive for the overall hydrogen consumption of the process. Based on the stoichiometry of both reaction pathways, it is clear that in an ideal case the hydrogen consumption is four times higher for HDO than for HDC of a saturated triglyceride (Fig. 5). However, when sulfidized hydrotreatment catalysts are used, carbon dioxide is partially converted to CO and methane[88,98]; the extent of these reactions depends once again on the catalyst and reaction conditions. Nevertheless, if all CO_2 was converted to methane, the consumption of hydrogen for HDC would be higher than that for HDO. Therefore, selective decarboxylation catalysts having negligible selectivity for the total hydrogenation of CO_2 are sought[101,102].

Hydrotreatment of triglycerides for production of hydrocarbons on an industrial scale can be implemented either by HDO of triglycerides in stand-alone units or by coprocessing of triglyceride feedstocks with crude-oil-derived fractions, e.g. atmospheric gas oil (AGO). Coprocessing offers the advantage of low implementation costs due to the possibility of using the existing hydrotreatment equipment[95]. However, several potential risks have been identified and it has been concluded that processing of vegetable oils in dedicated units was more cost-efficient. The drawbacks of coprocessing include (i) the potential need for a pretreatment reactor to remove contaminants, such as phosphorus and alkali metals; (ii) revamp of the recycle gas systems to deal with the deoxygenation products (CO_2, CO, H_2O); (iii) need for an increase in the quenching capacity as HDO is highly exothermic and (iv) the expected competition of HDO reactions with HDS leading to lower desulfurization efficiency[95]. The suggested negative impact of HDO on HDS reactions[42] has been recently confirmed in coprocessing of AGO with used frying oil (UFO). HDS of a mixture consisting of 90% AGO and 10% UFO required an increase of 4 °C in the HDS temperature as compared with pure AGO in order to obtain 10 ppm S in the final product[103] (Fig. 6).

Conversion of Bio-Oils into Fuels

The upgrading of bio-oils into transportation fuels by deoxygenation is not as advanced as production of fuels from vegetable oils. The main obstacles of bio-oil upgrading are its high moisture content (up to 30%, Table I) and

chemical instability. Moreover, the oxygen content is substantially higher than that of triglycerides (Table I) and, consequently, the hydrogen consumption could be prohibitively high. The quality of bio-oil varies significantly depending on the raw material used for pyrolysis and on the severity of reaction conditions and, therefore, the deoxygenation process is more difficult to optimize as compared with triglycerides deoxygenation. Bio-oils can be used for production of fuels either directly by using hydrotreatment[52,53,104] or zeolite upgrading[52,53,77,105–107], or indirectly by converting it first to synthesis gas and subsequently to fuels[2,58] (see next chapter). Hydrotreatment and upgrading of bio-oil over zeolites have been studied intensively using suitable probe compounds to reveal the underlying chemical mechanisms and to identify suitable catalysts[59,65–69,71–74]. Studies using bio-oil as feedstock are less common[52,53,77,104–107].

Hydrotreatment of bio-oils (hydrodeoxygenation) can be performed using conventional hydrotreatment catalysts, i.e. supported sulfidized metals, giving a naphtha-like product[52,53]. Due to chemical instability of the bio-oil it is necessary to treat it in a two-stage process. In the first step, bio-oil is stabilized under mild reaction conditions (250–275 °C) by hydrogenation of the most reactive double bonds to prevent its polymerization and fouling of the catalyst under typical hydrotreatment conditions. Only in the second step, the standard hydrotreatment temperatures (350–400 °C) can
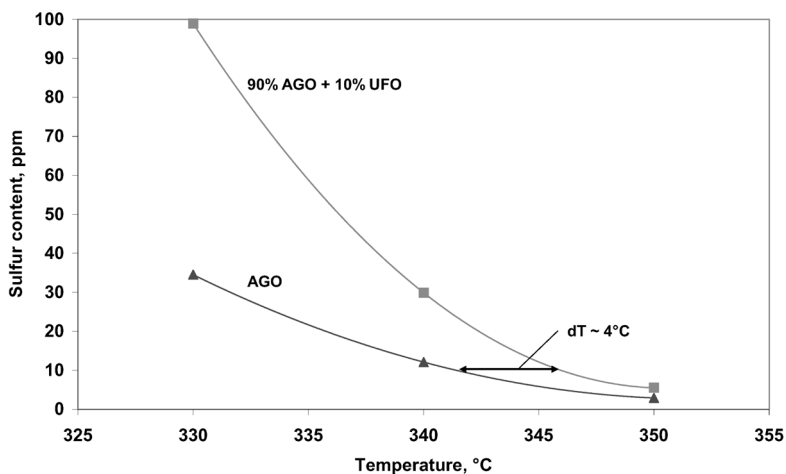

