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Advanced biofuels via catalytic deoxygenation and aldol condensation processes

HABILITAČNÍ PRÁCE

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Prohlašuji, že jsem předloženou habilitační práci vypracoval samostatně.

V Praze, 24. 7. 2020

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Souhrn

Předložená habilitační práce stručně shrnuje nejdůležitější výsledky vědecko-výzkumné činnosti uchazeče v oblasti aplikace heterogenní katalýzy pro zhodnocení biomasy na pokročilá biopaliva. Práce se zaměřuje na hydrogenační rafinaci kyslíkatých surovin a na uplatnění aldolové kondenzace při syntéze pokročilých biopaliv. V první části jsou studovány heterogenní katalyzátory pro aldolovou kondenzaci aldehydů a ketonů s cílem získat kyslíkaté suroviny s molekulovou hmotností vhodnou pro přípravu leteckých paliv a středních destilátů. Druhá část se věnuje hydrogenační rafinaci triglyceridů, pyrolýzních bio-olejů a produktů aldolové kondenzace. Pozornost je zaměřena jak na vliv reakčních podmínek a složení katalyzátorů na jejich deoxygenační aktivitu, tak na popis vlastností deoxygenovaných produktů. Výsledky jsou prezentovány formou komentářů k vybraným odborným publikacím uchazeče.

Klíčová slova

Zhodnocení biomasy; Zelená chemie; Triglyceridy; Bio-olej; Furfural; Deoxygenace; Hydrogenace; Aldolová kondenzace; Sulfidické katalyzátory; Bazické katalyzátory; Nosičové katalyzátory.

Summary

The presented habilitation dissertation briefly summarizes the most important results of scholarly and research activities of the candidate in the field of heterogeneous catalysis applied to valorization of biomass into advanced biofuels. The dissertation is focused on hydrotreatment of oxygenated compounds and on the use of aldol condensation in the synthesis of advanced biofuels. In the first part, heterogeneous catalysts for aldol condensation of aldehydes and ketones are investigated with the aim to obtain oxygenated compounds having molecular weight suitable for the preparation of aviation fuels and middle distillates. The second part is devoted to hydrotreatment of triglycerides, pyrolysis bio-oils and aldol condensation on their catalytic activity as well as to the description of the properties of the deoxygenated products. The results are presented in the form of commentaries of the selected scientific publications of the candidate.

Keywords

Biomass valorization; Green chemistry; Triglycerides; Bio-oil; Furfural; Deoxygenation; Hydrogenation; Aldol condensation; Sulfided catalysts; Basic catalysts; Supported catalysts.

Dedication

"Standing on the shoulders of the giants" is a motto recently adopted by Google Scholar. In my view, this ancient metaphor goes far beyond mere professional endeavors.

This is to my giants:

- to Iva, Šárka and Klárka
- to my parents and grandparents
- to Hacker
- to my colleagues who became my friends, my "sisters and brothers" in science.

Table of contents

Pr	eface.			1						
1	Intr	oduct	tion	1						
2	Ald	Aldol condensation								
	2.1	Basi	c concepts	5						
	2.2	Solic	d acid catalysts	7						
	2.2	.1	Zeolites in aldol condensation	7						
	2.2	.2	Potassium-modified zeolites in aldol condensation	10						
	2.3	Solic	d basic catalysts	13						
	2.3	.1	Mixed oxides in aldol condensation	14						
	2.3	.2	Reconstructed hydrotalcites in aldol condensation	17						
	2.3	.3	Deactivation in aldol condensation over hydrotalcite catalysts	20						
	2.4	Sum	ımary	24						
3	Cat	alytic	deoxygenation	26						
	3.1	Basi	c concepts	26						
	3.2	Deo	xygenation of triglycerides	27						
	3.2	.1	Key reactions	27						
	3.2	.2	Sulphided catalysts	29						
	3	.2.2.1	Active phase composition	30						
	3	.2.2.2	Effect of the support	33						
	3	.2.2.3	Deactivation	38						
	3.2	.3	Current technologies and products	42						
	3	.2.3.1	Commercial technologies	42						
	3	.2.3.2	Fuels and their properties	44						
	3	.2.3.3	Steam cracker feeds	48						
	3.3	Deo	xygenation of other feeds	50						
	3.3	.1	Deoxygenation of bio-oils	50						
	3.3	.2	Deoxygenation of aldol condensation products	52						
	3.4	Sum	ımary	55						
4	Cor	nclusic	ons and outlook	56						
5	List	of pu	blications	58						
6	References									

Preface

The habilitation dissertation is based on previously published research work in the field of catalytic deoxygenation and aldol condensation co-authored by David Kubička. The main findings and conclusions of these articles are compiled and used in the following chapters always with a reference to the original work at the end of a paragraph or a section. The figures and tables originate also from these articles or presentations delivered by the author. The original articles form an appendix that is an integral part of this dissertation.

1 Introduction

The rapid industrialization followed by globalization of both business and leisure activities fueled by fossil resources, at first by coal then by petroleum and natural gas, resulted in a substantial increase in our overall living standards. However, it caused rapid depletion of available resources, environmental pollution and climate changes. To sustain our living standards also for future generations while mitigating the negative environmental impacts of our activities, responsible utilization of resources is called for. At the center of these efforts are two key strategies. The first one is relying on the sustainable use of renewable resources while the other one is based on the application of circular economy principles.

When it comes to refining and petrochemical industry that consume most of our fossil fuel resources, biomass is an indispensable renewable resource since unlike the other renewable resources, such as solar or wind power, it is the only direct source of renewable carbon. Besides biomass, only utilization of carbon dioxide by its capture and utilization (*i.e.* using the circular economy approach) can be considered as a renewable carbon resource. To meet our future demands for refining and petrochemical products, it can be envisaged that only a combination of both strategies will facilitate the transition of our current society to a sustainable one. Such strategy would also help achieving the Sustainable Development Goals (SDGs) put forward by the United Nations [1].

To make the biomass utilization truly sustainable, it is important to focus not only on the resource and its production, but also on its exploitation. The processes used for the transformation of biomass and biomass-derived feedstocks have to abide by the Green chemistry principles [2] to maximize their sustainability. Apart from maximizing the atom economy and minimizing the use of hazardous chemicals, the efficiency of the transformations in terms of both maximum raw material valorization and minimum energy consumption can be further enhanced by using suitable catalysts. Targeted catalyzed conversions are the key to unlocking the immense potential of biomass as the main resource of renewable-carbon-based products.

1

While in the long-term one can expect a truly decarbonized transportation sector, *e.g.* due to a wide-spread use of electromobility, and production of many chemicals and monomers from biomassderived building blocks, *e.g.* so-called platform chemicals [ART-01, 3] in the short- to medium-term we still need carbon-based fuels, particularly in the aviation and heavy-duty transport to satisfy our needs [4]. However, it is crucial to act on the climate changes without any further delays to meet the targets of the Paris agreement on climate change mitigation [5, 6] and to prevent going beyond the point of no return. In this context, development of transition technologies for biomass valorization into advanced biofuels appears to be the only sensible way forward considering the huge contribution of the transport sector towards the world-wide emissions of carbon dioxide [ART-02, 7]. Besides contribution to CO_2 mitigation due to advanced biofuels production, the new technologies development will contribute to obtaining practical experience with biomass upgrading and will facilitate future biomass exploitation also in other areas of chemical industry.



Figure 1 Alternatives of biomass utilization and its integration in existing refining infrastructure.

The complexity of biomass composition offers several alternative upgrading technologies to produce fuels and chemicals that could be directly integrated into the existing value chains by utilizing the existing refining capacities (Figure 1). Among the main challenges is an efficient primary transformation of the solid lignocellulosic biomass into liquid or gaseous intermediates. The most promising strategies include fast pyrolysis yielding bio-oils that could be directly hydrotreated to transportation fuels [8, 9] and gasification of biomass followed by Fischer-Tropsch synthesis affording clean hydrocarbon fuels [10]. For feedstocks with high water content, hydrothermal upgrading of biomass yielding a heavy oil product is considered [11]. These strategies rely on a rather severe thermochemical deconstruction biomass followed subsequent deoxygenation of the intermediates. Whereas pyrolysis and hydrothermal upgrading suffer from low selectivity towards desired liquid products that are, moreover, difficult to upgrade, gasification and the cleaning and conditioning of the

resulting synthesis gas are energy intensive and advantageous currently only as large scale technologies, which is in contradiction with the distributed nature of biomass and its low volumetric density that make its transportation to such large facilities economically unviable [ART-02, ART-03].

These obstacles are reflected not only in the slow development and deployment of the new technologies, but also in the search for more selective alternatives. A prospective selective strategy that is investigated includes fractionation and depolymerization of the lignocellulosic biomass, *e.g.* using the so-called "Lignin-first" strategy [12, 13]. This strategy allows separate upgrading of the sugar and lignin monomers towards platform chemicals or chemical intermediates. These could be then used for design and targeted production of chemicals and/or advanced biofuels.

Biofuels have been put forward as a renewable alternative to fossil fuels to mitigate the greenhouse effect that can be linked to the ever-increasing CO_2 emissions. The continuous increase in the amount of the emitted CO_2 can be related to the global industrial development, in particular to the rapidly growing transportation sector. Biofuels are generally classified into three generations:

- the first generation uses food crops and its main representatives are bioethanol from sugar and starch plants and biodiesel produced from edible vegetable oils;
- the second generation relies on lignocellulosic feedstocks, non-edible oils and waste oils and fats;
- the third generation is produced aquatic biomass (*e.g.*, algae).

The importance of advanced biofuels, *i.e.* the second- and the third-generation biofuels, as outlined in the proposed RED II directive [14], continues to grow rapidly as their use is mandated by the Directive. They are proposed to gradually replace the first-generation biofuels whose contribution to the greenhouse gas reduction targets is only limited and that remain to be controversial as witnessed by the food vs. fuel debate and the related negative effects, such as deforestation in tropical regions.

The shift towards advanced biofuels brings forth new challenges due to the higher complexity of feedstocks and/or their lower quality as a result of the presence of various impurities and contaminants that may act as catalytic poisons. The higher complexity stems primarily from the substitution of easily obtainable sugars and triglycerides by lignocellulosic biomass while the increased presence of contaminants is a consequence not only of lignocellulosic biomass use, but also of replacing vegetable oils by waste fats and oils or tall oils.

Consequently, more complex upgrading strategies are needed than in the case of the firstgeneration biofuels that rely on fermentation of simple sugars to produce bioethanol and transesterification of triglycerides to produce methyl esters of fatty acids, *i.e.* biodiesel. Considering the high oxygen content in lignocellulosic biomass and, hence, the lower energy content in comparison with not only fossil fuels, but also with triglycerides, on the one hand, and the specific requirements on advanced transportation fuels, particularly for applications such as aviation or heavy-duty transport that are currently beyond the reach of electrification, on the other hand, it becomes clear that at least partial deoxygenation of the biomass-derived feeds is essential to obtain the desired advanced biofuels.

Deoxygenation is a robust, versatile technology capable of dealing with a wide variety of feedstocks [ART-04] and it can be expected that besides the already commercialized technologies for conversion of triglycerides and fatty acids to high quality hydrocarbon fuels for kerosene and diesel applications, other technologies for upgrading bio-oils as well as synthesized oxygenates will be commercialized. Nonetheless, the short carbon chain length in the monomers making up lignocellulosic biomass (5 to 9 carbon atoms) prevents their direct deoxygenation to valuable advanced biofuels as they could not be used directly or only in a limited extent to produce kerosene and diesel fuels. Therefore, strategies for prolonging the carbon-chain length in a controlled manner, such as aldol condensation or Sylvan process, are intensively studied.

The following chapters will, thus deal with aldol condensation to valorize sugars- or lignin-derived aldehydes and ketones by transforming them into oxygenates with carbon-chain length in the range of kerosene and/or diesel and with catalytic deoxygenation to convert biomass-derived oxygenates into premium hydrocarbon fuel components.

2 Aldol condensation

2.1 Basic concepts

Aldol condensation is a traditional organic reaction of aldehydes and ketones resulting in formation of carbon-carbon bonds. The prerequisite for the reaction to take place is the presence of hydrogen atoms on the carbon adjacent to the carbonyl group, *i.e.* on the a-carbon relative to the carbon of the carbonyl group. Therefore, acetone can undergo also self-condensation, but furfural cannot. The interest in aldol condensation in biomass platform molecules upgrading to advanced biofuels originates from the structure and size of biomass building units. The nominal length of carbon atom chains in these is 5, 6 and 9 carbon atoms for hemicellulose (*e.g.* xylose), cellulose (glucose) or lignin (*e.g.* coniferyl alcohol), respectively. Hence, direct deoxygenation of these building blocks would yield short chain hydrocarbons suitable only in petrol pool. Moreover, the former two would yield n-alkanes that are not directly suitable for petrol pool due to their low octane number. Consequently, aldol condensation is targeted as it would provide oxygenated products with longer carbon-atom chains that could be transformed into jet and diesel fuel components.

There are two potential sources of short chain aldehydes – pyrolysis and depolymerization followed by dehydration. The pyrolysis is an unselective strategy where biomass is degraded thermally in absence of air to a complex mixture of oxygenates including also aldehydes and ketones. The other strategy can be called selective as it exploits separation of biomass into hemicellulose, cellulose and lignin (by a pulping process) followed by acid hydrolysis of the sugar polymers into sugar monomers [15, ART-02] (*i.e.* xylose, arabinose, mannose, galactose from hemicellulose and glucose from cellulose). Acid-catalyzed dehydration of these sugars affords furfural (in case of C_5 sugars) or 5-hydroxymethylfurfural (in case of C_6 sugars) [ART-02]. In addition, phenols that make up lignin could be reduced to give cyclohexanones that could be used also as aldol condensation feeds.

Considering the availability and easiness of production, furfural was investigated as the aldolcondensation feed. Since it cannot undergo self-condensation, its condensation with acetone was studied. Acetone is not only an easily available by-product of phenol synthesis [16]; it could be also produced by ketonization of acetic acid [17] which is a common by-product in biomass pyrolysis – it originates from the decomposition of hemicellulose [18]. A simplified scheme of the reaction is depicted in Figure 2. The reaction of furfural with acetone yields 4-(2-furfuryl)-4-hydroxybutan-2-one (Fac-OH) as a primary product that undergoes facile dehydration to 4-(2-furfuryl)-3-butene-one (Fac), see Figure 2. Due to the availability of hydrogen atoms on the carbon in a-position to the carbonyl, FAc may react further with another furfural molecule yielding 1,4-pentadiene-3-one-1,5-di-2-furanyl (F₂Ac, Figure 2). In addition, acetone can undergo self-condensation (Figure 3) yielding primarily diacetone alcohol (DAA) that dehydrates to mesityl oxide (MO).



