Synthesis and conversion of furfural-batch versus continuous flow
Yantao Wang

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Par Yantao WANG

Synthesis and conversion of furfural-batch versus continuous flow

Thèse présentée pour l’obtention du grade de Docteur de l’UTC

Soutenue le 22 mars 2019
Spécialité : Génie des Procédés Industriels et développement durable : Transformations intégrées de la matière renouvelable (EA-4297)

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Université de Technologie de Compiègne

Ecole Doctorale : Sciences pour l’ingénieur

Thèse présentée par

Yantao WANG

Pour le titre de Docteur en Génie des Procédés Industriels et du Développement Durable

Synthesis and conversion of furfural-

batch versus continuous flow

Thèse dirigée par le Professeur Christophe LEN

Soutenue le 22 Mars 2019 devant le jury composé de :

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GENERAL INTRODUCTION

Our world, which is becoming more and more global every day, is confronted with the reduction of fossil resources, strong fluctuations (variation, instability) of fossil fuel prices and the increase of greenhouse gas emissions.\textsuperscript{1,2} These concerns require the discovery of bio-renewable resources such as intensive biotransformation processes to fossil fuels and chemicals. The use of plant wastes as raw materials is one of the alternatives for minimizing the dependence on fossil oil for transportation fuels and is the best strategy for replacing petrochemicals.\textsuperscript{3,4} The optimum upgrading of biomass through the exploitation of all opportunities in an integrated approach: "biorefinery". Biorefining can be defined as sustainable process of biomass transformation into biobased products (food, chemicals, and materials) and bioenergy (biofuels, electricity, heat).\textsuperscript{5}

The refinery of biomass converts the renewable bio-resources into biofuels, in platforms molecules for fine chemicals, agro-chemicals, and specialty chemicals such as bio-lubricants, natural fibers and bio-solvents.\textsuperscript{6} Several building blocks derived from renewable resources such as ethanol, glycerol, lactic acid, succinic acid and levulinic acid, are already in use or considered with potential importance in the near future.\textsuperscript{7} Among them, furanic compounds, such as furfural (FF) and 5-hydroxymethylfurfural (HMF), have various industrial applications (Figure 1), which conventionally produced from fossil feedstock via several steps that led to relatively lower overall yield. Recently years, many reports have shown that one-pot
and efficient production of furans could be achieved from biomass by well-optimized catalysts, solvents, equipment and processing technology upgrades etc. However, plenty of issues were also faced in most of studies, such as limited yield, longer reaction time, poor catalysts recycle performance etc. Besides, one of the main challenges is to respect the principles of Green Chemistry. As well-known, Green Chemistry was firstly introduced by Paul Anastas and John Warner in 1998, which was defined as the ‘design of chemical products and processes to reduce or eliminate the use and generation of hazardous substances’, and later, the Twelve Principles of Green Chemistry (as follows) were introduced as a guiding framework for chemists. These principles contributed to the development and the popularization of the concept of Green Chemistry:

1) Prevention. It is better to prevent waste than to treat or clean up waste after it is formed.

2) Atom Economy. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3) Less Hazardous Chemical Synthesis. Whenever practicable, synthetic methodologies should be designed to use and generate substances that pose little or no toxicity to human health and the environment.

4) Designing Safer Chemicals. Chemical products should be designed to preserve efficacy of the function while reducing toxicity.

5) Safer Solvents and Auxiliaries. The use of auxiliary substances (e.g. solvents, separation agents, etc) should be made unnecessary whenever possible and, when
used, innocuous.

6) Design for Energy Efficiency. Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7) Use of Renewable Feedstocks. A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8) Reduce Derivatives. Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9) Catalysis. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10) Design for Degradation. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11) Real-Time Analysis for Pollution Prevention. Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12) Inherently Safer Chemicals for Accident Prevention. Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.
Therefore, the aim of this PhD work is to: 1) realized the production of furfural with greener methods; 2) valorize furfural into high value-added products, such as 2-furonitrile, furfuryl alcohol etc. Several keys issues were identified in order to design processes greener than the current ones. For furfural synthesis, experiments were performed in water and in water and organic solvent when co-solvents (green or eco-friendly) are necessary. Microwave irradiation has been chosen as the heating method to accelerate the dehydration process, and microwave continuous flow reactor was also applied to improve furfural productivity. When starting from furfural to produce high value-added chemicals, flow reactors, such as Pheonix, H-cube Pro as well as microwave continuous flow with micro-reactor, were also identified as interesting alternatives to improve the productivities of target compounds.

The first chapter concerning furfural synthesis and the context of this thesis will be introduced from our "star"-furfural, then followed by the bio-resources and improved methods for its production. Finally, a review of the literature on furfural production in recent years will be discussed.

Chapter II will focus our contribution on the dehydration of D-xylose and xylan (from beechwood) to produce furfural using heterogeneous bio-based catalyst: sulfonated sporopollenin and homogenous catalyst (H$_3$PW$_{12}$O$_{40}$) in microwave continuous flow. Additionally, expeditious conversion of alginic acid to furfural using CuCl$_2$ was also investigated.
Chapter III will give an overview of furfural applications, and especially a brief review about furfural cyanation and furfural hydrogenation to (tetrahydro)furfuryl alcohol and 2-methyl(tetrahydro)furan in recent 5 years will be summarized.

Chapter IV mainly deals with the work we did concerning furfural cyanation in two steps continuous flow and furfural selective hydrogenation over various metals supported on activated carbon, and then the following alcoholysis of furfuryl alcohol to alkyl levulinates will be discussed.

In the last part, after the concluding remarks, the experimental procedures and supporting information will be offered.

Figure 1 Synthesis and application of two platform molecules: Furfural and 5-Hydromethylfurfural
References


CHAPTER 1 Furfural synthesis

Context and literature review

1.1 Furfural

1.1.1 General information

Furfural (formula C₄H₆OCHO) is one of the oldest renewable chemicals, like ethanol, acetic acid and sugar.¹ It could be found in many processed foods and beverages. The name of furfural comes from the Latin word furfur, meaning bran, referring to its originally preparation from the co-heating of rice bran with dilute acid. Furfural is a colorless, transparent, oily liquid with a distinctive odor similar to benzaldehyde, but the color quickly changed when exposed to light and air, that's why commercial samples are often amber. Furfural is the most important derivative of the furanic compounds, and it has high reactive activity due to its special function groups: aldehyde group and a dienyl ether group. The fundamental information of furfural was listed in Table 1.1.1.²
Table 1.1.1 Fundamental information of furfural

<table>
<thead>
<tr>
<th>IUPAC name</th>
<th>Appearance</th>
<th>Colorless oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furan-2-carbaldehyde</td>
<td>Odor</td>
<td>Almond-like</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other names</th>
<th>Formula</th>
<th>Density</th>
<th>Boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural, furan-2-carboxaldehyde, fural, furfuraldehyde, 2-furaldehyde, pyromucic aldehyde</td>
<td>C₅H₄O₂</td>
<td>1.16 g/mL</td>
<td>162 °C (324 °F; 435 K)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CAS Number</th>
<th>Solubility in water</th>
<th>boiling point</th>
</tr>
</thead>
<tbody>
<tr>
<td>98-01-1</td>
<td>83 g/L</td>
<td>162 °C (324 °F; 435 K)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EINECS Number</th>
<th>Vapor pressure</th>
<th>Molar mass</th>
<th>Flash point</th>
</tr>
</thead>
<tbody>
<tr>
<td>202-627-7</td>
<td>2 mmHg (20 °C)</td>
<td>96.09 g mol⁻¹</td>
<td>62 °C (144 °F; 335 K)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Melting point</th>
<th>⁰C (⁰F; K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>−37 (−35 °F; 236 K)</td>
<td></td>
</tr>
</tbody>
</table>

1.1.2 Development history

1. In 1821, German chemist Johann Wolfgang Döbereiner first discovered furfural as a byproduct of formic acid synthesis.

2. In 1840, the Scottish chemist John Stenhouse found that furfural could be produced by distilling a wide variety of crop materials, including corn, oats, bran, and sawdust, with aqueous sulfuric acid; he also determined an empirical formula of \((\text{C}_3\text{H}_4\text{O}_2)\).

3. George Fownes named this oil furfural in 1845.

4. German chemist Carl Harries deduced furfural's structure in 1901.

5. In 1922, American Quaker Oats Company first realized the industrialization of furfural, which was mainly applied to the decolorization of wood rosin and the refining of lubricating oil, and realized the application of furfural in the industrial field;

6. In the 1940s, furfural was widely used in the fields of synthetic rubber,
medicine, and pesticides;

7. After the 1960s, with the development of furfural derivatives, especially the widespread application of furan resins in the foundry industry, the development of furfural industry was greatly promoted.

8. Furfural was identified in 2004 as one of the top 30 high-value bio-based chemicals by the U.S. Department of Energy.

  Furfural is an important organic chemical raw material, which can be used to prepare maleic anhydride, oxalic acid, decyl alcohol and tetrahydrofuran. It can also be used to synthesize furfural resin, furan resin, rubber vulcanization accelerator, rubber anti-aging agent and preservative. Mainly used in medicine, pesticides, veterinary drugs, food and so on.

1.2 Bio-resources for the production of furfural

Generally, furfural could be produced by the acid catalyzed dehydration of 5-carbon sugars (pentose), particularly xylose, and these sugars may be obtained from hemicellulose which is second main component of biomass. However, recent researches have been demonstrated that other kinds of carbohydrates can be served as starting materials for furfural production. This part aims to mainly introduce the resources for the production of furfural.

1.2.1 C5 saccharides and polysaccharides

Furfural formation from pentose polymers is considered as a two-step mechanism (as drawn in Scheme 1.2.1). In the presence of acid catalyst, polysaccharides will first
hydrolyze to its monomers, and then the pentose units will loss three water molecules dehydrated to furfural. As we known, the most investigated C5 saccharides for the synthesis of furfural is D-xylose, which is the main building block for the hemicellulose xylan.

![Diagram of Furfural formation from pentose polymers](image)

**Scheme 1.2.1 Furfural formation from pentose polymers**

D-xylose contains five carbon atoms and includes an aldehyde functional group. As illustrated in Figure 1.2.1, D-xylose can adopt several structures depending on conditions, and in solution, the cyclic hemiacetal isomers (the pyranoses, which feature six-membered C5O rings (Figure 1.2.1d), and the furanoses, which feature five-membered C4O rings (with a pendant CH₂OH group, Figure 1.2.1c)) are more prevalent, even if all the conformations coexist.³

![Structure of D-xylose](image)

**Figure 1.2.1 Structure of D-xylose**

The conversion of xylose to furfural is a difficult reaction, and the reaction mechanism is quite complex, as it varied with different reaction conditions, such as the solvent, the type of catalyst etc. Several mechanistic studies reported that xylose
dehydration mechanism possibly via enolization\textsuperscript{4,5}, β-elimination\textsuperscript{6,7} or cyclic intermediates.\textsuperscript{8–10} However, there is no a reaction mechanism recognized definitively to date. Danon et. al attempted to group the mechanisms proposed, and the results were shown in Scheme 1.2.2\textsuperscript{11} At lower acidities, enolization and subsequent isomerization is favored, although the formation of furfurals is retarded and there are more options for side reactions (via 3e). Under these conditions ketoses may be detected, and enol intermediates such as 2 and 4 generally tautomerize respectively to 3 and 5 faster than they are dehydrated. Further enolization to 3e has been reported to be irreversible, seemingly leading to side reactions. Also β-elimination cannot be excluded under these conditions, offering a direct path to 4, hence reducing the possibilities for side reactions via 3e.

![Scheme 1.2.2 Grouped plausible mechanism of xylose reaction to furfural in acid media. X– indicates halides ions, and M\textsuperscript{3+} indicates metal cations. Adapted from Danon et. al\textsuperscript{11}](image-url)

However, most of the mechanisms proposed involved reaction intermediates
which have not been clearly identified or detected experimentally. Recent studies showed an isomer of xylose: xylulose, which was the key element of the reaction. Xylose would firstly isomerize to xylulose in the presence of Lewis acid, and then xylulose would further dehydrate to furfural, by analogy to the dehydration reaction of glucose to 5-HMF which goes through the formation of its isomer fructose, more reactive. In this case, Lewis acid acts an important role to isomerize xylose to xylulose, and decrease the reaction activation energy. On the other hand, xylose was supposed to isomerize to lyxose, and then dehydrate to furfural when catalyzed with zeolite\textsuperscript{12} or Mo (VI)\textsuperscript{13} catalysts. These works will be discussed in the following part.

As far as we known, except for xylose, only few of reports investigated the production of furfural with arabinose\textsuperscript{14}, ribose\textsuperscript{15} or lyxose\textsuperscript{6,16}. Most of studies focused on xylose that was reasonable, because xylose is commercial available from 1930, with a price close to sucrose. Correspondingly, the well-investigated polysaccharide for furfural synthesis is xylan, which comprises about 30 % of some plants (birch for example). Xylans thus represent a renewable resource available in large amounts in forestry, agriculture, and in wood, pulp and paper industries. Several types of xylans can be differentiated according to the nature of their substituents. Homoxylans (not substituted) are heteropolymers possessing a backbone composed of xylose units linked by $\beta$-(1→3) (Figure 1.2.2a) or mixed $\beta$-(1→3, 1→4) (Figure 1.2.2b) glycosydic bonds. Other three types of xylans are : 1) Glucuronoxylans which consist of a linear chain of xylose units branched with glucuronic acid and its O-methylated derivative; 2) Arabinoxylans which are grafted with arabinose substituents; 3) (Arabino)glucuronoxylan and (glucurono)arabinoxylan which can be ratified by the two previous types (Figure 1.2.2c).
According to Ebringerova et al., hemicelluloses was classified in four main groups: (i) xylans, (ii) mannans, (iii) xyloglucans, and (iv) β-glucans. Thus, except for xylans, the polymers combined C5 units and C6 units, for example, xyloglucans, can produce furfural, even C6 polysaccharides could be potentially served as the starting materials for furfural synthesis, which will be introduced in next part.

1.2.2 C6 saccharides and polysaccharides

The production of furfural from the compounds with six-carbon atoms emerged in recent years, especially with C6 polysaccharides- alginic acid. Some C6 monosaccharides, which are well-known as the starting materials for the production of 5-HMF, such as glucose and fructose, could also produce furfural through the retro-aldol reaction of these sugars in harsh conditions, for example high temperature. However, the yield of furfural was limited less than 40 %, in spite of the optimization of reaction conditions and starting from monosaccharides. Interestingly, similar results were observed with another C6 polymers- alginic acid.

Alginic acid, also called algin or alginate, is a polysaccharide distributed widely in
the cell walls of brown algae. It’s a linear copolymer with homopolymeric blocks of (1-4)-linked β-D-mannuronate (M) and its C-5 epimer α-L-guluronate (G) residues, respectively, covalently linked together in different sequences or blocks (Figure 1.2.3). The monomers can appear in homopolymeric blocks of consecutive G-residues (G-blocks), consecutive M-residues (M-blocks) or alternating M and G-residues (MG-blocks).