Fig. 6

The effect of addition of used frying oil (UFO) to atmospheric gas oil (AGO) on its hydrodesulfurization[103]

be used to deoxygenate bio-oil[52,53]. The hydrotreatment pressures may vary in a wide range (7–20 MPa)[52,53] depending on the composition of bio-oil on the one hand, and on the desired level of deoxygenation on the other. Oxygenated compounds are generally more resistant to hydrotreatment than sulfur-containing compounds[59] and require thus more severe reaction conditions[52] and optimization of the catalyst as well as optimization of the process conditions for a particular bio-oil feedstock[52]. Some applications of bio-oil do not necessitate full deoxygenation, e.g. fuels for stationary engines, and only partial hydrotreatment has been suggested for them[52]. This approach has the benefit of lower hydrogen consumption which is fairly high for complete hydrodeoxygenation (600–1000 $l_{H2}/kg_{bio-oil}$)[52] and is, therefore, the major inhibiting factor of its commercialization. The progress in hydroprocessing of bio-oils over the past 25 years has been recently reviewed by Elliot[104].

Upgrading of bio-oils over zeolites is a promising alternative to hydrotreatment, as this can be achieved at low-pressures (even atmospheric) and at temperatures similar to those used for bio-oil production. Thus it offers the advantage of combining the pyrolysis of biomass to produce bio-oil with its subsequent catalytic upgrading[52]. Oxygen is eliminated in the form of water (by dehydration) or in the form of carbon oxides (by decarboxylation or decarbonylation). As external hydrogen is not supplied, hydrogen necessary for partial hydrogenation (saturation, stabilization) of the unsaturated reaction intermediates originates from the hydrogen transfer reactions. Consequently, the product is highly aromatic and large amounts of hydrogen-deficient products, such as coke, tar and char, are formed[77]. The mechanism, however, is not yet fully understood. Due to the recent developments in transportation fuel specifications, the aromatics content has to be decreased and therefore it will become increasingly more difficult to use the highly aromatic product from bio-oil upgrading for blending of automotive fuels. Nonetheless, it could be utilized in the petrochemical sector as a raw material for production of aromatics and derived polymers.

Bio-oil is well-suited for production of specialty chemicals thanks to its complex chemical composition. In this case, the presence of oxygenated compounds becomes an advantage as they may be used directly in synthesis and, therefore, deoxygenation is not desired. The production of chemicals from biomass feedstocks, however, is out of the scope of traditional refineries and will not be, thus, discussed in this paper. The topic has been recently reviewed by several research groups[24,108,109].

BIOMASS TO GAS – A ROUTE TO TAILOR-MADE PRODUCTS

Biomass gasification is a universal tool for conversion of biomass to fuels and chemicals. While hydrodeoxygenation is limited to a special type of liquid feedstocks, such as vegetable oils (triglycerides) or bio-oils, gasification can be used basically for any biomass feedstock. This provides gasification with the inherent advantage of cheaper and more abundant raw materials as compared with HDO.

Gasification can be defined as partial combustion using air or oxygen to produce fuel gas or synthesis gas. Steam is often added to the feed to increase the heating value of the final product gas[52]. Its composition depends on the reaction temperature. Low-temperature gasification (800–1000 °C) yields, in the case of oxygen gasification, the so-called product gas consisting of CO, CO_2, H_2, H_2O, CH_4, hydrocarbons and tars, which is suitable mainly for direct power and heat generation[110]. On the other hand, the product of high-temperature gasification (1200–1400 °C) consists of CO and H_2 (so called biosyngas)[110]. In air gasification, nitrogen is present in addition to the above-mentioned compounds. Biosyngas can be alternatively obtained by catalytic gasification or by removing tar and hydrocarbons from the product gas by thermal cracking or reforming; it is chemically similar to syngas derived from fossil fuel sources[52,110]. When fuels and chemicals are desired, the product gas has to be processed to contain only CO and H_2 in a suitable molar ratio (the usage ratio); for some applications CO_2 may be present as well.