Figure 2 Basic scheme of aldol condensation of furfural with acetone. In addition to the names of products, their abbreviations used in the text are given. The schematic green lines depict the theoretical products of complete deoxygenation.

Acetone self-condensation



FAc dimerization over acid sites



Figure 3 Basic scheme of side reactions during aldol condensation of furfural with acetone – acetone selfcondensation and FAc dimerization. In addition to the names of products, their abbreviations used in the text are given. The schematic green line depicts the theoretical product of complete deoxygenation.

To demonstrate further the concept of aldol condensation for designing advanced biofuels, acetone was replaced by cyclohexanone in aldol condensation with furfural (Figure 4). As a result, the cyclic structure of cyclohexanone would be preserved and the final products upon complete deoxygenation would be 2-pentyl cyclohexane and 2,5-dipentyl cyclohexane, *i.e.* compounds suitable

for jet and diesel fuel production. Moreover, the self-condensation of cyclohexanone would afford C₁₂naphthenic products that could be deoxygenated to cyclohexyl cyclohexane.

Aldol condensation





Figure 4 Basic scheme of aldol condensation of furfural with cyclohexanone. The names of products are given just by their abbreviations used in the text. The schematic red lines depict the theoretical products of complete deoxygenation.

An interesting feature is that aldol condensation can be catalyzed by both acid and base catalysts. As the target were primarily advanced biofuels, *i.e.* a large-scale production, the research was aimed only at heterogeneous catalysts – namely zeolites as solid-acid catalysts (Section 2.2) and hydrotalcites as solid-base catalysts (Section 2.3) – to avoid future issue with scale-up of the process as well as with inherent environmental issues related to the use of homogeneous acid-base catalysts that require neutralization, laborious removal from the products and disposal.

2.2 Solid acid catalysts

2.2.1 Zeolites in aldol condensation

Zeolites have become the most widely used solid acid catalyst due to their large surface area as well as due to the possibility to fine-tune the number and strength of acid sites and also the access to these active sites. Here, several structurally different zeolites were investigated as catalysts for aldol condensation of furfural with acetone at mild conditions (20-60°C), namely ZSM-5 (MFI, 3D pore network, 10-membered rings), Beta (BEA, 3D pore network, 12-membered rings), Mordenite (MOR, 1D pore network, 12-membered rings) and ultra-stabilized Y (FAU, 3D pore network, 12-membered rings with cavities). They were tested both in their ammonium and proton form and zeolites with different Si/Al ratio were used to vary the concentration of acid sites in their H-forms. As expected, the activity of the NH₄-form was always significantly lower than that of the corresponding H-form. This was

attributed to the absence of Brønsted acid sites in the NH₄-forms. While no furfural conversion was observed at 20 and 60°C when using NH₄-zeolites, furfural was converted in their presence at 100°C. This was related to the presence of Lewis acid sites catalyzing also the aldol condensation reaction. Nonetheless, furfural conversion was much higher when H-zeolites were used due to the presence of Brønsted acid sites indicating that both Brønsted and Lewis acid sites are active in the reaction. The furfural conversion over H-zeolites increased in the sequence H-ZSM-5 \approx H-MOR < H-USY < H-Beta (Figure 5). It can be inferred that 10-membered rings (ca. 0.55 nm) in ZSM-5 zeolites were to narrow for the reaction to take place and that the unidimensional character of the 12-membered rings (ca. 0.7 nm) in Mordenite also prevented achieving high conversion [ART-05].



Figure 5 Conversion of furfural over different zeolites in H-form at 60 °C, the number in parenthesis corresponds to Si/Al ratio: (square) HMOR(20), (blue tringle) HZSM-5(28), (upside-down triangle) HZSM-5(50), (diamond) HSUSY(5), (brown triangle) HSDUSY(80), (circle) HBEA(25), (pink triangle) HBEA(38).

In contrast, the furfural conversion over 3D 12 membered-ring zeolites was significantly higher, however, differences in their activity could be also discerned. Inspection of Figure 5 reveals a dramatic drop in the reaction rate (based on the slopes it can be estimated that the initial reaction rates are 20-40 larger than the rates after several hours on stream. It can be thus concluded that the zeolites deactivate quickly which was corroborated by the TGA results on spent catalysts. The better performance of Beta zeolites over USY zeolites (Figure 5) can be explained by the formation of deposits in the cavities of the faujasite (zeolite Y) structure and by the large external surface area of zeolite Beta. The deactivation was connected to the formation of dimers (Figure 2) and possibly even oligomers. Experiments with regeneration of used zeolite Beta showed that in the second run with a previously used catalyst, furfural conversion was down to ca. 20% from the original ca. 40% when the catalyst was washed inn between the runs with ethanol. On the other hand, when the catalyst was calcined in between the experiments to burn out the deposits, the original furfural conversion of 40%

was restored in the second run. The data on product distribution also revealed that some of the sites responsible for dimer formation were blocked by the deposits since the selectivity to the dimer was lower in the second run on the ethanol washed catalyst than over fresh catalyst at a comparable conversion of furfural [ART-05].



Figure 6 (A) Furfural conversion obtained on different catalysts after 2 hours of the reaction at 100 °C and autogenous pressure. (B) Dependence of furfural conversion on the duration of reaction at 100 °C and autogenous pressure.

To provide deeper insight in the role of the external zeolite surface, several materials from the MWW family were studied. These included the original MCM-22 and MCM-49 zeolites as well as their delaminated analogues MCM-36 (using pillars to keep the MWW layers apart) and MCM-56 (delaminated material without pillaring). The furfural conversion over both MCM-36 catalysts with large external surface area (2-4 times higher than that of the other MCM materials and of Beta zeolite) was higher than over Beta zeolite (Figure 6A). However, the MCM-36 materials were unexpectedly outperformed by MCM-22, MCM-49 and MCM-56 catalysts (Figure 6A) that have 10-membered-ring pore opening (ca. 0.50-0.55 nm) and large supercages inside (diameter of 0.7 nm and height of 1.8 nm). When looking at the time-dependence of furfural conversion, it became clear that deactivation over MCM-22 was suppressed in comparison with MCM-36 or Beta zeolite. This could be explained by the fact that while the cups on the MCM-36 surface, where most of the acid sites were located, were coked rapidly by the oligomers due to their open nature, the confined space of the supercages prevented the formation of bulky molecules (oligomers) responsible for the deactivation by coking. Consequently, the acid sites inside the supercages remained protected due to the course of the reaction as they were accessible only to the raw materials and the aldol condensation products, mainly FAc, that could diffuse through the narrow pores where no reaction could take place. The performance of MCM-22 and MCM-49 catalysts can thus be regarded as an evidence for product-shape selectivity that protects the catalyst from deactivation by undesired products, *i.e.* oligomers [ART-06]. This is known from behavior of ZSM-5 catalysts in cracking where their coking by polyaromatic deposits is substantially suppressed as these cannot be formed inside the ZSM-5 porous structure due to their precursors being sterically hindered [19].

An important aspect in using acid catalysts is to identify whether Brønsted or Lewis acid sites or both are active in a particular reaction. It is a challenging task as it is virtually impossible to synthesize defects-free zeolites, *i.e.* free from Lewis acid sites (obviously, they always contain Brønsted acid sites). A study including metal-organic-frameworks (MOFs), Cu-BTC and Fe-BTC, besides zeolites helped to shed light on this aspect. Since the MOFs do not posses any acidic protons when properly dried, they can be considered as Lewis acid catalysts. The experiments showed that thermally treated (at 150°C) Cu-BTC and Fe-BTC did not possess any Brønsted acid sites, but they were able to catalyze aldol condensation of furfural with acetone at 100°C though the furfural conversion was low, <5%, despite high concentration of Lewis acid sites (>2 mmol/g, in contrast, zeolites had about 0.2 mmol/g of Lewis acid sites). It can be thus concluded that the Lewis acid sites can be active in aldol condensation, but their intrinsic activity is considerably lower than that of Brønsted acid sites. This was seen when testing moist MOFs samples that afforded higher furfural conversions. This was explained by water surrounding the cations (Cu²⁺ and Fe³⁺, respectively) in MOFs and forming weak Brønsted acid sites. Apart from the higher activity, formation of dimer, (FAc)₂, was detected when Brønsted acid sites were present, but not in their absence. It was particularly pronounced when using Fe-BTC or $Fe(NO_3)_3$ that was used corroborate the results obtained when using MOF catalysts [ART-07].

2.2.2 Potassium-modified zeolites in aldol condensation

In order to obtain insights into the role of Lewis and Brønsted acid sites as well as in the role of acid and base active sites, an in-depth study focusing on gradual modification of H-Beta zeolite catalyst to a K-Beta zeolite was carried out. To cover a wide range of acid-base properties, H-Beta was not ion-exchanged using a solution of KNO₃, but also impregnated KNO₃. Consequently, the former strategy (ion exchange, IE) resulted in catalysts with reduced Brønsted acidity due to replacement of acid protons by potassium cation, whereas the latter one (impregnation, IMP) led to catalysts with basic character due to the presence of supported K₂O formed upon catalyst calcination from the KNO₃ precursor. The addition of potassium, either by ion-exchange (IE) or by impregnation (IMP) resulted at first in a decrease in furfural conversion from the almost 40% for H-Beta to about 5% for 0.3K samples, *i.e.* using 0.3 M solution of KNO₃ (Figure 7). This decrease originated from the decrease in the number of acid sites. The maximum K/AI ratio in the ion-exchanged samples was 0.85 (for the three times ion-exchanged sample using 0.5 M KNO₃) suggesting that not all AI atoms related to the bridging hydroxyl groups (*i.e.* Brønsted acid sites), which was corroborated by the existence of Lewis acid sites. The virtually same performance of 0.3K and 0.5K ion-exchanged samples (Figure 7A) indicated the nearly complete ion-exchange (although the determined K/AI ration increased from 0.72 (in 0.3K sample) to

0.85 (in the 3-times ion-exchanged sample using 0.5 M KNO₃). In contrast, the impregnated sample with 0.3 M KNO₃ solution (0.3K-N sample) exhibited K/AI ratio close unity (1.07) suggesting that part of potassium in this sample was not related to the ion-exchange positions. Consequently, this sample presented the minimum on the furfural conversion curve as a function of the potassium content (or more precisely of the molarity of the solution used for impregnation) (Figure 7C). The other samples (from 0.5K-N up to 1.1K-N) had K/AI ratio from 1.2 to up to 2.5 and had already a basic character as evidenced by CO₂ adsorption microcalorimetry method. Therefore, furfural conversion over H-Beta catalyst (Figure 7C). Hence, H-Beta could be turned into a more efficient aldol condensation catalyst by its modification by potassium [ART-08].



Figure 7 Catalytic properties of K-BEA samples prepared by IE (A, B) or IMP (C, D) methods. A, C – Furfural conversion; B, D – Products selectivity. T = 100 °C, reaction time – 2 h. The number in the name of the sample represents the molarity of the KNO3 solution, i.e. the solutions were 0.1 – 1.1 M.

The modification by potassium did not change just the conversion of furfural, *i.e.* the catalyst activity, but also its selectivity. The key change concerned the reduced formation of the dimer, (FAc)₂, as the potassium concentration increased (Figure 7B,D). In fact, as soon as the catalyst did not possess Brønsted acid sites, the dimer was not formed [ART-08]. Comparison of acidity measurements (using the FTIR method of adsorbed pyridine) with the occurrence of the dimer in the aldol condensation products allowed concluding that aldol condensation of furfural with acetone was a more sensitive

method to detect Brønsted acid sites in the catalysts under reaction conditions. The reason is that the pre-treatment prior to the FTIR-pyridine measurements can convert some of the weaker Brønsted acid sites to Lewis acid sites (by dehydration). However, these sites can be rehydrated to Brønsted acid sites during aldol condensation as water is a reaction product.

The higher efficiency of zeolite Beta impregnated with potassium can be attributed to less pronounced deactivation than in the case where H-Beta was used as a catalyst. This can be attributed to the decreased formation of the dimer, which also signified suppressed oligomerization in general. Nonetheless, repeated catalytic cycles with a selected catalyst, 0.5K-N (K/Al=1.2) evidenced that the catalyst activity gradually decreased as the furfural conversion decreased from the original ca. 25% to ca. 20% in the second run (catalyst was washed at room temperature with ethanol between the runs) to ca. 12% in the fourth run / cycle (Table 1). When the catalyst was calcined between the catalytic runs to remove any carbonaceous deposits, the furfural in the second cycle was about 17% (a drop from the original 25%). However, after this initial drop, the conversion did not decrease further as in the fourth catalytic run conversion of ca. 19% was achieved. It could thus be concluded that after the initial drop the potassium impregnated catalysts gave a stable performance. The absence of basic sites was further reflected in the product composition where FAc-OH, *i.e.* the non-dehydrated aldol condensation product prevailed (Table 1) [ART-08].

Table 1 Catalytic performance of 0.5K-N-BEA in aldol condensation after three consecutive washing in ethanol (a) and regenerations at 530 °C (b). Reaction conditions: T = 100 °C, t = 2 h.

No. Exp.	Sample	Furfural Conversion, %	Selectivity, %				
			FAc	FAc-OH	F ₂ Ac		
1	0.5K-N- BEA – freshly calcined at 530 °C	25.6	36.0	61.1	2.9		
2a	1st washing in ethanol	19.6	31.4	65.9	2.7		
3a	2nd washing in ethanol	16.1	28.5	69	2.5		
4a	3rd washing in ethanol	11.8	24.1	74	1.9		
2b	1st regeneration at 530 °C	17.1	28.2	69.4	2.4		
3b	2nd regeneration at 530 °C	17.0	27.8	70.1	2.1		
4b	3rd regeneration at 530 °C	18.6	33.1	64.6	2.3		

This study was further extended to potassium ion-exchanged and impregnated Y-zeolite catalysts having different Si/Al ratio. The results of ion-exchange indicated that not all protons were accessible for ion exchange. As a result, the ion-exchanged catalysts possessed residual acidity which was reflected by the formation of the dimer and by the ratio of the FAc/FAc-OH product – the ratio decreased with the increasing Si/Al ratio, *i.e.* with the decreasing original acidity of the catalyst from >50 for Si/Al = 2.5 to <5 for Si/Al = 40. Upon impregnation, there was no significant residual acidity in all samples besides the one with Si/Al=2.5 and these samples had due to the impregnation with potassium basic character. This was reflected by the change in furfural conversion. While the potassium-impregnated zeolite Y with Si/Al=2.5 had a similar conversion of furfural as all the ion-exchanged catalysts (< 10%), the other two impregnated catalysts afforded furfural conversion >35%

(Figure 8). This was due to the change in the catalyst acid-base properties – the potassiumimpregnated Y zeolite catalysts with Si/Al of 15 and 40 had already a basic character that was reflected by the higher activity in aldol condensation. Moreover, the selectivity to the main products changed as well. First, dimer was not observed among the products. Second, the ratio of the FAc/FAc-OH product dropped <1 for the impregnated Y zeolite with Si/Al of 15 and 40, while it was still >20 for the impregnated Y zeolite with Si/Al of 2.5 (Figure 8) indicating that there were acid sites active in the reaction facilitating thus the dehydration [ART-09].