As mentioned above, furfural synthesis from xylan will experience hydrolysis and dehydration reactions. In case of alginic acid, these two processes are also needed; what's more, based on the structural differences between the monomers of alginic acid and xylose, the removal of the carboxyl group is necessary for the production of furfural from alginic acid. A plausible reaction pathway for the catalytic conversion of alginic acid to furfural was proposed by Jeon et al. (as shown in Scheme 1.2.3). Decarboxylation of alginic acid is as well as a key process in the production of furfural.
1.2.3 Origin biomass

Biomass is abundantly available currently, offering over 10% of the global energy supply, and being recognized as the top four energy sources in the light of world energy consumption in 2011. Lignocellulose mainly composed of cellulose, hemicellulose and lignin. From the industrial point of view, furfural is totally produced from origin biomasses, such as bagasse, corn cobs, oat hulls, wood chips etc. Figure 1.2.4 illustrated a schematic structure of lignocellulosic biomass. Generally, lignocellulosic biomass has three main families: woody plants, herbaceous plants and waste biomass. The relative content of each biopolymer can vary significantly depending on the biomass origin, as shown in Table 1.2.1. Plenty of pentosan-rich biomasses have been investigated in literatures for furfural production, such as wheat straw, corn stover, switchgrass, pinewood etc. Some of the work will be summarized in the part of literatures review.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Cellulose(%)</th>
<th>Hemicellulose(%)</th>
<th>Lignin(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Softwood</td>
<td>35-40</td>
<td>25-30</td>
<td>27-30</td>
</tr>
<tr>
<td>Hardwood</td>
<td>45-50</td>
<td>20-25</td>
<td>20-25</td>
</tr>
</tbody>
</table>
Wheat straw 33-40 20-25 15-20
Switchgrass 30-50 10-40 5-20

Figure 1.2.4 Schematic structure of lignocellulose. The hexagons represent the lignin subunits p-coumaryl alcohol (H), coniferyl alcohol (G) and sinapyl alcohol (S). From F. Streffer 23

1.3 Advanced methods for furfural production

As introduced, furfural production is facing environmental issues and yield limitation, especially its industrial production which largely relied on the batch dehydration of pentosan-rich biomass using sulphuric acid, with yields typically around 50%, such as the Quaker Oats process since 1921. Fortunately, researchers have not stopped the pace of innovation, and various advanced methods have been applied to improve furfural yield, to separate target products more easily, and to make the process more efficiency and greener. In this part, we will focus on the introduction of advanced methods for furfural production.
1.3.1 Microwave irradiation

Microwaves are generally defined as non-ionizing radiations, namely electromagnetic waves that are comprised of two perpendicular components (i.e., electric and magnetic fields). Microwave heating is different with conventional heating since it can be transmitted, reflected or absorbed toward the reagents. Figure 1.3.1 gives an intuitive view of microwave. It’s clearly showed that microwave is a kind of electromagnetic irradiation between the infrared and radio wave with the wavelengths ranging from 0.01 to 1 m, and the corresponding frequency varying from 0.3 to 300 GHz. However, to avoid any interference, all domestic “kitchen” microwave ovens as well as commercially available dedicated microwave reactors for chemical synthesis operate at a frequency of 2.45 GHz (corresponding to a wavelength of 12.25 cm).  

![Figure 1.3.1 The frequency and wavelength of microwave radiation region](image)

Microwave energy was originally applied for heating food. Until the mid-1980s,
Gedye et al. first reported the use of microwave heating to accelerate chemical synthesis. Since then, microwave technologies and equipment have been significantly developed, and the number of publications related to microwave-assisted organic synthesis increased dramatically (up to ≈ 5000). In 1998, Grant and Halstead provided a thorough explanation of the underlying theory of the microwave dielectric heating. The microwave heating involves two main mechanisms: dipolar polarization and ionic conduction as sketched in Figure 1.3.2 which adapted from Bilecka and Niederberger.

In case of dipolar polarization, to absorb microwaves irradiations, a substance structure must be partly negatively and partly positively charged. The dipolar polarization mechanism could be vividly exemplified with water. Under the microwave heating, water molecules try to orientate with the rapidly changing alternating electric field; thus heat is generated by the rotation, friction, and collision of molecules.

As for ionic migration, dissolved charged particles oscillate back and forth under microwave irradiation, and they also collide with neighboring molecules, thereby generating heat. As an example: if equal amounts of distilled water and tap water are heated by microwave irradiation, more rapid heating will occur for the tap water because of its ionic content in addition to the dipolar rotation of water molecules.
Under microwave irradiation conditions, the ability of a specific substance to convert electromagnetic energy into heat is determined by the so-called loss tangent, $\tan \delta$. The high $\tan \delta$, the high microwaves absorbing ability a material has. And the definition of the loss factor $\tan \delta$ is: $\tan \delta = \epsilon''/\epsilon$. Where the dielectric constant ($\epsilon$), describing the ability of molecules to be polarized by the electric field, and the dielectric loss ($\epsilon''$), indicating the efficiency with which electromagnetic radiation is converted into heat. Commonly used organic solvents with high ($\tan \delta > 0.5$), medium ($\tan \delta 0.1-0.5$), and low microwave absorbing ($\tan \delta < 0.1$) are summarized in Table 1.3.1.
Table 1.3.1 Commonly used organic solvents classified according to their heating efficiency (tan δ) in the microwave field. From Kappe et al. 30

<table>
<thead>
<tr>
<th>Solvent</th>
<th>tan δ</th>
<th>Solvent</th>
<th>tan δ</th>
<th>Solvent</th>
<th>tan δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene glycol</td>
<td>1.350</td>
<td>2-Butanol</td>
<td>0.447</td>
<td>Chloroform</td>
<td>0.091</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.941</td>
<td>Dichlorobenzene</td>
<td>0.280</td>
<td>Acetonitrile</td>
<td>0.062</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.825</td>
<td>NMP</td>
<td>0.275</td>
<td>Ethyl acetate</td>
<td>0.059</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.799</td>
<td>Acetic acid</td>
<td>0.174</td>
<td>Acetone</td>
<td>0.054</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.722</td>
<td>DMF</td>
<td>0.161</td>
<td>THF</td>
<td>0.047</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.659</td>
<td>Dichloroethane</td>
<td>0.127</td>
<td>Dichloromethane</td>
<td>0.042</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.589</td>
<td>Water</td>
<td>0.123</td>
<td>Toluene</td>
<td>0.040</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>0.571</td>
<td>Chlorobenzene</td>
<td>0.101</td>
<td>Hexane</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Why so many researchers devote to microwave chemistry? What are the advantages of microwave heating when vs conventional heating? As a fact, we can find that microwave is non-contact and volumetric heating, it’s energy transfer rather than heat transfer, it could reach desired temperature rapidly and efficiently, thus saving energy. Besides, as it can realize material selective heating, so it allows high flexibility of feedstock and products. What’s more, microwave heating has higher level of safety and automation, and easier operation (quick start up and stopping). However, it’s not well-investigated like conventional heating, or not easy to scale up concerning to the equipment. Some other disadvantages, such as low energy conversion efficiency, uncontrolled heating leads to safety concerns, inherent issue of temperature measurement and uniformity, especially difficulties of the scaling up
of microwave-assisted heating for biomass pyrolysis\textsuperscript{31} should be well concerned in the future.

1.3.2 Critical water

A new technology that can change waste woody biomass into useful resource by means of sub-critical or supercritical water is now attracting worldwide attention. The reason why this technology has great merit and is regarded as promising in near future lies in the facts that water is quite cheap, handy, and available almost everywhere in the world, and that water is chemically stable, safe, and harmless to environment.

Supercritical water (SCW) can be defined as water above its critical point (374 °C, 22.1 MPa, Figure 1.3.3). Water is supercritical existing as small but liquid-like hydrogen-bonded clusters dispersed within a gas-like phase, where physical properties, such as gas-like or liquid-like behavior, vary in response to changing temperature, pressure and density and the normal distinction between gas and liquid has disappeared.

For subcritical water, the definition is less strict and can describe as water above its boiling point at ambient pressure (> 100 °C and 0.1 MPa) and below its critical point (374 °C at 22.1 MPa, as shown in Figure 1.3.3). Other terms referring to subcritical water can be found in the literature, such as hot compressed water, superheated water or high temperature water. According to literature,\textsuperscript{32} the ion product of water (Kw) increases by three orders of magnitude from Kw = 10\textsuperscript{-14} mol\textsuperscript{2}/L\textsuperscript{2} to Kw ≈ 10\textsuperscript{-11} mol\textsuperscript{2}/L\textsuperscript{2} with increase temperature from 25 to 300 °C, which means plenty of
hydronium and hydroxide ions formed at 300 °C. That’s said that water becomes both a stronger acid and a stronger base as the temperature increases to the subcritical water range. Thus, reactions typically promoted by either acid or base can be performed in high-temperature water without the addition of any catalyst. In addition, while chemical reactions in supercritical water have mainly been applied to break up bonds, the milder temperature region of subcritical water allows bond formation, i.e., synthesis of organic compounds. Therefore, furfural production generally was performed in sub-critical water, and relative work will be showed in the review part.

![Figure 1.3.3 The Phase Diagram of Water.](image)

**1.3.3 Biphasic system**

In the production of furfural, one of the key factor that restricts furfural yield is that furfural formed could further react with xylose forming secondary products, namely
humins (as shown in Figure 1.3.4a). Besides, furfural has a poor thermal stability, when temperature is higher than 180 °C, furfural condensation and degradation will be easily occurred, especially under acidic environment. To avoid these problems, one of the remarkable methods is to introduce a co-solvent which can extract furfural at once it formed. As illustrated in Figure 1.3.4b, xylose dehydrated to furfural in aqueous phase, then furfural will be extracted into organic phase, and this process will avoid the contact of xylose with furfural, thus inhibit the occurrence of side-reactions. What’s more, the introduction of the co-solvent will protect furfural exposed in acidic environment, and further decreased possibly furfural condensation and degradation.

It's worth to mention that biphasic system leads to easier product separation as most of furfural was extracted in organic phase, and possibly energy saving. However, this extraction method utilizes the difference in solubility or partition coefficient of xylose and furfural in two mutually incompatible (or slightly soluble) solvents to transfer the compound from one solvent to another. So the choice of a green or environmental friendly organic solvent, which has good solubility for furfural and insoluble in water, will be a challenge and crucial point.

**Figure 1.3.4 Furfural production in a: monophasic system and b: biphasic system**
1.3.4 N$_2$-stripping

To improve furfural yield, another advanced method- N$_2$ stripping was also investigated. Stripping works on the basis of mass transfer. The idea is to make the conditions favorable for the component A, in the liquid phase to transfer to the vapor phase. Stripping is a physical separation process where one or more components are removed from a liquid stream by a vapor stream. In industrial applications the liquid and vapor streams can have co-current or countercurrent flows. Agirrezabal-Telleria et al designed a N$_2$ stripping methodology (Figure 1.3.5), and proved that the use of N$_2$ stripping showed better extraction efficiency of furfural than water/toluene biphasic system which benefits to environmental and products separation concerns.$^{34-38}$

![Figure 1.3.5 The N$_2$-stripping set-up for furfural production. Adapted from Agirrezabal-Telleria et al.$^{35}$](image)

1.3.5 Flow chemistry

Another solution for limiting the formation of side products is the use of a continuous flow reactor. In flow chemistry, a chemical reaction is run in a
continuously flowing stream (as shown in Figure 1.3.6). Flow chemistry is a well-established technique for use at a large scale when manufacturing large quantities of a given material. Indeed, the short residence times associated with this type of reactors could avoid long contact between reactants and products and thus increase desired products selectivity.

Figure 1.3.6 General schematic diagram of organic synthesis under continuous-flow conditions. Adapted from Glasnov and Kappe.39

Continuous processing is contrasted with batch production. In this regard, continuous flow processing has a number of significant and inherent advantages for biomass processing as compared to batch reactor technologies:

- Continuous flow processing allows a better control of reaction conditions.
- Flow processing also facilitates scaling up which is an important point taking into consideration that many of the biomass processes are still in the lab scale.
✓ The utilization of flow processing technologies allows intensification of the chemical processes, thereby significantly contributing to simplify technologies.

✓ Unlike batch processing, fixed-bed flow technologies do not require catalyst separation after reaction and regeneration, if required, is readily performed over the same catalytic bed.

✓ Safety is increased, as flow operation allows continuous removal of gases which may not interfere in the main catalytic process, however, gases build up in the reactor leading to increasing pressure and, potentially, new and uncontrolled processes in batch conditions.

✓ Multi step reactions can be arranged in a continuous sequence. This can be especially beneficial if intermediate compounds are unstable, toxic, or sensitive to air, since they will exist only momentarily and in very small quantities.

Of course, the drawbacks of continuous flow should be recognized, for example:

- Dedicated equipment is needed for precise continuous dosing (e.g. pumps), connections, etc.

- Start up and shut down procedures have to be established.

- Scale up of micro effects such as the high area to volume ratio is not possible and economy of scale may not apply. Typically, a scale up leads to a dedicated plant.

- Safety issues for the storage of reactive material still apply.

Encouragingly, most of furfural is produced by continuous processes in industry, such as the Huaxia/Westpro technology used in China. Another promising technology for improving the energy efficiency and yield of furfural production is the Supra Yield
process, which is utilized for furfural production in Australia. Some furfural production processes are briefly described in Table 1.3.2.

Table 1.3.2 Examples of furfural production in continuous processes. Adapted from Le Guenic et al.40

<table>
<thead>
<tr>
<th>Company /process</th>
<th>Process type</th>
<th>Operating temperature (°C)</th>
<th>Substrate</th>
<th>FF yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaker Oats</td>
<td>Continuous/aqueous</td>
<td>n/a</td>
<td>Bagasse</td>
<td>55</td>
</tr>
<tr>
<td>Huaxia/Westpro</td>
<td>Continuous/aqueous</td>
<td>160-165</td>
<td>Corn cobs</td>
<td>35-50</td>
</tr>
<tr>
<td>Vedernikovs</td>
<td>Continuous/aqueous</td>
<td>188</td>
<td>Wood chips</td>
<td>75</td>
</tr>
<tr>
<td>Zeitsch/Supryield®</td>
<td>Continuous/aqueous</td>
<td>240</td>
<td>n/a</td>
<td>50-70</td>
</tr>
<tr>
<td>Biofine</td>
<td>Continuous/aqueous</td>
<td>190-200</td>
<td>Paper sludge</td>
<td>70</td>
</tr>
</tbody>
</table>
1.4 Recent advances in furfural synthesis

1.4.1 Without catalyst

1.4.1.1 Critical Fluids

Critical solvents are characterized by a critical point which is obtained at specific pressure and temperature (Figure 1.4.1). When temperature and pressure used are higher than the critical point of the solvent, a supercritical solvent is obtained. When both: (i) the temperature and/or the pressure are lower than that of the critical point; and (ii) the temperature is higher than that of the boiling point with a pressure higher than 1 bar, subcritical solvent also called hot compressed solvent is obtained. Physical characteristics: viscosity, density, static dielectric constant and, for the protic ones, ion dissociation constant are deeply modified by heating solvent under pressure.

![Figure 1.4.1 Critical point in a pressure-temperature phase diagram.](image)

Hydrothermal conversion of D-xylose and hemicelluloses to furfural by
simultaneously furfural extraction with supercritical \( \text{CO}_2 \) (sc-CO\(_2\)) in catalyst-free conditions has been studied. Two common reaction models of pentose dehydration (model 1 and model 2) were chosen and compared in terms of their ability to predict the influence of sc-CO\(_2\) extraction on furfural yield (Scheme 1.4.1). By optimizing the reaction temperature, time, pressure, \( \text{CO}_2 \) flow rate and D-xylose concentration, a maximum furfural yield of 68 % was furnished from 4 % D-xylose initial loading at 230 °C for 25 min at the pressure of 12 MPa and 3.6 g/min \( \text{CO}_2 \) flow rate. Kinetics of D-xylose and L-arabinose dehydration demonstrated that the last model is more appropriate than the former one to explain the improvement of furfural yield by simultaneously extraction with supercritical \( \text{CO}_2 \) during its formation. Additionally, the method was extended to native biomass as feedstock to produce furfural, it is clear that supercritical extraction improved furfural yield significantly. However, the best result derived from wheat straw furnished furfural in 29 % yield, which was far lower than that from pure D-xylose. This result indicated side reactions with other hydrolysate components.

