5. Furfurals as chemical platform for biofuels production

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Abstract. In this chapter we present a review of the different conversion strategies for the catalytic upgrading of furfurals, specifically furfural and hydroxymethyl furfural, which are two chemical building blocks from lignocellulosic biomass for the production of transportation fuels, as well as useful acids, aldehydes, alcohols and amines. Reactions and catalysts for aldol-condensation, etherification, hydrogenation, decarboxylation and ring opening of furfurals are discussed. Specific examples are reviewed for hydrogenation and decarboxylation with emphasis on reaction pathways and kinetics analysis, comparing the behaviour of different metal catalysts.

1. Introduction

The conversion of lignocellulosic biomass to liquid fuels has attracted renewed attention in recent years due to its environmental, economic, and strategic advantages [361–3]. In contrast to fossil fuels, the biomass-derived fuels can be CO₂-neutral, since the CO₂ produced in their combustion can be
reabsorbed by green plants and algae during photosynthesis [4–7]. However, there are technical and economical challenges that have delayed the application of this technology to the commercial scale. An economically sustainable and competitive process will require versatility to accept different kinds of biomass feedstocks and the ability to produce low-oxygen, high energy content liquids, which should be fungible with conventional fuels [8].

There are different possible sources of biomass that could be used as feedstock in the production of biofuels. They include waste materials (agricultural or urban), forest products (wood, logging residues, trees, shrubs), energy crops (starch crops such as corn, wheat, barley; sugar crops; grasses; woody crops; vegetable oils; hydrocarbon plants), or aquatic biomass (algae, water weed, water hyacinth) [8]. The availability of enough quantities of biomass is a key factor in scaling up biofuels production. In the U.S., it is estimated that 1.3 x 10⁹ metric tons of dry biomass/year could be sustainably produced for biofuels, without a significant impact on human food, livestock feed, and export demands [9]. This amount of biomass would represent an energy content of 3.8 x 10⁹ boe (barrels of oil energy equivalent), which would account for 54 % of the current annual demand of crude oil in the U.S., Ref. [10,11].

Gasoline and diesel are commodities that have been optimized through many years of commercial practice and dedicated research. The notion of molecular management and molecular engineering of fuels has been put into action in refining operations of petroleum fuels. These terms entail having the right molecule in the right place, at the right time, and at the right price [12], and at even higher level of molecular manipulation, they imply a purposeful design of molecules with precise structures and well-defined properties. To achieve this high level of chemical specificity, the continuous development of better catalytic materials is crucial [13]. The arrival of biofuels in the energy scene, particularly those from second- and third-generation technologies, produced from non-food biomass resources, poses new challenges and research opportunities for fuel development and catalytic upgrade [14]. Among the properties that are required to qualify a given fuel type, one can mention octane number (ON), cetane number (CN), sooting tendency, water solubility, freezing point, viscosity, flash point, cloud point, autoignition temperature, flammability limits, sulfur content, aromatic content, density, boiling temperature, vapor pressure, heat of vaporization, heating value, thermal and chemical stability, and storability. Many of these properties can be improved by catalytic upgrading. Therefore, when designing an upgrading strategy, a refiner is required to know how each of these properties will be affected by the structure of the components that are being allowed into a
given fuel. Thus, it is important to develop predicting tools to determine how the structure of molecule added to the fuel will affect each of the properties of interest. Since for many fuel properties the overall value of the property for the mixture depends non-linearly on the individual contributions, the refiner also needs to be able to predict how new components behave in fuel mixtures [15].

The molecular engineering approach has been applied for upgrading of fossil fuels and there are many examples in the literature. However, the application of this rational approach in the upgrading of biofuels is just starting [16]. To optimize a fuel property of interest it is necessary to develop first an experimental database of known properties for components chemically similar to those to be incorporated in the fuels. Then, one needs to use correlations such as Quantitative Structure Property Relationships (QSPR) to expand the database to all the possible components of the fuel. QSPR utilizes molecular descriptors, (i.e., numerical values calculated from the molecular structure) to develop correlations with specific properties of the corresponding compounds. Molecular descriptors involve geometric, steric, and electronic aspects of the molecule and can range from very simple physical parameters such as the number of carbon atoms or branches in a molecule, to more complex parameters such as dipole moment or surface area. Application of QSPR to fuel properties has resulted in models that can estimate Cetane Number [17,18], Octane Number (RON and MON) [19], and sooting tendencies [20] of any fuel component, only on the basis of the molecular structure. With these structure-property relationships the researcher can evaluate whether a given potential catalyst and conversion process modify the structure of a given reactant in a favorable way regarding the desired fuel properties [21].

In this chapter we compare different conversion strategies involving furfural (FAL) and hydroxymethyl furfural (HMF), two chemical building blocks for the production of transportation fuels as well as a variety of useful acids, aldehydes, alcohols, and amines [22,23]. For example, C–O hydrogenolysis of HMF produces 2,5-dimethylfuran (DMF), a potentially good gasoline component, with heating value (35 MJ/Kg) and boiling point (93 °C) higher than those of ethanol (22.6 MJ/Kg and 78 °C, respectively) [24]. Being immiscible in water makes it even more suitable for transportation fuels. Similarly, the hydrodeoxygenation of the trimer obtained from the aldol-condensation of two molecules of furfural and one of acetone yields linear paraffins that could be used as jet or diesel fuel components, since they have the required properties for these fuels [25].

In the following sections we will first describe how furfurals are obtained from biomass and then compare potential upgrading strategies to produce transportation fuel components with desirable properties.
2. Biomass to furfurals

Photosynthesis uses solar radiation to convert energy-poor carbon dioxide and water into energy-rich carbohydrates \((\text{CH}_2\text{O})_n\) and molecular oxygen \((\text{O}_2)\), Ref. [26]. These carbohydrates are stored in the plants in the form of polysaccharides that include starch, cellulose, and hemicellulose and account for up to 75% of the plant mass. Although the energy efficiency of the photosynthesis process varies from 0.1 to 8.0%, the areal growth rate of the plants is usually very high (6 to 90 metric tons/ha-year).

