



Transformation of Sorbitol to Biofuels by Heterogeneous Catalysis: Chemical and Industrial Considerations

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PART 2

Second and Third Generation Biofuels: Towards Sustainability and Competitiveness

Deuxième et troisième génération de biocarburants : développement durable et compétitivité

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 68 (2013), No. 5, pp. 789-946

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Transformation of Sorbitol to Biofuels by Heterogeneous Catalysis: Chemical and Industrial Considerations

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Résumé — Transformation du sorbitol en biocarburants par catalyse hétérogène : considérations chimiques et industrielles — La raréfaction du pétrole et l'augmentation conjointe de la demande en carburants ont conduit à la recherche de carburants alternatifs. Dans un premier temps, la valorisation de ressources agricoles alimentaires pour la production d'éthanol et de biodiesel a permis de développer les biocarburants de première génération. Aujourd'hui les travaux de recherche s'orientent vers l'utilisation de biomasse lignocellulosique comme source de carbone renouvelable (biocarburants de deuxième génération). Alors que la filière de l'éthanol cellulosique est en plein développement, une nouvelle voie consistant à transformer des sucres et polyols d'origine lignocellulosique en alcanes légers par catalyse hétérogène bifonctionnelle en phase aqueuse a été récemment décrite.

Ce procédé s'effectue à basse température et pression modérée ($T < 300\text{ °C}$ et $P < 50\text{ bar}$). Il nécessite, d'une part, la formation d'hydrogène par reformage catalytique de carbohydrates en phase aqueuse et, d'autre part, la déshydratation/hydrogénation de polyols conduisant à un alcane par ruptures sélectives des liaisons C-O. Un défi lié à cette thématique réside dans le développement de systèmes catalytiques multifonctionnels stables, actifs et sélectifs dans les conditions de la réaction de transformation.

L'objectif de l'article est de présenter les réactions mises en jeu, les systèmes catalytiques décrits dans la littérature pour ce type de transformation ainsi que des exemples d'applications industrielles.

Abstract — Transformation of Sorbitol to Biofuels by Heterogeneous Catalysis: Chemical and Industrial Considerations — Decreasing oil supplies and increasing energy demand provide incentives to find alternative fuels. First, the valorisation of edible crops for ethanol and biodiesel production led to first generation biofuels. Nowadays, research is focused on lignocellulosic biomass as a source of renewable carbon (second generation biofuels). Whereas the cellulosic ethanol production is in progress, a new way consisting of the transformation of ex-lignocellulose sugars and polyols towards light hydrocarbons by heterogeneous catalysis in aqueous phase has been recently described.

This process is performed under mild conditions ($T < 300\text{ °C}$ and $P < 50\text{ bar}$). It requires on one hand hydrogen formation by catalytic reforming of carbohydrates in aqueous phase and on the other hand, the dehydration/hydrogenation of polyols leading to alkanes by selective C-O bond cleavages. The challenge here is to conceive multifunctional catalytic systems that are stable, active and selective under the reaction conditions.

The aim of this article is to present the involved reactions, the catalytic systems described in literature for that kind of transformation and examples of industrial applications.

INTRODUCTION

The scientific community currently acknowledges increasing oil prices and decreasing oil supplies as well as global warming caused by GreenHouse Gases (GHG) emissions produced by fossil fuels. Besides, global energy demands continue to rise sharply: according to the International Energy Agency (IEA), they should increase by 50% between now and 2030 and global oil demand should increase by 40% over the same period. Research to find sustainable alternatives to fossil energies should thus be a major global concern. There are nonetheless few alternatives in the area of fuels. Efforts have been focused on the production of new fuels from biomass, called “biofuels”.

Biomass is a renewable resource at a human timescale, unlike oil, coal and gas which are formed over millions of years. Its advantages include good distribution over the surface of the globe and significant potential for growth. Biomass can thus constitute a source of energy that would limit GHG emissions as the carbon emitted into the atmosphere upon use is then trapped by photosynthesis during plant growth. It is also the only renewable source of carbon [1].

We can currently distinguish between first-generation biofuels derived from plant storage organs, which are already present on the market, and second-generation biofuels produced from the entire plant (thus including the lignocellulosic part) that are under development (definition from ADEME, the French Agency for Environment and Energy Control). In this article, chemistry and production of second-generation biofuels will be examined.

Research on biofuels has over recent years turned towards lignocellulose. New processes, often involving green chemistry and the emergence of biorefineries, have appeared [2-5]. Lignocellulose is derived from agricultural residues (straw, bagasse, etc.), forestry waste, industrial by-products (from the paper industry, in particular) or even high annual-yield dedicated crops such as *Miscanthus* (a herbaceous plant) or Short Rotation Coppices (SRC, meaning small woods regularly cut over for regrowth) [6]. It has several advantages: it could be available at low cost; it could bypass the food/energy conflict for farms and can be produced nearly anywhere, thus allowing the creation of biorefineries supplied with local resources. However, lignocellulose-derived compounds have much higher oxygen levels than the compounds found in crude oil: the mass oxygen content of lignocellulose is close to 50% while that of oil is less than 5%.

The term lignocellulose actually designates three components constituting plant cell walls: lignin, hemicellulose and cellulose. Lignin is a macromolecule that contains several aromatic and phenol groups; cellulose and hemicellulose are 5- or 6-carbon sugar polymers. These three components are present in variable proportions in plants. The polysaccharides, cellulose and hemicellulose, constitute around 75% of lignocellulosic biomass [7, 8] and can be partially extracted from the other components

of lignocellulose using suitable pre-treatments. The sugars making up these polymers, such as glucose (C6) or xylose (C5), are then obtained by hydrolysis performed enzymatically or by acid catalysis. They can then be hydrogenated to produce the corresponding reduced sugars, sorbitol (C₆H₁₄O₆) or xylitol (C₅H₁₂O₅). This hydrogenation step can be performed by heterogeneous catalysis and sometimes is also combined with the hydrolysis step of the cellulose [9-12]. Sorbitol was selected as one of the 12 biomass-derived molecules that can be used for the production of fuels and/or chemicals, according to the US Department of Energy [13, 14].

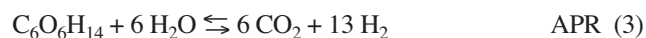
The transformation of sorbitol into hydrocarbons that can be used in the gasoline pool is currently considered to be a promising technology for the production of second-generation biofuels [15]. This review presents the current state of knowledge on the transformation of lignocellulosic polyols by heterogeneous catalysis into compounds to be used as raw materials for the fuel or chemical industries, with results on the reactivity of sorbitol, the most representative model molecule of polyols and the mechanisms proposed in the literature. We also examine the catalysts used for this transformation. The last part of this review examines the lignocellulosic biomass transformation processes used in industry, based on the polyols reactivity.

1 AQUEOUS PHASE REFORMING AND AQUEOUS PHASE DEHYDRATION/HYDROGENATION OF SORBITOL

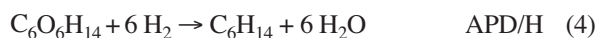
Sorbitol has long been considered as a reagent with high potential: in 1933, Zartman and Adkins [16] attempted to convert various sugars and polyols (including mannitol and sorbitol) dissolved in ethanol on a CuCrO_x catalyst in the presence of hydrogen and observed the formation of water, diols and triols (hexanetriol in particular). They also found that the reaction is hydrogen consuming [16]. In 1958, Clark proposed the synthesis of glycerol from lignocellulose-derived sorbitol using a nickel-based catalyst in a basic environment. He observed the formation of shorter polyols (glycerol, ethylene glycol, etc.) [17]. Between 1986 and 1996, Montassier, Giraud *et al.* studied the transformation of sorbitol and glycerol in an aqueous phase on supported metal catalysts, under hydrogen pressure [19]. This work helped to elucidate most of the mechanisms presented in Section 2. Since the year 2000, the transformation of polyols in aqueous phase has been focused on the production of hydrogen and alkanes, using APP (Aqueous Phase Processes): Aqueous Phase Reforming (APR) and Aqueous Phase Dehydration/Hydrogenation (APD/H) [21].

Cortright *et al.* [22] first studied the transformation of sugars and polyols into hydrogen in aqueous phase at low temperature (220-260°C), using a heterogeneous catalyst. They obtained a mixture of hydrogen, CO₂ and gaseous alkanes, as well as products in aqueous phase. They named this

process for the hydrogen production from biomass Aqueous Phase Reforming (APR) [22]. In theory, APR consists of two steps: Equation (1) corresponds to the reforming of sorbitol into hydrogen and CO. The CO produced is transformed into CO₂ and hydrogen by the Water Gas Shift (WGS) reaction, as shown by Equation (2). These two reactions are catalysed by a supported metal catalyst such as Pt/alumina:



In 2004, APR of sorbitol was oriented to the production of alkanes using a bifunctional catalyst combining a metal phase (platinum) on an acid support (silica-alumina) [23]. The support acidity then leads to dehydration reactions that eliminate oxygen in the form of H₂O; the resulting double bonds are then saturated by hydrogenation. The authors called this method for the transformation of polyols into alkanes Aqueous Phase Dehydration/Hydrogenation (APD/H) [24]. Equation (4) represents the APD/H reaction with hydrogen supply.



Huber and Dumesic [21] have considered the possibility to combine the APR reaction with the APD/H hydrogenation step in a one-pot process without any H₂ supply. It is theoretically possible to produce 1 mol of hexane from 1.5 mol of sorbitol through a series of dehydration/hydrogenation cycles, as shown by Equation (5) [21].