![Scheme 1.4.1 Kinetic models (model 1 and model 2) for pentose dehydration into furfural and the associated side-reactions in acidic or hydrothermal environment.](image-url)
The use of another feedstock: sodium alginate and another solvent in presence or not of catalyst permitted to have a fast decomposition of alginate at higher temperature.\textsuperscript{42} However, in catalyst-free sub-critical water (pH = 7), the average molecular weight of products obtained at 250 °C was higher than that for products generated under acid and base catalysts. These results suggested that catalyst-assisted hydrothermal treatment is favorable for the depolymerization of sodium alginate. Furthermore, only small amount of furfural formed without catalyst at 200 °C and 250 °C, this phenomenon could be explained by the composition of alginate mainly constituted of two monomeric subunits containing the carboxylic groups. They are respectively D-mannuronic acid and L-guluronic acid, which are both hexuronic acids. Therefore, decarboxylation process is necessary to realize the production of furfural. Obviously, the goal seems to be roughly achieved in subcritical water without catalyst. However, as reported, more than 15 % of furfural was produced in subcritical water at 250 °C instantly when pH was adjusted to 1 with HCl.

1.4.1.2 Hot Water Pretreatment

Production furfural assisted by hot water pretreatment did not use added acid catalysts. Nevertheless some acids could be generated during the process. A lignocellulose liquid hot water pretreatment process was developed by directly recycling spent liquor.\textsuperscript{43} During hot water pretreatment, approximately 10.0 g of corn stover and 200 mL of distilled water at 180 °C for 30 min furnished 8.0 g/L D-xylose
and 0.3 g/L furofural for the first time and further increased to 21.3 g/L D-xylose and 4.2 g/L furofural for the sixth time. The improvement of furofural yield was attributed to the fact that the formation of by-product acetic acid that will facilitate D-xylose dehydration to furofural, increased from 3.2 to 9.8 g/L as the number of recycling process increased from 0 to 6. In catalyst-free conditions (without added acid), integration of biomass pretreatment with fast pyrolysis by hot water extraction (HWE) and electron beam (EB) irradiation showed that HWE could be used to reduce the formation of carboxylic acid and ketones whilst improving the yield of organic target compounds.\[44\] Besides, EB irradiation has a good potential to increase the formation of useful furanic aldehydes (furofural and HMF) and decrease the yield of hydroxyacetaldehyde by-product.

The reaction kinetics in high-temperature water was studied for the production of furofural from D-xylose as monomer.\[45\] The results indicated that high-temperature water has the potential to substitute for solid and liquid acids as a catalyst by efficiently transfer furofural formed in water phase into organic phase. In this study, ethyl butyrate showed an excellent distribution coefficient of furofural and gave its yield of 75 % at 200 °C for 3 h, which was superior to the yield of 50 % obtained without extraction solvent. In addition, the author also calculated the kinetic order of D-xylose dehydration to furofural in high-temperature water from 160 °C to 200 °C that was 0.5, and dehydration rate constant $K_0 = 1.82 \times 10^5 \text{ (mol/dm}^3\text{)}^{0.5/\text{min}}$, here the activation energy (Ea) was 68.5 KJ/mol. In order to look insight the conversion of D-xylose to furofural, furofural formation mechanism from D-xylose and solvent effects
on its formation by density functional theory was investigated. Kinetic and thermodynamic analyses proposed that D-xylulose could be the intermediate that leads to the formation of furfural, and liquid water could stabilize both reactants and transition states with unsaturated C-C bonds, which is favorable to furfural production. This study also indicated a promising way to produce furfural from D-xylose by involving D-xylulose. Isomerization of D-xylose to its corresponding ketose isomer in high yield via a simultaneous-isomerization-and-reactive-extraction (SIRE) scheme was reported. Concentrated and purified D-xylulose by back-extraction into an acid medium, and then rapidly dehydrated the D-xylulose sugar to furfural at relatively low temperature with no additional catalyst was studied. Furfural yield of 68% was achieved from D-xylulose at 110 °C for 90 min, and was further improved to 90% with methyl isobutyl ketone (MIBK) as extract solvent or 85% in 5 min by replacing partial water with dimethyl sulfoxide (DMSO). The author also pointed out that the mild process conditions resulted in minimal chemical and energy inputs and have significant favorable impact on the overall process economics relative to D-xylose dehydration at 170 °C in spite of the additional unit operations involved. Besides, technical, economic and environmental performances for producing ethanol and furfural from Pinus patula bark, on a biorefinery concept was developed. Based on different levels of heat integration, three scenarios were evaluated, the results showed that fully integrated plus cogeneration scheme was superior to fully energy integrated and non-integrated scheme from both point view of production costs and environment.
Simultaneous extraction-hydrolysis of lignocellulosic biomass by means of high pressurized CO$_2$ and H$_2$O was developed.$^{49}$ In this work, the resulted water soluble hydrolysate was also exposed to CO$_2$ at the higher pressure and temperature in presence of MIBK as the extractive solvent and tetrahydrofuran (THF) as co-solvent. At 200 °C and 50 bar of CO$_2$, the residual hemicellulose was decomposed into its pentose sub-units with 81 % of conversion (Scheme 1.4.2). The optimized dehydration process required a temperature of 180°C and a residence time of 60 min giving a final furfural selectivity of 63 %. In another paper, the same research team was able to produce furfural directly from D-xylose using a mixture of water and THF.$^{50}$ The dehydration was carried out under higher pressure of CO$_2$ at 180 °C for 1 h. Respectively, they obtained 70 and 84 % of furfural yield and selectivity.

![Scheme 1.4.2 Production of furfural in an aqueous biphasic system using high pressure of CO$_2$ as catalyst.](image)

### 1.4.2 Homogeneous catalysts

Dehydration of D-xylose and derivatives was studied in presence of either mineral acids (H$_2$SO$_4$, HCl, H$_3$PO$_4$), organic acid (formic, methanesulfonic acid, maleic acid,
succinic acid) or metal salts (FeCl$_3$, AlCl$_3$, CrCl$_2$, CrCl$_3$, CuCl$_2$, NaHSO$_4$, KAl(SO$_4$)$_2$, Al$_2$(SO$_4$)$_3$) in water or in aqueous biphasic systems using thermal activation or microwave technology.

1.4.2.1 Mineral acid

In many industrial furfural production processes, conventional mineral acids, such as sulfuric acid, phosphoric acid, are generally used as catalysts. Nevertheless other mineral acids have been studied the last decade. A low acid hydrothermal fractionation was developed to transform hemicelluloses isolated from Giant Miscanthus into D-xylose-rich hydrolyzate which is converted at 180°C in presence of H$_2$SO$_4$ into ‘furfural side-product” with 53 % yield. Starting from a prehydrolyzate of aspen and maple chips, furfural was produced by means of H$_2$SO$_4$ when heated in a range of temperature from 160 to 260 °C. With 3.6 kg/m$^3$ of H$_2$SO$_4$, a value of 78 % furfural yield was reached at 240 °C. The authors noted that no significant enhancement of generated yield was observed with prior lignin removal from the pre-hydrolyzate.

Different additives such as thiourea, NaHSO$_4$, NaCl were used to improve the dehydration process. For example, the impact of thiourea additive in the furfural production process from corncobs treatment using H$_2$SO$_4$ was described. Thiourea has for effect to improve the furfural yield that reached 61 % under a liquid-solid ratio of 2:1 instead 34 % with only H$_2$SO$_4$. The transformation needed a temperature of 170 °C and an acid concentration of 0.5 M. The authors explained that thiourea as additive
is supposed to act as a blocking agent of the furfural resinification. In the same period, addition of NaHSO$_4$ as a catalyst promoter was reported for the direct production of furfural from bagasse.$^{54}$ The optimized condition was set up at 160 °C under 8 bar. With 23% of NaHSO$_4$ contents, a maximum of 9% furfural yield was reached after 50 min of residence time. NaCl as additive generated Cl$^-$ ions, which promote the formation of the 1,2-enediyl from the acyclic form of D-xylose, and thus enhances the production of furfural in aqueous acidic solution at temperatures between 170 °C and 200 °C.$^{55}$ The addition of NaCl in H$_2$SO$_4$ led to good furfural selectivity (90%). Variety of chloride salts as additives were studied and caused the use reduction of mineral acids. All of them showed positive effect on furfural yield and selectivity except for FeCl$_3$, however, they obtained exceptionally high D-xylose reaction rates which deserved more investigation.

In order to substitute water for the dehydration other eco-friendly solvents such as γ-valerolactone (GVL) were tested and quantification of the effects of polar aprotic organic solvents on the acid-catalyzed conversion of D-xylose into furfural was reported.$^{56}$ The use of GVL instead of water decreased the activation energy barrier for D-xylose dehydration from 145 KJ/mol to 114 KJ/mol, whereas the barrier for furfural degradation increased from 85 KJ/mol to 105 KJ/mol. Accordingly, furfural selectivity from D-xylose of up to 75% can be achieved in GVL using H$_2$SO$_4$ as the catalyst, compared to only 50% furfural selectivity from D-xylose in H$_2$O. The polar aprotic solvents have an influence on the stabilization of the acidic proton relative to the protonated transition states, which resulted in accelerated reaction rate for these
acid-catalyzed biomass conversion reactions. The author suggested that the proton of strong solid Brønsted acid catalysts, such as H-beta, become solvated during the liquid-phase catalytic reactions, and the conjugate bases of the associated strong Brønsted acid catalysts have little effect on proton reactivity.

Among the novel alternative technologies developed in chemistry and chemical engineering, microwave heating was applied to produce furfural from D-xylose. The highest furfural yield of 64 % was observed at 200 °C for 10 min at aqueous HCl concentration (4 mg/mL), simultaneously with 95 % of D-xylose conversion. The conversion of D-xylose and xylan to furfural by microwave-assisted reaction in HCl aqueous media was reported at 180 °C for 20 min with a solid-liquid ratio of 1:100 and a pH adjusted to 1.12 with a solution of HCl (0.1 M). This optimized conditions furnished furfural in 38 % and 34 % yields, respectively from D-xylose and xylan. However, furfural yield obtained from wheat straw, triticale straw and flax shives were 48 %, 46 % and 72 %, respectively. Under the optimized conditions, HCl is the most effective catalyst for furfural production from D-xylose and xylan compared to H$_2$SO$_4$, HNO$_3$, H$_3$PO$_4$, CH$_3$COOH and HCOOH. Hydrothermal transformation of giant reed (Arundo donax L.) to furfural and levulinic acid was described under microwave irradiation in the presence of diluted HCl. Furfural and levulinic acid theoretical yield of up to 70 % and 90 % were achieved under optimized conditions: biomass (0.35 g), water (5 g) with HCl (1.68 wt%) and 210 °C for 15 min. It was also demonstrated that microwaves were shown to represent a very efficient alternative to the traditional heating route to give furfural and levulinic acid. However, when water
was adopted as reaction medium, humins was often observed especially at high reaction temperature also under microwave irradiation.

Recently, the additions of organic solvents such as MIBK, THF, toluene, cyclopentyl methyl ether (CPME) which can isolate the furfural formed from aqueous phase and further inhibit the occurrence of side-reactions have been demonstrated as an efficient method to improve furfural yield. Catalytic performance of heteropolyacids (HPAs) in the dehydration of D-xylose to furfural in different solvent system (DMSO, water, water-toluene or water-MIBK) was studied.\(^6\) In this work, \(\text{H}_3\text{PW}_{12}\text{O}_{40}\) showed higher selectivity to furfural (64-69 %) in comparison with \(\text{H}_4\text{SiW}_{12}\text{O}_{40}\) (52-64%) and \(\text{H}_3\text{PMo}_{12}\text{O}_{40}\) (inferior than 27 %) in DMSO. However, \(\text{H}_4\text{SiW}_{12}\text{O}_{40}\) is the most effective one at 140 °C for 24 h in water-MIBK biphasic system with furfural yield of 51 %. For \(\text{H}_3\text{PW}_{12}\text{O}_{40}\) and \(\text{H}_4\text{SiW}_{12}\text{O}_{40}\) selectivity towards furfural production is higher for toluene-water than for DMSO for conversions up to 80 %. In this work, water-MIBK did not seem to be a good solvent system to produce furfural compared to water-toluene or DMSO with tungsten-containing catalytic system.

Using HCl as catalyst, water-MIBK biphasic system by mixing water phase with DMSO and butanol was reported.\(^6\) The results showed that furfural yield from D-xylose increased (65 % vs 29 %) with a 6-fold improvement in dehydration rate by decreasing pH (1.0 vs 2.0) in the presence of water-DMSO mixture (5:5, wt/wt) and MIBK-2-butanol (7:3, wt/wt) as an extracting solvent. With xylan as feedstock, 66 % of furfural could be achieved at pH = 1.0 in the same conditions. However, in
water-DMSO mixture (3:7, wt/wt) and dichloromethane (DCM) as an extracting solvent at 140°C without catalyst, 57 % and 76 % of furfural yielded from D-xylose and xylan respectively in 3 h. Although the large-scale use of DCM would be restricted due to environmental concerns, this system showed promise to solve the corrosion problem caused by adding mineral acids and effectively deal with insoluble and soluble biomass feedstocks. Evaluation of the effectiveness of MIBK for enhancing furfural yields was studied. Using maple wood solids (5 wt%) in aqueous sulfuric acid (0.1 M) and water-MIBK mixture (1:1, wt/wt), furfural yield can reach 85 % at 170°C for 50 min which is better compared to the result with less than 65 % of furfural yield in absence of MIBK extraction and superior to 67 % with hydrochloric acid catalysis for 60 min. Interestingly, when monosaccharide as D-xylose was offered as feedstock, HCl is more efficient which about 76 % of furfural yield. This result remained superior to the yield of 64 % with H₂SO₄ at 170°C for 30 min, simultaneously with MIBK as extract solvent. In 2017, the production of furfural from 8 wt% pentose-rich corn stover hydrolyzate was described. The optimized procedure employed a diluted aqueous sulfuric acid solution (0.05 M) and the mixture was heated up at 170°C for 20 min under conventional heating in presence of MIBK. The D-xylose contents were entirely converted into furfural with 80 % yield. CPME as an efficient eco-friendly co-solvent was used for the selective dehydration of lignocellulosic pentose to furfural. It has been clearly demonstrated that CPME leads to nearly 100 % furfural selectivity from lignocellulosic pentose under the following reaction conditions: H₂SO₄ (1 wt%), biomass (4 wt%) referred to aqueous
solution at 170 °C for 30 min, CPME/aqueous phase mass ratio equal to 2.33, and NaCl/aqueous solution mass ratio of 0.4 (Scheme 1.4.3). Like other organic co-solvents, CPME not only favors high furfural selectivity, but also prevents furfural degradation by keeping it in organic phase. In this study, NaCl addition was proved to play the role of accelerating furfural formation rate and shortening the reaction times.

Scheme 1.4.3 Production of furfural from cardoon in the presence of H₂SO₄ and NaCl in a mixture of CPME-H₂O.