Polysaccharides in plants have very distinct functions and their molecular structures are the most appropriate for each purpose. For example, to give structural resistance to the plant, cellulose is a large and well-organized polymer and is located in the primary cell wall. In contrast, hemicellulose is a branched polysaccharide that is less rigid and able to wrap around the cellulose structure (Figure 1). Finally, starch is a polymer of d-glucose with \(\alpha-1,4\)-glycosidic bonds (repeating unit \(\text{C}_{12}\text{H}_{16}\text{O}_{5}\)), Ref. [8,27]. Those linkages occur in chains of \(\alpha-1,4\) linkages with branches formed as a result of \(\alpha-1,6\) linkages, making its structure highly amorphous and readily attacked by enzymes in the digestive system of animals and humans. Starch is a main constituent of corn, rice, potato, etc. Although it has been widely used for fuels and chemicals production [10,28], starch should not be replaced as a source of food [29].

![Figure 1. Schematic representation of the composition of lignocellulosic biomass.](image-url)
Another major component of biomass is lignin (10–25 %), which has a noncarbohydrate polyphenolic structure that is encrusted in the walls of the cell and cement it together (Figure 1). This complex, cross-linked, highly aromatic structure (molecular weight ~10,000 g/mol) is derived from three monomers called monolignols (coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol). Coniferyl alcohol is the predominant lignin monomer found in softwoods, while p-coumaryl alcohol is a minor component of grass and forage type lignins. Both coniferyl and sinapyl alcohols are the building blocks of hardwood lignin [30,31]. Other compounds present in biomass in smaller quantities include pigments, sterols, triglycerides, terpenoids, resins, waxes, alkaloids, and terpenes.

2.1. Primary conversion of biomass

Although lignocellulose is one of the most abundant sources of biomass, its conversion into liquid fuels is a challenging task [32]. The more reactive sugar polymers in the plant are protected by the highly unreactive lignin fraction. For that reason, an effective pretreatment step is necessary to break down the refractory lignin seal, disrupt the crystalline structure of the cellulose, and increase the surface area of the biomass. A variety of methods are available to perform this pretreatment including immersion in hot water, dilute acid solutions, caustic lime/ammonia, and steam explosions [33,34].

Figure 2 summarizes the three major approaches suitable for primary processing of lignocellulosic biomass [35]. They are gasification to syngas [36,37], liquefaction (pyrolysis) to bio-oil [38] and hydrolysis for production of sugars [39]. Afterwards, further refining is necessary (secondary processing) to bring the mixture to the range of the desired fuel by reducing the oxygen concentration and maximizing the energy content of the liquid.

Several routes have been proposed for the secondary processing. They include (a) conversion of biomass-derived syngas into alkanes or methanol by Fischer-Tropsch or methanol synthesis [40-41], (b) catalytic aromatization, condensation and hydrodeoxygenation of bio-oil for hydrocarbons production [42–48], (c) enzymatic fermentation of sugars for methanol and butanol generation [49], (d) hydrogen synthesis by aqueous phase reforming of sugar-derived species [50], (e) conversion of monosaccharide molecules into aromatics and coke by zeolite upgrading [51–53], (f) fuels production by biphasic processing of sugars and oxygen-containing molecules [54–55], and (g) esterification of triglycerides for biodiesel synthesis [56].
Gasification is outside the scope of this chapter and the reader is referred to excellent reviews on this subject [37,57,58]. We will briefly discuss the other two primary conversion processes, with emphasis on those that lead to the production of furfurals.

2.1.1. Pyrolysis of lignocellulosic biomass

Pyrolysis oil is produced during the fast heating of lignocellulosic biomass in the absence of oxygen. Depending on the feedstock and the pyrolysis conditions, mainly temperature, heating rate, and residence time, it is possible to produce yields of bio-oil ranging from 50 to 95 wt. % [59]. Bio-oil is a dark brown, highly viscous, and oxygenated liquid with up to 40 wt. % water content [60,61]. In addition to water, pyrolysis oil comprises
catecols, syringols, guaiacols, phenolics, sugars, ketones, aldehydes, short carboxylic acids, and furfurals [62]. This mixture of highly reactive molecules makes the bio-oil an unstable system that requires further processing before its utilization for transportation fuels [38,63].

Pyrolysis of pure cellulose yields levoglucosan (up to 60 wt. %), via intramolecular condensation and sequential depolymerization of glycosidic units [64]. However, in the presence of alkali metals in concentrations as low as 0.005 mmoles/g, non-selective homolytic cleavage of carbon-carbon bonds occurs, favoring the formation of low molecular weight molecules including acids, furfurals, and linear aldehydes (Figure 3) Refs. [65–69].

These undesired reactions are controlled by the ionic nature of the inorganic salts, the Lewis acidity/basicity and/or their ability to form complexes that stabilize particular reaction intermediates. For example, when CaCl₂, Ca(NO₃)₂ and CaHPO₄ were added during the pyrolysis of cellulose, the yield of glycolaldehyde was reduced, while a remarkable increase was observed in the yield of formic acid and acetol. More interesting, the formation of furfural, hydroxymethyl furfural, and levoglucosenone is enhanced in the presence of CaCl₂, which indicates the participation of these salts in the dehydration reaction of the cellulose [67].

![Reaction scheme for cellulose conversion](image)

**Figure 3.** Reaction scheme for cellulose conversion a) in the absence and b) in the presence of metal ions (adapted from Refs. [66,68,69]).
2.1.2. Hydrolysis

The deconstruction of lignocellulosic biomass via hydrolysis is readily catalyzed by strong acids, which speed up the protonation of the oxygen bridges connecting the sugar monomers. Mineral acids (HCl, H$_2$SO$_4$, and HNO$_3$) are effective catalysts for depolymerization of hemicellulose and cellulose, as they have the necessary strength to break down the crystalline structure of the cellulose fibers. Acid catalyzed hydrolysis has been conducted in industrial scale for a long time. In 1922, The Quaker Oat Company developed the first commercial process for production of furfural from oat hulls in Cedar Rapids, Iowa, using liquid acid catalysts [70]. The first production of furfural was achieved by passing superheated steam through biomass. However, at high enough temperatures, sulfuric acid is not necessary since the acetic acid released during the depolymerization of hemicellulose is able to catalyze the dehydration reaction and produce furfural.

The acid catalyzed hydrolysis of polysaccharides comprises the following steps [71], (1) protonation of an oxygen link leading to a trivalent oxygen, (2) heterolytic cleavage of a C–O bond to form a carbocation and a hydroxyl group, (3) reaction of a water molecule with the carbocation, and (4) release of a proton from the resulting H$_2$O$^+$ with consequent regeneration of the catalyst and yield of a hydroxyl group. The sequence is repeated until the polysaccharide is fully converted into the corresponding sugars. However, during this process the lignin fraction cannot be dissolved and remains unreacted. Therefore, further refining is necessary. The catalytic effect of the acid is highly dependent on the proton transfer efficiency of the catalyst, rather than the proton concentration in the system. In fact, it has been observed that even negligible hydrogen ion concentrations may have a catalytic effect [72]. In this context, the hydrogen ion concentration is highly dependent on the temperature. It has been observed that the dielectric constant of water, responsible for the dissociation of the acids, decreases with temperature, which strongly diminishes the dissociation of the acid [73].