The APD/H could thus potentially constitute a biorefinery process for the synthesis of liquid hydrocarbons from ligno-cellulose-derived polyols in a single step. Though it was only very recently discovered, the APD/H of sorbitol and glycerol has been the subject of great interest on the part of the scientific community and leads to many publications since 2004. We should note that these works were focused more often on glycerol than sorbitol by a factor of four.

2 MECHANISMS OF THE SORBITOL TRANSFORMATION BY HETEROGENEOUS CATALYSIS

Very few publications on the transformation of sorbitol by heterogeneous catalysis concern the reaction mechanisms. The hypotheses regarding the reactivity of sorbitol are most often based on mechanistic studies performed on glycerol. Several mechanisms have been identified to explain the transformation of glycerol into diols and are presented in

reactions that lead to the cleavage of C-O or C-C bonds (propanediols and ethanediol, commonly called glycols). These transformations are generally carried out in an aqueous environment, at low temperatures (120-150°C), most often in a closed batch-type reactor with hydrogen supply.

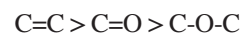
2.1 Mechanisms of the C-O Bonds Cleavage

Study of the glycerol reactivity has led to several suggested mechanisms for the cleavage of C-O bonds: dehydrogenation-dehydration-hydrogenation of an alcohol group, dehydration-hydrogenation of an alcohol group, direct hydrogenolysis of an alcohol group. These mechanisms have been extended to larger polyols (4 to 6 carbons). From four carbons and higher, the cyclodehydration mechanism also acts to cleave C-O bonds.

2.1.1 Dehydrogenation-Dehydration-Hydrogenation of an Alcohol Group

In 1989, Montassier *et al.* [18, 25] proposed the first mechanism for the sorbitol transformation in aqueous phase on a Raney Cu catalyst, then applied to a Ru/C catalyst and then Ru/C modified by sulphur, in the presence of hydrogen. This work showed that a first dehydrogenation of glycerol leads to glyceraldehyde, followed by a dehydration catalysed by an electrophilic site (M^{d+} metal site or acid site) (*Fig. 1*, mechanism E1). This mechanism was adopted in particular by Maris and Davis [26] who applied it to the Pt/C and Ru/C catalysts in a basic environment. The dehydration is thus catalysed by OH⁻ species by an E2 mechanism [26]. Huber and Dumesic [21] propose a similar mechanism for the reactivity of ethylene glycol on Pt/Al₂O₃. The hypothesis of an initial dehydrogenation has mainly been proposed under basic conditions [27, 28]. In that case, dehydrogenation allows the creation of a double bond that stabilises the dehydration product by a conjugated π system [29].

The unsaturated species produced by dehydration are then hydrogenated. The hydrogenation reaction takes place on the sites of the metal surface able to dissociate hydrogen. Based on the analysis of the sorbitol transformation products on Pt/SiO₂-Al₂O₃ [30], the relative rate of hydrogenation is as follows:



This order of reactivity has been confirmed by several studies on selective hydrogenations [31]. The bonds that are most difficult to hydrogenate are thus the ether bonds [30]. Hydrogenation is sometimes considered as a transfer of hydride that takes place on the metal surface. The protic aqueous environment promotes the transfer of protons (during the dehydration reaction) or hydride (during the hydrogenation reaction) [32, 33]. The hydrogen can be supplied externally or be produced *in situ* by APR: this mechanism has been identified in the case of Pt/NaY [34].

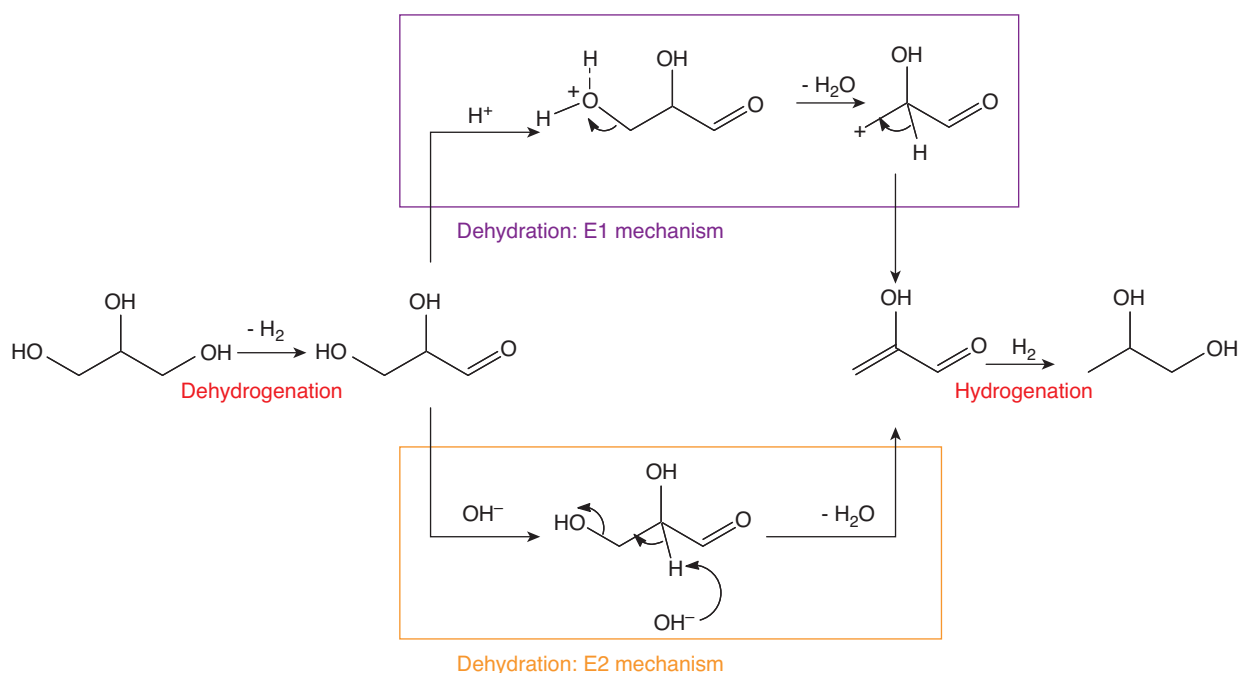


Figure 1

Mechanism of dehydrogenation-dehydration-hydrogenation of glycerol (from Montassier *et al.* [18, 25]).

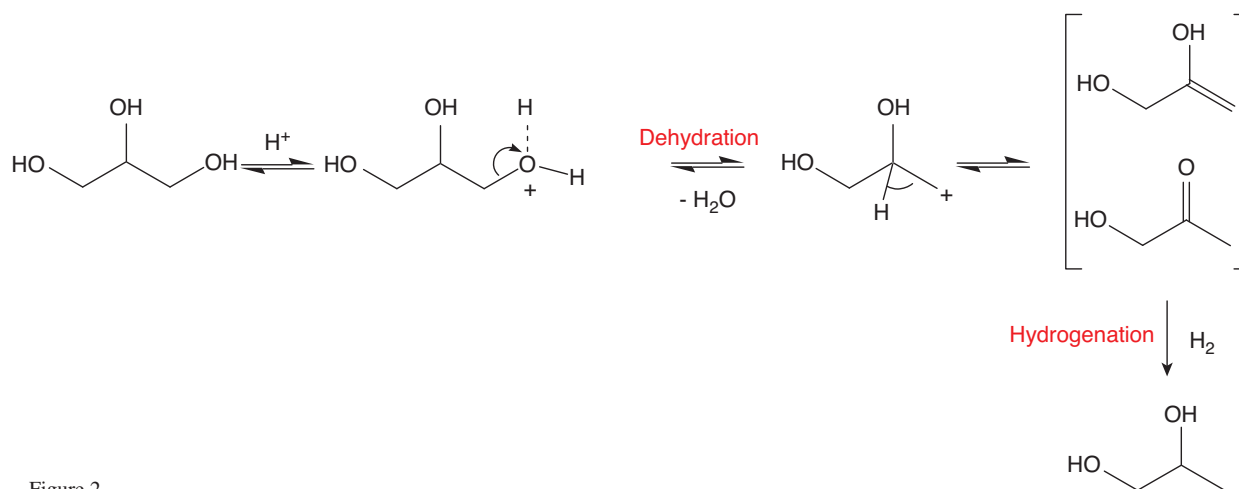


Figure 2

Dehydration/hydrogenation of glycerol into propanediol.

2.1.2 Dehydration-Hydrogenation of an Alcohol Group

It has been observed that, for a Ru/C catalyst + acid resin (Amberlyst), the increase in hydrogen pressure leads to an increase in the rate of C-O bond cleavage [35], which contradicts the hypothesis of a reversible initial dehydrogenation step. This is why, in most studies of bifunctional precious metal/acid solid catalytic systems, the C-O cleavage mechanism proposed consists of a dehydration step by an E1

mechanism followed by hydrogenation without an initial dehydrogenation step (Fig. 2). This sequence of steps is sometimes contracted with the name hydrodeoxygenation.

To obtain alkanes from long-chain polyols, the dehydration/hydrogenation mechanism must be repeated several times without undesired C-C bond cleavage. Under experimental conditions, the formation of several intermediate products has been observed: alcohols, ketones, alkenes.