In water-toluene biphasic system, the dehydration of D-xylose to furfural with H₂SO₄ as catalyst in association with an inorganic salt such as NaCl or FeCl₃ as promoter was described. The maximum yield of furfural (83 %) can be achieved when NaCl (2.4 g) was added to water-toluene mixture (10:150, v/v) with D-xylose (10 %) and H₂SO₄ (10 %), and heating at the boiling temperature for 5 h. As a promoter, FeCl₃ was better than NaCl. Aromatic solvent such as alklyphenol derivatives permitted the conversion of hemicellulose to furfural and levulinic acid using biphasic reactors with alklyphenol solvents that selectively partition furanic compounds from acidic aqueous solutions. Then, 2-sec-butylphenol has been identified as a new extracting solvent for the effective extraction of levulinic acid from acidic aqueous solution, and also for extracting furfural from aqueous phase with an exceptionally high partition coefficient when aqueous phase is saturated with...
NaCl. Some results of furfural production from D-xylose and corn stover were listed (Table 1.4.1).

Table 1.4.1 Conditions and results for the D-xylose dehydration with HCl as catalyst in an aqueous NaCl and 2-sec-butylphenol mixture.

<table>
<thead>
<tr>
<th>Entry</th>
<th>D-xylose (wt%)</th>
<th>HCl (M)</th>
<th>t (min)</th>
<th>Conv. (%)</th>
<th>Sel. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>0.1</td>
<td>20</td>
<td>98</td>
<td>80</td>
<td>78</td>
</tr>
<tr>
<td>2</td>
<td>1.1 (from corn stover)</td>
<td>0.1</td>
<td>30</td>
<td>95</td>
<td>74</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.25</td>
<td>15</td>
<td>92</td>
<td>82</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>0.1</td>
<td>15</td>
<td>92</td>
<td>77</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>2.1 (2 cycles from corn stover)</td>
<td>0.25</td>
<td>15</td>
<td>95</td>
<td>75</td>
<td>71</td>
</tr>
</tbody>
</table>

a Reaction conditions: HCl (0.1-0.25 M), saturated aqueous NaCl-2-sec-butylphenol mixture (6.67:1, wt/wt), 170 °C.

Alginate could yield furan compounds after acid treated at elevated temperature. In this regards, alginic acid direct catalytic conversion to furfural using 12-tungstophosphoric acid (HPA) and H$_2$SO$_4$ as catalyst was investigated. HPA exhibited higher catalytic activity than H$_2$SO$_4$, and gave the highest furfural yield (34 %) at 180 °C for 30 min. It was found that THF is more suitable than water as reaction solvent, and certain amount of water addition induced a synergistic effect, which will enhance the production of furfural.

Microwave irradiation as alternative technology was studied in the presence of HCl in the water-MIBK mixture and a kinetic model for the dehydration of D-xylose to furfural in a biphasic batch reactor was reported. It was demonstrated that the
organic phase, here MIBK, only act as “storage” for the extracted furfural improving the furfural yield, however, the biphasic system does not alter the fundamental kinetics compared to the current monophasic system. Moreover, microwave heating does not change the kinetics compared to heating by conventional means. Under optimal reaction conditions: D-xylose (10 wt%) and aqueous HCl (0.1 M) at 170°C for ~70 min in a water-MIBK solution (1:1, wt/wt) as a biphasic system, furfural yield can reach 85 %, which is more than two-fold of that obtained in monophasic system (30 %) under the same conditions.

The role of molecular structure on pentose dehydration to furfural has been examined using HCl as a Brønsted acid catalyst in a single phase aqueous media.\textsuperscript{69} It appears that the dehydration of D-xylose in the presence of Brønsted acid follows a direct path (Scheme 1.4.4).

![Scheme 1.4.4 Schematic representation of the overall pathways to produce furfural from D-xylose in the presence of a single Brønsted acid catalyst or both Lewis and Brønsted acid catalysts.](image)

When combined Lewis acid with Brønsted acid, D-xylose could isomerizes to D-xylulose and D-lyxose by Lewis acid and subsequently dehydrates to furfural combined with Brønsted acid (Table 1.4.2). With this combined catalyst
functionalities, a much higher yield (76 %) to furfural can be obtained in a biphasic system at low temperatures and short times.

### Table 1.4.2 Conditions and results for the dehydration of D-xylose with HCl and CrCl₃, 6H₂O and different solvents.⁷⁰

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Time (min)</th>
<th>Conv. (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HCl (0.1 M)</td>
<td>water</td>
<td>300</td>
<td>76</td>
<td>29</td>
</tr>
<tr>
<td>2</td>
<td>HCl (0.1 M)</td>
<td>water</td>
<td>150</td>
<td>75</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>CrCl₃, 6H₂O (2 mM)</td>
<td>water</td>
<td>90</td>
<td>90</td>
<td>38</td>
</tr>
<tr>
<td>4</td>
<td>CrCl₃, 6H₂O (6 mM)</td>
<td>water</td>
<td>60</td>
<td>96</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>CrCl₃, 6H₂O (13.5 mM) + HCl (0.1 M)</td>
<td>Water + toluene</td>
<td>120</td>
<td>96</td>
<td>76</td>
</tr>
<tr>
<td>6</td>
<td>HCl (0.1 M)</td>
<td>Water + toluene</td>
<td>120</td>
<td>31</td>
<td>27</td>
</tr>
<tr>
<td>7</td>
<td>CrCl₃, 6H₂O (6 mM)</td>
<td>Water + toluene</td>
<td>120</td>
<td>96</td>
<td>35</td>
</tr>
</tbody>
</table>

a. Reaction conditions: D-xylose 1 wt% (1 mL of aqueous solution for entry 1-4, 2 mL of aqueous solution and 2 mL toluene for 5-7), HCl (0.1 M) and/or CrCl₃, 6H₂O (2-13.5 mM), 145 °C.

An interesting study compared the furfural yields obtained respectively from the dehydration of D-xylulose and D-xylose in presence of H₂SO₄ under microwave heating in a range of temperature found between 180 and 220 °C.⁷⁰ According their kinetic model, the D-xylose isomerisation is not a crucial step in the pentose dehydration process.

### 1.4.2.2 Organic Acids

Although mineral acids are widely used organic acids are suitable alternatives to
minimize corrosion. The main organic acids used for the production of furfural are formic acid and methanesulfonic acid. Comparison of acid catalysts such as formic acid, sulfuric acid and phosphoric acid for dehydration of D-xylose to furfural at temperature range from 135 °C to 200 °C was reported.\textsuperscript{71} Formic acid performed the best furfural yield of 70 % at 180 °C against 62 % and 65 % for H\textsubscript{2}SO\textsubscript{4} and H\textsubscript{3}PO\textsubscript{4} at 160 °C, respectively. Response surface methodology was applied to optimize furfural yield and selectivity with formic acid as the catalyst, and the best furfural yield reached 74 % with D-xylose (40 g/L) and formic acid (10 g/L) initial concentrations at 180 °C. The effect of Kraft-lignin on acid-catalyzed D-xylose to furfural in formic and sulfuric acid using D-optimal design showed that lignin has an acid-neutralizing capacity and a negative effect on furfural formation from D-xylose.\textsuperscript{72} We have to bear in mind that at lower temperature, the yield of furfural is a bit better in the presence of lignin than without lignin in formic acid. Furthermore, the effects were greater in H\textsubscript{2}SO\textsubscript{4} than in formic acid. The same group also investigated the kinetics of formic acid-catalyzed D-xylose dehydration into furfural and furfural decomposition using batch experiments within a temperature range of 130-200 °C.\textsuperscript{73} By comparing three kinetic models, it is clear that the prediction model must take other reactions for D-xylose besides furfural formation into account. Moreover, the reactions between D-xylose intermediate and furfural play only a minor role. The study also showed that the pH of the reactant solutions has more effect on reaction rate of furfural decomposition when temperature raises, thus, the kinetic modeling of the D-xylose and furfural decomposition reactions should be considered in water. AlCl\textsubscript{3} as additive
was used to improve the role of formic acid as catalyst. The double effect of a catalytic combination of AlCl₃ with HCOOH on the furfural dehydration was studied. Herein, the production of furfural was permitted by D-xylose isomerisation into more reactive D-lyxose in presence of the Lewis acid before the dehydration by the organic acid. The optimized condition involved an aqueous solution of AlCl₃ (0.4 M) mixed with formic acid (55 wt%). The furfural selectivity reached a value of 74 % when the reaction was carried out at 130 °C.

Furfural was produced with a yield of 36 % directly from oil palm biomass using formic acid as catalyst when immersed in ethanol under supercritical conditions. Higher reaction temperature taken between 240 and 280 °C showed a great impact on the furfural yield. The supercritical ethanol had a significant role and the higher yield was obtained for an alcohol-acid ratio of 1:2, 0.4 g of solid loading for a mixture heated at 280 °C for 20 min.

The use of another organic acid such as methanesulfonic acid was reported in presence of other additives. Under optimized D-xylose (0.3 M) and methanesulfonic acid (0.25 M) loading, furfural yields reached values of 60 % at 160 °C for 60 min, 65 % at 180 °C for 15 min and 63 % at 200 °C for 8 min, which are similar with the results of 66 %, 62 % and 64 %, respectively with H₂SO₄. The results indicated that methanesulfonic acid is a promising alternative catalyst to H₂SO₄ for the production of furfural from D-xylose. It should be noted that the addition of D-glucose into D-xylose had a significant impact on furfural yield, as lower values obtained with both catalysts. For example, furfural yield catalyzed with methanesulfonic acid
decreased (45 % vs 63 %) as mentioned above with D-glucose addition (0.1 M), and decreased more (41 % vs 64 %) with H$_2$SO$_4$. It was considered that D-glucose addition resulted in the increase of furfural degradation. The same group produced furfural in high yield from exposure of pretreated sugarcane bagasse with methanesulfonic acid but the target furanic compound was obtained in association with larger amount of levulinic acid.\textsuperscript{77} The use of ionic liquid (IL) in presence of methanesulfonic acid was reported starting from lignocellulosic biomass.\textsuperscript{78} In this work, 25 % of furfural yield could be obtained at 100 $^\circ$C for 30 min starting from biomass-miscanthus which consist of 44 % cellulose and 24 % hemicellulose (0.1 g/cm$^3$) in the presence of IL (5 mL), methanesulfonic acid (0.11 mL), water (3 mmol/cm$^3$). It should be noted that recent works described thermal and combustion risk profiles of ILs as well as risks of toxicity\textsuperscript{79–82} and consequently a study of the stability of the ILs in the process should be studied.

In the optic to have a greener process, different biobased compounds obtained in the biorefinery have been tested as acid catalyst. Biobased maleic acid has been used as an efficient catalyst to convert xylan to D-xylose at high yields in aqueous solution at mild temperature of 160 $^\circ$C, and to subsequently dehydrate the resulting D-xylose to furfural.\textsuperscript{83} The kinetics of D-xylose dehydration to furfural using maleic acid predicted maximum furfural of 72 %, while the observed yield was 67 % at 200 $^\circ$C for 28 min with microwave heating. In 15 min, 54-61 % of furfural yields could be achieved with poplar, switchgrass and corn stover respectively as feedstocks, in comparison to a poor furfural yield of 29 % from pine. Maleic acid also showed some
promise in regards to reusability, although maleic acid is slowly hydrated to malic acid.

As mentioned above, the addition of organic solvents helps the extraction of furfural. Using organic catalysts, this process was also studied. o-Nitrotoluene acted as extraction solvent for furfural production. The maximum furfural yield of 74 % and selectivity of 86 % were obtained in 75 min when heated at 190 °C starting from D-xylose (80 g/L) and formic acid concentration (20 g/L) with 75 % o-nitrotoluene volume percentage. Additionally, the use of salts (KI, KBr, KCl and NaCl) was able to enhance the furfural yield and selectivity, but its concentration was reported as a minor factor. Len’s group demonstrated that formic acid combined with betaine chloride was an efficient and novel homogeneous catalytic system for direct transformation of D-xylose and xylan into furfural. Under optimized conditions at 170 °C for 1 h, 80 % and 76 % of furfural yields were respectively achieved from D-xylose and xylan in a CPME-water biphasic system by microwave-assisted (Scheme 1.4.5). Other mixtures of solvents such as water-GVL and water-2-methyltetrahydrofurane (MTHF) were used for the dehydration of D-xylose. Furfural yield (59 %) was achieved in the presence of p-toluenesulfonic acid for 10 min at 170 °C with D-xylose (0.4 g) in a mixture of water-GVL (1.5:15, v/v).
Biobased acid catalyst such as levulinic acid was explored to furnish furfural from pinewood and eucalyptus sawdust in a water or water-MTHF biphasic system. Using levulinic acid as the catalyst benefited to both hydrolysis and dehydration processes due to its solubility in the water and MTHF phase. As expected, biphasic system was superior to mono-system. In the presence of feedstock (0.4 g), levulinic acid (0.1 g) and water-MTHF (1:1, wt/wt) loading, eucalyptus isomer permitted to produce more efficiently furfural than pinewood (565 mg/L at 180 °C for 15 min vs 643 mg/L at 200 °C for 60 min), in spite of the fact that eucalyptus gave less C5 sugars which could be due to the different composition of hemicelluloses.

1.4.2.3 Metal Salts

Different metal salts have been studied for the production of furfural in a monophasic and biphasic system. Dehydration of xylan and D-xylose to furfural with
Cr (II) or Cr (III) as catalyst and N,N-dimethylacetamide (DMA) as solvent was reported. At 100 °C, D-xylose was converted into furfural in 30-40 % yield in DMA using CrCl₂ and CrCl₃. However, when LiBr was added as additive, furfural yield catalyzed with CrCl₂ increased up to 56 % and 47 % in case of CrCl₃. Other work on copper catalyst showed that Cu (II) is the most efficient among various metal cations for alginic acid hydrothermal treatment to produce furfural, which give 13 % of furfural yield at 200 °C for 30 min. In spite of low catalytic performance for degrading alginic acid, Cu (II) ions are favorable for the conversion of alginic acid to furfural. This study implied that algaes such as alginic acid could be potentially used as a sustainable alternative feedstock for the production of furfural in the future.

Sodium molybdate as metal salt in presence of HCl as acid co-catalyst permitted the stereospecific conversion of D-xylose and D-lyxose from xylan especially combined with microwave technology. Simultaneously the homogeneous catalyst leads to higher energy transfer to solution from a microwave source that will improve the yield of furfural. The process involves combined hydrolysis, epimerization and dehydration reactions in a single step and provided higher amounts of furfural (53 %) compared to reaction without Mo (VI) ions (42 %, 300 W for 5 min of heating). Xylan dehydration with conventional heating in the presence of molybdate yielded 36 % of furfural that is also higher compared to 28 % without Mo (VI) ions at 150 °C for 30 min. It was proposed that chromium acting as a Lewis acid catalyzed D-xylose isomerization. In fact CrCl₃ is an efficient Lewis acid to isomerize D-xylose to D-xylulose and further dehydrated it to furfural (76 %) at lower temperature (145 °C).
When xylan was used as the feedstock, the results implied that depolymerization is the major barrier for chromium-catalyzed furfural production, and less than 25 % of furfural was achieved at 140 °C with CrCl₂ as catalyst, HCl as co-catalyst in 1-ethyl-3-methylimidazolium chloride.

Only by using NaCl as catalyst, a comparison between conventional heating and microwave heating was made. Higher yields were obtained after 7 min of heating in presence of NaCl (3.5 wt%) at 200 °C. The D-xylose conversion was complete giving 76 % of furfural yield under microwave heating.