2.2. Dehydration of sugars

The formation of furfural and hydroxymethylfurfural can be accomplished by triple dehydration of xylose (pentose) and glucose (hexose), respectively, in the presence of an acid catalyst (Figure 4). Pentoses and hexoses are mostly present in the ring form, since the open-chain aldehydes only amount to less than 1 wt. %, Ref. [74]. Isomerization of glucose to fructose is desirable because the latter is more effective for production of
HMF. For example, Sn-containing zeolites have been found to be very active and selective towards fructose (31 wt. %), with small production of mannose (9 wt. %) at mild temperatures (110–140 °C), [75].

Figure 4. Production of furfurals (2-furfuraldehyde and hydroxymethylfurfural) from lignocellulosic biomass.

The transformation of the C₅, C₆ sugars is performed through the sequence of two 1,2-eliminations, followed by 1,4-elimination of water molecules. In the final step, ring formation occurs facilitated by the tendency of sp² carbon atoms to form planar structures [76]. After the 1,4-elimination, the hydrogen ion is eliminated and furfurals are obtained.

Ionic liquids have also been tested for the production of furfurals [77–79]. In this approach, the ionic liquid stabilizes the furfural (FAL) or hydroxymethylfurfural (HMF) product from the reaction mixture and increases the reaction selectivity. However, the detailed role of the ionic liquid in the catalytic cycle is still under study [80].

Possible mechanisms have been proposed for the dehydration of fructose in the presence of halides, as well as for the isomerization of glucose to fructose catalyzed by hexacoordinated chromium (II) complexes (Figure 5), Ref. [79]. It appears that the halide (X⁻) attacks the oxocarbenium ion to form
Figure 5. Putative mechanisms of dehydration of fructose and isomerization of glucose in the presence of halides and hexacoordinate chromium (II) complex, respectively, [77,79].

A 2-deoxy-2-halo-intermediate that is more stable and, therefore, less prone to oligomerization and reversion reactions (Figure 5a).

An alternative explanation has been given by Zhao et al. [77] (Figure 5b), who proposed that, when ionic liquids like 1-methyl-3-methylimidazolium chloride [EMIM]Cl are mixed with chromium chloride (CrCl₂), the Lewis acid formed (CrCl₃⁻) plays a critical role in the proton transfer, which facilitates the mutarotation of glucose.

3. Catalytic strategies for conversion of furfurals to fuel components

Several pathways for conversion of furfurals are considered in Figures 6 and 7. Among these routes, aldol-condensation has been proposed to increase the molecule length through the formation of carbon–carbon bonds [81,82], and etherification has been presented as an alternative to produce specialty chemicals for pharmaceutical industry [83].

3.1. Aldol-condensation

Biomass-derived sugars can be upgraded to conventional fuels through the combination of aldol-condensation reactions and hydrogenation/dehydration reactions. Dumesic et al. [35,54,84–87] have
Figure 6. Catalytic pathways for the conversion of furfural.

done seminal work in this area, applying molecular engineering concepts to formulate refining strategies for the production of renewable fuels.

The aldol-condensation reaction is initiated by the abstraction of the \( \alpha \)-hydrogen from aldehydes and ketones, in the presence of a basic catalyst. The resulting enolate reacts with the carbonyl carbon of another molecule to form the aldol-product that, after dehydration, forms an \( \alpha,\beta \)-unsaturated carbonyl molecule.

Although furfural molecules do not have \( \alpha \)-hydrogens, it is possible to perform cross-condensation reactions with other aldehydes and ketones, like acetone and propanal. In this approach, diesel and jet fuel can be produced by the coupling of \( C_5-C_6 \) furfural molecules with \( C_3 \) aldehydes and ketones (Figs. 6 and 7, respectively), Ref. [88]. The cross-condensed products, ranging from \( C_8 \) to \( C_{15} \), can be hydrogenated at low temperatures (100–150 °C) to decrease their solubility in the aqueous phase and their oxygen content. High temperatures and bifunctional catalysts (acid and metal) are required to perform dehydration and hydrogenation reactions in order to remove the residual oxygen and produce \( C_8 \) to \( C_{15} \) alkanes. Another route proposed by these authors [88] was based on the partial hydrogenation of the aromatic ring in the furfural molecules, in which an \( \alpha \)-hydrogen is generated and 5-hydroxymethyl-tetrahydrofurfural (HMTHFA) and tetrahydro-2-furfural (THF2A) are formed as products. These molecules can then react by self aldol-condensation to generate \( C_{10} \) to \( C_{12} \) products.
Figure 7. Catalytic pathways for the conversion of hydroxymethylfurfural.

The aldol-condensation reactions are carried out in polar solvents, such as water or water-methanol, and usually catalyzed by homogeneous bases like NaOH or Ca(OH)$_2$, Ref. [89]. However, in homogeneous catalysis, for every 10 parts of product formed, one part of spent catalyst is generated, which increases up to 13% the selling price of the product due to required purification, recovery, and waste treatments [89]. In contrast, heterogeneous catalysts are readily separated by filtration methods and, depending on the reactor configuration, they can be used for vapor-phase [90,91], liquid-phase [92,93] or biphasic liquid [55,82] systems.

3.2. Etherification

The production of chemical intermediates derived from fossil resources is of great importance for the pharmaceutical and polymer industries, as more than 90% of the major organic chemicals manufactured in the US in 1995 were produced from conventional hydrocarbon sources [94]. Nevertheless, the diminishing of the crude oil reserves and the ever-increasing environmental regulations has boosted the interest in the conversion of biomass into chemicals [95]. A perfect example of this is the etherification of hydroxymethylfurfural to produce 5,5-oxy(bis-meth-ylene)-2-furaldehyde (OBMF), which can be used in the synthesis of imine-based polymers with
high glass transition temperatures (300 °C), as well as in the preparation of hepatitis antiviral precursors [83]. In that case, the catalysts used were zeolites and mesoporous aluminosilicates with Bronsted and Lewis acid sites, which offer high temperature resistance and size-shape selectivity [96].