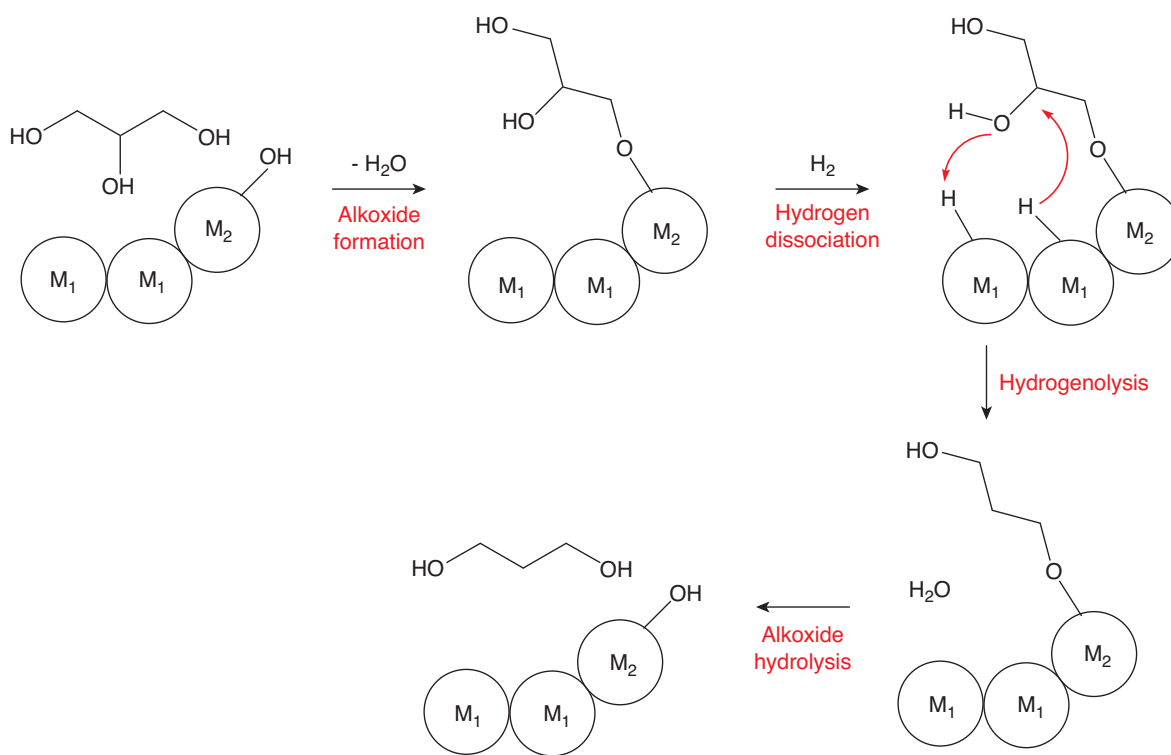


Figure 3

Direct hydrogenolysis of glycerol over a bimetallic particle composed of a noble metal (M1) and a metallic oxide (M2). From Nakagawa *et al.* [27].

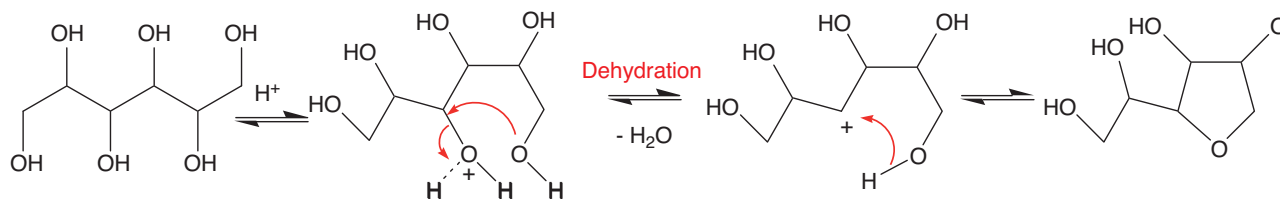


Figure 4

Mechanism of sorbitol cyclodehydration (adapted from Montassier *et al.* [39]).

For the dehydration-hydrogenation mechanism, the position of the C-O bond cleavage depends on the stability of the carbocation intermediate formed during the dehydration. Secondary carbocations are known to be more stable than primary carbocations; as a result, an alcohol at the end of a chain is more difficult to eliminate than one in the middle of a chain. For example, the dehydration of 2-butanol is more rapid than that of 1-butanol [30]. The carbocation can also be stabilised by a conjugated π system if there is an adjacent double bond or by the keto-enol tautomerism in the case of dehydration of the neighbouring diols [29]. The rate of the

dehydration reaction is thought to be correlated with the strength of the C-O bond and thus to decrease as the number of alcohol groups in the molecule decreases [36]. So, during successive dehydrations of polyols, mono-alcohols are the most difficult alcohols to dehydrate as no adjacent group stabilises the intermediate carbocation.

2.1.3 Direct Hydrogenolysis of an Alcohol Group

The term hydrogenolysis is often used abusively to designate the dehydration-hydrogenation reaction. Hydrogenolysis,

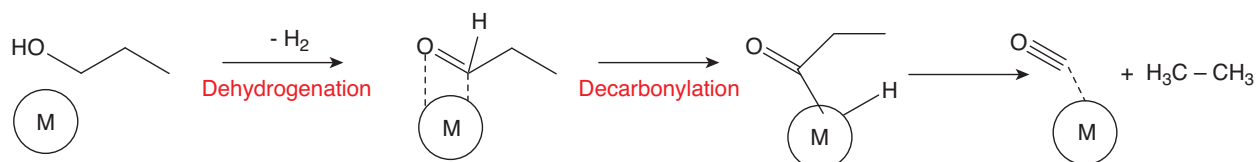


Figure 5

Dehydrogenation/decarbonylation of 1-propanol into ethane.

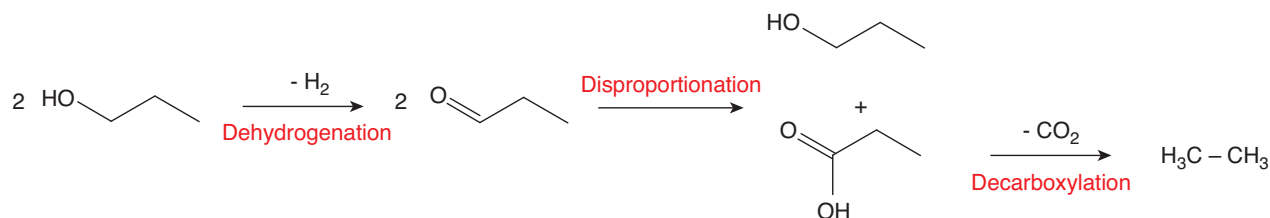


Figure 6

Disproportionation/decarboxylation of 1-propanol into ethane in basic medium (adapted from Wawretz *et al.* [44]).

defined as hydrogenation of a covalent bond leading to its cleavage, is a special case that was identified in particular in the case of rhodium-rhenium and iridium-rhenium catalysts in the presence of hydrogen [33]. The active site would thus be located at the edge of a rhenium cluster deposited on a precious metal particle (rhodium or iridium). The rhenium is thought to adsorb the polyol in the form of an alkoxide, thus allowing cleavage of the adjacent C-O bond by the neighbouring metal site (*Fig. 3*) [27].

2.1.4 Cyclodehydration of an Alcohol Group

If the number of atoms in the carbon chain allows the formation of a thermodynamically-stable heterocycle, as for polyols with four or more carbons, intramolecular dehydration is possible (*Fig. 4*) [20, 37]. Isosorbide is synthesised from sorbitol on bimetallic copper-based catalysts by this type of mechanism [20, 38, 39].

In the case of cyclodehydration, the C-O bond cleavage location depends on the stability of the heterocycle formed: furan derivatives with four carbons and one oxygen are more stable than pyran derivatives that have five carbons and one oxygen. Cycles with less than four carbons are not favoured.

2.2 Mechanisms of the C-C Bonds Cleavage

2.2.1 Dehydrogenation of an Alcohol Group

The initial dehydrogenation step remains a point of controversy in the case of C-O cleavage reactions but is unanimously accepted for C-C cleavage reactions. It is thought to take

place on the metal surface; the primary alcohols are dehydrogenated into aldehydes, the secondary alcohols into ketones, with each dehydrogenation reaction producing one mole of hydrogen [40]. These carbonyl intermediates are adsorbed onto the metal surface [25, 26]. The aldehydes are not detected in the reaction products, though a theoretical study of the transformation of ethanol on platinum confirms that they exist [41]. Adsorbed aldehyde and ketone intermediates have also been observed *in situ* by IR spectroscopy during the conversion of glycerol on a platinum-based catalyst, thus validating the hypothesis of dehydrogenation/adsorption of polyols [42].

A recent DFT study also demonstrated that the dehydrogenation of a C-H bond is theoretically possible in the case of glycerol [43].

2.2.2 Decarbonylation of an Aldehyde or Ketone Group

The decarbonylation reaction corresponds to the C-C bond cleavage of aldehydes adsorbed on the metal surface, thus leading to the formation of adsorbed CO. The decarbonylation leads to the loss of a terminal carbon atom from a polyol, which is first adsorbed in the form of CO and then desorbed in the form of CO₂ by the Water Gas Shift reaction (*Fig. 5*).

2.2.3 Dismutation/Decarboxylation of an Aldehyde Group

Alternatively, Wawretz *et al.* [44] proposed a mechanism for the C-C bond cleavage of aldehydes by a dismutation reaction followed by a decarboxylation reaction (see *Fig. 6*). They observed the formation of propionic acid during the conversion of 1-propanol. Cortright *et al.* [22] had already

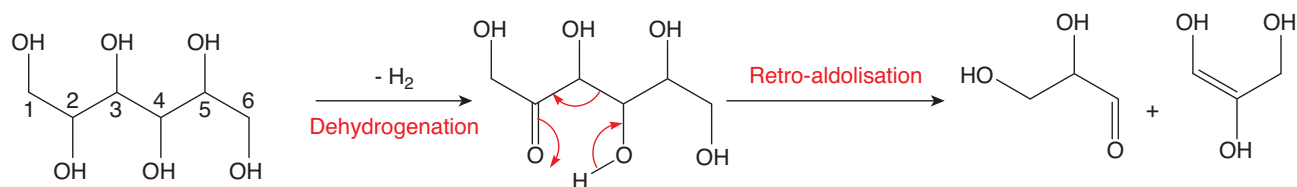


Figure 7

Retro-aldol condensation of sorbitol (adapted from Li *et al.* [30]).

mentioned the formation of carboxylic acids during the conversion of sorbitol. Analysis of the products from the APR reaction on sorbitol and 1-propanol on Pt/Al₂O₃ also supports this mechanism [36, 45].