Figure 8 Furfural conversion (A) and product selectivity (B) observed for impregnated potassium Y zeolites

2.3 Solid basic catalysts

The results of aldol condensation over potassium-modified zeolites clearly showed the potential of solid basic catalysts (section 2.2). Therefore, the performance of inherently basic solid materials, hydrotalcites, *i.e.* layered-double hydroxides, was studied in detail. In particular, the effect of hydrotalcite composition (their Mg/Al ratio and replacement of Ga by Al in the structure) and post-synthesis treatments (mixed oxides obtained by calcination and rehydrated hydrotalcites obtained by rehydration of the mixed oxides) were assessed. The structure of hydrotalcites and its changes due to thermal treatment (calcination) affording mixed oxides and due to subsequent rehydration of mixed oxides resulting in the reconstruction of the hydrotalcite structure thanks to the so-called "memory effect" is depicted in Figure 9. It is obvious, that the as-prepared hydrotalcite does not possess any significant basicity and, thus, cannot be catalytically active in aldol condensation which was also verified experimentally. The initial studies allowed identifying the reaction network consisting of the initial condensation reaction of furfural with acetone, followed by dehydration of the initial aldol condensation product and a further condensation of the dehydrated product with furfural (Figure 2). It was also established that acetone self-condensation did take place, but its conversion was limited; the selectivity to diacetone alcohol did not exceed 5% [ART-10].



Figure 9 Schematic depiction of hydrotalcites structure and its changes due to calcination and rehydration (scheme taken from [20]).

2.3.1 Mixed oxides in aldol condensation

Mixed oxides are prepared from hydrotalcites by calcination at temperatures typically in the range of 400 – 550°C to decompose fully the hydrotalcite structure while at the same time avoiding the formation of spinel possess Lewis basicity. In contrast, reconstructed hydrotalcites prepared by rehydration of these mixed oxides have Brønsted basicity. This change was also reflected in the catalytic performance of both catalytic materials. The results obtained for aldol condensation of cyclohexanone with furfural over MgAl mixed oxide and MgAl reconstructed hydrotalcite demonstrated the superiority of the reconstructed hydrotalcite and, thus, Brønsted base active sites over mixed oxide with its Lewis base active sites (Figure 10). One can observe a dramatic increase in the initial reaction rate at all three studied temperatures. For instance, furfural conversion was only about 3% after 30 minutes at 25°C over mixed oxide while it was as high as 80% over reconstructed hydrotalcite at the same reaction conditions. It was hence concluded that reconstructed hydrotalcites were considerably more efficient catalysts which was ascribed to the change in the type of active sites from Lewis base to Brønsted base. It needs to be, however, mentioned that due to their high reactivity, the Brønsted base hydrotalcites are very sensitive to exposure to carbon dioxide that adsorbs rapidly on the active base site rendering them inactive. Therefore, in-situ activation treatments are crucial to maintain the high catalytic activity [ART-11].

This relationship between the activity of mixed oxides and reconstructed hydrotalcite counterparts was shown to be valid also for other elemental composition than MgAl; namely MgGa and MgFe mixed oxides and hydrotalcites. All catalysts had the molar ratio of Mg²⁺ to M³⁺ (with M being Al, Ga or Fe) equal to 3. This comparison also revealed that MgAl hydrotalcites provided mixed

14

oxides as well as reconstructed hydrotalcites having better catalytic performance in aldol condensation of acetone with furfural (Figure 11). The superiority of the MgAl catalytic system was pronounced particularly in the comparison of the mixed oxides while after reconstruction to the hydrotalcite structure the differences were much lower (Figure 11). Thus, both iron and gallium could replace aluminum in the hydrotalcite structure and after calcination followed by rehydration active aldol condensation catalysts would be obtained [ART-12, 21].



Figure 10 Furfural conversion over MgAI mixed oxide (A) and reconstructed MgAI hydrotalcite (B) in aldol condensation of cyclohexanone (CH) with furfural (F) with CH/F = 5 at different temperatures.



Figure 11 Furfural conversion during its aldol condensation with acetone over mixed oxides (left) and reconstructed hydrotalcites (right) at 50°C.

The performance of MgAl mixed oxides was also investigated with respect to their initial composition (different Mg/Al ratio in the range 2 to 4) and method of preparation. One set of hydrotalcite samples was prepared by an industrial production method by Eurosupport Manufacturing Czechia and the other was prepared using a laboratory co-precipitation method. This comparison shed light on the relationship between the structure of the as-prepared hydrotalcite material, its properties and performance of the derived mixed oxide in aldol condensation. All mixed oxides from laboratory prepared samples exhibited higher furfural conversion in aldol condensation with acetone than their industrial counterparts. This was related to better structural parameters of the as-prepared laboratory hydrotalcites that were phase pure hydrotalcites while admixture of MgO was found in the industrially

produced samples. As a result, the BET surface area of the industrial samples was in the range $160 - 170 \text{ m}^2/\text{g}$ whereas the laboratory samples had BET in the range $200 - 250 \text{ m}^2/\text{g}$. This difference was reflected in the total pore volume – the laboratory sample has almost three times higher pore volume than the industrial samples (0.96 - 1.20 vs. $0.33 - 0.41 \text{ cm}^3/\text{g}$) the main difference being in particular in the mesopore region (pores with a diameter of 2 - 10 nm):the volume of these pores was 6 - 10 times higher in the laboratory prepared samples. The larger surface and better accessibility of the active sites through larger pores facilitated larger furfural conversion over the laboratory-made samples. Moreover, the better textural properties together with a higher hydrotalcite phase purity were responsible for a better dispersion of the two elements (Mg and Al) in the mixed oxide and allowed better rehydration and reconstruction of the hydrotalcite structure [ART-13].



Figure 12 Furfural conversion during its aldol condensation with acetone as a function of Mg/Al molar ratio of the mixed oxide catalysts. Conversion after 120 minutes at 50°C. PAIC, PMgC are Al2O3 and MgO prepared using the same precipitation and calcination procedures that were used for preparation of the mixed oxide catalysts.

A detailed investigation of MgAl mixed oxide catalysts brought further insights into the relationship between their activity and structure and properties. It was established that the unusual dependence of furfural conversion on the MgAl mixed oxide composition (Figure 12) was given not by the overall number of basic sites but rather their surface density which is depicted in Figure 13. In particular, there was a clear dependence of the furfural conversion on the density (μ mol/m²) of the so-called strong basic sites, *i.e.* those that release adsorbed CO₂ in the TPD measurements at >200°C (the maximum of the high temperature desorption peak is at >250°C) described often as surface O²⁻ ions (Figure 13D). Although the correlation was the strongest between the determined density of basic sites and the conversion of furfural, participation of the less strong basic sites, mainly the so-called medium strong sites (assigned in literature to Mg²⁺–O²⁻ pairs) could not be excluded (Figure 13C). In

addition to the density of basic sites, the size of the crystallites was seen to affect the catalytic performance. It was observed that over smaller crystallites that imposed lower diffusional resistance, and thereby their active sites were more readily accessible, bulkier products such as F2Ac were formed with a higher selectivity [ART-14].



Figure 13 Furfural conversion in dependence on the density of total (A), weak (B), medium (C), and strong (D) basic sites. Treac. = 50 °C, time = 120 min.

2.3.2 Reconstructed hydrotalcites in aldol condensation

As discussed above, reconstructed hydrotalcites gave significantly better performance than the corresponding mixed oxides. Hence, the rehydration process was studied in detail for an MgAl mixed oxide in order to understand how long rehydration treatment was needed and what was the effect of water on the performance of a reconstructed hydrotalcite in aldol condensation of furfural with acetone. It was established that the rehydration was reflected in the properties of the catalyst and could be best observed by XRD as the change in the phase composition of the catalyst and as evolution of water from catalyst sample heating up resulting in a decrease of sample weight observable by TGA. These changes are depicted in Figure 14. To facilitate the observation of the structural changes, acetone containing different amounts of water was used. It is obvious that when increasing the amount of water, higher crystallinity (Figure 14, left) was attained which was corroborated by TGA where more structural water from the dehydroxylation of the hydrotalcite structure was released (Figure 14, right).



Figure 14 Transformation of mixed oxide into hydrotalcite by rehydration using different concentration of water in acetone followed by XRD (left) and TGA (right) methods.

Nonetheless, the aldol condensation itself was found as the most sensitive method to detect these structural changes. Consequently, it was determined that already a very short contact time with deionized water (15 s) was enough to result in significant reconstruction of the original hydrotalcite structure and that extension of the treatment beyond 30 seconds led only to minor improvements in the catalyst activity (Figure 15) [ART-15].





Due to the rehydration procedure, it has to be assumed that water will remain physically bonded in the interlayer space of the reconstructed hydrotalcites and affect the catalytic performance. Therefore, careful removal of the water in excess was performed and the remaining water content was monitored and correlated with catalyst activity in aldol condensation. For this purpose, the classical evaluation of TGA data was modified since the initial weight of rehydrated samples depended on the amount of water captured and could not be used as a constant starting value. Consequently, the weight of mixed oxide was taken as a constant well-defined value and the amount of water above this value was determined. At the same time the amount of water needed to obtain a hydrotalcite without physisorbed was water was also calculated. The data are depicted in (Figure 16A) where the red dashed line depicts the theoretical amount of water to be released from a hydrotalcite and the values above this value thus represent the excess of water in the samples, *i.e.* water that is not structurally bound. It is obvious as the drying time increased the water content dropped and for sample dried for 60 minutes the water content determined by TGA corresponded to that calculated for a hydrotalcite of the given composition (Mg/Al molar ratio was 3). In other word, mild drying in a rotary evaporator at 25°C for 60 minutes was necessary to remove all physisorbed water from the interlayer space. When looking at the catalytic data a surprising conclusion was to be made. A fully rehydrated catalyst without water in the interlayer space was completely inactive and also the sample dried for 40 minutes that had significantly reduced amount of water present in the interlayer space had a reduced activity while the non-dried catalyst and those dried for <20 minutes exhibited similar catalytic performance (Figure 16B). Thus, it was concluded that water is essential for obtaining high catalyst activity in aldol condensation [ART-15].



Figure 16 A). The influence of drying time on the weight of reconstructed hydrotalcite produced by the rehydration of Mg-Al mixed oxide (weight of Mg-Al mixed oxide is taken as 100%). Red dashed line stands for the theoretical weight of totally reconstructed water-free HTC. B). The dependence of furfural conversion observed over dried hydrotalcites on time of their drying. F:Ac = 1:5 (mol:mol), mfeed:mcat.= 105, Treac.= 25 °C.

To better understand the effect of trace amounts of water, further experiment focused on the performance of a reconstructed hydrotalcite (10 minutes treatment of a mixed oxide) dried under mild conditions for 2 hours. In line with the previous discussion, this benchmark catalyst was inactive in aldol condensation in absence of water. However, as the concentration of water was increased in the reaction mixture from 0 to 10%, the conversion of furfural increased. While addition of 1% water had only a minor impact, 3% of water improved the furfural conversion dramatically (Figure 17). Further increase in concentration of water in the reaction mixture resulted in maximized catalyst performance – there was virtually no difference between 5 and 10% water in the reaction mixture (Figure 17). This seems to be promising aspect from the application point of view as the biomass-derived feed contain often significant amounts of water. Nonetheless, additional experiments were performed with even

higher amount of water (the mixtures contained 19 and 38 wt% of water) and a gradual decrease in furfural conversion was observed. The conversion of furfural after 20 minutes dropped from the initial ca. 70% for the reconstructed hydrotalcite to ca. 50 and 30% for the mixtures containing 19 and 38 wt.% of water, respectively [ART-15].



Figure 17 The dependence of furfural conversion on the amount of water post-added to furfural-acetone reaction mixture. Catalyst – HTC-10-120. F:Ac = 1:5 (mol:mol),mfeed:mcat.= 105, Treac.= $25 \circ C$. The amount of post added water – 0-10% to the amount of furfural-acetone mixture.

2.3.3 Deactivation in aldol condensation over hydrotalcite catalysts

The stability of catalyst activity is an essential aspect of any catalyst evaluation. In the previous section (section 2.2) the rapid deactivation of acid zeolites was attributed to the formation of dimers and possibly even oligomers that remained trapped in the internal pore structure and contributed to formation of carbonaceous deposits. It was also shown that dimers were not formed over potassium-modified zeolites with basic properties and formation of dimers was not observed over mixed oxides or reconstructed hydrotalcites as well. Thus, this cause of deactivation could be excluded from consideration. However, a flow experiment (50 hours time-on-stream) in a fixed bed of calcined MgAI hydrotalcite (molar ratio Mg/AI = 3), i.e. mixed oxide, using mixture of acetone and furfural (molar ratio acetone/furfural = 10) at 50°C and weight-hourly space velocity of 2h⁻¹ revealed formation of large amounts of high-molecular-weight products that could contribute to catalyst deactivation. The products were different aldol condensation products with several acetone (Ac) and furfural (F) "building blocks" in various combinations as schematically depicted in Figure 18 [ART-16].

As demonstrated in Figure 19, under the selected reaction conditions full conversion was achieved over ca. 45 hours on stream and then a rapid decrease in activity (furfural conversion) took place. It coincided with an increase in the selectivity to FAc-OH (Figure 19A), *i.e.* the primary non-dehydrated product. It could, thus, be concluded that the inability of the catalyst to efficiently

dehydrated FAc-OH to FAc reflected its loss of activity. Moreover, the heavier products were formed with a relatively high selectivity that at first gradually increased due to the initial build-up of the necessary intermediates on the catalyst surface and reached a maximum at about 20 hours on stream (Figure 19B). At this time, these heavy products made up more than one third of all products formed. The decrease in the selectivity to these heavy products was attributed to the already diminished activity of the catalyst [ART-16]. These results indicated a serious limitation of the reaction system and alternatives were investigated.