Gasification Challenges

The high diversity of biomass composition makes the production of fuels and chemicals a complex and demanding task as the final products need to have rather well-defined and uniform composition. Gasification enables to convert practically any carbon- and hydrogen-containing feedstock into synthesis gas with a desired usage ratio for a particular application. Nevertheless, the biomass feedstock diversity makes the production of synthesis gas more complex and sophisticated as compared with gasification of fossil fuels (mainly methane and coal)[111]. The main challenge lies in the scattered occurrence of biomass and its low volume energy density in comparison with fossil fuels (e.g. straw bales and diesel fuel have about 2 and 36 GJ/m³, respectively)[111]. Therefore, collection of biomass from large areas and its transportation over long distances that affects negatively the total costs and energy inputs is necessary. Moreover, gasification, particularly purification

and conditioning of synthesis gas, and conversion technologies of syngas are technically demanding and require intensive investment and, hence, large-scale units are preferred. Regional fast pyrolysis of biomass to obtain pyrolysis oil and char has been proposed[111]. The char is then suspended in the pyrolysis oil and the resulting slurry holds up to 90% of the original biomass energy content[111]. More importantly, the volume energy density increases from about 2 to ca. 25 GJ/m^3 and the intermediate can be thus transported over larger distances to central gasification units.

From the view point of crude-oil refinery, the slurry could become one of the raw materials for manufacturing biofuels. Conceptually, the slurry could be either coprocessed by gasification or partial oxidation together with liquid hydrocarbon feedstocks or the synthesis gas could be produced in a separate gasification reactor and then purified and conditioned together with the fossil-based syngas. The use of the existing gas purification and conditioning equipment would decrease the investment intensity of biomass-to-syngas units and biosyngas would get access to downstream conversion processes at the same time. The integration of bio-oil slurry or biosyngas into refineries is an opportunity that needs to be further studied.

Synthesis gas resulting from biomass gasification has typically the C/H ratio equal to about unity[111] and cannot be directly used for synthesis of hydrocarbons as a C/H ratio of less than 0.25 is needed. The concentration of hydrogen can be increased either by addition of hydrogen-rich gas or by partial conversion of CO by water-gas-shift reaction (WGS). Once again, if integrated into a refinery, the existing WGS capacities and excesses of refinery hydrogen could be used. Alternatively, direct removal of CO_2 during gasification resulting in an increased hydrogen concentration in the synthesis gas has been proposed[112]. It relies on addition of a heat carrier capable of forming carbonates, which are then decomposed in a regeneration unit and CO_2 is released during burning off the deposited tar[112].

From the viewpoint of production of fuels, synthesis gas with an adjusted usage ratio (UR) can be converted to fuels either directly by Fischer–Tropsch synthesis (FTS, UR = 2.05–2.15) or methanation (UR = 3) or indirectly via methanol synthesis (UR = 2) and its subsequent conversion into hydrocarbons or dimethyl ether (DME)[113]. In addition to fuels, a broad spectrum of chemicals can be obtained from syngas. The main conversion pathways of syngas[113] are depicted in Fig. 7. The thermal efficiency of liquid fuels production from methane (via syngas) is the highest for methanol, followed by FTS diesel and gasoline from the methanol-to-gasoline (MTG) process[114]. The liquid fuels offer several advantages over methanol, such as high

energy density, low vapor pressure, insolubility in water, and compatibility with existing engines and fuel infrastructure[114].

Fischer–Tropsch Synthesis

The importance of Fischer–Tropsch synthesis (FTS) will grow in the years to come, as crude-oil reserves will be depleted and alternative feedstocks for the production of fuels and base chemicals will be used. The traditional synthesis gas sources, natural gas and coal, will be accompanied by biomass as a result of public awareness of the adverse environmental effects of CO_2 emissions. FTS has been developed with varying intensity over the past 80 years. As FTS competes with crude oil for the fuel market, its economic viability depends on the price of crude oil[115]. The FTS technology has been industrially proven in coal-based FTS plants in Germany in 1930's and currently both coal-based (Sasol, South Africa) and methane-based FTS plants (Mossgas, South Africa; Bintuli, Malaysia) are operated[114,115].