The dismutation is carried out by a Cannizzaro reaction (basic catalysis) [18, 46] or a Tischenko reaction (Lewis acid catalysis). The carboxylic acid formed then undergoes decarboxylation and produces a CO₂ molecule. This hypothesis of decarboxylation is corroborated by the fact that, in the case of the conversion of glycerol, the partial CO₂ pressure is above the value predicted by the balance of the WGS reaction, which means that CO₂ is formed in excess by another route [44].

Based on the results of Wawrzetz *et al.* [44], decarbonylation and dismutation/decarboxylation are two mechanisms that take place simultaneously.

2.2.4 Retro-Aldol Reaction

Cleavage of the C-C bond by retro-aldol reaction takes place on highly oxygenated molecules such as sorbitol [25, 26]. The retro-aldol mechanism can occur on metallic sites under basic conditions, according to the study of Wang *et al.* [47] on 1,3-diols model compounds. It involves the carbon adjacent to the carbonyl formed by a dehydrogenation reaction [47]. The sorbitol is first dehydrogenated, probably on a metal site, and forms a ketone group in position 2 or 3; that ketone is involved in the retro-aldol reaction mechanism that leads to the formation of an aldol and an aldehyde (Fig. 7). These two products are then hydrogenated on the metal surface. The aldehydes are not detected in the reaction environment. Their hydrogenation is thus very rapid.

2.3 Sorbitol reactivity: Contribution of the Different Mechanisms

Only Li and Huber [30] have proposed a general reaction scheme for sorbitol conversion into alkanes on a Pt/silica-alumina catalyst, with details on the formation of partially oxygenated reaction intermediates (Fig. 8). Their scheme is con-

stituted of four key reactions that control the polyol transformation processes in aqueous phase [30], based on some of the mechanisms described above. Most of these hypotheses are built using reactions fed with hydrogen. The four main reactions are consecutive and/or parallel, which gives many potential intermediate products during the conversion of sorbitol. Li and Huber [30] present around thirty compounds in their reaction scheme. In particular, the selective conversion of sorbitol into hexane involves two dehydration reactions that give 1,4-anhydrosorbitol followed by isosorbide, then four dehydration-hydrogenation reactions that successively give 1,2,6-hexanetriol, followed by 1,2-hexanediol, 1(or 2)-hexanol and then hexane, as shown in Figure 8.

The sorbitol can also undergo a retro-aldol reaction that leads to the formation of glycerol (Fig. 8, blue arrows). Lastly, all oxygenated intermediates containing at least one terminal alcohol could react by a decarbonylation or decarboxylation reaction (Fig. 8, green arrows) and form shorter compounds as well as CO or CO₂ (not shown in Fig. 8). It is important to note that the authors assimilated the dehydration and hydrogenation reactions to one single step of the mechanism in the case of an alkene or carbonyl intermediate based on the hypothesis that hydrogenation of these compounds is rapid. In the same way, the C-O-C rupture and the subsequent hydrogenation are noted as simple hydrogenation reaction, whereas hydrogenolysis would be more correct. The number of potential intermediate products thus largely exceeds the 32 shown in Figure 8.

The reactivity of polyols by heterogeneous catalysis is thus complex and still poorly understood at this time. There are few mechanism studies and those that exist are sometimes contradictory, which could in part be explained by the variety of experimental conditions and types of catalysts used. During the transformation of sorbitol in aqueous phase, the presence of multiple reaction products is an illustration of the contribution of the various mechanisms cited. The experimental studies have also shown that the design of the catalyst is important for the orientation of the reaction pathways towards the selective production of certain products.

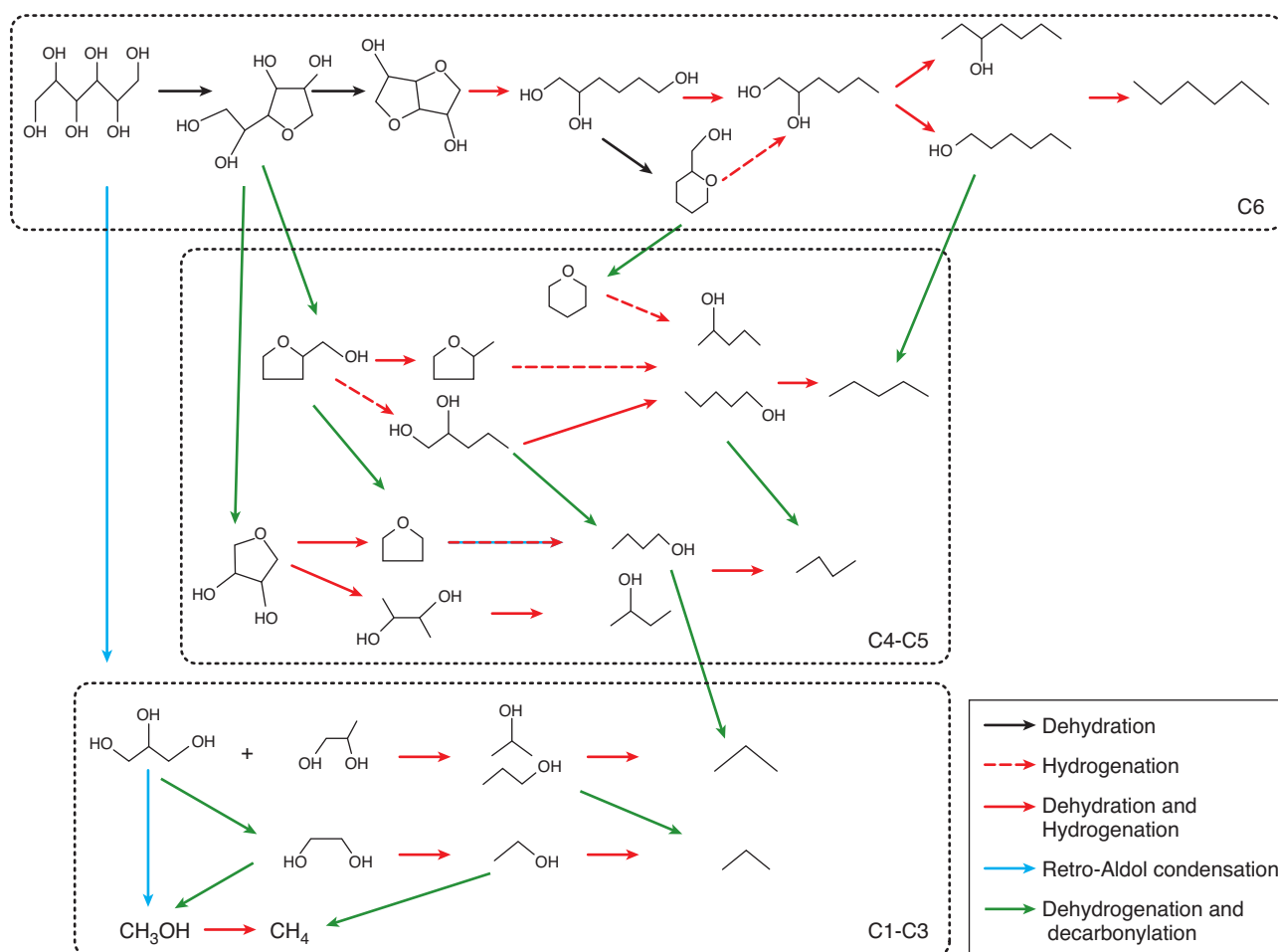


Figure 8

Transformation of sorbitol over Pt/silica-alumina [30].

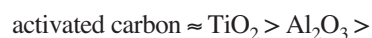
3 CATALYSTS FOR SORBITOL TRANSFORMATION

Several studies presenting new catalysts for sorbitol transformation have been published over recent years. They are most often based on the reactivity of glycerol but also on work concerning the reactivity of ethylene glycol as a model molecule or on sorbitol. The products sought-after in these transformations may vary: hydrogen, hydrocarbons or oxygenated intermediates. The design of the catalyst is adapted to fit the desired application.

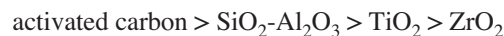
A supported metal catalyst is generally used when the target product is hydrogen; to product hydrocarbons, a bifunctional catalyst composed of a metal phase and an acid phase is more often chosen; lastly, when the reaction is oriented towards the production of oxygenated compounds such as isosorbide or glycols, the catalysts used are metals, sometimes as a complement to a base used to promote mid-chain C-C cleavages by retro-aldol reaction.

3.1 Role of the Support

A few authors have compared the impact of the support on polyol transformation reactions in aqueous phase. It is clear that the support has an influence on the catalyst activity, as shown for example by a comparative study of the ethylene glycol conversion on platinum catalysts on different supports in aqueous phase [48]. It provides, in particular, acidic sites for dehydration and basic sites for retro-aldol reaction. Platinum supported catalysts can be classified according to the ethylene glycol conversion in decreasing order as follows:



$\text{SiO}_2\text{-Al}_2\text{O}_3 \approx \text{ZrO}_2 > \text{platinum black} > \text{CeO}_2 > \text{SiO}_2 > \text{ZnO}$
The most selective for alkanes are, by decreasing selectivity:



Complex support effects may also be explained by degradation of the support in an aqueous environment. During this

experiment, partial dissolution of the silica and cerium oxide was observed.