Using metal salts, biphasic systems were developed with similar solvents as mentioned above. Isolation of hemicelluloses from Rubescens using a water-GVL biphasic system heated at 180 °C was studied. The hemicelluloses rich lignin fraction was then warmed up in presence of NaCl and THF giving a furfural yield of 77 %. NaCl was also responsible of all reactions such as hydrolysis, epimerization and dehydration involved in the processes at the higher temperature of 200 °C. A production of furfural was set up in association with bromomethylfurfural and HMF from cellulose and lignocellulosic biomass. The biphasic system water-DCM (1:3, v/v) involving an organic solvent and a molten lithium bromide hydrate solution was heated for 2 h at 120 °C and permitted to obtain furfural in 70 % yield. The use of high pressure of CO₂ in a mixture of aqueous isopropanol in the presence of NaCl furnished furfural in 70 % yield. The high CO₂ concentration reduced the pH of the sugar solution and the optimized condition required a temperature of 200 °C for 3 h in a 2:1 ratio of water-alcohol. Different works described the use of iron-catalyzed
furual production in biobased biphasic systems. FeCl$_3$ was selected as the catalyst, NaCl as additive and MTHF as biomass-derived solvent. Without NaCl, furfural yield only reached 27% catalyzed with FeCl$_3$ at 140°C, however, the same reaction condition involving NaCl (20 wt%) for 4 h afforded furfural (70%). Furfural formation rate increased with a factor of more than two. Xylan from beech wood was first hydrolyzed to D-xylose in a concentration of 30 g/L (2.5 mL), then FeCl$_3$, 6H$_2$O (0.12 M), NaCl (30 wt%), were added together in 2.5 mL of MTHF, and the reaction yielded furfural (37%) at 140°C for 2 h. Furfural yield of 75% from D-xylose in a water-THF biphasic medium containing AlCl$_3$, 6H$_2$O and NaCl under microwave heating at 140°C. It was clear that AlCl$_3$ could isomerize D-xylose into D-xylulose, followed by the dehydration of the latter to produce furfural, similar to isomerization catalysts CrCl$_3$ or NaMoO$_4$ mentioned above. Moreover, this system was effective in the hydrolysis of xylan and lignocellulosic hemicelluloses to D-xylose, which resulted in some important of furfural yields from lignocellulosic biomass (Table 1.4.3).

Table 1.4.3 Conditions and results for the production of furfural starting from various sources of lignocellulosic biomass in presence of AlCl$_3$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Biomass</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
<th>Yield (%)</th>
<th>D-Furfural</th>
<th>D-Xylose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Corn stover</td>
<td>140</td>
<td>60</td>
<td>51</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Pinewood</td>
<td></td>
<td></td>
<td>29</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Switchgrass</td>
<td></td>
<td></td>
<td>50</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Poplar</td>
<td></td>
<td></td>
<td>45</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Corn stover</td>
<td>160</td>
<td></td>
<td>55</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Pinewood</td>
<td></td>
<td></td>
<td>38</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Switchgrass</td>
<td></td>
<td></td>
<td>56</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Poplar</td>
<td></td>
<td></td>
<td>64</td>
<td>&lt;1</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Pinewood</td>
<td>180</td>
<td>30</td>
<td>61</td>
<td>&lt;1</td>
<td></td>
</tr>
</tbody>
</table>

a Reaction conditions: Biomass 0.05 g, AlCl$_3$, 6H$_2$O 0.1 mmol, NaCl 6.0 mmol, water 1 mL, THF 3 mL.
Our team also studied furfural production catalyzed with FeCl₃ and NaCl as additive. With the aid of microwave irradiation and the eco-friendly mixture: water-CPME (1:3, v/v), the highest furfural yield (74 %) was achieved at 170 °C for 20 min in the presence of iron chloride (10 mol%) and NaCl 100 (mol%) (Scheme 1.4.6). Addition of NaCl was found to increase the catalytic activity of FeCl₃ and allowed to reduce the amounts of FeCl₃ used from 20 mol% to 10 mol%. This system was extended to xylan and afforded furfural yield of 52 % at 200 °C for 20 min or 170 °C for 70 min.

Scheme 1.4.6 Microwave-assisted production of furfural from D-xylose in the presence of FeCl₃ and NaCl in a mixture of CPME-H₂O.

Sulfate derivatives such as NaHSO₄, KAl(SO₄)₂ and Al₂(SO₄)₃ were tested for the production of furfural. Furfural was obtained from various raw lignocellulosic materials in water-THF by using NaHSO₄ as catalyst. Many reaction parameters were optimized, such as reaction temperature, time, solvent volume ration, feedstock concentration as well as catalyst loading. Under the optimum conditions: 190 °C, 90 min, biomass concentration (11.1 wt%), NaHSO₄ (3.31 wt%), H₂O (0.8 mL) and THF (8 mL), 50-60 % furfural yields were obtained from diversified lignocellulosic
biomass such as corncob, wheat straw, bagasse. Under conventional heating, using KAl(SO$_4$)$_2$ in a water-MIBK biphasic system, furfural was efficiently produced from D-xylose when heated for 6 h at 190 °C, 55 % of furfural yield was obtained.$^{96}$ The catalytic activity of Al$_2$(SO$_4$)$_3$ metal salt for the D-xylose dehydration was reported using a water-GVL biphasic system.$^{97}$ Al$_2$(SO$_4$)$_3$ decomposes into SO$_4^{2-}$ anions and the hexacoordinated Lewis acidic species [Al(OH)$_2$(HO)$_4$] able to isomerizes D-xylose into D-xylulose, easily converted into furfural. The optimized conditions afforded furfural in 88 % yield.

1.4.2.4 Ionic liquids

ILs are known as organic salts with melting points below 100 °C composed solely of cations and anions, which have many unique properties, such as very low volatility, good dissolving capacity, chemical and thermal stability, non-flammability, non-toxic nature and recyclability. Ils are considered as an example of more sustainable solvents, which contribute to a greener processing of biomass, and are suitable for furfural production.$^{98}$ Some neutral ILs such as 1-butyl-3-methylimidazolium chloride$^{99–101}$ has been employed as efficient solvents and 1-ethyl-3-methylimidazolium chloride used as additive.$^{88}$ Generally, acidic ILs were applied as catalysts which performed as reaction mediums,$^{102}$ such as 1-butyl-3-methylimidazolium hydrogen sulfate,$^{103–105}$ 1-ethyl-3-methylimidazoliumhydrogen sulfate,$^{106}$ 1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate.$^{107,108}$ Even though ILs have showed many advantages for the production of furfural, scientists are also facing plenty of
challenges to realize their industrial utilization, such as the cost of ILs, deep understanding of their properties, their recovery and recycling problems and also environmental issues. Meanwhile, the recovery of furfural from IL should also become difficult. Moreover, our group reported that ILs could generate fire induced toxicity and induce ecological disturbance for organism. In order to limit the use of ILs, different groups reported the production of furfural with acid ILs used as reagent and not as solvent.  

1.4.3 Heterogeneous catalysts

Production of furfural starting from pentose derivatives has been reported using carbon acids, clays, ion-exchange resins, oxides, phosphates, silicates and zeolites assisted by alternative technologies or not.  

1.4.3.1 Carbon-based Acids

Carbonaceous materials are effective solid acid catalysts due to their high thermal stability, high chemical activity and low production costs, which make them an interesting alternative for sugar dehydration in aqueous environment. Activated carbon catalyzed D-xylose dehydration to furfural was compared with an autocatalytic reactions. The use of Norit as commercial-activated carbon permitted to have a better control over the unwanted side reactions such as acids and humin formations. It was found that the main isomer with carbon catalyst was D-xylulose and in case of non-catalyzed reaction was D-lyxose. This result demonstrated that activated carbon
catalyst could avoid unwanted side reactions by offering acidic sites and could permit isomerization D-xylose into more reactive keto sugars, which benefits to furfural production. Other carbon sources such as graphene derivatives were studied for the production of furfural to improve the conversion and selectivity. In this regard, four kinds of carbon-based catalysts: graphene, graphene oxide, sulfonated graphene, and sulfonated graphene oxide (SGO) were elaborated and tested\textsuperscript{116} (Table 1.4.4).

### Table 1.4.4. Conditions and results for the production of furfural starting from D-xylose and grapheme derivatives in water.

<table>
<thead>
<tr>
<th>Entry\textsuperscript{a}</th>
<th>Catalyst</th>
<th>Conv. (%)\textsuperscript{b}</th>
<th>Sel. (%)\textsuperscript{b}</th>
<th>Yield (%)\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>76</td>
<td>58</td>
<td>44</td>
</tr>
<tr>
<td>2</td>
<td>Graphene</td>
<td>75</td>
<td>68</td>
<td>51</td>
</tr>
<tr>
<td>3</td>
<td>Graphene oxide</td>
<td>80</td>
<td>66</td>
<td>53</td>
</tr>
<tr>
<td>4</td>
<td>Sulfonated graphene oxide</td>
<td>83</td>
<td>75</td>
<td>62</td>
</tr>
<tr>
<td>5</td>
<td>Sulfonated graphene</td>
<td>86</td>
<td>64</td>
<td>55</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: D-xylose (2.25 g), catalyst loading 2 wt%, 35 min, 200 °C. \textsuperscript{b} Data averaged over 3 runs.

SGO was proven to be a rapid and an active catalyst for improving furfural yield from D-xylose aqueous solution even at very low catalyst loadings down to 0.5 wt% vs D-xylose. Furthermore, $\text{SO}_3\text{H}$ groups, which are the active acidic sites for dehydration of D-xylose to furfural, have been demonstrated water-tolerant and more thermally stable under the reaction conditions than COOH or OH groups. After 12 tested repetitions at 200 °C for 30 min, an average furfural yield of 61 % was maintained in comparison to 44 % for the uncatalyzed system.
Often the carbon-based catalysts are prepared by carbonization of sugar molecules in acid to form sulfonate-functionalized carbon particles. Solvothermal conversion of cassava waste to furfural using a sulfonated carbon-based catalyst was investigated.\textsuperscript{117} Results obtained in presence of $\text{H}_2\text{SO}_4$ and without catalyst was compared, the carbon-based catalyst showed its effectiveness for the hydrolysis of xylan to D-xylose and then D-xylose dehydration to furfural. However, during this study, less than 3\% of furfural yielded from cassava waste and 12 \% from D-xylose and xylan. Sulfonated biochar was prepared successively by carbonization and sulfonation.\textsuperscript{118} The resulted acidic carbonaceous solid was employed for the direct transformation of a pre-hydrolyzed aqueous solution of corncob in a biphasic system involving DCM on the organic layer. When the system was heated at 170 °C for 60 min, 83 \% of furfural selectivity was finally recorded.

Other source of carbon was reported by successively carbonization of sucrose and sulfonization, successively.\textsuperscript{119} This solid catalyst was able to dehydrate D-xylose and corn stalk into furfural at 170 °C for D-xylose and 200 °C for the plant waste. The yields were 79 and 61 \% respectively for residence time varying between 30 and 100 min. Recently, a carbonized resorcinol-formaldehyde resin and sulfonated to become a catalyst.\textsuperscript{120} The material was efficient for furfural production from D-xylose and corn stover in GVL. When heated at 170 °C for 15 min with enough catalyst, the best dehydration conditions afforded furfural in 80 \% yield with a D-xylose conversion of 100 \%. In comparison, 69 \% of furfural yield was achieved from corn stover at 200 °C after 100 min of heating with higher amount of catalyst. The sulfonation of
carbonaceous carbon-coated alumina (SC-CCA) prepared by carbonization of sucrose using 4-benzene-diazeniumsulfonate as a sulfonating agent produced furfural in 79 % yield in sole GVL as solvent at 170 °C for 30 min. \(^{119}\) Starting from corn stalk furfural was obtained in 60 % yield for 100 min at 200 °C or for 60 min at 210 °C. In case of corn stalk, it is noteworthy that addition of water (10 wt%) severely decreased furfural yield. Nevertheless, sulfonated groups grafted onto the carbon-based material have been demonstrated to be significantly stable, and SC-CCA could be reused up to 5 runs without the loss of furfural yields. Calcium citrate was used as novel source of biomass for the preparation of sulfonated catalyst. \(^{121}\) Sulfonation of carbonaceous residue obtained from the calcinations of bio-based calcium citrate and dehydration of raw corn stover furnished furfural (93 %) in GVL at 200 °C. The authors mentioned that using the same conditions in water instead of GVL, furfural was obtained in 51 % yield.

### 1.4.3.2 Clays

Only one report described the use of clays for the dehydration of pentose derivatives into furfural. Four kinds of pillared clays catalysts with different quantity of aluminum and hafnium (labeled as Al-Hf 11-1, Al-Hf 10.5-1.5, Al-Hf 10-2 and Al-Hf 8-4), and applied them into the conversion of D-xylose to furfural. \(^{122}\) The selectivity of furfural reached 53 % with Al-Hf 11-1 and increased to 65 % with Al-Hf 10.5-1.5 at 140 °C, however, D-xylose conversion were only 45 % and 35 %, respectively. Increasing reaction temperature to 170 °C raised D-xylose conversion,
but a loss of selectivity was observed. As a conclusion, an increase of the hafnium content reduced the selectivity for furfural on Al-Hf vermiculites. A maximum Hf content of 2 mmol Hf/g (clay) is promising catalyst for the dehydration of pentose in water as a solvent, producing furfural with an average conversion rate of 78 % and a selectivity rate of 50 % at 170 °C for 4 h in four consecutive reactions.

1.4.3.3 Ions-exchange resins and ionomers

Furfural production catalyzed by an ion-exchange sulfonic resin was largely studied. The nature and properties of the resins: Amberlyst, Nafion with different acidity, pore diameters and thermal stability permitted to generate the dehydrated chemicals depending of the process used. The kinetic parameters of furfural production in water and water-toluene biphasic system with or without catalyst at different reaction temperatures and time, D-xylose loading and its simultaneous stripping using nitrogen were studied. In this work, 65 % of the stripping furfural was achieved from D-xylose and almost 100% of selectivity in the condensate was observed. Later, the effect of D-glucose addition into D-xylose on furfural production was conducted under different operating configurations. D-Glucose addition to D-xylose has a negative effect on furfural yield at 175 °C, but a positive effect at 200 °C, which is considered as “entropy-effect” at high reaction temperature, leading to slower side-reactions. The mixture of D-xylose and D-glucose at similar ratios to the real pentosan-rich biomass led to furfural yields of up to 75 % at 200 °C, and even 78 % with lower D-xylose concentration. The same group showed that Amberlyst-70 with
strong sulfonic acid sites presented a higher furfural selectivity than Nb$_2$O$_5$ supported catalyst.$^{36}$ In all of their studies, the strategy of nitrogen stripping was proved more industrial feasibility with respect to other biphasic water-solvent systems. Using the same catalyst, Amberlyst-70, the research of specific formation of humins has been done starting from D-xylose in a mixture of methanol-water.$^{123}$ It was found that high reaction temperature, long residence time, low methanol-water mass ratio, and high catalyst dosage were favorable for its formation. Although furfural can be protected to form 2-(dimethoxymethyl)-furan (DOF) in the methanol-rich medium, this did not remarkably suppress polymerization at high reaction temperature. Additionally, the acid treatment of furfural also produced methyl levulinate in methanol and levulinic acid in water due to the degradation furfural. Later, further study of acid-treatment of C5 and C6 sugar monomers/oligomers with the same catalyst in water or DMSO system was conducted.$^{124}$ The interaction or cross-polymerization of D-xylose-D-glucose, D-fructose-raffinose, furfural-D-glucose, and furfural-D-fructose exists. In water, yields of the insoluble polymer from the sugars (furfural) increase in the order: D-fructose ~ raffinose > D-glucose > D-xylose > furfural. In another hand, furfural can be preserved by DMSO and less insoluble polymer formed.