Figure 18 Tentative reaction network leading to the formation of heavier condensation products of furfural (F) and acetone (Ac).



Figure 19 Furfural conversion and selectivity to main reaction -FAc, FAc-OH and F2Ac (A), selectivity to heavier reaction products (B).

A comparison of different activation procedures showed that the performance of mixed-oxides and hydrotalcites could be significantly improved by catalyst pretreatment. The catalyst without activation (Figure 20) was mixed oxide that was calcined in-situ at 450°C and then feedstock containing furfural and acetone (Ac/F = 10) was directly introduced. The catalyst lifetime was doubled (estimated as full conversion at given set of reaction conditions, *i.e.* 45 vs. ca 100 h TOS) when the mixed oxide was first treated by acetone alone. In this way water formed during acetone self-condensation could partially rehydrate the mixed oxide. The most significant enhancement was observed when the catalyst was pretreated with acetone containing 10% water that was used also to prepare the mixture with furfural. In this case, full conversion of furfural was obtained for nearly 300 hours on stream (*i.e.* six-times longer than in the mixed-oxide catalyst) and the subsequent decline in furfural conversion was less steep than in the other two experiments (Figure 20). It can be inferred that there is still room for improvement by optimizing the catalyst pre-treatment and feedstock composition – particularly in terms of its water content.



Figure 20 Furfural conversion as a function of time-on-stream (TOS) for differently activated Mg/Al mixed oxide catalyst (Mg/Al = 3, Ac/F = 10, WHSV = 2 h-1, p = 0.5 MPa, N2, T = 50°C (no activation) or 60°C (remaining experiments)).

As initial experiments in batch experimental set-up indicated that the mixing order of feedstock components with catalysts played an important role. Specifically, when acetone was mixed with catalyst (MgAl mixed oxide) first and only then furfural was added, good performance (20% conversion of furfural after 3h) was observed whereas it was much worse (3% conversion of furfural after 3h) when catalyst was first mixed with furfural and acetone was add last (Figure 21). On the other hand, when catalyst was added to the mixture of acetone and furfural nearly the same performance as when adding acetone first was obtained (Figure 21). The results, hence, indicated an adverse effect of furfural on the catalyst.

Detailed analytical investigations revealed presence of furfuryl alcohol. Since the experiments were performed in absence of hydrogen or any other reducing compounds, reduction of furfural by direct or transfer hydrogenation could be excluded. Therefore, the formation of furfuryl alcohol from furfural by Cannizzaro reaction was put forward and later also confirmed. In Cannizzaro reaction (), two molecules of an aldehyde (here furfural) react together and give rise to an alcohol (here furfuryl alcohol) and an acid (here furoic acid). While furfuryl alcohol was detected among the reaction products, furoic acid was not. The reason for that was that it immediately reacted with the basic sites of the solid catalyst and remained chemisorbed on the surface thereby blocking the basic active sites and hence deactivating the catalyst [ART-17].



Figure 21 Furfural conversion in its aldol condensation with acetone for different order of mixing of catalyst (Cat) with acetone (Ac) and furfural (F).



Figure 22 Cannizzaro reaction in the presence of hydrotalcite as a basic catalyst.

This hypothesis was confirmed by catalyst performing experiments with a different contact time between furfural and catalyst before adding acetone and starting the aldol condensation reaction. At first, experiments with furfural over Mg/Al mixed oxide revealed that in presence of water furfuryl furoate was formed and its amount increased with the increasing amount of water. This proved that furoic acid was really formed. The one order of magnitude lower concentration of the ester in comparison with the alcohol indicated that most of the acid remained bound to the surface causing catalyst deactivation. This was further supported by the changes in furfural conversion in aldol condensation with acetone in dependence on the contact time (5 to 180 minutes) of furfural (containing water to achieve mixed oxide rehydration) with the catalyst. Whereas furfural conversion in aldol condensation was nearly complete after 60 minutes for catalyst-furfural contact times of 5 and 30 minutes, it dropped to ca. 50% after 60 minutes when the contact time was extended to 180 minutes (Figure 23, left). A relationship between the extent of Cannizzaro reaction (indicated by higher formation of furfuryl alcohol) and the catalyst deactivation (lower furfural conversion) was also established; the higher concentration of furfuryl alcohol was observed at the end of the experiments (*i.e.* after 3 hours), the lower conversion of furfural was achieved (Figure 23, right). It is obvious that

Cannizzaro reaction contributes to deactivation of hydrotalcite-based catalysts as it leads to formation of furoic acid [ART-17].



Figure 23 Furfural conversion in aldol condensation with acetone after differently long contact-time of furfural with catalyst prior to the aldol condensation experiment (left), dependence of furfural conversion on the content of furfuryl alcohol (signifying the amount of furoic acid formed and chemisorbed on the catalyst surface) (right).

2.4 Summary

Aldehydes and ketones that can be obtained by selective upgrading of lignocellulosic biomass consisting of its fractionation and depolymerization followed either by dehydration of sugar monomers or by partial hydrogenation of lignin-derived phenolics are a valuable renewable resource. They could be used to synthesize oxygenated precursors of either advanced biofuels or prospective chemical building blocks, *e.g.* diols. Among the various valorization pathways of these short-chain aldehydes and ketones (having 5 to 9 carbon atoms in their molecules), aldol condensation appears to be a promising route to produce selectively oxygenates having 11 to 18 carbon atoms in their molecules which corresponds well to the required carbon-chain lengths in jet and diesel fuels. By a suitable combination of the reactants, their ratios and reaction conditions, it would be possible to design the structure and molecular mass of the oxygenates and, hence, also of the hydrocarbons obtained upon their deoxygenation. By including cyclic ketones (derived from phenolics), it is possible to introduce naphthenic ring in the oxygenates that would be retained in the resulting hydrocarbons and improve their fuel properties.

It is important to employ heterogeneous catalysts to enhance the sustainability of the transformation of aldehydes and ketones to the aldol condensation products. Both acid catalysts, such as zeolites, or base catalysts, *e.g.* mixed oxides or hydrotalcites, can be used to catalyze the aldol condensation reactions. The advantage of the heterogeneous base catalysts is their significantly higher activity in comparison with acid catalysts. However, they show insufficient stability of the catalytic activity due to deactivation by possible acid impurities in furfural, furoic acid formed by Cannizzaro reaction and heavier aldol condensation products. This could be overcome by catalyst regeneration,

but an efficient regeneration protocol of hydrotalcite-based catalysts remains to be developed. The acid catalysts, on the other hand, are less active and they suffer from deactivation due to oligomerization reactions leading to carbonaceous deposits blocking the active sites in zeolites. Nonetheless, they can be regenerated by burning off the deposits that results in full restoration of their activity. Moreover, oligomerization of the aldol condensation products affords branched products that are desirable from the fuel properties point of view. Thus, the challenge in acid catalyzed aldol condensation is not only to enhance their catalytic activity, but also to gain control over the oligomerization by limiting it only to dimerization.

3 Catalytic deoxygenation

3.1 Basic concepts

Biomass-derived feedstocks contain in contrast to petroleum fractions significant amounts of oxygen that needs to be at least partially removed for the produced fuels to comply with the requirements on the fuels. The typical oxygen content in the biomass-derived feedstocks lies in the range from 10 wt% found in triglycerides to as high as 40 wt%, which is the oxygen content in fast pyrolysis bio-oils. The products of aldol condensation of furfural with acetone have about 22 wt% due to the inherent dehydration of the first reaction intermediate. The removal of oxygen not only increases the energy content of the targeted fuels, but it also contributes to a further improvement of their properties, such as oxidation stability or corrosiveness. This is critical particularly in case of bio-oil that cannot be upgraded in conventional refineries, unlike triglycerides, due to their high water content, low thermal and oxidative stability, high polarity and low pH, and immiscibility with petroleum-derived fractions.

In general, hydrogen addition or carbon abstraction are possible strategies to reduce the oxygen content. Hydrogen addition necessitates an external source of hydrogen be it molecular hydrogen applied at high pressures or suitable hydrogen donor, such as 2-propanol, which, on the one hand, can be detrimental from the cost point of view (hydrogen cost as well as high-pressure equipment), but, on the other hand, allows maximizing the liquid product in transportation fuel range. Oxygen is eliminated in the form of water. In contrast, carbon-abstraction does not require external hydrogen source and could be carried out at low pressure, but it leads inevitable to a decrease in yield of the targeted hydrocarbon fuels since oxygen is removed as CO or CO₂. In absence of hydrogen, undesired side reactions, particularly coking, can be hardy controlled and they cause rapid catalyst deactivation. In practice, carbon abstraction pathway would be suitable only for feeds with low oxygen content as the reduction in yield is proportional to oxygen content. From chemical composition point of view, carbon abstraction is suitable only for acids (decarboxylation) and aldehydes (decarbonylation) where it could be highly selective.

Deoxygenation consists of four basic types of reactions – hydrodeoxygenation, decarboxylation, decarbonylation and dehydration that are discussed in detail below (see 3.2.1). The extent of these reactions obviously depends on the feedstock composition. Consequently, decarboxylation as well as hydrodeoxygenation are prominent reactions in deoxygenation of triglycerides, while only hydrodeoxygenation and dehydration take place in deoxygenation of aldol condensation products. Due to its complex composition, all mentioned deoxygenation reactions can be observed during hydrotreating of bio-oils. The presence of phenols in bio-oils, furanic rings in aldol condensation products and olefins in all three feeds indicate that hydrogenation of these structures will take place

26

in upgrading of these feedstocks. The fundamental as well as practical aspects of deoxygenation will be discussed first on the example of triglycerides (Section 3.2) and only then deoxygenation of bio-oils and aldol condensation products will be explored (Section 3.3).

3.2 Deoxygenation of triglycerides

3.2.1 Key reactions

Deoxygenation of triglycerides encompasses four main chemical reactions that take place under reducing conditions – namely hydrodeoxygenation, dehydration, decarbonylation and decarboxylation – ultimately resulting in three main oxygen-containing products, *i.e.*, water, carbon monoxide and carbon dioxide (Figure 24). In addition, other products (such as alcohols) originating from demethoxylation or hydrogenolysis reactions involving ethers and esters, respectively, could be considered as deoxygenation products as well. This makes the deoxygenation chemistry more complex than that of hydrodesulfurization (HDS) and hydrodenitrification (HDN), which under reducing conditions yield hydrogen sulfide and ammonia, respectively, as the only heteroatomcontaining by-products. Obviously, the rich chemistry of deoxygenation has its origins in the complex composition of biomass; however, even relatively simple oxygenates, such as triglycerides, can undergo a wide range of deoxygenation reactions depending on the catalyst and reaction conditions employed. [ART-04, ART-18].

Main deoxygenation reactions of triglycerides



Important side reactions during deoxygenation

со + зн ₂	→	CH ₄ ∔ H ₂ O	methanation
CO ₂ + 4H ₂	→	CH ₄ + 2H ₂ O	methanation
СО + H ₂ O	→	$CO_2 + H_2$	water-gas shift

Figure 24: Main deoxygenation reactions and important parallel reactions.

Considering only the three main reactions (Figure 24), it could be concluded that steering the overall deoxygenation process towards decarboxylation towards selective decarboxylation is the most advantageous strategy as it results in the lowest hydrogen consumption. This is, however, true only when hydrogenation of carbon dioxide can be avoided, which is a challenging task under relevant hydrotreating conditions. Depending on the reaction conditions (particularly hydrogen pressure and temperature), carbon dioxide as well as carbon monoxide undergo hydrogenation that yields ultimately methane making the decarboxylation pathway more hydrogen-demanding than the hydrodeoxygenation pathway. Moreover, decarboxylation as well as decarbonylation pathways result in a lower yield of liquid hydrocarbons than the hydrodeoxygenation due to the CO₂ or CO production [ART-19]. Thus, a decision on the preferred reaction pathway is never straightforward and hydrogen consumption, reduced yield of the liquid products as well as other aspects related *e.g.* to further treatment / disposal of CO (a known catalytic poison) and CO₂ have to be considered.



Figure 25: Changes in product distribution over a NiW/Al2O3-SiO2 catalyst due to a change in reaction temperature (left) and in hydrogen pressure (right).

The selectivity towards either hydrodeoxygenation or decarboxylation can be governed by the catalyst choice as summarized in [ART-04] as well as reaction conditions as demonstrated in [ART-19]. Metals (Pd, Pt, Ni) supported on carbon were shown as highly selective catalysts towards decarboxylation [22, 23], while molybdenum carbide catalysts were reported as selective hydrodeoxygenation catalysts [24]. Traditional sulphided catalysts catalyze both pathways at the same time, although it is possible to adjust the ratio of the hydrodeoxygenation and decarboxylation/decarbonylation pathways as discussed in Section 3.2.2. Besides the catalyst choice,

there is a pronounced influence of reaction temperature and hydrogen pressure that in some cases has a dramatic impact on the selectivity. While over a NiMo/Al₂O₃ sulfided catalyst only moderate changes can be observed that can be interpreted by help of the Le Chatelier's principle – *i.e.*, at higher hydrogen pressure hydrodeoxygenation is preferred at the expense of decarboxylation whereas at higher reaction temperature decarboxylation is preferred over hydrodeoxygenation, the over NiW/Al₂O₃-SiO₂ the selectivity can be completely reversed by changing the hydrogen pressure (Figure 25). Specifically, hydrodeoxygenation was the main reaction at 280°C when operating at 7 MPa H₂ while decarboxylation prevailed when the hydrogen pressure was reduced to 0.7 MPa [ART-19].



Figure 26 Effect of reaction pressure on the production of hydrocarbons from triglycerides (a) and deoxygenation reaction pathway (b) at 320 °C sulfided CoMo/MCM-41.

The effect of hydrogen pressure on triglyceride conversion as well as on the reaction pathway (decarboxylation vs. hydrodeoxygenation) was studied in more detail using a CoMo/MCM-41 catalyst. The positive effect of increased hydrogen pressure on rapeseed oil conversion was expected and is well documented over a broad range of weight-hourly space velocities (Figure 26). From the fundamental point of view, it is important to note that hydrogen pressure affects also the distribution of hydrocarbon products due to having impact on the two reaction pathways. As the hydrogen pressure increased the ratio of the hydrodeoxygenation rate to the decarboxylation reaction rate increased as documented by the increase in the C_{18}/C_{17} ratio. Hence, hydrogen pressure can be used to control the ratio of hydrocarbons with even and odd carbon atom number [ART-20].