3.1.1 Acidic Solids

In the ground-breaking study of Shabaker *et al.* [48] silica-alumina was found to be one of the most selective catalytic supports for alkanes during the ethylene glycol transformation reaction in aqueous phase. Later studies performed on the topic mainly examined silica-alumina catalysts [23, 30, 49-51]. This support has acidic properties but is sensitive to the hydrothermal conditions of sorbitol transformation [51].

Other acidic catalysts have also been studied in the literature. A comparative study of platinum-based catalysts on different acidic supports during the transformation of sorbitol yielded the following classification of activity (conversion to gas phase) after 26 h on stream, with a hydrogen supply (245°C, 29 bar) [50]:

phosphated zirconia > niobium oxide >
HZSM-5 zeolite > phosphated titanium oxide > phosphated
niobium oxide > silica-alumina > HY zeolite > tungstated
zirconia > molybdenum doped zirconia

This classification consists of different types of solids. Zeolites (HZSM-5, H-mordenite and HY) are well known for their acidic properties in various refining processes in hydrocarbon environments. They have been found to be active for the aqueous phase transformation of sorbitol [50, 52, 53] or glycerol [42, 54] in hydrocarbons. However, these catalysts might not be stable under hydrothermal conditions (liquid water between 150 and 250°C). Ravenelle *et al.* [55] studied the stability of Y and HZSM-5 zeolites in aqueous phase between 150 and 200°C. They demonstrated that Y zeolites amorphise within a few hours under hydrothermal conditions by mechanisms that differ from those observed in gaseous phase. In condensed phase, the silicon atoms solubilise partially to come out of the crystal network, unlike the generally accepted aluminium migration mechanisms in gaseous phase. However, under the conditions of their study, HZSM-5 zeolite (Si/Al = 15 to 40) was found to be stable [55]. This result was contradicted by Li *et al.* [50] who observed that the catalyst Pt/HZSM-5 (Si/Al = 60) deactivates in 24 h during the conversion of sorbitol at 245°C. This difference can be explained on one hand by the higher temperature in the study of Li *et al.* [50] and, on the other, by the Si/Al ratio that was also higher in latter case. In the example of HY zeolite, deactivation is faster and deeper as the Si/Al ratio increased. The use of non modified zeolites in aqueous phase processes should thus be considered with caution.

The second category of acidic solids used in APP is composed of niobium oxide (Nb_2O_5) and its derivatives (phosphated derivatives in particular) [56, 57]. Niobium oxide is second in the ranking of platinum supports for the conversion of sorbitol by APP. Furthermore, West *et al.* [57] compared the activity of Pt/silica-alumina and platinum on

niobium-based supports (niobic acid, niobium phosphate, phosphated niobic acid) for the transformation of sorbitol. They observed better alkanes yield with niobium-based supports, that they explained by the presence of stronger acid groups. The authors suggested the hypothesis of strong interactions between the support and reagents, polyols or alcohols, that promotes dehydration. It should be noted that this solid is also known for its stability in aqueous phase [58], although a study on g-valerolactone transformation in water at 300°C shows a deactivation of a commercial niobia catalyst [59].

The other solids studied for the APP of sorbitol are prepared by a classic method that consists of doping a weakly acidic solid such as ZrO_2 or Al_2O_3 with a transition metal (molybdenum or tungsten) or with phosphorus in order to obtain Lewis acidic sites. Indeed, Lewis acids seem to be active in an aqueous environment, though their exact nature (Brønsted or Lewis) has not yet been clearly defined [36]. This strategy gives good results with phosphated zirconia and phosphated titanium oxide in the classification cited above. These results are corroborated by a model acidity study of fructose dehydration in water that showed good activity for phosphate zirconia [60]. Of course, the properties of the support such as the surface, pore size and stability under hydrothermal conditions and those of the doping species play an important role in the activity and stability of this type of acidic catalyst. For example, Li *et al.* [50] observed deactivation of tungstated zirconia (fixed bed reaction at 245°C, 15% WO_3 - ZrO_2) while Weingarten *et al.* [60] did not observe modification of the tungstated zirconia during the post-test analysis of the fructose dehydration (reaction in batch reactor at 160°C: 15% WO_3 - ZrO_2). Sun *et al.* [61] deposited phosphotungstic acid particles ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) on different non-acidic supports to convert sorbitol into isosorbide.

The development of new stable and active acidic solids in hydrothermal environments could improve the dehydration rate that is currently a key point of research on APD/H.

3.1.2 Other Supports

When no acidic property is required (production of hydrogen, glycols), the desired characteristics for a support are the stability and the specific surface that promotes dispersion of the metal phase. For this purpose, carbon supports such as activated carbon, carbon nanofibers or carbon nanotubes are considered to be good candidates [35, 39, 62-64]. Titanium oxide and silica are also highly valued [18, 54, 65]. Lastly, alumina, as a conventional support for heterogeneous catalysis, is often studied for the transformation of sorbitol, though its stability in aqueous phase is questionable: gamma alumina rehydrates into boehmite in a few hours under hydrothermal conditions close to APP or APR [22, 23, 49, 66].

It should be noted that “neutral” supports are sometimes studied in association with bases [53, 62, 63, 65] or mineral

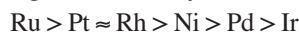
acids [23] that allow the orientation of reactivity such as solid catalysts.

Lastly, when the target products are short polyols (glycerol or glycols) obtained by retro-aldol reactions, solid bases can be used: NaY (sometimes acidified by $\text{Na}^+ - \text{H}^+$ exchanges) [34, 53], ZnO [19], MgO [67].

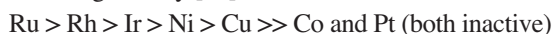
3.2 Role of the Metal Phase

3.2.1 Monometallic Catalysts

The deciding element for the activity and selectivity of a catalyst is still the type of metal used. Group VIII metals supported on silica were compared for the APR of ethylene glycol [68]. These metals can bring the hydrogenation sites necessary for the dehydration-hydrogenation mechanism but they are also known to be active in C-C cleavages [69]. They can be classified by decreasing activity (alkane yield, *i.e.* dehydration-hydrogenation activity) as follows:



Other authors have obtained different orders of reactivity when considering the conversion of the reagent during reactions under hydrogen. For example, during the conversion of glycerol on metal supported on silica, under 100 bars of hydrogen, Montassier *et al.* obtained the following ranking by decreasing activity [18]:



A study by Amada *et al.* [33] of the glycerol transformation by metals supported on silica promoted by ReO_x gave the following classification:



which is close to the data obtained by Davda *et al.* [68], with the exception of platinum. Based on these three different classifications, we can see that ruthenium, rhodium and nickel have good activity for APP. The metal nature has a significant effect on selectivity. In the case of conversion of glycerol under hydrogen pressure, the resulting classification of metals supported on silica by decreasing selectivity for alkanes is as follows [18]:



Based on the results of the ethylene glycol APR on different metals supported on silica, the most selective metals for the production of alkanes are, in decreasing order [70]:



These results on the influence of the type of metal on selectivity are not highly commented in the literature. The state of the catalyst and in particular its degree of hydration and partial oxidation during the reaction is poorly understood, certainly due to the lack of techniques allowing *in situ* characterisations of catalysts for the conversion of polyols in aqueous environments.

Nevertheless, sintering and leaching of metallic particles occurs easily in water, for example over platinum catalysts

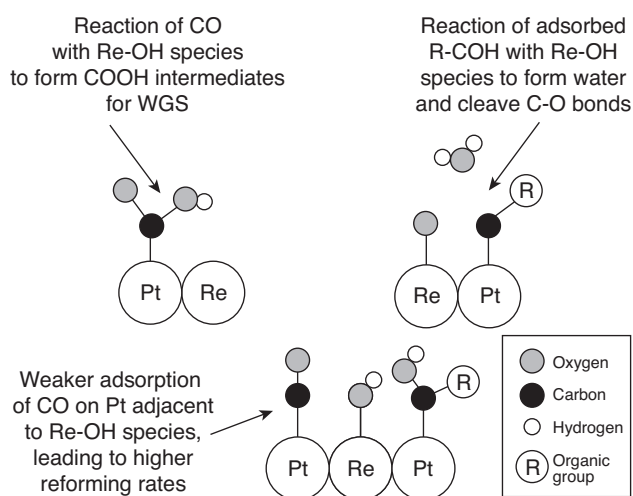


Figure 9

Effect of rhenium addition on Pt/C catalyst [79].

[51, 71], ruthenium catalysts [72], etc. The support plays an important role in the metallic phase stability in hydrothermal conditions [72-74]. Several studies of supported nickel have shown that this metal deactivates very rapidly under APR conditions [67, 68, 75, 76]. This deactivation is attributed to oxidation of the metal, sintering, carbon deposit on the metal particles or strong interactions between the active sites, water and the reagents leading to some metal leaching. The use of promoters such as Ce, Mg, Zr, La has been said to slow down the deactivation, but does not allow sufficient stability for APR [76].