FTS can be operated in high-temperature (HTFTS) and low-temperature (LTFTS) mode. The HTFTS uses iron-based catalysts at temperatures 300–350 °C and yields low-molecular-weight olefins and gasoline[114,115]. The
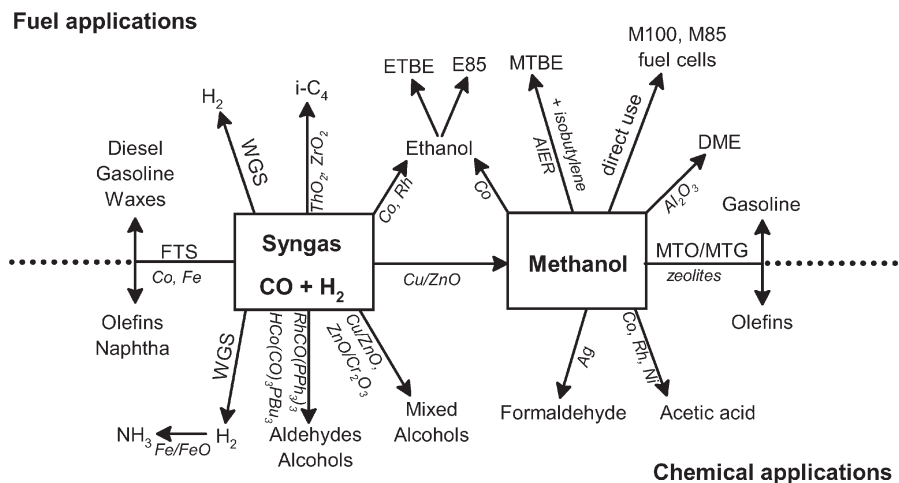

FIG. 7

Synthesis options from synthesis gas[113]. FTS, Fischer–Tropsch synthesis; WGS, water-gas shift; AIER, acid ion-exchange resins; MTO/G, methanol-to-olefins/gasoline; DME, dimethyl ether; E/MTBE, ethyl/methyl *tert*-butyl ether; E85/M100, the fuel containing 85% ethanol/ 100% methanol

LTFTS is operated at temperatures 200–240 °C to produce high-molecular-weight linear waxes and either cobalt- or iron-based catalysts are employed[114,115]. In both operating modes, it is crucial to ensure high heat-exchange rates as FTS reactions are highly exothermic (ΔH = –165 kJ/mol). These are achieved by a suitable reactor setup – fluidized-bed reactors are used in HTFTS and slurry-bed reactors or multitubular fixed-bed reactors and high gas velocities are used in LTFTS [114,115].

Just four metals – Co, Fe, Ni, Ru – have been found to be active FTS catalysts. However, nickel and ruthenium are disqualified from the industrial use, Ni due to its high selectivity for methane and Ru because of its very high price and limited availability[115]. Iron-based catalysts without support can be used both in LTFTS and HTFTS. Catalysts for LTFTS are prepared by precipitation and for HTFTS by fusing magnetite; their main promoter is K_2O [114,115]. On the other hand, cobalt-based catalysts are used only in LTFTS as they have too high selectivity for methane at high temperatures. Since Co is significantly more expensive than Fe, it is used on high surface-area supports, such as Al_2O_3, SiO_2 or TiO_2, with a loading 10–30% (ref.[115]). To improve the reducibility of dispersed Co crystallites, the cobalt-based catalysts are promoted with small quantities noble metals such as Pt, Re or Ru [115].

As a result of the different reaction conditions and catalytic systems employed, products from LTFTS differ from those obtained in HTFTS. HTFTS products contain several per cent of oxygenates and are rich in olefins, particularly α-olefins[114], being suitable for production of chemicals rather than fuels. Moreover, due to the lower chain growth probability (see below) at high temperatures, the product distribution is shifted towards light hydrocarbons[114]. On the other hand, an LTFTS product consists mainly of linear paraffins with smaller amounts of olefins and oxygenates[114]. The product distribution is shifted towards middle distillates and waxes (i.e. high-molecular-weight paraffins) as a result of a higher chain growth probability.

An inherent advantage of FTS is that the products are virtually sulfur-free and aromatics-free. The FTS follows a polymerization-type kinetics resulting in a statistical distribution of hydrocarbons determined by Anderson–Schulz–Flory distribution (ASF). The key parameter of ASF is the chain growth probability α; by changing α the product distribution can be manipulated (Fig. 8). However, with the exception of the two extremes (when α = 0 only methane is formed, when α = 1 an infinite paraffin chain is formed) the product will consist always of a wide range of hydrocarbons. For wax production by FTS α has a value of about 0.9, this means that the

C-atom selectivity for C_{10+} products is about 74% [116]. It has been calculated and experimentally verified that the maximum attainable gasoline and diesel yields are about 42 and 20%, respectively[114]. The achievable product distribution, hence, differs significantly from the demanded product slate as the yield of the desired fuel products (gasoline and diesel) cannot exceed 60%. Moreover, the yield of gasoline is higher than that of diesel, which is in contrast with the current as well as the expected fuel demands[16].