The use of Amberlyst-15 instead Amberlyst-70 has been applied to the hydrothermal reaction of alginic acid to produce furfural.$^{125}$ The maximum of 19 % furfural yield was obtained at 180 °C for 30 min. The catalyst could be recycled for 5 times with approximately 30 % loss of furfural yield. Unfortunately, recovered catalyst could not be regenerated with H$_2$SO$_4$ because by-products covered its surface.
inhibited its regeneration. In water-THF mixture, Amberlyst-15 gave furfural in 17 % yield at 170 °C for 60 min. The thermal stability of Amberlyst-15 could explain this result. In comparison with the use of 12-tungstophosphoric acid inferior catalytic result has been obtained. Successive dehydration of D-xylose by Amberlyst-15 and furfural hydrogenation over a hydrophobic Ru/C catalyst in a single biphasic reactor have been studied. Organic solvents butan-1-ol, MTHF and cyclohexane were used. The amounts of the catalysts, solvent, temperature and pressure were optimized in the water-cyclohexane system. The main product tetrahydrofurfuryl alcohol was obtained at 135 °C with a selectivity and a conversion of 50 % and 32 %, respectively. In addition, co-products such as GVL, levulinic acid and pentanediols were also observed with comparable yields.

A more promising heterogeneous catalyst, Nafion 117 furnished furfural in 58-62 % yields in DMSO at 150 °C with 15 consecutive runs with a conversion higher than 90 %. Activation energy values for Nafion 117 at 5 % and 20 % catalyst weight loading were 86.4 and 89.3 kJ/mol, respectively which were lower than other solid acid catalysts obtained. Our group has tested perfluoroalkane sulfonic resin, Nafion NR50 as an efficient superacid catalyst for the production of furfural. In a water-CPME biphasic system under microwave irradiation D-xylose, L-arabinose and xylan gave in the presence of NaCl furfural with maximum yields of 80 %, 42 % and 55 %, respectively (Scheme 1.4.7). It was found that the association of Nafion NR50 and NaCl generated an unusual stability of the resin, which have synergetic effect in acid catalysis. Unfortunately, gradual deactivation due to humin deposition was also
observed after the fourth cycle.

Three kinds of micro-mesoporous sulfonic acid catalysts—silylated MCM-41-SO$_3$H, coated MCM-41-SO$_3$H and hybrid-SO$_3$H have been prepared, characterized, and tested in the dehydration of D-xylose to furfural.\textsuperscript{120} The hybrid-SO$_3$H gave a lower furfural selectivity compared to MCM-41-SO$_3$H materials, which may be due to the hydrophobicity of the surface enhanced the adsorption of furfural at the surface, and further accelerated it to react with intermediates on the accessible acid sites. Coated MCM-41-SO$_3$H yielded slightly higher yield ($> 75\%$) than silylated MCM-41-SO$_3$H (69\%) in DMSO or water-toluene biphasic system at 140 °C for 24 h. However,
silylated MCM-41-SO$_3$H have a better selectivity than that of coated MCM-41-SO$_3$H (96 % vs 83 %) in water-toluene. Increase of reaction temperature shortened reaction time, also benefited furfural yield. For example, 70 % of furfural yield was achieved at 170 °C for 4 h with coated MCM-41-SO$_3$H. Unfortunately, apparently catalyst deactivation was observed from the second run in spite of its regeneration.

Using the same strategy, a new porous sulfonated triphenylamine was developed to dehydrate pentoses and hexoses in lactone-type organic solvents.$^{130}$ When GVL was used at 175 °C furfural was obtained in 74 % yield.

### 1.4.3.4 Oxides

Different oxides derivated from Zr, Ti and Nb have been studied for the production of furfural. Well-ordered mesoporous and super strong acidic sites catalysts SO$_4^{2-}$/ZrO$_2$-Al$_2$O$_3$/SBA-15 were tested and the most efficient catalyst SO$_4^{2-}$/12 % ZrO$_2$-Al$_2$O$_3$/SBA-15 gave 99 % of D-xylose conversion and 53 % furfural yield at 160 °C for 4 h by Shi et al.$^{131}$ It was found that the addition of Al to SO$_4^{2-}$/ZrO$_2$/SBA-15 stabilized the tetragonal ZrO$_2$ phase and enhanced the activity of the catalyst by increasing the number of acid sites. The reasons for catalyst deactivation and regeneration were evaluated. In spite of sulfur leaching, catalyst deactivation was related to the accumulation of humin, which might cover the surface of the catalyst, leading to the passivation of the acid site. Furthermore, deactivated catalyst can be completely regenerated with H$_2$O$_2$, but furfural yield decreased by increasing the number of recycling tests, which mainly caused by the presence of
monoclinic ZrO$_2$ that decreased the acid strength and acid concentration of the catalyst. Ultraviolet irradiation was tried with a screening of heterogeneous catalysts for the production of furfural from D-xylose$^{132,133}$ and from corncob.$^{134}$ The optimized photocatalyst 1.0 M-SO$_4^{2-}$/TiO$_2$-ZrO$_2$/1.0wt%-La$^{3+}$ gave 32 % of D-xylose conversion and 216.6 µmol/g of furfural yield at 120 °C for 4 h under ultraviolet irradiation, which is sharply higher than non-catalytic process and no ultraviolet irradiation process.

Some other scientists studied the simultaneous hydrolysis/dehydration of sugarcane bagasse, rice husk and corncob under hot compressed water in the presence of TiO$_2$, ZrO$_2$ and TiO$_2$-ZrO$_2$ at 200-400 °C.$^{135}$ In all case, TiO$_2$ showed more efficiency to convert lignocellulosic biomass to furfural than ZrO$_2$. It was found that catalysts prepared by co-precipitation method gained higher reactivity than those prepared by sol-gel and physical mixing methods. The suitable calcination temperature for TiO$_2$ and ZrO$_2$ was formed at 500 °C. The employ of mixed-oxide TiO$_2$-ZrO$_2$ offered the highest furfural yield (10 %) from corncob at 300 °C with less by-products selectivity when compared with TiO$_2$ or ZrO$_2$ at the same conditions. Reusability of five cycles furnished furfural (10 %) indicated long-life of this catalyst. Additionally, this catalyst has the bi-functionality of both acidity and basicity properties, which benefit to hydrolysis, dehydration and also isomerization processes, leading to high furfural production. The suitable calcination temperature for TiO$_2$-ZrO$_2$ was 600 °C, which is higher than that for TiO$_2$ and ZrO$_2$.

Note that the introduction of sulfate ion and lanthanum can enhance the
photocatalytic performance of metal oxides by increasing the acidic sites.\textsuperscript{132} Subsequently, this kind of catalyst was applied in the hydrothermal pretreatment of corncob into D-xylose and furfural.\textsuperscript{134} After optimizing the reaction parameters, the highest furfural yield (6.18 g of furfural for 100 g of corncob) could be obtained at 180°C for 120 min when the corncob-water ratio of was 10:100. From xylan, furfural yield of 21% was achieved using Cr-LaCo\textsubscript{0.8}Cu\textsubscript{0.2}O\textsubscript{3} (1.5%) as catalyst within 10 h in the 1:600 weight ratio of xylan to water at 160°C.\textsuperscript{133} We have to mention the amount of chromium in solid catalyst decreasing from 1.26% to 0.38% after the first recycling run, which led to the reduction of furfural yield to 13%. Importantly, there is no effect on pentose formation.

An environmentally-friendly two-step process for furfural production starting from corncob.\textsuperscript{136} Hydrothermal pretreatment was firstly investigated at a temperature range from 160-190°C for 0-60 min, and then the resulted hydrolysate was catalyzed with SO\textsubscript{4}\textsuperscript{2-}/SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}/La\textsuperscript{3+} as a solid acid catalyst at 150°C for 2.5 h. The maximum yield of furfural achieved was up to 21% from the hydrolysates (total D-xylose yield 7.01 g/L) obtained at 190°C for 60 min in the hydrothermal process, and there was no obvious decrease of furfural yield observed after four consecutive runs.

A mesoporous and amorphous nobium oxide was used to dehydrate D-xylose into furfural through a ketone-type intermediate called D-xylulose.\textsuperscript{137} Furfural selectivity (48%) was obtained when the reaction was carried out at 120°C, in sole water; however the yield increased in a water-toluene biphasic system (2:3, v/v) to reach 72% of selectivity. The catalyst activity was also compared to other solid catalyst such as
titan oxide (TiO$_2$).

1.4.3.5 Sulfated oxides

Several bulk and ordered mesoporous silica-supported zirconia catalysts for the dehydration of D-xylose into furfural in a water-toluene solvent mixture at 160 °C furnished furfural yields higher than 50 % and a conversion higher than 90 %.\textsuperscript{138} It should be noted that the initial catalytic activity correlated fairly well with the sulfur content. Unfortunately, sulfur leaching was observed compromising the reusability of the catalyst. The sulfated AZ-MCM-41 (prepared with 3.0 mmol ZrOCl$_2$, 8 H$_2$O and 0.1 mmol Al(NO$_3$)$_3$, 9 H$_2$O) seems to be the most attractive catalyst for aqueous phase conversion of D-xylose, since it was the most stable to sulfur leaching and exhibited increasing activity and no significant loss of selectivity to furfural in three recycling runs, regardless of negative effect of Al addition on D-xylose conversion.

Recently, sulfonated carbonaceous materials revealed their potential for furfural production because of their high acidity, water tolerance and metal oxides having Lewis acidic sites. A carbonaceous heterogeneous catalyst, which combined the sulfonic acid (-SO$_3$H) groups with Lewis acidic TiO$_2$ by a one-pot synthesis method was prepared.\textsuperscript{139} When applied it into furfural production from D-xylose, furfural was obtained in 51 % yield in DMSO as solvent at 140 °C for 60 min or in water-MTHF biphasic system at 180 °C for 30 min. Maximum furfural yield of 37 % was also recorded in 5 min at 180 °C in DMA/LiCl-mediated reaction.
1.4.3.6 Niobium-based oxides

Few works using niobium-based oxides were related for the dehydration of pentose into furfural. The activities of Lewis acid catalysts (Nb₂O₅ supported on a mesoporous silica Cabosil) and Brönsted acid catalysts (Amberlyst 70) were studied.³⁶ Lewis acid sites gave a higher rate to convert D-xylose into furfural than Brönsted acid sites, because Lewis acid sites could isomerize D-xylose into D-xylulose, while Amberlyst-70 with strong sulfonic acid sites presented higher furfural selectivity. To improve furfural production, the use of N₂ stripping methodology showed better extraction efficiency than water-toluene biphasic system which benefits to environmental and products separation concerns. A mesoporous Nb₂O₅ catalyst was prepared by a neutral templating route.¹⁴⁰ The catalytic behavior was compared with that of a commercial Nb₂O₅. Higher than 90 % of D-xylose conversion and 54 % of furfural yield was attained at 170 °C after 90 min with a D-xylose-catalyst (3:1, wt/wt). It is noteworthy that 41 % of furfural can be achieved at 150°C for the same reaction time. In addition, D-xylose conversion in the non-catalyzed process was practically negligible, and commercial Nb₂O₅ only gave low D-xylose conversion (22 %) and poor furfural yield (3 %). It was demonstrated that no significant niobium leaching has been observed, the catalytic activity reduced could be attributed to the presence of a large amount of carbonaceous deposits on the catalyst surface. Silica-zirconia supported niobium catalysts were prepared by impregnation (Nb/SZi) or sol-gel (Nb/SZsg) in comparison with pure niobic acid (NBO) were presented for D-xylose dehydration in green solvents: water, water-isopropanol, water-GVL, and
In all the solvents, NBO was more active than the other supported niobium catalysts. All the supported niobium catalysts had got the same activity and showed the highest D-xylose conversion and furfural yield in presence of GVL and CPME. During the recycling and continuous catalytic tests, in spite of the deactivate trend of D-xylose conversion, furfural yield is more stable. The niobia supported catalysts furnished around 45-50 % of furfural yield and almost 80 % selectivity after 7 runs at 180 °C for 4 h. These catalysts have lower activity than bulk niobia but higher stability. Note that furfural yield could reach around 60 % by increasing reaction time to 4 h at 180 °C or reaction temperature to 190 °C for more than 2 h catalyzed with NBO.

1.4.3.7 Phosphates

Different phosphates associated with Vanadium, Niobium and Tantanum were used as catalysts for the dehydration of pentose derivatives. The orthorhombic vanadyl pyrophosphate (VO)$_2$P$_2$O$_7$, prepared by calcination of VOHPO$_4$, 0.5H$_2$O at 550 °C for 2 h, exhibited superior catalytic performance amongst the investigated materials. In this work furfural yield (53 %) in consecutive batch runs at 170 °C for 4 h was reported. Interestingly, this heterogeneous catalyst actually acted as a source of very active water-soluble species, which are responsible for the observed catalytic activity. A series of zirconium phosphate catalysts have been synthesized. The calcined mesostructural zirconium phosphate ZrP-HT-Am-C exhibited inspiring catalytic performance than others include H$_3$PO$_4$. At 170 °C, D-xylose conversion
(96 %) and furfural yield (52 %) were measured in aqueous-phase after 2 h. The reuse property of the catalyst for 3 runs seemed fairly good by thermally treated in air at 500 °C for 4 h before the next run. Association of niobium and phosphate was done and the corresponding nobium phosphate (NbP) was tested for the furfural production. Nb$^{5+}$ ions were supported to act as Lewis exposed sites, showing medium strength acidity. Their previous study showed that NbP catalyst recovered gave furfural in 43 % yield and D-xylose conversion in 82 % at 160 °C for 30 min in water. After three consecutive catalytic runs, furfural yield and D-xylose conversion slightly decreased to 36 % and 70 %, respectively. When corn stover was applied as feedstock, 23 % of furfural yield was achieved. The next part was the introduction of tantalum. In this regards, different mesoporous tantalum phosphates with various P/Ta molar ratios were prepared and tested for evaluating their respective catalytic activities to convert D-xylose into furfural. A high Bronsted to Lewis acid site ratio is required to enhance the furfural selectivity. The best candidates afforded a furfural selectivity of 72 %.

1.4.3.8 Silicates

The main silicates used for the dehydraion of biomass into furfural were mesoporous silicates MCM-41 and SBA-15 and derivatives having sulfonated group or metal were used for the dehydration of pentose into furfural. Among different silicates, H-MCM-41 gave the highest furfural yield from unusual C6 sugar levoglucosan at 300 °C. Unfortunately, catalysts were deactivated due to coke.
The conversion of D-xylose into furfural with mesoporous molecular sieve MCM-41 as catalyst in presence of NaCl and butanol as the extraction solvent at 170 °C for 2 h furnished furfural in 48 % yield. In three consecutive runs, its value decreased slightly, which can be due to inefficient removal of by-products adsorbed on the catalyst surface after each run. It was noteworthy that the same process without NaCl gave only the aldehyde in 39 % yield.