3.2.2 Bimetallic Catalysts

The bimetallic catalysts $\text{NiPt}/\text{Al}_2\text{O}_3$, $\text{CoPt}/\text{Al}_2\text{O}_3$, $\text{FePt}/\text{Al}_2\text{O}_3$ [77] and RuPt/C , RePt/C , OsPt/C [78] were prepared from $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/C and tested for APR. The bimetallic catalysts were more active and more selective for hydrogen than their parent monometallic catalysts. This effect has been explained by a reduction of the adsorption enthalpy of hydrogen and CO on the metal surface, which promotes the desorption of these products and leaves more sites accessible for the reaction [77, 79]. Indeed, Bligaard *et al.* [80] calculated that Fe, Co, Ni and Ru have dissociative chemisorption energies for CO and H_2O much lower than Pt (in vacuum). In addition, certain co-metals are also promoters of the WGS reaction: rhenium, ruthenium and cobalt are thus known to be highly active in the presence of water and CO [81]. This effect can be seen by the increase in the H_2/CO ratio and the decrease in the CO/CO_2 ratio [79]. Lastly, certain co-metals such as rhenium can chemisorb hydroxyl groups formed from water and thus form alkoxides [33, 82]. These hydroxyl

groups are expected to play a role in the WGS reaction by promoting the oxidation of CO adsorbed on platinum. They are also thought to catalyse C-O cleavages by dehydration reactions or even direct hydrogenolysis in some cases. The improved activity of platinum is thus due to the combined effects of bimetallic catalysis. Figure 9 illustrates the effect of the addition of rhenium on platinum.

Nickel is also a potentially interesting metal when used in SnNi bimetallic catalysts. Indeed, though the Ni/SiO₂ catalyst deactivates rapidly, Raney nickel is relatively stable under APR conditions [83-86]. The addition of tin to this catalyst improves the selectivity for hydrogen and partially inhibits the methanation reaction from CO and CO₂ [70]. A Ni:Pt alloy (33:1) supported on alumina has also been shown to have good activity [87]. The addition of platinum has been said to increase the number of active sites on nickel by increasing its reducibility. Furthermore, the WGS reaction is promoted by the weakening of the adsorption enthalpy of CO, which frees up the active sites on nickel.

The activity of the metal surface sites can thus be modulated by the use of bimetallic catalysts. This effect allows the possibility of more selective, more stable and more active catalysts.

3.3 Relationship Between Acidic and Metal Sites

Cortright *et al.* [22] demonstrated that a Pt/SiO₂-Al₂O₃ catalyst and a Pt/Al₂O₃ catalyst mixed with SiO₂-Al₂O₃ had the same selectivity for the same ratio of Pt/number of acidic sites. The proximity of the acidic sites and the metal sites is thus not a deciding factor in the mechanism [21]. This means that dehydration and hydrogenation involve both distinct mechanisms located at remote sites of the catalyst, in agreement with the mechanisms discussed in the first part. There is adsorption of a reactive molecule, then dehydration-desorption of an unsaturated intermediate, then re-adsorption-hydrogenation-desorption [88].

Nevertheless, a recent DFT study on glycerol transformation over Ni, Rh or Pd surfaces suggests a synergetic effect between metal and acid for the dehydration step: the reaction is more exothermic when the reactant and intermediates are adsorbed on the surface [89].

Publications on the transformation of sorbitol in aqueous phase currently mainly focus on the Pt/silica-alumina catalyst and there are very few comparative studies on different catalysts. However, we can draw conclusions from a careful review of articles on the transformation of polyols. The catalysts containing zeolite, cerium oxide, silica or alumina phase are not stable in liquid water at temperature. Though certain zeolites have interesting acidic properties, this type of catalysts does not seem to be suitable for APD/H. The supports with good stability in aqueous environments are the carbon supports, TiO₂ and ZrO₂. Doped oxides prepared

from these supports, such as ZrO₂-PO₄, show good stability and activity for dehydration. Lastly, niobium-based supports have been examined in a few publications: these solids seem to be stable and their acidity increased by the aqueous environment. The most commonly used metal in the literature is platinum, which is known for its hydrogenation and dehydrogenation properties; it has also a fairly good activity for the WGS reaction under the operating conditions. However, the stability of platinum in water is poorly understood. Other metals have been tested: the most promising are ruthenium and rhodium that show good activity for APD/H. For economic reasons, nickel was also considered as an APR catalyst but deactivates rapidly in water in the presence of oxygenated compounds.

4 PROCESSES FOR THE TRANSFORMATION OF LIGNOCELLULOSIC BIOMASS INTO BIOFUELS IN AQUEOUS PHASE

We have just seen that the polyol transformation reaction in aqueous phase by heterogeneous catalysis involves complex reaction mechanisms. In order to improve our understanding of these reactions, academic studies have been performed on model molecules such as glycerol or, more rarely, sorbitol.

The production of polyols from lignocellulosic resources requires a series of pre-treatment, fractionation, purification steps to even out the variability of the resources. However, the real charge is still more complex than the model molecules studied. Moreover, the profitable use of APP products in the fuel and chemistry sectors also requires purification and separation upgrading steps in order to meet market specifications. The resources, processes and range of products obtained through the transformation of polyols are described and compared with certain existing sectors.

4.1 Processes to Make Profitable Use of Lignocellulosic Biomass: Background

A large number of pathways for the transformation of sugars of various origins have been described in the literature and currently mainly concern the fuels market rather than that of biosourced chemicals [90]. Economic and environmental comparisons performed by lifecycle analyses of the various pathways at the preindustrial stage are often difficult as the target products and technologies differ from one process to the next.

According to Savage [91], the ideal biofuel must be cheap, stable and energetically dense. This should thus limit the use of alcohols (ethanol, butanol that can mainly be used in gasoline) and oxygenated compounds such as dimethyl ether or plant-derived methyl esters, and promote transformation pathways that produce “conventional” hydrocarbons (particularly for jet fuel and Diesel fuel).

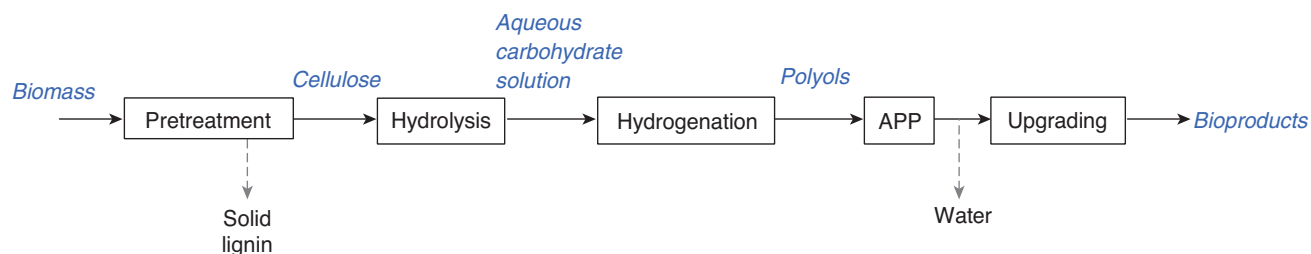


Figure 10

Production of Bioproducts [50].

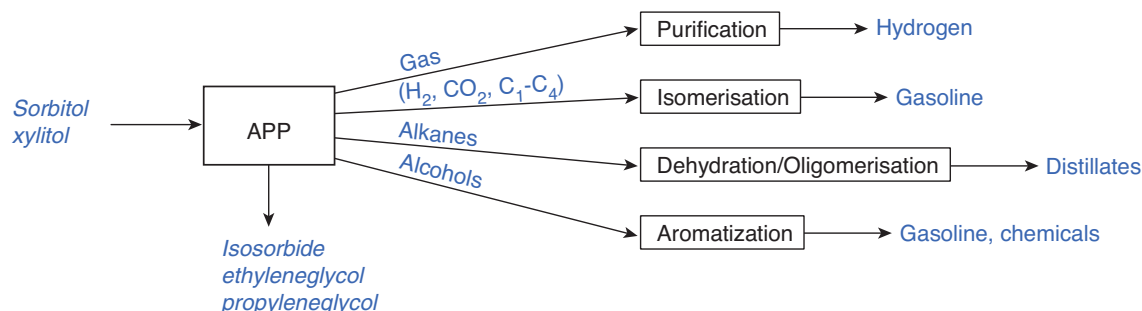


Figure 11

Upgrading of APP products.

The pathways for fuel production from lignocellulosic biomass at the industrial or preindustrial stage are currently mainly biochemical or thermochemical transformation pathways. In the first case, this involves the production of ethanol (or butanol) through the fermentation of sugars from enzymatic hydrolysis, while the lignin fraction is used for the production of electricity by combustion. In the second case, this concerns the production of paraffinic effluent by Fischer-Tropsch synthesis from a synthetic gas produced by gasification of the biomass or production of liquid through thermal liquefaction processes (pyrolysis, liquefaction). The oils produced by pyrolysis must undergo severe hydrotreatment steps (especially hydrodeoxygenation) in order to allow their use as fuel [92].

These processes require hydrogen and involve steps that are costly in energy, or that use toxic or corrosive chemicals. In regard to these observations, a demand for clean processes involving heterogeneous catalysis has emerged.

According to Huber and Dumesic [21], the technology of the future for biofuels production will combine a large number of different processes to best use the biomass resource in a biorefinery, as it is currently the case in oil refineries.

In this context, polyol transformation processes in aqueous phase in the presence of heterogeneous catalysts can constitute an interesting possibility.

4.2 Aqueous Phase Process (APP): Transformation of Polyols by APR/(APD/H)

As explained previously (cf. *Sect. 1*), the Dumesic group described various polyol transformation pathways from biomass in the presence of one or more heterogeneous catalysts under controlled operating conditions to obtain a target product [21]. As a result, a wide range of hydrocarbon products for use as fuels or chemicals can be obtained from lignocellulose. In this case, the use of a process on biomass involves different complex steps (see *Fig. 10*), including pre-treatment of the native biomass, hydrolysis to extract the sugars, hydrogenation of the sugars into polyols and the reaction in aqueous phase (APP, aqueous phase process). An upgrading step may be added to obtain certain bioproducts. For example dehydration, aromatization or oligomerization reactions may be used to obtain targeted products (aromatics, olefins, alcohols, etc.) (*Fig. 11*).