Two different etherification processes can be found in the literature (Figure 8), Ref. [83]: 1) etherification of HMF catalyzed by acids in organic solvents [97–99] and 2) the Williamson reaction of HMF and 5-chloro-methyl-2-furfural in an excess of base [100].

![Figure 8. Synthetic pathways for the production of 5,5'-oxy(bis-methylene)-2-furaldehyde (OBMF). Reproduced from Ref. [83].](image)

### 3.3. Hydrogenation

Hydrogenation of furfural with hydrogen gas on metal catalysts produces mainly furfuryl alcohol. This alcohol finds uses as a solvent, but is primarily used as an ingredient in the manufacture of chemical products such as foundry resins, adhesives, and wetting agents [74]. The catalysts most typically used in furfural hydrogenation are metals because they are able to dissociate hydrogen, thus making hydrogenation possible. The choice of catalyst support is based on its ability to disperse and stabilize metal particles enhancing the active surface area. Compared to other aldehydes, in addition to the carbonyl group, furfural contains an aromatic furanyl ring that could be also hydrogenated. While carbonyl hydrogenation is usually preferred due to the high stability of the aromatic ring, metal catalysts that have strong interactions with the unsaturated C= C bonds can still saturate the ring. Therefore, the selectivity toward aromatic alcohols is strongly dependent on the metal catalyst used. Furthermore, the geometric and electronic properties of different metals can affect both hydrogenation activity and selectivity by
influencing the type of adsorption intermediates. In this section we will primarily discuss the differences observed in furfural hydrogenation on group IB and VIII metals.

Among the group IB metals, Cu has been the most intensively investigated as a catalyst for furfural hydrogenation [101–107]. Silver has been used in a few studies while there is no report on Au catalysts [108]. The group IB metals are significantly less active than other metals. However, they exhibit a remarkable selectivity towards hydrogenation of the carbonyl group leaving the C=C double bonds in the furanyl ring unreacted. In this sense, Cu has been found to be the most selective among all tested metal catalysts. Selectivities above 98 % to furfuryl alcohol have been achieved over monometallic Cu/SiO₂ catalysts [107]. Also, monometallic Ag catalysts have been found able to hydrogenate the C=O group of furfural with relatively good selectivity, but not as high as that of Cu. For example, 80 % selectivity was obtained over a Ag/SiO₂ catalyst prepared by the sol-gel method [108].

The group VIII metals (Ni, Pd, and Pt) have also been used for furfural hydrogenation in both vapor and liquid phases on different supports; they all exhibit significant activity and selectivity [108], particularly at low temperatures (i.e., below 200 °C). For example, Ni catalysts have been used at low temperatures (100 °C) in liquid phase, exhibiting > 95 % selectivity to furfuryl alcohol [109,110]. Likewise, supported Pt catalysts doped with transition metal oxides have exhibited high selectivity, e.g., Pt/TiO₂/SiO₂ (selectivity = 94 %) and Pt/ZrO₂/TiO₂ (selectivity = 95 %), Ref. [111]. However, at higher temperatures (> 200 °C) the selectivity to alcohols on group VIII metals drops significantly upon the appearance of other reactions. For example, over a Ni/SiO₂ catalyst at 230 °C and excess of hydrogen (H₂/feed ratio = 25), only 25 % selectivity to furfuryl alcohol was observed [112]. On Pd catalysts, it is even lower, e.g., a Pd/SiO₂ catalyst at 230 °C yielded 14 % selectivity [113] and a Pd-Y catalysts at 350 °C rendered only 1 % selectivity to furfuryl alcohol [101]. The lower selectivities observed at high temperatures on group VIII metals can be ascribed to the emergence of decarbonylation and ring opening reactions. In addition, hydrogenation of the furanyl ring yielding the saturated alcohol is also observed over group VIII metal catalysts due to a stronger interaction of the furanyl ring with the metal surface than that obtained with group IB metals [114]. As a result, Cu and Ag should be the preferred catalysts if high selectivity to furfuryl alcohol is desirable, particularly at high temperatures. However, the intrinsic activity for furfural hydrogenation is lower on group IB metals than on group VIII metals, which is typically explained by the difference in extent of d-orbital filling. That is, the d-orbitals are filled in group IB, reducing the bond strength.
3.3.1. Reaction intermediates and mechanisms for furfural hydrogenation

DFT (density functional theory) calculations and HREELS (High Resolution Electron Energy Loss Spectroscopy) studies have been used to investigate the reaction intermediates and mechanisms for the hydrogenation of furfural on metal surfaces. For example, the preferential adsorption configurations of the furfural molecule on a Cu(111) surface have been investigated by DFT [107]. These calculations have shown that the perpendicular adsorption mode (see Figure 9) is the most stable configuration with the carbonyl group directly bonded to the surface through the O lone pair, which acts as a Lewis base. This type of adsorption mode is termed $\eta^1$-(O) and it seems to occur exclusively on group IB metals [115].

![Figure 9. Adsorption geometry of furfural on Cu(111), Ref. [107].](image)

In contrast, the parallel ring adsorption is highly unstable on the Cu(111) surface. This instability arises from the overlap of the filled 3d band of the surface Cu atoms with the $\pi$ orbitals of the aromatic furanyl ring, which causes a repulsion that results in a net positive (i.e., endothermic) adsorption energy.

A simple analysis of these results leads to a clear explanation of the observed high hydrogenation selectivity of the carbonyl group on these metals. That is, since the most stable configuration over group IB metals is the $\eta^1$-(O) mode, only the carbonyl group can be hydrogenated, while the predicted repulsion between the aromatic ring and the Cu surface makes the hydrogenation of the furanyl ring much more difficult.
Starting from the $\eta^1$-(O) adsorbed species on Cu surface two different reaction paths have been calculated by evaluating the possible transition states [107]. As shown in Figure 10, the hydrogen attack to the carbonyl group can occur in two different ways. In the first case (mechanism (a)), the addition of the H atom first occurs on the C atom of the carbonyl, leading to an alkoxide. The second H atom is added to the O of the alkoxy intermediate, yielding the alcohol product. In the second case (mechanism (b)), hydrogenation occurs first on the carbonyl O atom with formation of a hydroxylalkyl intermediate, followed by addition of the second H atom to the carbon to produce the furfuryl alcohol.

The DFT calculations indicate that the first H attack to the O atom of the carbonyl (hydroxyalkyl species, mechanism (b)) would have a lower energy barrier than the first H attack to the C atom of the carbonyl (alkoxy intermediate, mechanism (a)). The difference in stability between the two intermediates can be ascribed to the role played by the aromatic furanyl ring. That is, the addition of the first H atom to the O atom produces a negative charge on the C atom, which can be stabilized by the presence of furanyl ring (delocalization), favoring the formation of the hydroxylalkyl intermediate. This stabilization would not occur with aliphatic aldehydes, for which only mechanism (a) is possible.