Apart from the unsuitable product slate, the properties of FTS gasoline and diesel do not meet the respective fuel specifications and need to be further upgraded. As the FTS products are n-alkanes and n-alkenes, they have a high cetane number and are well-suited for diesel fuel blending except for their poor cold-flow properties. Conversely, high concentrations of straight-chain paraffins make the FTS products unsuitable for direct gasoline blending due to their low octane number. The mismatch between the demands for automotive fuels (both in terms of their yields and properties) and the yields and quality of FTS products initiated recently numerous research efforts in this area[114,117–132]. Generally, two basic concepts have been followed: (1) production of FTS waxes (at $\alpha = 0.95$) as these can be obtained in very high yields and their subsequent conversion into desired products by hydrocracking technologies[114,117–122] and (2) use of acid supports or acid co-catalysts (e.g. zeolites) for partial cracking and isomerization of longer paraffins to enhance the yield of gasoline fraction[114,123–132].
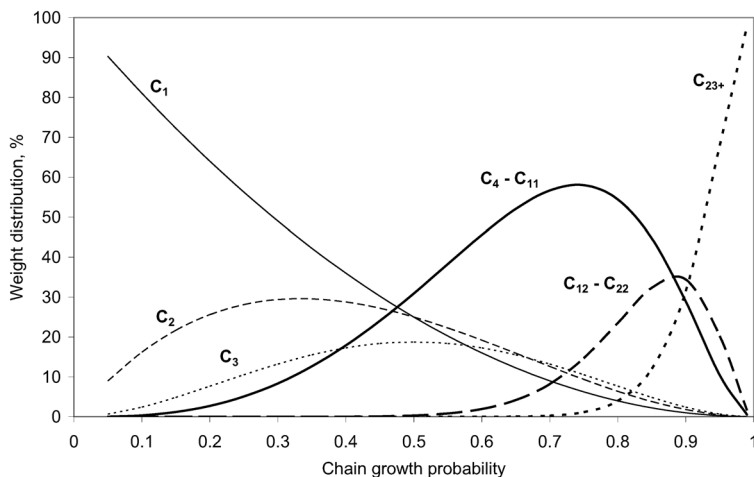

FIG. 8
ASF distribution in FTS

Mild hydrocracking and hydrotreating processes have been applied to convert FTS products in the diesel fuel and wax range into high quality diesel fuel[114,117–122]. The main objectives of the upgrading, apart from increasing diesel yield, are saturation of olefins, removal oxygenates and partial isomerization of n-alkanes into isoalkanes. Traditional refinery hydrotreatment and hydrocracking catalysts can be used[114,118]. Alternatively, modified catalysts containing noble metals (Pt) have been used[119]. Oxygenates, i.e. alcohols and carboxylic acids, have been shown to influence the hydrocracking selectivity for diesel and hydrocracking conversion[120]. It has been proposed that oxygenates present in the feed affected the balance of acid- and metal-active sites in hydrocracking catalysts, thereby modifying the catalyst selectivity[120]. As FTS products are virtually sulfur-free, noble metal catalysts could replace the traditional sulfides (e.g. NiMo, CoMo) for hydrogenation; however, in the case of significant concentration of oxygenates (in particular from HTFTS), the hydrotreatment (hydrodeoxygenation) activity of NiMo or CoMo catalysts is a benefit (see above – HDO section).

Due to the limited number of FTS installations, FTS products are usually processed on-site to final products which are then blended with crude-oil-based products. In the future, however, a tighter bond between crude-oil refineries and FTS units can be expected. Consequently, the straight-run FTS products will be upgraded in crude-oil refineries together with crude-oil streams. Therefore, optimization of refinery processes including the catalysts employed will be crucial to obtain the desired product slate. The key aspects will be the introduction of long-chain paraffins (waxes) and their selective conversion into diesel fuel by hydrocracking and isomerization. Moreover, oxygenates will have to be deoxygenated and their inhibition effects on hydrogenation and hydrodesulfurization will have to be dealt with as well (see chapter on HDO).