4.2.1 Production of Polyols from Lignocellulosic Biomass

We have seen that the first step consists first of extracting the sugar fraction from the biomass through pre-treatment and hydrolysis steps and then of hydrogenating that fraction into polyols.

As introduced above, lignocellulosic biomass is composed of three main components: cellulose, hemicellulose and lignin. The relative proportion of cellulose and hemicellulose varies according to the origin of the biomass but one can assume that more than half of the composition of wood is cellulose [93]. Hemicellulose polymers surround the cellulosic microfibrils and play the role of a “cement” within the plant. Due to its microfibril crystalline structure as well as its interconnection with lignin and hemicellulose, raw cellulose is more resistant to hydrolysis compared with shorter carbohydrates such as cellobiose or a partially crystalline glucose polymer exhibiting more reactive α 1-4 linked glucose such as starch.

At industrial scale, lignocellulosic biomass should be used in its raw state, with its three main components. For transport facilities, raw biomass can be crushed in shavings or powder. Thereafter, biomass is often treated, in order to improve its reactivity thanks to higher accessibility. All actions done in this purpose are called pre-treatment processes. Their nature depends on the targeted product and process of interest but pre-treatment actions always refer to solubilisation and separation processes to make the remaining solid biomass more accessible to further chemical or biological treatments. According to experimental conditions, treatments will decrease cellulose crystallinity by cellulose defibrillation and amorphisation. Furthermore, partial or total solubilisation of lignin and/or hemicellulose will occur. Pre-treatments have to be selective and particular attention must be paid to minimise degradation of the desired product, cellulose in general. Industrial application of biomass pre-treatments is well known in paper processes for pulp cellulose extraction. The Kraft process is a technology for converting wood by treatment with NaOH or Na₂S into wood pulp consisting of pure cellulose fibres [93, 94]. Other pre-treatments types are varied and can be classified in as follows: mechanical (milling, grinding), thermochemical (high temperature treatment with alkali, diluted acid, oxidising agents or organic solvents), mechanical and thermochemical (steam explosion, AFEX: ammonia fibre explosion) or biochemical [95-97]. The impact of mechanical treatments exceeds simple reduction of particle size, by enhancing the cellulose accessibility and reactivity through decrystallisation and increase of exchange surface area. Most common physical treatments combine chipping, grinding and/or milling. Thermochemical pre-treatments of lignocellulosic biomass include high temperature biomass transformation (150-170°C) in the presence of diluted acid media (usually sulphuric acid but phosphoric, acetic, formic acid are possible), alkaline media (sodium or lime for example) or oxidising media. Alcohol solvents are employed in the Organosolv process [98]. While acid pre-treatment will solubilise the hemicellulosic part, alkaline pre-treatment removes lignin, but a part of the hemicellulose is degraded simultaneously. In the Organosolv process, the lignin network and sometimes the hemicellulose

fraction is removed or decomposed. At industrial scale, lignocellulosic bioethanol production, pre-treatments are applied to reduce the recalcitrant nature of cellulose in order to enhance enzymatic hydrolysis productivity. Process design studies have indicated that pre-treatment steps are the costliest part of the whole process [99, 100].

At the end of the pre-treatment, the following step thus consists in extracting the sugars from the pre-treated biomass residue. There are different processes that generally use enzymatic or acidic hydrolysis of the cellulose and/or hemicellulose fractions, in the presence or absence of lignin.

The enzymatic hydrolysis processes generally act on biomass from which the hemicellulose fraction was extracted during pre-treatment. This is the most common case of hydrolysis processes for the production of ethanol [101]. These processes use cellulase-type enzymes. They have several advantages such as the mild reaction conditions (40°C, neutral pH), few by-products formed and low energy consumption. The shortcomings of enzymatic hydrolysis are the efficacy of the hydrolysis of cellulose, a slow and more difficult reaction than the hydrolysis of starch, and the high cost of the enzymes [102]. The ideal enzymatic hydrolysis process should thus convert the maximum amount of pre-treated biomass into sugars in the shortest period of time with the least amount of enzymes. Applied research is heavily exploring new pathways for improvement of this process. For example, the NREL and Novozymes have formed a partnership for research and development on new enzymes for the hydrolysis of biomass-derived sugars using an integrated process optimisation approach. The efforts have focused on the study of different enzymes and the factors that influence the efficacy of the reaction, such as the accessibility of the substrate, the crystallinity of the cellulosic material, the impact of the presence of hemicellulose and residual lignin and optimization of the enzymatic cocktail [103].

Processes involving acidic hydrolysis in a very low or very high concentrated media are historical processes and constitute an alternative to the enzymatic pathway. This type of process was first discovered in the 19th century but is still used for the production of ethanol. Sulphuric acid is the acid the most commonly used. The drawbacks of these processes in an acidic environment are degradation of the sugars, operational problems caused by corrosion and the salt content after neutralisation of the acid. The efficacy of the acid recycling rate also has a significant impact on the operational costs of the process [102]. There was recently a report of new acidic hydrolysis processes. *BlueFire Ethanol* is currently in the process of commercialising a concentrated acidic hydrolysis process, probably based on the technology patented by *Arkenol* [104]. In this case, a liquid rich in hexoses and pentoses is obtained. We should also cite *HCL CleanTech*, founded in 2007 and now become *Viridia*, that developed the CASE™ process that converts lignocellulosic biomass into sugars and lignin using concentrated hydrochloric acid [105]. Lastly, *Eni* has developed a process using a water-soluble

organic acid derived from the result of the hydrolysis reaction by extraction with an organic solvent [106].

Alongside acidic hydrolysis processes, *Renmatix* has proposed a *Plantrose*TM process that produces water-soluble sugars by hydrolysis in an aqueous environment under supercritical conditions. This technology would allow *Renmatix* to avoid the cost of recycling and the production of degraded products associated with acidic hydrolysis and the operational costs connected with enzymatic hydrolysis. According to the company, the demonstration unit converts 3 tons of biomass into sugars per day [107].

The critical point of technologies involving acidic hydrolysis is to preserve the sugar from secondary reactions that lead to the production of products such as furfural, levulinic acid, formic acid, etc. The formation of these products reduces yield and, in certain configurations, affects the downstream process, by inhibiting the fermentation of glucose into ethanol for example.

For example, sorbitol was produced through the hydrogenation of glucose during the Second World War as a substitute for glycerine that was reserved for military use. Since the 1950s, sorbitol has found new applications, particularly as a humectant in cosmetics or a sugar-substitute sweetener for non cavity-causing sweets. Other polyoxygenated compounds such as mannitol, maltitol, xylitol, isomalt, isosorbide also have diverse applications in these sectors.

Roquette Frères, *Cargill* and *SPI* are the largest global producers of sorbitol, with polyols, and they hold 70% of the market. (source: market, according to International Polyols Chemicals.)

Sorbitol is produced through the catalytic hydrogenation of aqueous glucose solutions (glucose concentrations up to 65% weight) in discontinuous reactors (autoclave) or continuous reactors (trickle bed), under high hydrogen pressure [108]. The most commonly used catalysts contain nickel. Historically, Raney nickel was used, followed by supported nickel; these have been the subject of patent applications [109, 110]. The drawback of these catalysts under these reaction conditions is the leaching of nickel that causes deactivation of the catalyst and the presence of metal in the sorbitol solution. This requires purification of the resulting solution for food and medical applications. Research is currently ongoing to limit these effects, by modifying the metal-support interaction [111] or using other metals such as ruthenium [112]. The challenge is to obtain sorbitol selectivity above 99% to 100% of glucose conversion and catalyst stability for long operating periods. Under certain conditions, the hydrogenation of polyols can be accompanied by hydrogenolysis reactions to obtain other polyols of interest [22]. These hydrogenation processes are currently used on a glucose feeds derived from starch. The use of second-generation sugar feeds and, even more importantly, in a mixture with hexoses and pentoses, has not, to our knowledge, been described in the literature.

4.2.2 Profitable Use of Polyols by a Process in Aqueous Phase

The APD/H reaction, described in the first part of this article, allows the production of liquid hydrocarbons from sugars and/or polyols under mild pressure and temperature conditions which thus require moderate energy input [23]. When APR and APD/H reaction are combined, the process involves no external hydrogen supply. The separation of the products is supposed to be simplified as the alkanes theoretically form a hydrophobic phase that separates in an aqueous environment [21]. Alkanes can then be integrated into the classic refinery circuit and be distributed by existing infrastructure. Unlike oil-derived hydrocarbons, they contain no sulphur. Another advantage of the process is that APD/H can be applied to a wide range of polyols, particularly C₅ polyols derived from hemicellulose, while the fermentation of C₅ sugars into ethanol is still at the fundamental research stage [15].

Hydrogen Production

The team of Dumesic demonstrated that the production of hydrogen is feasible from sugars or polyols by heterogeneous catalysis [22]. At temperatures close to 225°C, conventional platinum catalysts supported on alumina allow the selective conversion of reactants into a mixture of hydrogen, CO₂ and light hydrocarbons. The selectivity towards hydrogen increases with the decrease in the number of carbons: 66% for sorbitol, 75% for glycerol at 225°C, to the detriment of selectivity towards hydrocarbons. Selectivity is higher for sorbitol than for glucose (50%). A recent study demonstrated that the production of hydrogen from biomass is economically viable using a combination of glucose fermentation and APR [113]. The hydrogen produced by APR must undergo purification steps depending on its use.