Figure 10. Formation of a) alkoxide and b) hydroxylalkyl intermediates over Cu/SiO$_2$ [107].
As opposed to group IB metals, on which $\eta^1\text{-}(O)$ aldehyde is the preferred surface species, clean group VIII metal surfaces tend to adsorb aldehydes in the so-called $\eta^2\text{-}(C,O)$ configuration, in which both C and O atoms of the carbonyl group are bonded to the metal surface. In fact, DFT calculations of furfural on Pd(111) clearly show that an $\eta^2\text{-}(C,O)$-aldehyde is the preferred configuration on Pd (Figure 11), Ref. [113]. These results fully agree with the experimental HREEL spectroscopic observations of Barteau et al. [116]. The DFT calculations also demonstrate that the preferred adsorption of furfural is with the furanyl ring oriented essentially parallel to the metal surface. Therefore, this configuration makes hydrogenation of the furanyl ring on Pd readily possible, yielding the saturated alcohol as a major product, as experimentally observed.

The first H attack to the O atom of the $\eta^2\text{-}(C,O)$ aldehyde can result in a C-bonded hydroxyalkyl surface species, which can become the reaction intermediate in the hydrogenation of furfural on Pd to produce furfuryl alcohol. However, when the temperature is high enough, the $\eta^2\text{-}(C,O)$ aldehyde may further convert on the surface to a more stable acyl species, which is a precursor for decarbonylation, leading to hydrocarbon fragments and CO [117]. This tendency lowers the alcohol selectivity on Ni and Pd catalysts, at the expense of furan, which is the direct product of decarbonylation, discussed in Section 3.4.

### 3.3.2. Hydrogenation kinetics

The heterogeneously catalyzed hydrogenation of furfural over supported surfaces exhibits several elementary steps, including adsorption of the reactants, surface reaction, and desorption of the products.

$E_{\text{ads}} = 55.4 \text{ kcal/mol}$  
$E_{\text{ads}} = 9.6 \text{ kcal/mol}$

**Figure 11.** Adsorption geometry of furfural on Pd(111) and PdCu(111), Ref. [113].
A Langmuir-Hinshelwood model is usually a good approximation to describe the kinetics of this reaction [118]. The model can contemplate competitive and non-competitive adsorption, as well as dissociative and non-dissociative adsorption of reactants. In cases in which hydrogen is used in high excess, its partial pressure remains essentially unchanged and it is typically incorporated in the reaction constants. Furthermore, the kinetic model can assume one or two types of adsorption sites.

For example, a single-site Langmuir-Hinshelwood kinetic model based on dissociative adsorption of hydrogen was used by Sithissa et al. [107] to describe the gas phase hydrogenation of furfural over Cu/SiO₂. In that study, the adsorption of hydrogen, the aldehyde, and the products was assumed to involve one type of site.

Adsorption of the organic compounds was assumed to be rapid compared to the reaction steps, implying quasi-equilibrium for the adsorption and desorption steps. That is, the irreversible hydrogenation step was assumed to determine the rate of product formation. In addition to furfuryl alcohol (FOL), methyl furfural (MF) is also obtained in small amounts by cleavage of the C–O bond over Cu/SiO₂. After writing the mass balance for consumption and formation of each compound (FAL, FOL, and MF), the following rate equations were obtained:

\[
\begin{align*}
\dot{r}_{\text{FAL}} &= -k_1 K_{\text{FAL}} P_{\text{FAL}} + \frac{k_1}{K} K_{\text{FOL}} P_{\text{FOL}} - k_1 K_{\text{FOL}} P_{\text{FOL}} - k_2 K_{\text{FOL}} P_{\text{FOL}} + K_{\text{MF}} P_{\text{MF}} + K_{\text{H}_2}^{1/2} P_{\text{H}_2}^{1/2} \\
\dot{r}_{\text{FOL}} &= k_1 K_{\text{FAL}} P_{\text{FAL}} - \left[ \frac{k_1}{K} K_{\text{FOL}} P_{\text{FOL}} + k_2 K_{\text{FOL}} P_{\text{FOL}} \right] - k_1 K_{\text{FOL}} P_{\text{FOL}} - k_2 K_{\text{FOL}} P_{\text{FOL}} + K_{\text{MF}} P_{\text{MF}} + K_{\text{H}_2}^{1/2} P_{\text{H}_2}^{1/2} \\
\dot{r}_{\text{MF}} &= k_2 K_{\text{FOL}} P_{\text{FOL}} - k_1 K_{\text{FAL}} P_{\text{FAL}} - k_2 K_{\text{FOL}} P_{\text{FOL}} - k_1 K_{\text{FOL}} P_{\text{FOL}} + k_2 K_{\text{FOL}} P_{\text{FOL}} + K_{\text{MF}} P_{\text{MF}} + K_{\text{H}_2}^{1/2} P_{\text{H}_2}^{1/2}
\end{align*}
\]

where \( k_1 \) and \( k_2 \) are the rate constants for hydrogenation and hydrogenolysis, respectively (including hydrogen pressure), \( K_i \) is the adsorption constant and \( P \) is the partial pressure of component \( i \) (FAL = furfural, FOL = furfuryl alcohol, MF = 2-methyl furan).

By fitting the kinetic data with a LH model, all the thermodynamic and kinetic parameters were obtained. They include the heat of reaction (\( \Delta H_{\text{reaction}} \))...
short title

The heats of adsorption of furfural (12.3 kcal/mol) and 2-methyl furan (3.7 kcal/mol), Ref. [107]. The calculated heat of reaction was in the same order of that experimentally measured in the production of furfuryl alcohol over a copper chromite catalyst (-14.5 kcal/mol), Ref. [119]. The significant difference between the heats of adsorption of furfural and 2-methyl furan can be explained from the DFT calculations, which as indicated above, show that the strongest interaction of furfural with the Cu surface is via the carbonyl O forming $\eta^1$-(O) aldehyde. Since methyl furan does not have a carbonyl O and the furanyl ring is repelled by the Cu surface, a very weak adsorption is expected. This behavior of Cu strongly contrasts with that of other group VIII metals such as Pd or Pt, which strongly bind the furanyl ring [114].