3.2.2 Sulphided catalysts

Sulphided catalysts are the catalysts of choice for the industrial deoxygenation despite triglycerides comprise virtually no sulfur-containing compounds. The sulfur content of triglycerides is

typically <5 ppm which is even well below the sulfur content in the so-called sulfur-free fuels, *i.e.* <10 ppm. This counter-intuitive choice is based on the robustness of sulfided catalysts, the strong knowhow in their synthesis and characterization and previous experience in upgrading feeds containing wide-range of heteroatoms including S, N and O. While oxygen-content in petroleum-derived fractions is generally low in contrast to sulfur and nitrogen, the upgrading of coal-based liquids had to deal also with oxygen-containing compounds next to sulfur- and nitrogen-containing components. The following sub-sections discuss the influence of active phase composition (3.2.2.1), the effect of the support and active-phase–support interactions (3.2.2.2), and aspects of deactivation related to feed composition (3.2.2.3) on the activity and selectivity in deoxygenation of triglycerides.

3.2.2.1 Active phase composition

Sulfided catalyst are primarily used in refineries in hydrotreating, particularly supported NiMo or CoMo catalysts or their combination, *i.e.* NiCoMo catalysts, and in hydrocracking where in addition to the above-listed catalysts NiW supported catalysts are used. Therefore, four bimetallic active-phase compositions supported on Al₂O₃, *i.e.* NiMo, CoMo, NiW and CoW sulfides, were studied in rapeseed oil deoxygenation together with two trimetallic compositions, *i.e.* NiCoMo and NiCoW sulfides. Among them, catalysts combining Co and W sulfides (CoW/Al₂O₃ and NiCoW/Al₂O₃) were identified as the least active ones (Figure 27). On the other hand, NiMo/Al₂O₃ catalyst exhibited the best deoxygenation activity among the tested catalysts followed by the other catalyst based on molybdenum sulfide and sulfided NiW/Al₂O₃ (Figure 27). It was also found that the CoMo catalyst was more selective towards hydrodeoxygenation than the NiMo catalyst and as a result the ratio between hydrodeoxygenation and decarboxylation products was about 20 over the CoMo catalyst, but only 3-4 over the NiMo catalyst at 270°C [ART-21].



Figure 27 Comparison of rapeseed oil deoxygenation at 270°C and 5 MPa over different alumina-supported bimetallic and trimetallic sulfides.

The NiMo active phase was, thus, studied in more detail with respect to the changes in active phase composition as well as supports used (see 3.2.2.2). The active phase composition study included determination of the optimum Ni/(Ni+Mo) atomic ratio as it is known from hydrodesulphurization chemistry that such an optimum exists and elucidation of the performance of individual sulphided phases, *i.e.* nickel and molybdenum sulfides supported on alumina. Considering the Ni/(Ni+Mo) optimum for hydrodesulphurization being 0.3, catalysts with Ni/(Ni+Mo) equal to 0.2, 0.3 and 0.4 were investigated. The differences in their performance were, however, only minor indicating that this parameter is not crucial. Nonetheless, the experiments with sulfided Ni/Al₂O₃, NiMo/Al₂O₃ and Mo/Al₂O₃ confirmed that there was a synergy between both sulfides since sulfided NiMo catalyst outperformed both sulfided Ni/Al₂O₃ and sulfided Mo/Al₂O₃ (Figure 28). The higher activity of NiMo sulfided catalysts was accompanied by its higher selectivity to hydrocarbons, at triglyceride conversion in the range of 30 – 80%, the selectivity to hydrocarbons was about 50% over sulfided NiMo, but only 10-20% over sulfided Ni or Mo catalysts. The monometallic sulfided catalysts exhibited at this conversion range high selectivity (80-90%) to oxygenated compounds, namely carboxylic fatty acids, fatty acids and their mutual esters, *i.e.* typically stearyl stearate as the double bonds of the rapeseed oil used as a feed were saturated already at temperatures <240°C [ART-22].



Figure 28 Conversion of triglycerides over alumina-supported sulfided NiMo (diamond, Ni/(Ni+Mo)=0.3); Mo (square) and Ni (circle) catalysts at 260°C and 3.5 MPa.

A closer look at product selectivities of the sulfided monometallic catalysts revealed that decarboxylation was the almost exclusive reaction pathway over sulfided Ni/Al₂O₃ whereas hydrodeoxygenation was strongly preferred over the sulfided Mo/Al₂O₃ (Figure 29). The selectivity of the sulfided NiMo catalysts was in between (Figure 29). It can be, thus, inferred that both NiS and MoS₂ phases contribute to the observed overall selectivity, *i.e.* that decarboxylation products are formed on the NiS phase whereas the hydrodeoxygenation products are produced on the MoS₂ phase, or that the

bimetallic sulfide phase, NiMoS_x phase, is active in both decarboxylation and hydrodeoxygenation reactions. The differences in the activity of both phases affected also the composition of the oxygenated intermediate products. Over NiS phase, only carboxylic acids were observed as their decarboxylation prevented the formation of alcohols and, hence, also esters. On the other hand, esters were the main products over MoS₂ phase since the alcohols formed by hydrogenation of the respective carboxylic acids reacted immediately with the acids, which resulted in the formation of the esters with high molecular weight, *e.g.* stearyl stearate [ART-22].



Figure 29 Selectivity within the hydrocarbon products group to main hydrocarbons – n-heptadecane (A) and noctadecane (B) as a function of total yield of hydrocarbons for alumina-supported NiMo (diamonds, Ni/(Ni+Mo)=0.3); Mo (squares) and Ni (circles) catalysts; T = 260–280°C, p = 3.5 MPa, V/F = 0.25–4 h.

A further investigation was aimed at understanding the role of NiMo/Al₂O₃ catalyst calcination on its activity and selectivity. The nickel precursor was calcined at 450, 600 or 800°C while the Mo phase was calcined only at 600°C due to its volatility at higher temperatures. The deoxygenation activity of the catalyst calcined at 450°C was slightly higher than that of the other two catalysts. This could be attributed to a better dispersion of the Ni phase in the NiMo catalyst. This conclusion was corroborated by studying sulfided Ni on alumina where the catalyst calcined at 450°C was significantly more active than the one calcined at 800°C. When looking at the selectivity to oxygenates and hydrocarbons as a function of conversion, all three sulfided NiMo catalysts exhibited the same selectivity at a given conversion. However, a closer look at the product distribution within the hydrocarbon group reveled that the NiMo catalyst calcined at the highest temperature (800°C) was more selective to hydrodeoxygenation than the NiMo catalyst calcined at 450°C (Figure 30). It can be inferred that the lower the calcination temperature the more pronounced the effect of the NiS phase, *i.e.* the more favored decarboxylation pathway. By UV-Vis investigation of the calcined catalysts it was observed that there was also a change in the NiO phase structure, namely higher calcination temperature resulted in formation of more tetrahedrally coordinated NiO species on the catalyst surface than calcination at 450°C that favored the formation of octahedrally coordinated species. The XPS results indicated a higher degree of sulfidation of the Ni phase in case of the catalysts calcined at lower temperature [ART-23].



Figure 30 The dependence of the ratio of the selectivity to C18 to the selectivity to C17 deoxygenated products as a function of rapeseed oil conversion over sulfided NiMo catalysts calcined at 450, 600 and 800 °C).

In summary, it was shown that sulfided NiMo phase is more active than the other sulfided phases in deoxygenation of triglycerides. Moreover, it was demonstrated by varying the NiMo composition both activity and selectivity can be modified. In particular, NiS phase was seen to be selective towards decarboxylation whereas MoS₂ phase was selective to hydrodeoxygenation. The selectivity in deoxygenation of rapeseed oil could be further varied by calcination of the Ni precursors as this led to variation in the coordination of the NiO species (tetrahedral vs. octahedral) and different degree of sulfidation and dispersion of the sulfided Ni phase on alumina.

3.2.2.2 Effect of the support

The catalyst deoxygenation performance is determined not only by the active phase (*i.e.*, its intrinsic activity in dependence on the active phase composition), but also by the support used for supporting the active phase. The influence is direct as well as indirect. The direct influence comprises specific adsorption and pre-activation of the reactants or even their conversion (by *e.g.* cracking or isomerization reactions) whereas the indirect influence includes the effects of the support on the

active-phase dispersion as well as the electronic interactions between the support and active phase resulting in the modification of the active phase properties and ultimately its intrinsic activity. Different supports were studied [ART-21] and the interactions between the support and active phase were analyzed [ART-24]. As alumina is the most common support of sulfided catalysts, the influence of the properties of the alumina used as a support on the deoxygenation performance of the sulfided catalysts was investigated as well [ART-25, ART-26].



Figure 31 The comparison of support materials (alumina, titania, SBA-15, hydrotalcite and silica) loaded with NiMo; the comparison of the deoxygenation extent as a function of the residence time, W/F (h), (A and B) and yields of hydrocarbons as a function of triglycerides conversion.

The screening of sulfided NiMo catalysts over different supports including alumina, titania, silica, mesoporous silica (SBA-15) and hydrotalcite showed significant differences in their performance. As the active phase composition, preparation and pre-treatment were the same for all catalysts, these differences could be attributed to the different nature and properties of the support used. Alumina (BET=198 m²/g) and SBA-15 (BET=650 m²/g) clearly outperformed the other supports, suggesting that titania (BET=109 m²/g), silica (BET=57 m²/g) and hydrotalcite (BET=171 m²/g) were less suitable than alumina (Figure 31). The good performance of the SMA-15-supported sulfided NiMo phase, however, indicated that silica is not necessarily bad support, but large surface area to achieve better active phase dispersion is important. SBA-15 had BET surface area $650m^2/g$ while silica only 57 m²/g. It is also important to note that at a comparable conversion of triglycerides alumina supported sulfided NiMo was significantly more selective towards hydrocarbons than the SBA-15-supported catalyst (*Figure*

31C,D). This suggests that apart from the triglyceride conversion there are also differences in the deoxygenation reactions caused by the nature of the support [ART-21].

Therefore, a more detailed investigation into the origin of the observed differences was performed using alumina, mesoporous silica and titania with large surface area (). It can be clearly seen that while alumina and titania with virtually the same BET area were obtained, the BET surface area decreased due to the impregnation more significantly in case of the titania support (Table 2). The sulfur content in the catalysts after catalytic tests was used to characterize the dispersion of the active NiMo phase. It is obvious that the best dispersion was obtain for the silica-supported catalyst having the largest surface area while the worst was obtained in case of the titania supported catalyst (Table 2). The carbon content in the catalysts suggested that there was approximately the same amount of carbonaceous deposits in the catalysts (Table 2) [ART-24].

Table 2 Basic physico-chemical properties of studied catalysts

	BET (m^2/g)	S (wt.%)	C (wt.%)
NiMo/SiO ₂	343 (524) ^a	15.6	5.6
NiMo/Al ₂ O ₃	177 (198) ^a	9.8	5.9
NiMo/TiO ₂	117 (203) ^a	7.1	5.5

^a The number in parentheses gives the BET surface area of the support.

The differences in the performance of the catalysts expressed in terms of triglycerides conversion and in their deoxygenation are presented in Figure 32. It should be noted that conversion of triglycerides reflects the disappearance of triglycerides from the reaction mixture, *i.e.* it is related to formation of both hydrocarbons and oxygenated products, such as acids, alcohols and esters, whereas deoxygenation reflects the decrease in oxygen content in the products compared to its original value in the feed. In other words, if only acids were formed from triglycerides, a conversion of 100% could be reached and deoxygenation would remain 0%. The comparison of the two charts (Figure 32A and B) indicates that although similar performance of all catalysts was achieved, the alumina supported sample was the most selective towards hydrocarbons, while the silica supported catalyst showed the lowest selectivity towards hydrocarbons. Considering the different dispersions of the active phase among the catalyst, it can be concluded that sulfided NiMo on silica has intrinsically lower activity than sulfided NiMo on alumina and that the better dispersion over these two catalysts was compensated for the intrinsic lower activity since the triglyceride conversion over these two catalysts was comparable (Figure 32) [ART-24].



Figure 32 Conversion, A, and deoxygenation, B of rapeseed oil as a function of reaction temperature (260–300 °C) at 4 h–1, 3.5 MPa and 50 molH2 /molfeed.



Figure 33 Molar ratio of yields of n-octadecane to n-heptadecane (C18/C17) as a function of deoxygenation performance of the catalysts at 260–300 °C, 2–8 h–1, 3.5 MPa and 50 molH2 /molfeed.

The differences in active phase dispersion (and hence in active phase cluster size) contributed together with the different acido-basic properties of the supports to modification of the reducibility of the NiO species in calcined catalysts (determined by temperature programmed reduction) and of the

coordination of the NiO species (tetrahedral vs. octahedral coordination determined by UV-Vis measurements. These changes were then reflected not in the activity itself, but in the selectivity towards decarboxylation (formation of C_{17} hydrocarbons) and hydrodeoxygenation (formation of C_{18} hydrocarbons). This manifested itself by the variation in the C_{18}/C_{17} yield ratio over different catalysts which is presented in Figure 33. It is obvious that decarboxylation was the main reaction over the silica supported sulfided NiMo phase (ratio C_{18}/C_{17} was in the whole temperature range <1) while the hydrodeoxygenation was predominant over the titania-supported sulfided NiMo phase (ratio C_{18}/C_{17} exceeded the value of 10 at high deoxygenation levels, >80%). These results confirm the hypothesis that the catalyst performance and particularly selectivity could be fine-tuned not only by the active phase composition and pretreatment, but also by the choice of the support [ART-24].



Figure 34 (A) Dependence of the conversion of rapeseed oil on temperature in the deoxygenation of rapeseed oil at W/F 0.25 h over NiMo–alumina/meso (dashed line) and NiMo–alumina (solid line) catalysts; (B) dependence of the conversion of rapeseed oil on catalyst weight/total flow (W/F) ratio in the deoxygenation of rapeseed oil at 260°C over NiMo–alumina/meso (dashed line) and NiMo–alumina (solid line) catalysts; and (C) dependence of the selectivity of oxygenates (solid symbols) and hydrocarbons (open symbols) as a function of the conversion of rapeseed oil at 260°C over NiMo–alumina/meso (squares) and NiMo–alumina (circles) catalysts.