Metal-containing silicates (Nb, Al) were tested and compared. In this regards, the microporous and mesoporous niobium silicates (AM-11 and MCM-41) as solid acid catalysts were studied for the dehydration of D-xylose in a water-toluene solvent mixture. The proton form of AM-11 (H-AM-11) showed a stable reusability and gave the highest furfural yield (50 %) and a D-xylose conversion (89 %) at 160 °C for 6 h after 3 runs. For fresh catalysts, their activities followed the order: H-AM-11 (46 % at 85 % conversion) > ex H-AM-11 (H-AM-11 after ions-exchange, 39 % at 85 % conversion) ≈ HY5 (the protonic form of Y-zeolite, with Si/Al = 5, 39 % at 94 % conversion) ≈ MCM-41 (Nb50-MCM-41, ex Nb50-MCM-41, Nb25-MCM-41 and ex Nb25-MCM-41, ca. 39 % at 92 ~ 99 % conversion) > Na,H-AM-11(31 % at 77 % conversion) > mordenite (with Si/Al = 6, 28 % at 79 % conversion). Developing the same idea, the effect of surface acidity on the dehydration of D-xylose was examined using SiO₂-Al₂O₃ catalysts with varying alumina contents by You et al. D-xylose conversion in water as solvent at 140 °C for 4 h increased more than 9 folds with the increase of alumina content from 0 to 1. Simultaneously, humin yield reached 45 % with Al₂O₃ compared to no humin formed with SiO₂. It was considered that Lewis
acid sites significantly affected D-xylose conversion and humin formation. The best furfural yield of ca. 27 % was obtained with SiO$_2$-Al$_2$O$_3$ (0.6) while SiO$_2$-Al$_2$O$_3$ (0.1) provided the highest furfural selectivity more than 60 %. The highest yields of D-lyxose and D-xylulose were attained over SiO$_2$-Al$_2$O$_3$ (0.4) and SiO$_2$-Al$_2$O$_3$ (0.8).

Silicates with sulfonated groups have been tested for the model reaction. Two kinds of sulfonic MCM-41 catalysts: the propyl sulfonic acid catalyst (PrSO$_3$H-MCM-41) and the methyl propyl sulfonic acid catalyst (MPrSO$_3$H-MCM-41) have been prepared.$^{151}$ After testing their activities for furfural production from D-xylose in water-toluene biphasic system at 155 $^\circ$C for 2 h, it was found that PrSO$_3$H-MCM-41 was quite efficient and gave 96 % of furfural selectivity and 92 % of D-xylose conversion compared to 26 % and 99 % for MCM-41. The authors explained that the preparation of MPrSO$_3$H-MCM-41 have a significant effect on their acidic densities and pore diameters, which further affect furfural yield and D-xylose conversion.

MPrSO$_3$H-MCM-41 prepared by co-condensation method using dodecyltrimethylammonium bromide as a surfactant template and aged at room temperature gave the smallest pore diameter (3.4 nm). The modification of the catalyst permitted to furnish the highest furfural yield (93 %) and furfural selectivity (98 %). The reusability of the MPrSO$_3$H-MCM-41 needs to be concerned as furfural yield rapidly decreased to less than 50% for the second time. Mesoporous shell silica bead (MSHS) served as support and modified with sulfonic acid (MSHS-SO$_3$H) and aluminium (MSHS-Al) were prepared.$^{152}$ Their catalytic performance with dehydration reaction of D-xylose into furfural under water phase was investigated.
MSHS-Al gave a higher D-xylose conversion than MSHS-SO$_3$H (45 % vs 32 %), but furnished a lower furfural selectivity (35 % vs 57 %). Moreover, MSHS-Al isomerized D-xylose to D-lyxose at a concentration of 14 %. When compared general mesoporous catalysts MCM-41-SO$_3$H and HMS-SO$_3$H, MSHS-SO$_3$H is more efficient than HMS-SO$_3$H (18 % vs 13 % for furfural yield at 170$^\circ$C for 1 h), but less efficient than MCM-41-SO$_3$H (24 % in furfural yield) which attribute to its almost three times the number of sulfonic acid groups compared to MSHS-SO$_3$H. In addition, MSHS-SO$_3$H showed a better hydrothermal stability than MCM-41-SO$_3$H.

1.4.3.9 Zeolites

Different zeolite have been prepared and tested for the dehydration of carbohydrate derivatives into furfural. Zeolite catalysts (zeolite SM-25, mordenite 13 (Si/Al = 13), mordenite 20, faujasite 13) acidified with H$_3$PO$_4$ or H$_2$SO$_4$ were tested for D-xylose dehydration to furfural in a continuous two-liquid-phase (water-toluene) plug-flow reactor. The optimal conditions was determined: powdered mordenite (H$^+$) 13 as catalyst, 12 % w/w D-xylose solution, reactor temperature of 260$^\circ$C, pressure of 55 atm, toluene/D-xylose aqueous solution volumic ratio of 2, residence time of 3 min. For the first cycle, the furfural molar yield reached 98 % with a conversion rate of 99 %, and the second pass gave the furfural yield of 90 % with the same conversion rate. This indicated that the regeneration of the mordenite cannot recover its original activity.

A series of solid catalyst were tested for selectively converting hemicellulose from
crop waste into C5 sugars and furfural. The HUSY (Si/Al = 15) catalyst showed the highest activity to convert hemicellulose (> 90 % conversion) at 170°C within 3 h in the presence of water, followed by H-Beta zeolite (Si/Al = 19), HMOR zeolite (Si/Al = 10), and K10 clay. However, herein, less than 12 % of furfural formed. Other catalysts: γ-Al₂O₃, Nb₂O₅, and Al-containing mesoporous silicas have less activity. The application of biphasic solvent mixture furnished higher furfural yield. For example, 54-56 % of furfural yield were obtained in water-toluene or water-MIBK or water-xylene biphasic systems catalyzed with HUSY (Si/Al = 15) at 170°C for 6 h. Zeolites seemed to be hydrolytically stable in the reaction mixture and mineral impurities such as Na and K in biomass may be responsible for the reduction in the activity of the catalysts. ZSM-5 zeolite catalyzed the furfural production from aqueous hemicelluloses solution (which contains D-xylose (164 g/L), D-glucose (11 g/L) and arabinose (4.5 g/L)). The effects of reaction temperature, time, catalyst loading, organic solvents and inorganic salts or metal oxides addition were investigated in detail. The maximum furfural yield of 82 % and the D-xylose conversion of 97 % were achieved at 190 °C in the presence of ZSM-5 (1.0 g), NaCl (1.05 g) and organic solvent-to-aqueous phase ratio of 30:15 (v/v) for 3 h. Applying these conditions into pure D-xylose solution decreased the yield of furfural (51 %) which attributed to easier occurrence of excessive hydrolysis of D-xylose and condensation reactions. Besides, ZSM-5 has a relative stability and can be reused at least five times with the furfural yield still up to 67 %.

HZSM-5 zeolite was used to improve the production of monoaromatic
hydrocarbons, such as benzene, toluene, xylene and ethylbenzene. In fact, there is only little amount of furfural formed (less than 0.59 wt% with respect to dry basis sugar maple). The same catalyst HZSM-5 helped to produce furfural from steam explosion liquor of rice straw (which contains mainly D-xylose oligomers 2.27 kg/m$^3$ in 3.61 kg/m$^3$ total sugar). The maximum furfural yield was 310 g/kg under the optimum conditions: HZSM-5 addition 60 g/kg sugar, reaction temperature 160 °C, extraction steam flow rate 2.5 cm$^3$/min and total sugar concentration 61.4 kg/m$^3$. It was worth noting that polymerization inhibitor 4-methoxyphenol and tert-butylcatechol were added into the reaction system to improve furfural yield. It was found that 4-methoxyphenol was more efficient than tert-butylcatechol at the same additive amount, especially with 15 g/kg 4-methoxyphenol addition increased furfural yield to 375 g/kg, which increase by 21 % compared with that without polymerization inhibitor. HZSM-5 catalysts could be reused for 3 runs and the catalytic activity recovered 88 % after regeneration through calcinations.

D-Xylose dehydration activity of arenesulfonic SBA-15 catalysts synthesized at high aging-temperature (180 °C) revealed that the catalyst was more selective and hydrothermally stable. For example, SBA-15 modified with 0.2 mole ratio of 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane (A180-0.2) gave furfural in 82 % yield with a conversion of 98 % at 160 °C in water-toluene biphasic system for 20 h. Modification of the catalyst with 0.3 organosiloxane molar loading led to furfural in 86 % yield with a conversion of 99 %. Amberlyst-70 was compared with arenesulfonic SBA-15 catalysts, which presented obviously lower furfural selectivity.
Moreover, regenerated A180-0.2 by using a thermal treatment at 290 °C gave furfural in 75 % yield and a conversion of 88 % after three consecutive runs. The catalysts aged at lower temperature showed important deactivation rates.

Microporous silico aluminophosphates SAPO-5, SAPO-11 and SAPO-40 were tested as solid acid catalysts in the dehydration of D-xylose into furfural under water-toluene biphasic system at 170 °C.\textsuperscript{158} Furfural yields in 4 h using SAPO-11 (34-38 %) are comparable with that for HMOR zeolite with Si/Al ≈ 6 (34 %), under similar reaction conditions, while SAPO-5 and SAPO-40 gave less than 25 % of furfural yield, with respect to H\textsubscript{2}SO\textsubscript{4} (0.03 M), only 2 % of furfural was formed. Complete D-xylose conversion is reached within 16-24 h, with furfural yields of up to 65 %. No decrease of Si, P or Al contents and furfural yield were observed in all catalysts for three consecutive runs. Regardless comparable furfural yield achieved by this kind of catalyst, their preparation process are more convenient. In another work, SAPO-44 was superior to SAPO-5, SAPO-11, SAPO-46 for one-pot conversion hemicellulose into furfural as it has a higher acid amount and surface area.\textsuperscript{159} With respect to HMOR (Si/Al = 10), even it has an equal total acid amount of 1.2 mmol/g and a higher surface area than SAPO-44, an inferior activity was observed because of its weaker hydrophilic nature. SAPO-44 could give a furfural yield of 63 % with 88 % of mass balance at 170 °C within 8 h and no loss of catalytic activity was observed after 8 cycles. Later, more kinds of hemicellulose as feedstock were applied,\textsuperscript{160} and extraordinarily high yields of furfural catalyzed with SAPO-44 (about 86-93 % from bagasse, rice husk and wheat straw) were obtained at 170 °C in a water-toluene
biphasic system. This catalyst could also keep consistent activity. Subsequently, effects of careful designing of SAPO-44 catalysts on the efficient synthesis of furfural from xylan were conducted.\textsuperscript{161} It was found that SAPO-44 having 1.0 mole of Si content is the best catalyst for the xylan-D-xylose conversion to furfural. Use of biphasic ratio of 1:2 (v/v) showed the highest amount of furfural (82 \%) production from xylan at 170 °C and within 10 h. Other kinds of catalyst such as H:\textbeta\ (Si/Al = 19), HMOR (Si/Al = 10), HUSY (Si/Al = 15), were also compared with SAPO-44. Recently, small pore zeolites SAPO-34 and SAPO-56 were applied to furfural production from D-xylose and switchgrass in water-GVL monophasic system.\textsuperscript{162} ZSM-5, Amberlyst-70 and H\textsubscript{2}SO\textsubscript{4} led a better furfural yields (70 \%, 63 \%, 67 \% from D-xylose respectively), but leaching studies indicated that these good results were attributed to homogeneous catalysis by the acid sites that leached from the catalysts. The commercial SAPO-34 catalyst gave a moderate furfural yield of 40 \% from D-xylose and 31 \% from switchgrass, and showed a good recyclability. These small pore zeolites may be rationally designed to increase the yield from biomass reactions. The use of a chabazite-type zeolite prepared from the chemical transformation of a faujasite-type natural one was studied.\textsuperscript{163} The hemicellulose contained in ball-milled pretreated bamboo powder was directly transferred into furfural when it was stirred in a water-toluene biphasic system under conventional heating. At 170 °C for 10 h, furfural was finally produced in 55 \% yield.

A special zeolite displaying iron, tin and zirconium site was synthesized using from H-type by means of an ion-exchange procedure.\textsuperscript{164} The catalysts hold both Bronsted
and Lewis acid sites. Surprisingly, by using the more effective Sn-beta, D-glucose became the substrate to produce furfural when heated at 180 °C. In a water-GVL biphasic system, furfural was obtained in 69 % yield.

1.4.3.10 Supported catalysts and others

Mesoporous silica-supported HPA catalysts showed a significant effect on the catalytic performances relating to several variables, such as the catalyst preparation method, type of support, HPA loading, and the reaction conditions.\textsuperscript{165} In water-toluene biphasic system, catalysts prepared in 1-butanol are more stable in recycling runs than that in water. Besides, higher HPA loadings and temperatures leaded to higher furfural yield. The furfural yields and catalyst stabilities are higher in DMSO than in water-toluene. Furfural was produced at 140 °C for 4 h in DMSO in 52 % yield when the catalyst was prepared in 1-butanol with 34 wt% of HPA supported on medium-pore micelle-templated silica. However, the best catalytic stability was obtained in DMSO using either the 15 wt% HPA inorganic composites, or HPA immobilized in the aminopropyl-functionalized silicas. Generally, the catalyst deactivation was due to HPA leaching and catalyst surface passivation.

Later, they supported cesium salts of 12-tungstophosphoric acid on medium-pore MCM-41 (3.7 nm) or large-pore (9.6 nm) micelle-templated silicas and investigated their catalytic performance for D-xylose dehydration to furfural in water-toluene and DMSO solvent system.\textsuperscript{166} In this work, similar conclusions have been observed. The initial catalytic activities decreased in the order silica-supported CsPW > Cs2.5PW >
Cs2.0PW > HPW. Increasing the CsPW loading from 15 to 34 wt% or using a support with a larger pore diameter nearly doubled furfural yields.

A series of MCM-41-supported niobium-oxide catalysts were tested and in general, the catalytic activity is related to the presence of niobium species over the silica support, and this increases with niobium-oxide content. However, the catalyst with 16 % of Nb$_2$O$_5$ loading (MCM-Nb16) is more efficient than that with 33 % of Nb$_2$O$_5$ loading which resulted in closure of the pore entrances and partial destruction of the mesoporous framework. MCM-Nb16 has a stable ability for furfural selectivity in spite of the increase in conversion or the reaction temperature, and in addition of 0.5 g NaCl/g aqueous solution, furfural yield significantly increased to 60 % from 36 % at 170 °C for 180 min in water-toluene biphasic system. After three consecutive runs, no catalytic activity decrease was observed with the recovered catalyst. Subsequently, the study of niobium oxide incorporated on different supports indicated that the textural properties of the supports and the total acidity played significant roles in D-xylose dehydration and furfural selectivity. $\gamma$-Al$_2$O$_3$ showed the highest D-xylose dehydration activity but poor furfural selectivity as it has higher Lewis acidity than Brønsted, which might favor side reactions on the catalyst surface. Commercial fumed silica supported catalyst presented larger pore sizes, favoring the diffusivity of D-xylose and consequently the dehydration activity. Whereas SBA-15 and MCM-41 showed higher acid site densities, their intermediate micro-mesoporous structure could provide higher D-xylose dehydration rates to furfural. SBA-15 with 12 wt% niobium oxides loading showed the highest amount of acid sites than that of 4 wt%
and 20 wt% loadings, and gave a D-xylose conversion of 85 % and furfural selectivity of 93 % at 160 °C for 24 h in water-toluene mixture. Moreover, the regenerated catalyst showed similar furfural selectivity with 4 % of D-xylose conversion decrease. With respect to co-solvent toluene, the use of N₂ stripping is more comparable.