Likewise, a similar Langmuir-Hinshelwood model of a single site has also been applied for the hydrogenation of furfural towards furfuryl alcohol over Ir/TiO$_2$ [120]. In this study, the adsorption of furfuryl alcohol was not taken into account in this kinetic model and the rate expression was expressed as:

$$r_{FAL} = -\frac{k_1 K_{FAL} C_{FAL} K_{H_2}^{1/2} P_{H_2}^{1/2}}{1 + K_{FAL} C_{FAL} + K_{H_2}^{1/2} P_{H_2}^{1/2}}$$

(Eq. 4)

Two alternative single-site mechanisms (with and without dissociation of hydrogen) were proposed in a furfural hydrogenation study conducted in the liquid phase over a Pt/C catalyst [121]. From these models, rate expressions were developed for cases in which either the adsorption of furfural, or hydrogen, or the surface reaction was rate-controlling. However, all these cases resulted in some negative parameters and hence they were rejected. By contrast, a model involving a dual-site mechanism with hydrogen molecularly adsorbed on active sites different from those involved in the adsorption of furfural and furfuryl alcohol resulted in all positive parameters. In this case, the surface reaction between adsorbed furfural and adsorbed hydrogen was assumed to be rate-controlling. The rate expression derived for this case is

$$r_{FAL} = -\frac{k_1 K_{FAL} K_{H_2} C_{FAL} C_{H_2}}{(1 + K_{FAL} C_{FAL})(1 + K_{H_2} C_{H_2})}$$

(Eq. 5)

The activation energies ($E_a$) for hydrogenation of furfural to furfuryl alcohol obtained over different catalysts are summarized in Table 1.
Table 1. Activation energy of furfural hydrogenation for various catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$E_a$ (kcal/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SiO$_2$</td>
<td>11.8</td>
<td>107</td>
</tr>
<tr>
<td>Copper-chromite</td>
<td>$11 \pm 2$</td>
<td>119</td>
</tr>
<tr>
<td>Ir/TiO$_2$</td>
<td>11.8</td>
<td>120</td>
</tr>
<tr>
<td>Ir/Nb$_2$O$_5$</td>
<td>$\sim 9$</td>
<td>122</td>
</tr>
<tr>
<td>Pt/C</td>
<td>6.7</td>
<td>121</td>
</tr>
</tbody>
</table>

The activation energy for furfural hydrogenation on both Cu/SiO$_2$ and Cu-chromite catalysts is close to 12 kcal/mol. This activation energy is in the range of the values typically observed in the hydrogenation of other carbonyl compounds over Cu [119]. The significantly lower activation energy observed on Pt/C compared to Cu catalysts might be ascribed to the different adsorption phenomena occurring on Pt and Cu. Since on Pt the furfural adsorption occurs exclusively in the $\eta^2$ mode while on Cu it occurs in the $\eta^1$ mode, the carbonyl C and O atoms are closer to the metal surface in the former than in the latter. Therefore, it could be expected that the H attack is energetically unfavorable on Cu, which should result in a higher activation energy. The activation energies observed on Ir catalysts seem to depend strongly on the type of support used, i.e. Ir on TiO$_2$ and Nb$_2$O$_5$ supports [120,122]. That is, not only the type of metal but also the nature of the support may have a crucial effect on the hydrogenation reaction.

### 3.4. Decarbonylation

The decarbonylation of furfural results in the production of furan, which could be utilized as a fuel component, but also as a chemical intermediate. For example, furan can be subsequently hydrogenated to tetrahydrofuran, which is commonly used as solvent and as a starting material for polyurethane manufacture [74].

While decarbonylation of furfural can be carried out in both the vapor and liquid phases [123–125], the former is generally preferred due to the advantage of a simpler operation and the possibility of easier catalyst regeneration and reuse. Different catalysts have been tested for this reaction. They include metal oxides such as Mn, Zn, Cd, Sr, K, Fe, Mo, and Cr oxides [126–128] or group VIII metals such as Pd, Pt, Rh, Ni [112,123,129]. The
latter are known to be effective catalysts and to result in high yields at rather mild conditions. By contrast, the former require more severe operating conditions and promote formation of heavy products that may cause catalyst deactivation.

Among the group VIII metals, Pd has been the most intensively investigated as the active metal in furfural decarbonylation [124,125] while Pt and Ni have been used less often [112,129]. It has been found that the high decarbonylation activity of Pd may be modified by the incorporation of a second metal (alloy formation) Ref. [113] or additives such as alkali and alkaline-earth metals [125,130]. Although Pd catalysts are relatively more active than other catalysts, the yield of furan decreases sharply with time on stream. For example, after 3 h on stream a Pd/C catalyst was found to lose most of its decarbonylation activity. An even faster deactivation was observed on a Pd/Al₂O₃ catalyst [123,127]. Among the various possible reasons for the observed deactivation, the most commonly proposed is carbon deposition, which could be due to side reactions, such as condensation and/or decomposition of furfural. Earlier studies demonstrated that a rapid loss in the activity of Pd/Al₂O₃ was observed in the absence of hydrogen, but the activity could be partially recovered by increasing the hydrogen partial pressure [124].

3.4.1. Reaction intermediates and mechanisms for furfural decarbonylation

The possible reaction paths for furfural conversion on Pd are illustrated in Figure 12. As mentioned above, the interaction of furfural with Pd involves a side-on complex (η²-(C-O) aldehyde) in which the furan ring lies parallel to the surface. In this configuration, the carbonyl binds to the metal surface through the carbonyl π orbital, with overlap between d electrons of the metal and the π* orbital of the carbonyl. The back-donation from the metal results in a stronger metal-aldehyde bonding than in the case of the η¹- mode. This stronger adsorption leads to a higher reaction rate, not only for hydrogenation of the η²-(C-O) surface aldehyde, but also to its decomposition into a more stable acyl surface species (see Figure 12), in which the C atom of the carbonyl remains strongly attached to the surface. This acyl species may in fact be a precursor for the decarbonylation reaction, producing furan and CO. In fact, it has been shown that the selectivity to decarbonylation significantly increases as a function of temperature, which is consistent with an activated conversion of η²(C,O) into the acyl species that increases decarbonylation while reducing hydrogenation [113].
The decarbonylation activity and selectivity of Pd catalysts may be modified by formation of bimetallic alloys and addition of additives such as alkali and alkaline-earth metals. For example, a comparison of the behavior of Pd-Cu alloys to that of pure Pd indicates that Pd may be electronically modified by the addition of Cu [113]. It has been observed that the stability of the di-sigma $\eta^2$-(C-O) species is greatly reduced on the Pd-Cu alloy due to a lower extent of back-donation. Theoretical calculation of the adsorption of furfural on Pd(111) and PdCu(111) surfaces suggest that the presence of Cu significantly reduces the interaction strength of furfural with the metal surface (see Figure 11). In fact, the heat of adsorption on the bimetallic surface is significantly reduced relative to that on the pure Pd. That is, the adsorption strength of furfural was predicted to drop from 13.2 kcal/mol on Pd(111) to 2.3 kcal/mol on PdCu(111). This dramatic reduction in the strength of interaction can be ascribed to the role played by the furanyl ring, which has a strong affinity for Pd, but not for Cu. As shown on the side view of Figure 11, the repulsion between the ring and the Cu atoms makes the molecule bends away from the surface.