To improve economics of the process, the 3% weight precious metal contents announced for the heterogeneous catalyst composition must be significantly reduced. Furthermore, the metal and alumina phases are significantly modified by the hydrothermal operating conditions [51, 55]. Their stability must also be improved in order to increase productivity.

Fuel Production

Concerning the production of molecules of interest for a fuel composition, the combination of APD/H of sugar-alcohol (preferably sorbitol, xylitol) with different conventional refining catalytic processes yields a wide range of hydrocarbons that can be used as fuels [114, 115]. For example, *n*-pentane and *n*-hexane are converted into gasoline suitable compound by an isomerisation reaction. The conversion takes place in the presence of acidic catalysts, generally chlorinated alumina, that require strong drying of the feeds upstream of the process. This process yields gasoline that is free of lead and aromatics and that thus meet current environmental constraints. The isomerisation process coupled to alkylation also

transforms the *n*-butane into a hydrocarbon fraction that may indirectly feed the gasoline pool [116].

Another pathway for profitable use is based on the transformation of olefins into fuels through oligomerisation processes. The feeds for these processes are mixtures of short olefins that can be obtained from polyols by dehydration of alcohols or by dehydrogenation of paraffins. The oligomerisation process converts olefins into basic jet fuel or gasoline fuels in the presence of acidic catalysts such as Supported Phosphoric Acid (SPA) or amorphous silica alumina [116, 117]. The use of zeolite catalysts allows production of medium distillates. One example is the Mobil Olefin to Gasoline and Distillate (MOGD) process that transforms a mixture of olefins with a ZSM-5 zeolite into Diesel fuel after hydrogenation [116]. The direct use of oxygenated loads can also be considered.

Lastly, aromatisation reactions are ways to obtain aromatic bases that can be used, for example, to produce high octane car fuels. The conventional feed is composed of a mixture of light aliphatic hydrocarbons. The reaction, favoured by high temperatures and low pressures, is catalysed by acidic solids such as ZSM-5 promoted by zinc or gallium. For feeds derived from the transformation of polyols in aqueous phase, a preliminary hydrogenation step is required [118].

All of these conventional refining processes can thus convert new feeds derived from the conversion of polyols. Fractionation, purification and in certain cases transformation (dehydration, hydrogenation) steps are nevertheless unavoidable and can turn out to be a costly steps in the process as a whole.

Alongside the use of these new products in conventional refining processes, new pathways for their transformation have been described. Long C7-C15 alkanes can be produced by aldol condensation of aldehydes and ketones derived from ADP/H. This transformation produces compounds that can be added to Diesel fuel and jet fuel but that still require a series of subsequent steps: fractionation, aldol condensation, hydrogenation [114].

Lastly, solutions have been proposed in the literature to directly add high octane-index effluents derived from ADP/H and containing yet more oxygen like alcohols and furan derivatives (for example, tetrahydrofuran). The suitability of these compounds for use in current engines has not however been demonstrated [50].

Chemical Production (Glycols, Isosorbide, Aromatics)

The transformation of sugar-alcohol polyols allows the production of fuels, hydrogen and, depending on the operating conditions, oxygenated molecules of interest.

Glycerol was long a target molecule to be produced from polyols or sugars-alcohols. Processes used to produce biodiesel through the transesterification of vegetable oils have now made glycerol widely available on the market. Interest has now shifted towards the transformation of sorbitol into ethylene glycol or propylene glycol, potential

platform molecules for the production of polymers [119]. Ongoing research on different processes for the hydrogenolysis of polyols into molecules of interest was recently the subject of a very complete review [112].

The isosorbide obtained by dehydration-cyclisation of sorbitol is also of interest for surfactant, polyester applications. Research has focused on the substitution of homogenous mineral acidic catalysts with heterogeneous acidic catalysts. *Petrobras* and *Bioecon*, a Dutch company, announced in 2010 that they were developing a new process to convert lignocellulosic biomass from bagasse into chemicals for the production of green plastics or for transformation into Diesel fuel additives. BiCHEM process uses a solvent to breakdown cellulose into sugars. The use of molten salts has been proposed [120]. The sugars are then hydrogenated and converted into platform molecules such as isosorbide or transformed into fuel additives [121]. A demonstration unit is planned for Brazil.

As discussed previously, aromatisation reactions yield aromatic bases from feeds derived from the conversion of polyols. Aside from their use as basic gasoline, Benzene/Toluene/Xylene compounds (BTX) resulting from extraction constitute an interesting alternative to fossil aromatics in the field of petrochemicals. These biosourced compounds are potential sources of polymerisation precursors: styrene, phenol, terephthalic acid, etc.

Integration of APP Processes in a Biorefinery – Economic Issues

We have shown that it is possible to produce multiple products for diverse applications: hydrogen, glycols, aromatics, hydrocarbons, etc. through the transformation of polyols and sorbitol in particular in aqueous phase.

The Bioforming process developed by *Virent* thus converts soluble sugars in water into products that can be used as gasoline, jet fuel and Diesel fuel. A demonstration unit in collaboration with *Shell* has been producing 38 000 litres per year of Bioforming gasoline since 2009 [122]. This process was first proven with first-generation sugars and also seems to be compatible with sugars derived from cellulosic biomass. Based on the data from *Virent*, the BioForming process could produce gasoline at \$60 the barrel [123], using first-generation transformed sugar (starch-derived), with a molar yield of 85% [114]. The process can also transform pentoses derived from the hemicellulose fraction of biomass, thus maximising the overall hydrocarbon yield for a gain of up to 30% compared with the use of cellulose alone.

Though the hydrogen can be generated *in situ* during APP reactions, the majority of processes rely on reactions fed with hydrogen from an external source. However, hydrogen supplies remain problematic for several transformation processes of biomass-derived products (HDT of vegetable oils, HDO of pyrolysis oils, etc. [15]). Indeed, a process can only be considered green if it is independent of fossil resources, including the hydrogen supply. The APR of biomass-derived products

[124, 125], the use of photocatalysis are under study for the production of “green” hydrogen [126]. Huber and Dumesic [21] have thus developed the concept of an integrated biorefinery using APD/H as the central process, with the production of hydrogen [21, 115].

The economic assessment of biorefineries shows that their profitability would only be guaranteed with the production of bioproducts alongside the production of biofuels. The transformation of polyols in aqueous phase offers this solution. Very recently, *Virent* and *Coca-Cola* Company announced a partnership for the commercialisation of biomaterials for packaging. This agreement is based on the technology for the production of paraxylene developed by *Virent BioformPX™*, for the synthesis of PET resin for plastic bottles [127]. This process uses the APP technology from sugars [128], followed by an aromatisation process on a modified ZSM-5 zeolite. The resulting aromatic effluent is sent to a petrochemical complex for the production of paraxylene, a precursor of PET.

4.3 Alternative Pathways to the APP of Polyols

The APD/H of polyols to hydrogen and various hydrocarbons seems to be an effective method to product fuels and/or biosourced chemicals. However, it requires the use of transformed polyols. The direct use of more widely available molecules such as glucose or sugars in general or the cellulosic fraction would be profitable as it would eliminate the steps required to prepare the feed (hydrolysis and/or hydrogenation).

Glucose, which is less thermally stable than sorbitol, leads to the formation of several degradation products and does not seem to be suitable for the APD/H reaction. Researchers at *Mobil* have developed a process to produce aromatic compounds by reaction of glucose on ZSM-5 zeolite catalysts. The thermal conditions are more severe than those for ADP/H and 40 to 50% of the carbon is thus transformed into coke [129]. More recently, Carlson *et al.* [130] obtained similar results on ZSM-5 zeolites with glucose, xylitol, cellobiose and cellulose, thus suggesting that there is a common intermediate derived from glucose.

The production of hydrogen from cellulose was studied by researchers at Dalian University [131]. This process implies gentle hydrolysis of the cellulose, followed by reforming of the glucose into hydrogen in one single step.

Moreover, certain patent applications have claimed direct transformation of carbohydrates (cellulose) into polyols and/or hydrocarbons in one single step, under hydrogen and in the presence of a heterogeneous acidic catalyst [132].

Lastly, another route would be to produce the hydrogen from pyrolysis oils. Bio oils are not very expensive to produce from biomass. However, their quality is very poor and they must be transformed in order to be added to the fuel

pool or transformed into molecules of interest. In this context, hydrogen and hydrocarbons can be produced using processes in aqueous phase from the aqueous fraction of bio-oil, in the presence of heterogeneous catalysts [49, 133].

Processes involving transformation in aqueous phase currently propose polyvalent transformation of polyols into products for use in the fuel and chemistry industries. Projects for demonstration units and several ongoing partnerships are illustrations of the potential they represent. Indeed, these processes should be adapted to various polyols derived from biomass and produce a diversified range of products. Furthermore, the hydrogen required at certain steps of the process can be autogenerated. The economic blocks are in part connected with the large number of steps required to transform lignocellulosic biomass and to adapt it to existing processes: pre-treatment, purification, hydrogenation. The effective fractionation of the resulting products and their transformation into products suitable for current engines or specifications in the chemical industry are also costly steps in the process that must be improved. However, the flexibility of the process to combine the production of fuels with that of high-value chemicals is a plus for the biorefining economy.

CONCLUSION

The transformation of lignocellulose-derived polyols in aqueous phase constitutes an attractive, emerging way to produce high-value compounds for the fuel or chemistry industries. The processes considered currently include a large number of steps that should be reduced, particularly through a better understanding of the reactivity of more complex, less refined feeds such as cellulose, for example. Lastly, optimisation of the entire process chain must necessarily include a catalytic design that is suited for the new conditions and new feeds and the development of effective characterisation methods for these new sugar transformation reactions performed under hydrothermal conditions.

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