As significant improvement in deoxygenation of triglycerides was observed for silica supported sulfided catalysts due to the use of a high-specific-surface-area support (mesoporous SBA-15), alumina support having a large specific surface area was prepared and investigated in deoxygenation of rapeseed oil. Two commercial alumina samples (from Eurosupport Manufacturing Czechia) were used to prepare NiMo catalysts, one with BET surface area of 255 m²/g and the other with BET surface area of 520 m²/g that dropped upon impregnation to 193 and 273 m²/g, respectively. Moreover, the latter

alumina had a broader pore size distribution shifted towards larger pore radii (ca. around 10 nm instead of 5-6 nm) and significantly higher total pore volume (0.84 vs. 0.36 cm³/g) that would improve the access of the large triglyceride molecules to the active sites. This hypothesis was confirmed by the catalytic results – the conversion of rapeseed oil was significantly higher for the sulfided NiMo phase supported on the mesoporous alumina (Figure 34) [ART-25].

These conclusions were corroborated also for sulfided CoMo catalysts supported on alumina and three mesoporous support (two organized mesoporous alumina supports and aluminumcontaining aluminosilicate MCM-41). The mesoporous supports had larger specific surface area and total pore volume than the ordinary alumina and, consequently, all three mesoporous supports allowed obtaining higher conversion than when the sulfided CoMo phase was supported on an ordinary alumina support. The differences could be observed particularly at lower reaction temperatures (<280°C) since at higher temperatures complete conversion of triglycerides was obtained. In terms of selectivity towards hydrocarbons, catalysts based on organized mesoporous alumina supports were slightly better than the ordinary alumina-supported catalyst. However, the MCM-41-supported sulfided CoMo phase had the lowest selectivity to hydrocarbons that was caused by the presence of silica in the support (MCM-41 is an aluminosilicate). Above, silica was shown to be a less suitable support as silica supported sulfided catalysts had lower intrinsic deoxygenation activity despite comparable conversion of triglycerides as alumina-supported catalysts [ART-26].

3.2.2.3 Deactivation

Catalyst deactivation and its investigation forms an integral part of any catalyst study as not the activity alone, but its durability and restorableness through catalyst regeneration are essential for understanding catalyst performance and its applicability. Two specific aspects pertinent to catalyst deactivation were studied – (i) the effect of an external H_2S source and (ii) the influence of impurities present in the triglyceride feed on the catalytic activity of the sulfided catalysts and its stability [ART-27].

The importance of an external H₂S source demonstrates Figure 35. When rapeseed oil was used without adding an external H₂S source, the deoxygenation performance deteriorated significantly during 6 days on stream. However, when dimethyl disulfide (DMDS) was added to the rapeseed oil (the resulting feed contained 0.5 wt.% DMDS) the deoxygenation performance remained stable for more than ten days on stream (Figure 35). To investigate the nature of the deactivation caused by the absence of sulfur in the feed leading to decreased catalyst activity due to its desulfurization and possibly reduction, an experiment was performed where sulfur-free and sulfur containing rapeseed oil feeds were used. It is obvious that the first twelve-hours long pulse of DMDS-containing rapeseed oil restored nearly completely the deoxygenation performance, while the second pulse was not able to

38

restore the catalyst performance completely (Figure 35). This indicates that the changes in the sulfided deoxygenation catalyst caused by the absence of sulfur in the feed are reversible only partially. Therefore, the sulfur-free feeds can be deoxygenated over sulfided catalysts only when doped with an external H_2S source [ART-27].



Figure 35 Deoxygenation of refined rapeseed oil as a function of time on stream: refined rapeseed oil (diamond); refined rapeseed oil (black square) with pulses of sulfured refined rapeseed oil (black square with white dot); sulfured refined rapeseed oil (circle).



Figure 36 Changes in the yield of C17 hydrocarbons as a function of time on stream for sulfur-free and sulfur-containing rapeseed oil feeds (description of feeds same as in Figure 35).

Besides the changes in catalyst activity due to presence or absence of sulfur, modification of catalyst selectivity was observed as well (Figure 36). It is obvious that due to the presence of H_2S formed by decomposition of the added DMDS decarboxylation reaction was promoted at the expense of hydrodeoxygenation as the yield of C_{17} hydrocarbons when using sulfur-containing feed was twice as high as the yield of C_{17} hydrocarbons when using sulfur-free rapeseed oil (Figure 36). This was the case also when the pulses of sulfur-containing rapeseed oil were used, *i.e.* the change in the selectivity

was rapid and unequivocally related to the presence of H₂S. This can be attributed to the increased acidity of the catalytic system leading to further promotion of the decarboxylation reactions [ART-27].

Vegetable oils contain in addition to triglycerides also different minor components. While tocopherols that ensure the natural oxidation stability of vegetable oils should not have a significant impact on catalyst performance, inorganic elements, namely alkali and alkaline-earth metals and phosphorus present in phospholipids could be deposited on the solid catalysts and thereby modify their performance. Therefore, different rapeseed oil feeds differing in the content of these minor components were deoxygenated and their influence on catalyst performance was evaluated. The oils originated from rapeseed oil refining and their composition in terms of the concentration of the inorganic elements is presented in Table 3 where RRO stands for refined rapeseed oil, PRO for primaryrefined rapeseed oil (i.e. product of degumming that is used to remove phospholipids) and NRO for neat rapeseed oil (*i.e.* oil obtained from the seeds by pressing and extraction). The remaining two feeds were waste rapeseed oil (WRO) collected from the waste-water treatment of the plant and trap grease (TG), which was the oil collected during washing the oil tanks, etc. The acid number of the last two oils (Table 3) indicates that they comprised also free fatty acids in addition to triglycerides. It can also be seen that there is only small difference between RRO and PRO, and although having high content of inorganic elements, the amount anionic (phosphate) and cationic (alkali and alkaline-earth metal cations) species were balanced in NRO where as there was more metals than phosphorus in RRO and RRO. Besides, the WRO feed was richer in the alkali and alkaline-earth metals than in phosphorus and had a substantial concentration of both (in comparison with RRO and PRO), whereas phospholipids and, thus, phosphorus prevailed over the metals in the TG feed (Table 3) [ART-27].

Table 3 Concentration of main impurities in processed vegetable oils.

Feed	Acid number (mg/g) ^a	Ca (mg/kg)	Mg (mg/kg)	Na (mg/kg)	K (mg/kg)	P(mg/kg)	M eq. (mmol/kg) ^b	P(mmol/kg)
RRO	0.08	3.80	0.40	4.70	1.80	<0.5	0.237	< 0.016
PRO	0.82	3.50	0.45	3.30	1.50	0.71	0.197	0.023
NRO	0.70	146.00	45.90	7.20	24.60	188.00	6.003	6.070
WRO	49.02	74.10	0.91	4.50	4.00	37.90	2.035	1.224
Trap grease	61.00	6.60	2.60	4.80	5.30	310.00	0.444	10.010

^a mg/g of KOH.

^b M eq. = $\frac{\sum_{(\text{cation charge × cation concentration)/cation atomic weight}}{|anion charge|}$, where anion charge was equal to -2, as the phosphate group is bound to the glycerol backbone in phospholipids.

When looking at the catalytic deoxygenation of these feeds, some differences can be observed, but they are not as pronounced as one might expect. In particular, it is very surprising that NRO with high concentration of impurities was deoxygenated in the same way as RRO, *i.e.* the most refined rapeseed oil. This could lead to a wrong conclusion that the metals and phosphorus do not affect the catalyst performance. When removing the catalyst after the experiment, it was observed that just prior to the catalyst bed, the reactor was already partially blocked by solid deposits which were identified as phosphates. This shows that even a 144-hours long experiment is not enough to capture this effect (Figure 37). An even slightly better performance was observed when using PRO, which could not be satisfactorily explained. It resembled the catalyst performance when using analytical grade oleic acid (Figure 37), which demonstrates that the worse performance of WRO should not be attributed to its higher acidity due the presence of free fatty acids, but rather to the presence of impurities. Considering the better performance when using NRO than with WRO (Figure 37) and, at the same time, the higher content of inorganic impurities in NRO than in WRO (Table 3), the worse performance has to be attributed to the disbalance between metals and phosphorus. Based on the experience with NRO it can be inferred that when in balance, metal cations remain as a part of the phosphates and do not reach the catalyst bed. Hence, in case of WRO the alkali and alkaline-earth metals (or their cations) reached the catalyst bed and deteriorated the catalyst performance. [ART-27].



Figure 37 Deoxygenation of rapeseed oil obtained from different stage of its processing as a function of timeon-stream: (full circle) RRO – refined rapeseed oil (food grade), (square) PRO – primary refined rapeseed oil (after degumming, without bleaching and desodoration), (diamond) NRO – neat rapeseed oil (oil before degumming), (triangle) WRO – waste rapeseed oil; (open circle) oleic acid

The detrimental effect of the disbalance between alkali and alkaline-earth metals and phosphorus is best demonstrated on the example of the trap grease (TG) that was rich in phosphorus, which indicates that the decomposition of phospholipids resulted in formation of phosphoric acid rather than phosphates observed during the deoxygenation of NRO. Consequently, rapid catalyst deactivation was observed, and the catalyst lost completely its deoxygenation activity during the first 48-hours on stream when deoxygenating the TG feed. When diluted by the primary refined oil (PRO) the performance could be improved (Figure 38). The results can be explained by the formation of phosphoric acid that acted as an oligomerization catalyst and caused thus rapid coking of the catalysts by these oligomers. This was also confirmed by heating up rapeseed oil with added phosphoric acid present [ART-27].

In summary, deoxygenation of vegetable oils over sulfided catalysts requires that an external source of H₂S added to maintain the catalytic activity. Moreover, any impurities have to be removed from the feedstock prior to its deoxygenation since phosphorus will either afford phosphoric acid resulting in rapid catalyst deactivation by coking or alkali or alkaline-earth metals phosphates that will deposit in the reactor and cause eventually its plugging. The alkali and alkaline-earth metals may also deposit on the catalyst surface and deteriorate the catalytic activity as well.



Figure 38 Deoxygenation of rapeseed oil obtained from different stage of its processing as a function of timeon-stream: Trap Grease (diamond); Primary refined oil (square) and a mixture of TG and PRO (1:2) (circle).

3.2.3 Current technologies and products

3.2.3.1 Commercial technologies

Catalytic deoxygenation was commercialized by the Finnish refining company Neste Oil Oy under the name NexBTL in 2007. The two units built in their refinery in Porvoo in 2007 and 2009 (each with capacity 210 kt/y) were followed by units in Singapore and Rotterdam (each with capacity 1000 kt/y) in 2010 and 2011, respectively. It is a stand-alone two-stage technology processing different types of triglycerides containing feeds (Figure 39). The first stage consists of hydrotreating (deoxygenation) over a sulfided catalysts, while the second stage comprises isomerization (or mild hydrocracking) of the n-alkanes produced in the first stage over a Pt modified zeolite catalyst. The first stage necessitates a pre-treated feedstock, in particular removal of phospholipids and alkali and alkaline-earth metals. The second stage allows not only adjusting the cold-flow properties of the fuel, but it also provides the flexibility to produce either diesel or kerosene (jet fuel) [ART-04, ART-28].



Figure 39 Schematic flow scheme of the NexBTL process.

A similar technology has been also developed by ENI in partnership with UOP. It is called Ecofining and it is currently operated in the USA (capacity ca. 600 - 1500 kt/y) and Italy (capacity ca. 1100 kt/y). It is as well a stand-alone two-stage technology (Figure 40). Although the two stages are not specified in detail, the scheme reveals that both water and CO₂ are removed in the process, *i.e.* that both hydrodeoxygenation and decarboxylation reactions take place [ART-04, ART-28].

Most recently, two other stand-alone technologies were announced, namely Vegan by AXENS/IFP to be installed since 2018 in a Total refinery in south of France (capacity 500 kt/y), and BioVerno of the Finnish pulping company UPM that deoxygenates crude tall oil (100 kt/y), a residue of pulp making process. Unlike the other technologies based on vegetable oils and possible animal fats, the BioVerno process is the first one to use wood-processing residues, which makes it truly 2nd generation biofuels technology [ART-04].



Figure 40 Schematic flow scheme of the Ecofining process.

The stand-alone technologies presented above provide a great deal of flexibility as they facilitate production of premium fuels and even allow controlling the split between kerosene and diesel produced. This is, however, accompanied by considerable investment costs and alternative

solutions have been sought. Typically, such that would allow utilizing already existing refinery capacity via co-processing biomass- and petroleum-derived feeds [ART-01]. It should be noted that the Ecofining unit in the refinery in Venice was based on revamp of unused hydrotreating unit. There are two known examples of co-pressing technologies, although the existence of other in-house process cannot be excluded. The first one is the process called H-Bio developed by the Brazilian refining company Petrobras around 2008 based on addition of triglyceride feeds to the feed for a refinery hydrotreater. It appears, however, that the technology is not currently operated. The other example is the technology operated in the Swedish refinery Preem. The catalytic part of the technology was developed by the Danish company Haldor Topsoe. The technology co-processes light gas oil with up to 30% of refined tall oil (Figure 41). As seen in the scheme (Figure 41) the technology uses quenching after the first catalyst bed by fresh refined tall oil in order to cope with the high exothermicity of the deoxygenation reaction [ART-04].



Figure 41 Coprocessing of tall oil with light gas oil in Preem refinery.

3.2.3.2 Fuels and their properties

The products of deoxygenation of triglycerides are aromatics- and sulfur-free and can be, thus, compared to the synthetic fuels produced from synthesis gas by Fischer-Tropsch synthesis. Their n-alkane character has, however, a negative influence on the cold-flow properties of the deoxygenated vegetable oils and limits, thus their direct applicability. The main industrial technologies consist of two stages – the first being deoxygenation and the second one isomerization (or mild hydrocracking) of the deoxygenated product as discussed in section 3.2.3.1. Considering the high capital investment needed for the two-stage technology, the influence of operating parameters during deoxygenation on the

quality of the resulting fuels was investigated. Moreover, the feasibility of improving the cold-flow properties by existing commercial additives was explored as well [ART-29 - ART-32].

The hydrotreating experiments at 7 MPa and in the temperature range 260-340°C using three different NiMo/Al₂O₃ catalysts at weight-hourly space velocity of 1 h⁻¹ showed that reaction temperature of at least 310°C is needed to produce a mixture of alkanes, *i.e.* to achieve full deoxygenation. The products consisted of alkanes in the range C_{15} - C_{18} with majority being n-alkanes. Nonetheless, the increase in the reaction temperature resulted in a gradual increase in the yield of *i*-alkanes that are the desired reaction products from the cold-flow properties improvement point of view (Figure 42). One can observe significant differences among the catalysts at the final temperature of 340°C where the yield of *i*-alkanes is in the range of 10 to 40 wt.% depending on the catalyst choice [ART-32]. The associated decrease in the cetane number is not detrimental as the final cetane number remains even after isomerization well above 50.