Lopez and Norskov [131] have shown that alloying Pd with Cu causes a change in the position of the d-band center of Pd. This shift causes a lower extent of $\pi$-backdonation from Pd to $\pi^*$ orbital of the C=C and C=O bonds in the furfural molecule, which results in a significant weakening of the furfural adsorption strength. Moreover, relatively long distances are predicted by DFT between the carbonyl C and the metal surface in the case of the alloy, which greatly hinders the formation of the acyl intermediate, needed for decarbonylation. The destabilization of this crucial intermediate results in a drastic decrease in the rate of furan decarbonylation as the percent of Cu in the alloy increases.

A strong electronic modification of the properties of the Pd surface can also be obtained by doping it with K [130]. In this case, the Pd-K interaction results in an enhanced strength of furfural adsorption. This enhancement has been experimentally verified by the temperature-programmed surface reaction (TPSR) and FTIR. At the same time, an improvement in
decarbonylation rate is observed in the presence of K. It has been proposed that this improvement is due to an enhanced stability of the acyl intermediate.

### 3.4.2. Decarbonylation kinetics

Obtaining reliable kinetic parameters for furfural decarbonylation has been found to be more difficult than for furfural hydrogenation because the extent of catalyst deactivation has been much greater. In fact, while almost no deactivation was observed under conditions of hydrogenation reactions, almost 85% of the initial activity was lost after 4 h under decarbonylation reaction conditions [123]. Two possible reasons have been suggested for this rapid deactivation. They are the formation of coke, which is more significant at the temperature needed for decarbonylation, and catalyst fouling by either adsorbed furfural or some product formed during the reaction, including some of the high-molecular-weight by-products resulting from dimerization of furan [124,125].

A possible solution to avoid this problem has been attempted in a study of vapor phase decarbonylation of furfural on Pd/Al₂O₃ catalyst [124]. These authors obtained rates of reaction at zero time on stream (−r_{FAL})₀ by extrapolating the curves (X_{FAL})₀ vs. W/F_{FAL₀} using a second-order polynomial, followed by analytical differentiation and analyzing the data according to the method proposed by Froment and Hosten [132]. Using a Langmuir-Hinshelwood approximation they were able to satisfactorily fit the data on the basis of single-site mechanism that resulted in the expression:

\[
(r_{FAL})₀ = -\frac{kK_{FAL}P_{Furan}}{(1 + K_{FAL}P_{Furan} + K_{RS}P_{Furan})^2} \quad \text{(Eq. 6)}
\]

where \( K_{RS} \) is the adsorption constant of furan and CO. With this methodology, the authors were also able to develop kinetics and mechanism for the deactivation process. It was concluded that the deactivation occurred in parallel with the main reaction and the deactivation kinetics was governed by the reaction of two adjacent furfural molecules on the surface, resulting in the formation of the coke precursor. The deactivation rate (−da/dt) expression that most satisfactorily correlated with the data was the following

\[
\frac{-da}{dt} = \frac{k_d K_{FAL}^2 P_{Furan}^2}{(1 + K_{FAL}P_{Furan} + K_{RS}P_{Furan} + K_{FAL}P_{FAL})^2 a^{1.5}} \quad \text{(Eq. 7)}
\]

This expression was derived from the mechanism involving two adjacent adsorbed furfural molecules. It was found that resulting values for the
equilibrium constants of the adsorption of furfural that yields the coke precursor ($K_{\text{FAL}^*}$) are significantly higher than the equilibrium adsorption constant for furfural ($K_{\text{FAL}}$) used in the reaction kinetics. This enhancement would indicate that deactivation is enhanced by adsorbate-adsorbate interactions that strengthen the adsorption of furfural. Interestingly, the activation energy for deactivation derived from the fitting was 6.7 kcal/mol, which is much lower than that of the main reaction (14.8 kcal/mol). The former is associated with a condensation step, the latter with a C–C bond cleavage, which requires significant energy.

3.5. Opening of the furanyl ring

Ring opening is another potentially important reaction in the conversion of furfural over metal supported catalysts. Several pathways have been proposed for the ring opening, as shown in Figure 13. It can be seen that the products obtained from this reaction are predominantly alcohols, which could be promising biofuel components, such as butanol. It may also be used as valuable intermediates in the production of chemicals. For example, 1,5-pentanediol can be used as a monomer in the production of polyesters and polyurethanes [133]. At high enough temperatures and under acidic conditions, 1,5-pentanediol can be dehydrated to pentanes, which has a reasonable octane number (ON), but an unacceptably high vapor pressure to be incorporated in gasoline [134].

Several metal catalysts could be used to catalyze the ring opening reaction. Some of the metal catalysts mentioned in the literature include Ni [112,134,135], Rh [136], Pt [137] and Cu-chromite [103]. It is interesting to point out that by changing the catalyst one can obtain different alcohols since different catalysts have different selectivities towards the various possible reaction paths, particularly the first step. For example, 1,5-pentanediol and 2-pentanol were observed when hydrogenation and hydrogenolysis, respectively, occurred as the first step in the reaction sequence, while butanol was produced when the reaction started with the decarbonylation of furfural. A 33 % yield of 2-pentanol and 2-pentanone was achieved at 300 °C over a catalyst containing Cu/Cr/Ni/Zn/Fe with molar ratios of 43:45:8:3:1 [103]. In this case, the hydrogenolysis of furfural to 2-methyl furan was reported as the primary reaction. In contrast, butanal, butanol, and butane, which are derived from the ring opening of furan were observed as the main products from the conversion of furfural over Ni/SiO$_2$ catalyst at $> 200$ °C since furfural decarbonylation to furan is readily catalyzed by Ni at these high temperatures, as mentioned above [112]. On the other hand, at lower temperatures (140 °C) hydrogenation of furfural to furfuryl alcohol is
preferred over Ni catalyst. As a result, the ring opening produces mainly 1,5-pentandiol, which as mentioned can be later dehydrated to C$_5$-hydrocarbons over an acidic support (SiO$_2$-Al$_2$O$_3$) Ref. [134].