Production of gasoline from FTS requires a more severe upgrading than FTS diesel production[114]. Due to the paraffinic nature and absence of aromatics the straight-run FTS naphtha is an excellent steam cracker feed (for production of ethene and propene) and its transformation into gasoline (fuel) calls for catalytic reforming or aromatization and isomerization to achieve sufficient octane number values. Zeolites and mesoporous materials have been investigated either as co-catalysts (in hybrid catalysts)[126,127,131] or as support materials[123,124] to obtain higher yields and higher degrees of branching of the FTS products in the gasoline boiling range. In the case of hybrid catalysts, two-stage catalyst beds are used –

a conventional FTS catalyst, e.g. Co/SiO_2, is placed in the upper bed and a zeolite catalyst is placed in the lower bed where it can crack the high-molecular-weight FTS products. The two-bed concept makes it possible to use, at the same time, the optimum reaction temperature for the FTS catalyst and for the zeolite catalyst since they are in separate beds[131]. H-zeolites of various topologies (USY, Beta, Mordenite, ZSM-5) have been found to increase the yield of gasoline range products, the highest gasoline selectivity has been observed for ZSM-5, followed by H-Mordenite and H-Beta[126]. Similarly, an increase in selectivity for gasoline-range products together with an increase in the isoalkane/n-alkane ratio has been achieved by using Pt- or Pd-Beta catalysts in the second catalyst bed[127]. The investigations of various combinations of the composition of the first and the second catalysts have indicated that the product selectivity in FTS, particularly concerning the yield of gasoline and its degree of branching, can be adjusted[131]. It has been shown that zeolites can improve the quality of gasoline-range FTS products. However, important issues such as the detrimental effect of water formed during FTS and hydrocarbon deposits on the activity and selectivity of zeolite catalysts have to be yet solved.

CONCLUSIONS AND OUTLOOK

The crude-oil refineries will remain the unrivaled producer of automotive fuels in the years to come. Nevertheless, they will face changes in the feedstock supply. The gradually deteriorating quality of crude oil (higher density and S content) will be newly accompanied by introduction of synthetic crudes (from tar sands upgrading), biomass feedstocks (such as triglycerides and bio-oils) and FTS-derived products (based on gasification of biomass, methane and coal) into the refinery feedstock portfolio. The environmental and health concerns together with public awareness will dictate deeper upgrading of fuels (lower S and aromatics contents) and higher share of renewable resources. Consequently, the refinery upgrading processes will have to be further developed to keep up with the new challenges.

The new biomass-derived feedstocks will bring oxygen-containing compounds into refineries. Due to the interference of deoxygenation reactions and their products with other hydrotreatment reactions (mainly HDS), hydrotreatment catalysts will be further developed to cope both with increasing heteroatom levels in the feeds and, at the same time, with the ever-lower levels of heteroatoms required in the products. Moreover, advanced support materials will be sought to (1) enable better dispersion and thus more efficient use of active components, (2) resist new refining by-

products, such as water and CO_2 and (3) accommodate feeds with larger molecules, such as triglycerides and waxes.

The current refining catalysts will undergo changes to satisfy the need for higher isomerization and mild cracking activity which will be required for upgrading of FTS waxes into the demanded fuel product slate. Particularly, the production of high-quality gasoline will be difficult in comparison with the production of diesel fuel and feedstocks for steam cracking to produce light olefins. Moreover, improvements in conventional FTS catalysts can be expected to be accompanied by efforts aimed at development of modified catalyst systems, such as hybrid catalysts, to achieve deviations from ASF distribution and, thus, to increase the yields of gasoline- and diesel-range products at the expense of FTS waxes.

LIST OF ABBREVIATIONS USED

AIER	acid ion-exchange resin
AGO	atmospheric gas oil
ASF	Anderson–Schulz–Flory
DME	dimethyl ether
ETBE	ethyl *tert*-butyl ether
FAME	fatty acid methyl esters
FCC	fluid catalytic cracking
FTS	Fischer–Tropsch synthesis
HDC	hydrodecarboxylation
HDN	hydrodenitrogenation
HDO	hydrodeoxygenation
HDS	hydrodesulfurization
HHV	higher heating value
HTFTS	high-temperature Fischer–Tropsch synthesis
LTFTS	low-temperature Fischer–Tropsch synthesis
MP	methylphenol
MTBE	methyl *tert*-butyl ether
MTG	methanol to gasoline
MTO	methanol to olefins
UFO	used frying oil
UR	usage ratio
VGO	vacuum gas oil
WGS	water-gas shift

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