Figure 42 Dependence of i-alkanes content (C15–C18) in the deoxygenated rapeseed oil product on reaction temperature and the catalyst used.

Considering the promising effect of increased reaction temperature, further investigations were carried out using a commercial hydrocracking catalyst for deoxygenation of sunflower oil under hydrocracking reaction conditions, *i.e.* at H₂ pressure of 18 MPa and in the temperature range of 360 – 420°C in a fixed bed reactor while maintaining weight-hourly space velocity of 0.7 h⁻¹. It was demonstrated that due to the increase in reaction temperature the content of n-alkanes decreased from ca. 65% at 360°C to ca. 20% at 420°C (Table 4). At the same time the content of i-alkanes and cycloalkanes increased from about 31% to about 74% and even aromatics were observed at the highest temperatures. Overall, the composition of the deoxygenation product obtained at 420°C resembled that of a typical petroleum-derived diesel (Table 4) although having less aromatics (5 vs. 19%) and more *i*-alkanes and cycloalkanes (74 vs. 60%) [ART-29].

Component	Reaction co	nditions	Petroleum-derived diesel		
	360 °C	380 °C	400 °C	420 °C	
<i>n</i> -alkanes < <i>n</i> -C ₁₅	2.0	4.6	9.1	9.8	11.7
n-C ₁₅	3.2	3.1	3.6	2.4	1.8
n-C ₁₆	3.5	4.0	3.7	2.1	1.5
<i>n</i> -C ₁₇	24.7	10.0	5.7	2.8	1.4
<i>n</i> -C ₁₈	26.5	13.7	5.1	1.8	1.1
$n-C_{19}$	0.5	0.5	0.4	0.3	1.0
$n - C_{20}$	0.5	0.5	0.3	0.2	0.7
$n-C_{20}$ to $n-C_{33}$	3.9	3.6	0.8	0.6	1.4
Total <i>n</i> -alkanes	64.7	40.0	28.7	19.8	20.6
Total aromatics	0.1	0.5	2.0	5.2	19.1
<i>i</i> -alkanes + cycloalkanes	31.2	50.5	63.3	73.5	60.3
Other hydrocarbons ^a	4.0	9.0	6.0	1.5	0.0

Table 4 The composition (wt.%) of the deoxygenated sunflower oil products obtained at various reaction temperatures.

Reflecting the changes in composition, the properties of the deoxygenated sunflower oil changed as well. Most importantly, there was a dramatic improvement in the cold-flow properties. The cold-filter plugging point (CFPP) and cloud point decreased from >15°C and 19°C, respectively, determined for the product obtained by deoxygenation at 360°C, to -14°C and -11°C, respectively, measured in the product of deoxygenation at 420°C. These values (at 420°C) are fully acceptable for diesel fuels as the appropriate European standard (EN590) specifies cloud point of -8°C for grade F diesel (*i.e.* "winter grade") and CFPP of -10°C and -15°C for diesel grade D and E (*i.e.* "spring and autumn grade"), respectively. It should be noted that no additives that are typically used in the final diesel formulation to achieve "winter grade diesel" specifications (CFPP of -20°C), were used. The more severe deoxygenation conditions resulted in a decrease in cetane index from 91 (product obtained at 360°C) to 65 (product obtained at 420°C) that is well above the limit value of 46 specified by EN590 [ART-29].

The good quality of the deoxygenation products obtained at 400 and 420°C made it possible to investigate their blending with an atmospheric gas oil (AGO). The blends of deoxygenated products and AGO contained 10, 30 and 50% of the deoxygenated sunflower oil and were further evaluated based on their physicochemical properties (Table 5) that were compared with the requirements of the European standard EN590. It should be noted that the base AGO was not fully refined and hence did not meet the EN590 specifications, namely its sulphur content was too high (65 ppm, Table 5). As shown in Table 5, the addition of either of the deoxygenated products had a positive influence on the properties of the resulting blend. In particular, cetane index increased and sulphur content decreased with the increasing concentration of the deoxygenated sunflower oil in the blend. Moreover, the CFPP was improved as well. It can be also seen that the final boiling point of the blends increased (Table 5), which was a consequence of using the as-produced deoxygenation product (*i.e.* without distillation) [ART-29].

Parameter	Content	of the produc	EN 590 (temperate climate)					
	0	Product obtained at 400 °C			Product obtained at 420 °C			
		10	30	50	10	30	50	
Density at 15 °C (kg m ⁻³)	825.0	823.8	821.5	819.1	823.1	819.3	815.1	820-845
Kin. viscosity at 40 °C (mm ² s ⁻¹)	2.32	2.47	2.81	3.21	2.35	2.41	2.47	2.00-4.50
Distillation								
at 250 °C recovered (vol.%)	50	44	37	30	49	45	42	<65
at 350 °C recovered (vol.%)	95	93	88	85	95	93	92	>85
95 vol.% recovered at (°C)	350	357	370	380	350	360	367	<360
Flash point in closed cup (°C)	69	68	71	72	66	60	57	>55
Cetane index	52.5	55.0	58.4	62.3	53.8	56.4	59.2	>46
Sulfur (mg kg ⁻¹)	65	59	48	37	60	49	38	<10
Nitrogen (mg kg ⁻¹)	16	15	12	9	15	13	12	-
Water (mg kg $^{-1}$)	14	17	24	30	16	19	22	<200
Low-temperature properties								
Cloud point (°C)	-8	-4	3	4	-8	-8	-8	<-8 ^a
CFPP (°C)	-12	-16	$^{-14}$	-10	-12	-14	-15	b
Pour point (°C)	-25	-12	-9	-7	-22	-19	-19	-

Table 5 The physicochemical properties of the fuel blends containing various amounts of the sunflower oil deoxygenation products at 400 and 420 °C.

As an alternative strategy to hydrocracking of neat vegetable oils (triglycerides), followed by blending of the deoxygenated product in atmospheric gas oil, hydrocracking of vacuum gas oil with vegetable oil (so-called co-processing) was investigated as well. The experiments were performed again at 400 and 420°C and 18 MPa. The feed consisted of 95% of vacuum gas oil and 5% of rapeseed oil. The products were then distilled into kerosene, atmospheric gas oil and distillation residue fractions. The former two were then blended and evaluated along with the neat gas oil fractions in accordance with EN590. It was established that high quality diesel blending fractions were obtained by hydrocracking of both neat vacuum gas oil as well as its blend with rapeseed oil. Despite the low percentage of added rapeseed oil, the middle distillate properties were improved in terms of cetane index and aromatics content, while the decrease in CFPP was still acceptable to produce grade F diesel. As a result of the selective transformation of vegetable oils into diesel-fuel-range hydrocarbons, it was estimated that the content of biomass-derived hydrocarbons in the diesel-fuel fraction from hydrocracking blends containing 5% rapeseed oil was in the range 5 to 8 wt.% depending on the severity of reaction conditions and over-cracking of the rapeseed-oil-derived alkanes into products below the diesel-fuel boiling-point range [ART-30].

Besides deoxygenation under severe reaction conditions to promote hydrocracking and isomerization reactions that improve cold flow properties of the final fuels, the influence of additives (so-called cold-flow improvers) was studied with the aim to determine if milder reaction conditions combined with the use of cold-flow improvers would allow obtaining fuels with acceptable cold flow properties. It was demonstrated that when a low-quality deoxygenated rapeseed oil (having CFPP >20°C) was blended into diesel fuel without additives (having CFPP of -12°C), the CFPP of the final blend increased from the original -12°C to -3°C for the blend containing 30% of the deoxygenated rapeseed oil (Figure 43). The main difference between the diesel and the blends containing the deoxygenated rapeseed oil was in the sensitivity towards the flow improving additives. While the addition of 100 to

500 ppm of flow improver resulted in a drop in CFPP from -12°C down to -30°C, the blends were practically insensitive to the flow improver added and only a small decrease in CFPP (2 to 5°C), if any, was observed for the blends containing 5 or 10% of the deoxygenated product (Figure 43). The blend comprising 20 or 30% of the deoxygenated product did not exhibit any decrease in CFPP even when 500 ppm of flow improver was added (Figure 43) [ART-31].



Figure 43 Cold filter plugging point (CFPP) of diesel fuels containing various amount of deoxygenated rapeseed oil (processed at 360 °C and 7 MPa) treated with flow improver Keroflux[®]3566 (BASF).

These results suggest that full upgrading involving isomerization and cyclization of the primary deoxygenation products in addition to deoxygenation is essential to produce fuel components with good cold-flow properties. They also demonstrate that it is possible to obtain high-quality diesel fuel fractions in a single upgrading step, *i.e.* that under hydrocracking reaction conditions when using a suitable hydrocracking catalyst, vegetable oils can be both deoxygenated and isomerized.

3.2.3.3 Steam cracker feeds

The products of deoxygenation are primarily n-alkanes whose carbon chain length depends on the distribution of fatty acid in the original triglycerides. The prevalence of n-alkanes reflects the nonbranched character of the original fatty acid moieties in the triglycerides. Although there are only fatty acid chains with an even number of carbon atoms in the natural triglycerides, the deoxygenated products consist of n-alkanes with even as well as odd carbon number due to the concurrent occurrence of hydrodeoxygenation and decarboxylation reactions over sulfided catalysts. The straight chain with typically 15 to 18 carbon atoms in products of deoxygenation of the most common vegetable oils (*i.e.* palm oil, rapeseed (canola) oil, sunflower oil, soybean oil) makes these products suitable to produce light olefins (ethylene and propylene) by their steam cracking. This hypothesis was verified by laboratory pyrolysis of a product of rapeseed oil hydrotreatment that consisted only of hydrocarbons where n-heptadecane and n-octadecane corresponded to 26 and 63 wt.% of this product, respectively [ART-33].

The results of laboratory pyrolysis of the deoxygenated rapeseed oil product clearly show its superiority in comparison with naphtha and distillation residue of hydrocracking products (HCVD), *i.e.* two common steam cracking feeds used to produce ethene and propene in Unipetrol. While naphtha and HCVD yielded only 19 and 31% ethene, the deoxygenated rapeseed oil yielded 43% ethene (Table 6). Besides, propene yield of 19% for deoxygenated rapeseed oil was higher than that for naphtha and HCVD (13.5 and 15.5%, respectively, Table 6). The positive influence of the deoxygenated rapeseed oil was also confirmed in co-processing experiments where mixtures containing 5, 10 or 20% of deoxygenated rapeseed oil and naphtha or HCVD were pyrolyzed (Table 6). The addition of the deoxygenated rapeseed oil improved the yields of light olefins (ethene, propene, 1-butene) and reduced the yields of branched olefins (i-butene), aromatic hydrocarbons and pyrolysis oils (Table 6) [ART-33].

Table 6 Yield of laboratory pyrolysis of mixtures of crude-oil fractions and products of rapeseed oil hydrotreatment. N – naphtha, H – distillation residue from hydrocracking, R – products of rapeseed oil hydrotreatment (composition: n-C18 – 63 wt.%, n-C17 – 26 wt.%,

Sample	R	Ν	Н	N + 5% R	N + 10% R	N + 20% R	H + 5% R	H + 10% R	H + 20% R
Methane	8.0	9.2	7.2	8.9	8.8	9.0	7.2	7.8	7.6
Ethane	3.3	2.2	1.7	2.1	2.1	2.8	1.7	2.1	2.0
Ethene	43.4	19.2	31.3	20.6	21.6	23.1	33.4	32.3	34.3
Propane	0.6	0.3	0.4	0.3	0.3	0.4	0.4	0.5	0.5
Propene	19.0	13.5	15.5	13.7	13.8	14.6	16.0	16.1	16.4
Acetylene	0.3	0.3	0.6	0.3	0.3	0.3	0.6	0.5	0.5
2-Butene	0.9	1.1	0.9	1.1	1.1	1.1	0.9	0.9	0.9
1-Butene	4.8	2.2	3.7	2.3	2.4	2.6	4.1	3.6	4.0
iso-Butene	0.2	2.2	1.7	2.1	2.0	1.8	1.5	1.5	1.3
1,3-Butadiene	8.3	6.4	8.3	6.6	6.6	6.2	8.4	8.2	8.4
Fraction C _{5–6}	4.5	10.5	6.0	10.3	10.1	9.1	5.6	6.1	5.7
Benzene	2.8	5.8	5.3	5.7	5.7	5.3	4.9	5.5	5.0
Toluene	0.9	7.7	2.8	7.4	7.2	6.5	2.5	2.9	2.6
Ethylbenzene	0.1	1.3	0.4	1.3	1.3	1.0	0.4	0.4	0.4
Xylenes	0.1	4.1	0.7	3.9	4.0	3.3	0.6	0.7	0.6
Styrene	0.3	1.5	0.7	1.4	1.4	1.3	0.7	0.8	0.7
Naphthalene	0.1	0.5	0.6	0.4	0.4	0.5	0.5	0.6	0.5
Other C ₇₋₁₂	0.8	8.7	3.4	8.6	8.2	7.4	3.0	3.3	2.9
Pyrolysis oils	1.2	2.5	7.6	2.3	2.2	3.0	6.6	5.4	4.7

3.3 Deoxygenation of other feeds

Deoxygenation of triglycerides and the relevant model compounds, such as fatty acids or esters, to produce hydrocarbons is the most studied reaction system with respect to production of oxygen-free renewable fuels. Although deoxygenation allows production of advanced biofuels going beyond the traditional 1st generation biofuels, *i.e.* biodiesel and bioethanol, the availability of triglycerides that would not compete with food production is rather limited. Hence, to progress towards sustainable advanced biofuels other, more abundant feeds have to be used. Lignocellulosic biomass, which is the most abundant source is an obvious choice. With respect to liquid biofuels by deoxygenation, two major alternatives can be envisaged – (i) deoxygenation of bio-oil, liquid organic products from biomass fast pyrolysis and (ii) deoxygenation of oxygenates produced by condensation aldehydes and ketones, *e.g.* furfural and cyclopentanone obtained from selective depolymerization and dehydration of cellulose and hemicellulose. In section 3.3.1, deoxygenation of biooil from ablative fast pyrolysis of straw or wood is discussed [ART-34 - ART-36], while deoxygenation of oxygenated products obtained by aldol condensation of furfural with acetone [ART-37 - ART-39] is described in section 3.3.2.