**Figure 13** Reaction scheme for the ring opening of furfural on metals.

**Figure 14.** Ring opening reaction of tetrahydrofurfuryl alcohol over Rh/SiO$_2$ and Rh-MoO$_x$/SiO$_2$ [136].
Finally, Rh has also been used to catalyze the ring opening reactions. For example, the ring opening of tetrahydrofurfuryl alcohol was observed on Rh/SiO$_2$ after hydrogenation of furfuryl alcohol in aqueous solution [136]. Without any modification, Rh/SiO$_2$ showed very low activity for this reaction and the main product was 1,2-pentanediol (66 % selectivity). However, after addition of MoO$_x$, a remarkable increase in activity was observed and the product selectivity was observed to change from 1,2-pentanediol to 1,5-pentanediol (> 93 % selectivity), as shown in Figure 14. This interesting change in behavior might have been explained in terms of an enhancement of adsorbate interaction with the catalysts via the OH group of the molecule and the MoO$_x$ species. According to this proposal, tetrahydrofurfuryl alcohol is adsorbed on MoO$_x$ species via the OH group and the cleavage of the C–O bond is then catalyzed by the neighboring Rh particles.

4. Molecular engineering of fuel components derived from furfurals

A quick examination of the different furfural conversion strategies reviewed above indicates that by choosing the right catalyst and reaction conditions the researcher can pick and choose from a broad range of potential fuel components. As summarized in Figure 15, starting with furfural, one can start with hydrogenation on a metal (Cu, Pd, Ni, Pt). The product furfuryl alcohol would not be the most desirable fuel component since it is fully miscible in water (see Table 2). If the furanyl ring is further hydrogenated and then the ring opened (e.g. on Pd and Ni, respectively), 1,5-pentanediol can be obtained. As shown in Table 2, this diol has a very good octane number, but its high solubility in water may also hinder its applications as a fuel component, similar to furfuryl alcohol. A similar situation may occur with butanol, which can be relatively easily obtained with a combination of decarbonylation/hydrogenation and ring opening (on Ni). While this potential fuel component has a relatively good octane number and vapor pressure, its water solubility is also high. However, it must be noted that, in this sense, butanol appears much better than ethanol, a fuel component widely used today despite its high water solubility. Two interesting alcohols that can be obtained from furfural and methyl furfural via hydrogenolysis followed by ring opening are pentanol and hexanol, respectively. While their octane numbers are not as high as those of the shorter alcohols, their vapor pressures and water solubilities are very attractive for gasoline components. This is an example of the fuel component analysis that can be done with the molecular engineering approach, in which the researcher may have the possibility of choosing reaction path that optimize several fuel properties simultaneously.
Figure 15. Catalytic strategies for the conversion of furfural to fuel components and chemicals. The possible reaction steps are indicated with lowercase letters and the corresponding catalysts listed in the inset.

Avoiding ring opening produces furan and methyl furan, aromatic compounds that have remarkably high octane numbers and low solubility in water. The only serious limitation of these compounds that may hinder their use as fuel components is their high vapor pressure, which is much higher than those of their corresponding ring-opening derivatives.

Finally, the path that combines aldol-condensation with hydrogenation and hydrodeoxygenation appears greatly attractive for the production of diesel fuel components. As shown in Figure 15, while the C$_8$ compound that results from the condensation of one molecule of acetone with one molecule of furfural is in the gasoline range, the C$_{13}$ compound that results from two furfurals and one acetone is in the diesel range and has a high cetane number, even after hydrodeoxygenation, resulting in an appealing alternative for green diesel fuel.

In this contribution we have reviewed the possible reaction paths that could be followed for upgrading furfurals (e.g. 2-furfuraldehyde and 5-hydroxymethyl furfural), intermediates from biomass to fuel components and chemicals. It is concluded that by varying the catalyst composition (metal,
Table 2. Summary of the possible reactions taking place in the conversion of furfural (FAL) and hydroxymethylfurfural (HMF), with the respective products and their properties.

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Reactions</th>
<th>Products</th>
<th>ON or CN*</th>
<th>RT Vapor Pressure (mm Hg)</th>
<th>Water solubility (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAL</td>
<td>Hydrogenation</td>
<td>furfuryl alcohol</td>
<td>134</td>
<td>3</td>
<td>Fully miscible</td>
</tr>
<tr>
<td>FAL</td>
<td>Hydrogenation + Ring opening</td>
<td>1,5-pentanediol</td>
<td>69</td>
<td>0.02</td>
<td>Fully miscible</td>
</tr>
<tr>
<td>FAL</td>
<td>Decarbonylation</td>
<td>furan</td>
<td>109</td>
<td>490</td>
<td>0.0</td>
</tr>
<tr>
<td>FAL</td>
<td>Hydrogenolysis</td>
<td>methyl furan</td>
<td>131</td>
<td>140</td>
<td>7</td>
</tr>
<tr>
<td>FAL</td>
<td>Decarbonylation + Ring opening</td>
<td>butanol</td>
<td>96</td>
<td>6</td>
<td>77</td>
</tr>
<tr>
<td>FAL</td>
<td>Hydrogenolysis</td>
<td>pentanol</td>
<td>57</td>
<td>1.8</td>
<td>22</td>
</tr>
<tr>
<td>HMF</td>
<td>Ring opening</td>
<td>hexanol</td>
<td>55</td>
<td>0.93</td>
<td>8.2</td>
</tr>
<tr>
<td>HMF</td>
<td>Hydrogenolysis</td>
<td>dimethylfuran</td>
<td>119</td>
<td>26</td>
<td>2.3</td>
</tr>
<tr>
<td>HMF</td>
<td>Aldol-condensation</td>
<td>4-2-(furyl)buten-3-en-2-one</td>
<td>128</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HMF</td>
<td>Aldol-condensation</td>
<td>1,5-di-2-furyl pentan-1,4-dien-3-one</td>
<td>75*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HMF</td>
<td>Aldol-condensation + Hydrogenation</td>
<td>1,5-di-furylpentan-3-ol</td>
<td>100*</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

additives, support), as well as reaction conditions (pressure, temperature, liquid/vapor phase, etc.), one can obtain a rich variety of products with different fuel properties.

References