3.3.1 Deoxygenation of bio-oils

Deoxygenation of bio-oils is more demanding than deoxygenation of triglycerides due to the very complex composition of bio-oils and the presence of oxygen-containing compounds with very different reactivity. Bio-oil comprise, on the one hand, very reactive compounds, such as aldehydes and ketones, and, on the other hand, phenols and furanics that are hard to deoxygenate. The deoxygenation is further complicated by the high content of water in bio-oils (>20 wt.%), high acidity due to the presence of acetic acid from hemicellulose pyrolysis and other acids and relatively high viscosity.

The investigation of two commercial catalysts, sulfided NiMo and sulfided CoMo supported on alumina allowed concluding that the NiMo catalyst was more stable during bio-oil deoxygenation. As single-stage upgrading was targeted, the deoxygenation at the top of the catalytic bed was essential to stabilize the bio-oil by deoxygenating the most reactive compounds before they could undergo undesired condensation and oligomerization reactions. To improve the overall deoxygenation efficiency the strategy included setting up an increasing temperature gradient along the catalyst bed, *i.e.* having 230°C, 240°C and 350°C in the top, middle and bottom part of the catalyst bed (usually, the reactors are operated with an isothermal or adiabatic temperature profile) and diluting the feed with methanol. Mixing the feed so that in contained 4 wt.% of methanol and 96 wt.% bio-oil helped to decrease the feed viscosity and to partially reduce its acidity by allowing the formation of respective methyl esters. As a result, it was possible to deoxygenate bio-oil and even control the properties of the

products by varying the weight-hourly-space velocity (WHSV). Figure 44 shows that bio-oil deoxygenation at WHSV = 0.2h⁻¹ yielded primarily petrol-like product, but when the contact time was reduced (higher WHSV), products with higher molecular weight resembling diesel fuel were obtained.



Figure 44 SIMDIS curves of bio-oil deoxygenation products obtained at WHSV of 0.2 and 0.3 h-1 and of two reference fossil fuels – petrol and diesel.

The deoxygenation strategies may differ. Either the production of fully deoxygenated, i.e. hydrocarbon-type fuel to be used as drop-in biofuel is targeted, or the aim is to obtain partially deoxygenated product to be blended with appropriate fossil fractions in a refinery to be subsequently co-processed by the conventional hydrotreating to afford final hybrid fuel, *i.e.* fossil fuel containing bio-derived hydrocarbons. The latter strategy was used to hydrotreat straw bio-oil from ablative fast pyrolysis. The experiments using a commercial sulfided NiMo/Al₂O₃ catalyst were performed at 240-360°C and 2-8 MPa. Full miscibility with straight-run gas oil was achieved only under the most severe reaction conditions (360°C, 8 MPa). The development of the yields of the organic and aqueous phase is demonstrated in Figure 45. Although the yield of the organic products may seem low, it has to be kept in mind that the water and oxygen contents of the bio-oil feed were 23 and 39 wt.%, respectively, whereas the water and oxygen contents were <1 and ca. 4-12 wt.%, respectively, for the best products, *i.e.* those obtained at $>300^{\circ}$ C and 8 MPa. When looking at the energy balance, these products contained >85% of the energy content of the original bio-oil, the main energy losses being to the gas phase due to the demethoxylation and decarboxylation reactions. Due to the deoxygenation at 360°C and 8 MPa, the carboxylic acid number dropped down to 0 from the original value of >50 mg KOH / g and the lower heating value increased to nearly 40 MJ/kg from the original value of 21.5 MJ/kg [ART-34].



Figure 45 Yields of organic and aqueous phases under different reaction temperatures at pressures 2; 4 and 8 MPa.

Due to the complex composition of bio-oils as well as products of their deoxygenation, it is impossible to describe the changes during deoxygenation by means of individual reactants, intermediates and products. It was shown that even a detailed GC-MS analysis does not allow detecting all oxygenates, *e.g.* phenols, acids or aldehydes and ketones, and alternative titration methods have to be used as well to assess the composition of bio-oils and their deoxygenated products. A comparison of the two strategies revealed that in case of acids about 70% of total acids (determined by titration to measure carboxylic acid number) could be detected by GC-MS method, while in case of phenols only about 30-40% of phenols could be determined by GC-MS. Thus, combination of both classical titration methods with detailed GC-MS analysis is a valuable approach to gain more insights into the deoxygenation of bio-oils. Moreover, these traditional methods allow quantifying oxygenates also in the aqueous phase after deoxygenation. Consequently, it was seen that at milder conditions deoxygenation extent could be overestimated when using only organic phase analyses as particularly acetic acid and some phenols were extracted into the aqueous phase rather than deoxygenated [ART-36].

3.3.2 Deoxygenation of aldol condensation products

An alternative strategy to bio-oil upgrading to produce advanced biofuels is to deoxygenate the products of aldol condensation. As can be seen in section 2, the products of aldol condensation of furfural with acetone or cyclohexanone comprise several different functional groups – namely a furanic ring, a carbonyl group, a double bond and, in some cases, also a hydroxyl group. Each of these groups require different optimum reaction conditions and catalyst functionality or functionalities for their efficient upgrading, *i.e.* hydrogenation and/or deoxygenation.

To understand the reaction pathways, various supported Pt catalysts were investigated and based on the identified reaction products and their distribution, a reaction network was proposed (Figure 46). It was seen that the aliphatic double bond hydrogenation was rather facile, but further hydrogenation and particularly opening of the furanic ring were limited. Among the tested catalysts, the best hydrogenation performance was found for Pt/TiO₂, but the yield of the ring-opening products that would afford aliphatic alcohols and subsequently even hydrocarbons was limited. The extent of the ring-opening reactions could be, however, improved when using acidic supports such as zeolite Beta, mesoporous molecular sieve Al-SBA-15 or WO₃-ZrO₂. Since the feed was directly the product of aldol condensation, it contained the excess acetone as well as other compounds than FAc, which made the analysis too complex as these compounds took part in various side reactions. The most prominent wad the formation of oligomerization products over the acid supports. Thus, a well-balanced catalyst composition in terms of the hydrogenation function needed for saturation of double bonds and acid function crucial for opening of the (hydrogenated) furanic ring and dehydration of alcohols was found to be necessary. To prove this concept, a two-stage experiment was performed where the aldol condensation products was first hydrogenated over Pt/TiO₂ and then further treated over the mildly acidic Pt/Al-SBA-15. As a result, the yield of the aliphatic C8 products (M and N in Figure 46) was increased from 3.7% and 5.3 for Pt/TiO₂ and Pt/Al-SBA-15, respectively, to ca. 23% over the dual catalyst system [ART-37]. The results indicated that total deoxygenation to octane was demanding, but they also suggested that formation of linear alcohols would be more viable. Particularly the production of diols from renewable resources could be of interest from the green and sustainable chemistry point of view.



Figure 46 Proposed reaction scheme for the hydrodeoxygenation of 4-(2-furyl)-3-buten-2-one (F–Ac) into octane.

The initial experiment also showed that excess acetone was prone to reacting under the selected reaction conditions (200°C, 5 MPa H₂). Therefore, the influence of solvent was studied in more detailed using the Pt/TiO₂ catalyst. In this study, pure FAc was used as a feedstock to eliminate the issues with too many side reactions faced when real aldol condensation product (containing several products and the excess acetone was used). It was established that the nature of the solvent indeed played an important role. There were differences between protic and aprotic solvents and within both group of solvents (Figure 47). In case of the protic solvents (a series of aliphatic alcohols C1 to C5), it was found that initial hydrogenation rate correlated well with the dielectric constant of the solvents – the lower the dielectric constant the higher the initial hydrogenation rate. In case of the aprotic solvents, it was seen that the initial hydrogenation rate was higher for solvents with lower desorption energy of the solvent (determined in TPD experiments) and its donor nucleophilic number. The significantly better performance in acetone than in tetrahydrofuran and dimethylformamide could be caused (in addition to its low desorption energy) also by its transformation to 2-propanol under the reaction conditions that would then act as a protic solvent and a hydrogen donor [ART-38].



Figure 47 Solvent effects on the conversion of 4-(2-furyl)-3-buten-2-one over Pt/TiO2catalyst; (a) protic and (b) aprotic solvents.

Furthermore, the applicability of the mesoporous SBA-15 was investigated further in a study that involved different supported metals both noble (Pt, Pd and Ru) and non-noble (Ni and Cu). Over the Si-SBA-15, *i.e.* a neutral support, a bimetallic Ni-Cu catalyst was found to outperform not only Ni-SBA-15 and Cu-SBA-15, but also the supported noble metal catalysts. It afforded the highest yield of the fully hydrogenated products – 4-(2-tetrahydrofuryl)-butan-2-ol (63%) and even 2-butyl furan (16%), *i.e.* a dehydration product. The only catalyst gave similar products yields was Ru/SBA-15 with 57 and 6%, respectively, of the two fully hydrogenated products. From the sustainability point of view, Ni-Cu catalyst is, however, a better choice. Moreover, having the formation of C8 diols as potentially

important intermediates in mind, Ni-Cu/Al-SBA-15 was used to introduce also mild acidity and make the catalyst bifunctional. Consequently, C8 diols were produced with a yield of ca. 20% [ART-39].

3.4 Summary

Deoxygenation is an indispensable tool to transform biomass-derived oxygenates into high quality biofuels that can be used as blending components modern transportation fuels. It comprises four key reactions – hydrodeoxygenation, decarboxylation, decarbonylation and dehydration. The extent of the individual reactions is governed by the feedstock composition, on the one hand, and catalyst and reaction condition choice, on the other hand. In the most thoroughly studied and understood deoxygenation of triglycerides, the choice of a catalyst and, to a lesser extent, of reaction conditions allows controlling the reaction pathway (hydrodeoxygenation *vs.* decarboxylation) and, thereby, the resulting hydrogen consumption, which is a crucial aspect from the economics and sustainability point of view. Nonetheless, deoxygenation of triglycerides alone does not guarantee high quality of fuels and the resulting linear hydrocarbons need to undergo isomerization or mild hydrocracking to introduce branching in the hydrocarbon chains that is essential to improve the cold-flow properties of the final product.

While deoxygenation of triglycerides (and related feeds) has been already commercialized due to the low complexity of these feedstocks, deoxygenation of more complex raw materials comprising particularly bio-oils produced by fast pyrolysis of lignocellulosic biomass and oxygenates obtained by aldol condensation of aldehydes and ketones continues to be a challenge. The main reason is the very complex composition of these feeds where different oxygen-containing functional groups having different reactivity are present. Consequently, catalysts need to be optimized to be active in conversion (deoxygenation) of all types of carbon-oxygen bonds while suppressing catalyst deactivation due to coking. The research performed on deoxygenation of aldol condensation products evidences that it is a challenging task and multifunctional catalysts need to be designed. Moreover, the adverse inhibiting effects of *e.g.* water or alkali and alkaline-earth metals present in lignocellulosic biomass-derived bio-oils have to be considered as well together with the competitive adsorption of different reactants in these very complex feedstocks.

4 Conclusions and outlook

Our current highly efficient use of petroleum to produce fuels as well as petrochemicals has been enabled by using catalytic technologies that allow meeting our demand on petroleum-derived products regardless the petroleum quality. Nonetheless, the actual challenges related to the everincreasing concentration of carbon-dioxide in the atmosphere necessitate a raw material change from fossil-based feeds towards renewable ones, such as biomass. This habilitation dissertation summarizes the research work of the candidate over the past 15 years in the field heterogeneous catalysis applied to biomass upgrading into advanced biofuels. The research results obtained up to now clearly show that although it is a challenging task a significant progress was achieved in the past decades and that with the help of novel selective upgrading strategies sustainable biomass utilization is possible.

It has been demonstrated that it is possible to convert in a controlled (and tunable) way biomassderived oxygenates, specifically aldehydes and ketones, into attractive intermediates of advanced biofuels. By focusing on the use of heterogenous catalysts, it has been shown that hydrotalcites-based basic catalysts are good candidates with a high catalytic activity and selectivity. The conducted research has allowed identifying challenges that need to be tackled in order to get closer to an industrial implementation of the advanced biofuels. They key challenges include fine-tuning the composition of the catalysts as well as optimizing their pre-treatment / activation procedures to improve their stability and tolerance to deactivation. This encompasses deactivation due to catalyst structural changes, due to side-reactions, such as Cannizzaro reaction, as well as due to traceimpurities in the raw materials. It can be inferred that tailor-made multifunctional systems will have to be developed.

It has been also clearly shown that deoxygenation may take-over the role of the refinery working horse that is currently held by hydrodesulfurization. Now, the deoxygenation technology of triglycerides is already a commercial process thanks to the demand for biofuels fully compatible with the current fuels and engine technologies, and the low complexity of triglyceride feeds. It has been demonstrated that the technology can be further developed and that it can be flexible in terms of the product selectivity. Nevertheless, non-food and waste triglycerides are not an abundant feedstock and hence do not provide the ultimate solution for meeting the demand for advanced biofuels. Therefore, other feedstocks derived particularly from lignocellulosic biomass or algae need to be considered. Here, bio-oils from fast pyrolysis of biomass and oxygenates obtained by aldol condensation of short-chain aldehydes and ketones have been investigated. The challenge is once again the design and development of robust catalysts that would tolerate the demanding upgrading conditions and wide

variety of compounds with very different reactivities present in bio-oils. It has been shown that it is possible to design catalysts even for a single stage upgrading although the deactivation rates are still prohibitively high. A similar situation is faced also with aldol condensation products as the intermediate oxygenates entail several different functionalities that demand specific upgrading functionalities of the catalysts. Thus, multifunctional catalyst development constitutes the key future challenge. In an ideal case, integrating aldol condensation with the consecutive deoxygenation could be the so much needed breakthrough enabling a competitive production of advanced biofuels from lignocellulosic biomass.

In summary, biomass is a feedstock of the future. To use its great potential to the maximum extent, future research has to focus on all aspects along the complete value chain. In addition to the conversion aspects discussed here, where heterogeneous catalysis is going to play a pivotal role, production, harvesting and primary fractionation and depolymerization of biomass have to be further developed while considering the complete lifecycle to make the future technologies truly sustainable. Although the personal transportation sector will be most-likely gradually electrified, it will not be the case of heavy-duty transport nor aviation. Hence, the advanced biofuels should be developed for these applications. It is to be expected that developments of upgrading strategies to produce advanced biofuels will give rise also to new routes to important petrochemicals making thus our chemical industry more sustainable.

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