Hydrothermal pretreatment of corncob with microwave-assisted have been systematically studied and the hydrolysates with the maximum D-xylose content (160 °C, 90 min), the maximum xylobiose content (180 °C, 15 min), and the maximum total D-xylose content in monosaccharide and oligosaccharides (DP ≤ 6) (160 °C, 60 min) were further conducted to produce furfural using tin-loaded montmorillonite (Sn-MMT) as the catalyst in the 2-sec-butylphenol/NaCl-DMSO system, respectively. The highest furfural yield (58 %) was obtained from the hydrolysates with the maximum D-xylose content, and the hydrolysate with the maximum xylobiose content gave the lowest furfural yield (less than 10 %) which indicated that the production of furfural has a direct connection with the monomeric pentose. Controlled experiments with pure D-xylose solution showed lower furfural yield than that from the hydrolysates with the same total D-xylose amount in monosaccharide and oligosaccharides, which may be ascribed to the reason that the slow release of pentose monomers from the oligomers can impede the formation of humins.

A silica supported poly(styrene sulfonic acid) was prepared. The silica particles were first functionalized by means of aminopropyltriethyilsilane and showed primary amine moieties on its surface to attach the polymer through electrostatic interactions. The catalysts were tested for their capacity to dehydrate D-xylose in
the organic solvents. The best performance was obtained using a 10 wt% D-xylose aqueous solution in water-CPME biphasic system. When the medium was heated at 180°C for 60 min, finally the furfural yield reached a value of 57%.

A series of functional IL supported silica nanoparticles with different acidity (ILs/SiO₂) have been prepared by covalent bonds using novel, non-toxic ethanol as solvent. With respect to furfural production from D-xylose, the catalytic performance followed the order: IL/SiO₂ < IL-SO₃H/SiO₂ < IL-HSO₄/SiO₂ < IL-SO₃H-HSO₄/SiO₂, and furfural yield increased from 31% to 50% at similar D-xylose conversion of 94-96%. In the catalyst IL-SO₃H-HSO₄/SiO₂, the strong acid sites from SO₃H and HSO₄⁻ have played the roles as active centers. As for IL/SiO₂, 31% of furfural yield was attributed to positive effect of chlorine anion from IL.

Other catalysts were tested for their activity regarding the production of furfural. Vanadium (10 wt%) contained H-MCM-41 catalysts showed the highest catalytic activity for the production of furanic compounds (e.g. the most abundant furanic compound was furfural) during the ex situ catalytic pyrolysis of cellulose, levoglucosan and xylan. It was found that furanic compounds were mainly derived from levoglucosan over weak acid sites of vanadium contained H-MCM-41.

The catalytic activity of functionalized partially hydroxylated MgF₂ catalysts for D-xylose dehydration into furfural was reported. Partially hydroxylated MgF₂ which contains Lewis and Brønsted sites, was further modification with perfluorosulfonic or methanefluorosulfonic. The former sulfonic precursor showed higher selectivity for furfural than the later one due to a lower sulfur atom.
incorporation and as a consequence of the reduction in furfural resinification reaction rates. Well-optimized Lewis/Brønsted ratios catalyst synthesized by one-step grafting technique could give a maximum furfural selectivity of 90 % at 160 °C in water-toluene biphasic system. Another part of their research investigated D-xylose conversion to furfural with partially hydroxylated MgF$_2$ catalysts synthesized using different HF concentrations. MgF$_2$-71 (synthesized with 71 wt% HF) gave 86 % of furfural selectivity with 94 % of D-xylose conversion in water-toluene and a furfural selectivity of 87 % could be achieved using N$_2$-stripping. The catalyst MgF$_2$-40, which is rich in Lewis acid-sites promoted the D-xylose conversion rather than furfural selectivity, and MgF$_2$-87, which has lower Lewis acid-sites content gave opposite conditions. It was found that the addition of D-glucose as a co-carbohydrate decreased furfural selectivity in all case. The change of reaction mechanism depended on the catalysts containing different Lewis/Brønsted ratios was also elaborated.

Furfural production using solid acid catalysts in GVL was studied in the presence of γ-Al$_2$O$_3$, Sn-SBA-15 and Sn-beta, which contain only Lewis acid-sites. In their hands, furfural was obtained in poor yields (< 40%). Sulfonic acid functionalized catalysts Amberlyst-70, Nafion SAC-13, sulfonated carbon, and propylsulfonic acid functionalized SBA-15, zeolites (H-ZSM-5, H-mordenite, and H-beta), sulfated inorganic metal oxides (sulfated zirconia), and even mineral acid H$_2$SO$_4$ have been tested. The effect of water content (as it has a significant influence on furfural degradation reactions) in GVL was investigated. Under the best conditions, 81 % furfural and 4 % formic acid were obtained in GVL with 10% water using H-M as
catalyst, and no decrease in furfural yield after five cycles, which is more stable than A70 and S-SBA-15. Interestingly, the main product of D-glucose conversion using zeolite catalysts and GVL as the solvent is furfural with yield superior to 30%.

A mechano catalytical strategy to simultaneously release hemicelluloses from the corncob cells and depolymerize the polysaccharide into its pentose subunits in presence of a solid acid catalyst (SO$_4^{2-}$/SiO$_2$/Al$_2$O$_3$/La$_3^+$) was published.$^{173}$ Herein, ball-milling treatment played an important role in the decomposition of the plant material. During the sonication step, the acid catalyst is responsible of the conversion of the hemicelluloses content into furfural. Finally, furfural yield of 83% was obtained at 190°C for 30 min from the pretreated waste material.

Currently metal organic frameworks (MOFs) are becoming promising new materials for as catalysts for various reactions. An good example employed Zn$_2$(Bim)$_4$ as an organic filter embedded in polymethylphenylsiloxane (PMPS).$^{174}$ Both are components of a porous composite membrane potent for the vapor permeation and isolation of produced furfural. After recovery of the product, the furfural was obtained with 41% of yield at 140°C in aqueous solution.

### 1.4.4 Conclusions

In conclusion, we try to summarize all synthesis of furfural using various kinds of catalysts. With respect to homogenous catalysis, mineral and organic acid catalysts mainly consisting of Brønsted acid need to get over a high activation barrier for furfural production. From this point of view, their combination with Lewis acid salts
which benefit to D-xylose isomerization to D-xylulose, a more reactive intermediate, seems to be more promising, thus lower energy is required and higher furfural yield and selectivity could be obtained. However, the corrosive, environmental and handled problems should be well concerned with this kind of catalysts. As for ILs, even if extraordinary results are obtained, due to its separation difficulty it appears to be impossible to realize their industrial applications. The limitations of solid catalysts basically lie in their complicated synthesis processes, relatively higher costs and easier inactivation after reaction. In despite of these drawbacks, some of them are significantly potential applications, such as sulfonated carbonaceous materials (SGO), zeolites (ZSM-5, SAPO-44, H-M) and partially hydroxylated MgF$_2$ etc. The crucial application of catalyst would be comprehensively evaluated by its efficiency, cost, stability, reusability and so on. Additionally, the design of more efficient reactors and furfural extraction with organic solvents, N$_2$ stripping or permeation membrane will be also preferable to improving furfural production on an industrial scale with a higher yield.
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CHAPTER 2

2.1 Sulfonated sporopollenin as an efficient and recyclable heterogeneous catalyst for dehydration of D-xylose and xylan into furfural

2.1.1 Introduction

As we reviewed in the last chapter, acid catalysts are leading the production of furfural. Regardless of promising results obtained with homogeneous acids such as HCl\(^1\),\(^2\) H\(_2\)SO\(_4\)\(^3\), or H\(_3\)PO\(_4\)\(^4\), some key issues should be concerned such as corrosion, safety and handling problems. In contrast thereto, acidic heterogeneous catalysts are less corrosion, more safe and easy-to-handle. Sulfonated organic polymers, Nafion\(^7\),\(^8\), have shown promising results in the field of green chemistry. Both materials are sulfonyl group-decorated polymers and are alternatives to other types of heterogeneous catalysts such as zeolites\(^9\),\(^10\) or heteropolyacids.\(^11\)

Sporopollenin is a potential alternative to synthetic organic polymers for a variety of supported catalyst applications. It is the main component of the outer walls of plant spores and pollens, and this biopolymer is extremely resistant to biological and chemical degradation as well as high temperatures.\(^12\) Its stability is due to its being a highly cross linked structure involving tertiary carbons and ethers. It possesses aliphatic chains bound to aromatic moieties, conjugated phenols, aliphatic alcohols, lactones and carboxylic acids. Morphologically it is relatively similar to the spores and pollens from which it is extracted; hence, it is isolated in the form of an empty microcapsule (exine). Due to the presence of a large hydrophobic cavity in the exine, sporopollenin exines have been shown to sequester edible oils from emulsions.
efficiently, encapsulate various polar and non-polar materials and act as a drug delivery system with excellent enhanced bioavailability.\textsuperscript{13} Sporopollenin has also acted as an efficient green support for covalent immobilization of a lipase.\textsuperscript{14} As a naturally occurring alternative polymer to the synthetic sulfonated polymers, Amberlyst or Nafion, sporopollenin exines were converted into a heterogeneous acidic catalyst by attaching sulfonyl groups to their surfaces \textit{via} sulfonation of the aromatic components of sporopollenin. Whilst a form of sulfonated sporopollenin was previously reported as part of a preliminary study to examine the potential of sporopollenin to act as an ion-exchange support,\textsuperscript{15} the product of sulfonation was not fully characterized or explored as a potential strong acid catalyst. This present work focuses on the employment of sulfonated sporopollenin (SSP) as heterogeneous catalyst in the presence or absence of NaCl in an aqueous biphasic system under microwave irradiation.

In this part, the characterization of SSP by elemental analysis, SEM, EDX, FTIR, XRD and XPS, the effect of various reaction parameters on the yield of furfural and xylose conversion and catalyst recycling performance will be discussed.

\textbf{2.1.2 Modification of the surface of sporopollenin}

SSP was produced by successive treatments starting from raw spores of Lycopodium clavatum. After conventional treatment,\textsuperscript{16} the desired naked material was obtained and then treated with chlorosulfonic acid affording sporopollenin derivatives with sulfonic acid and hydrogen sulfate. Successive treatment in basic and in acidic conditions afforded the target SSP without detectable presence of hydrogen sulfate. For all following experiments, SSP with average acidity of 1 mmol/g was chosen as the main candidate. A simple pH measurement gave us a value of 2.3 before starting
the experiments. Elemental analysis of SSP showed the presence of sulfur atom (51.3 % C, 5.8 % H, 0 % N and 6.6 % S) although no sulfur detection was observed with natural sporopollenin (62.7 % C, 7.3 % H, 0 % N and 0 % S). The initial morphology of the material was controlled by SEM observations. SEM images confirmed no significant damage of sporopollenin morphology as a consequence of the sulfonic acid loading (see ESI, Figure S2.1.1). The presence of the sulfur containing groups showed with elemental analysis was confirmed by EDX spectra (Figure 2.1.1 a and b). To confirm the nature of the group having sulfur atom, FTIR and XPS was done. The absorption bands at 1166 cm\(^{-1}\) and 1038 cm\(^{-1}\) can be assigned to O=S=O stretching vibration of SO\(_3\)H groups.\(^{17,18}\) Moreover, FTIR spectra indicated the presence of hydroxyl group in the native sporopollenin and in SSP (see ESI, Figure S 2.1.2). The results obtained by XRD method showed that SP and SSP have got amorphous structure (see ESI, Figure S 2.1.4). The XPS spectra were used to clarify the surface property of the sporopollenin and SSP. The total survey scans showed the existence of elements like C and O for the sporopollenin and C, O and S for SSP (Figure 2.1.1 c). For the sporopollenin, the XPS peaks of O1s can be deconvoluted into two dominated peaks (Figure 2.1.1 d) along with one weaker band associated with hydroxyl group confirmed by FTIR spectra. For SSP, the XPS peaks of O1s can be deconvoluted into only one main band. The S2s spectra have one peak assigned to sulfur in SO\(_3\)H group.\(^{19–21}\) Its deconvolution gave two peaks S2p3/2 and S2p1/2. The above results confirm that the presence of SO\(_3\)H group in the SSP. Besides, the BET analysis showed that SP and SSP materials are non-porous as expected with a negligible surface area (below 10 m\(^2\)/g).
2.1.3 Effect of reaction temperature

Reaction temperature is an essential factor showing a great influence on the reaction of dehydration. In our case, variation of temperature from 130 °C to 210 °C for 60 min under microwave irradiation in batch was investigated in order to determine the most favorable temperature catalyzed by SSP. CPME, considered as a promising green co-solvent, can greatly enhance the dehydration of D-xylose to furfural by isolating the formed aromatic aldehyde derivative just after its formation in the aqueous layer. According previous studies, the optimized water-CPME biphasic ratio was set as (1:3, v/v)²² in the whole study, and catalyst loading was initially
blocked at 10 wt % of D-xylose. At temperature below 180 °C, conversion of D-xylose and yield of furfural were inadequate (Fig. 2.1.2). However, it was noteworthy that conversion of D-xylose catalyzed by SSP reached 45 % even at the lowest temperature of 130 °C, whereas hardly furfural produced. Obviously, the catalyst can realize D-xylose partial dehydration, even at relatively lower temperature, but was not able to accomplish the complete production of furfural from the produced intermediates. Interestingly, furfural yield reached maximum value of 56 % yield, with a quite complete conversion of D-xylose at 190 °C.

Figure 2.1.2 Effect of temperature on the yield of furfural and D-xylose content. Reaction conditions: SSP (10 wt%), D-xylose (1.0 mmol), water (1 mL), CPME (3 mL), MW, 60 min.

It was noticeable that at temperature higher than 170 °C, humin formation was also observed even in our bi-phasic system. Interestingly, on the corresponding SEM photograph of the recovered SSP after reaction (see ESI, Figure S2.1.3), only a slight
amount of humin was really adsorbed in the cavities of the catalyst surface, but the presence of carbonaceous material masking the sulfonic groups was proven by the partial suppression of sulfur signal on EDX spectrum. The experiments showed that the optimized reaction temperature is obtained at 190 °C, displaying furfural selectivity of 56 %. Furthermore, a blank test was realized as follow: reaction was carried out at 190 °C in the same condition with 10 wt % of the non sulfonated sporopollenin. In this case, only 19 % of furfural was finally formed. This result convinced us to pursue these experiments with SSP.

### 2.1.4 Effect of reaction time

According to the literature, reaction time has a crucial effect on furfural production. By the way, the residence time effect on furfural yield and D-xylose conversion was investigated at 180 °C and 190 °C (Figure 2.1.3). At 190 °C, conversion of D-xylose increased with the reaction time, and yield of furfural reached its maximum value of 56 % at 40 minutes. Here the maximum of selectivity gave a value of 59 % for the best reaction time. This phenomenon was in accordance with the results currently found in literature for other type of heterogeneous catalysts. It was noticeable that addition of CPME to reaction mixture is favorable to inhibit formation of humins when the reaction temperature is lower than 180 °C. Unfortunately, despite the possible non-diffusion of the acid species in the organic layer, the best temperature in our case was always superior to 170 °C and it could promote side reactions which reduces the selectivity of the reaction. Nevertheless, by decreasing the temperature,
the yield obtained at 180 °C (53 % yield for 70 minutes) was inferior to the result obtained at 190 °C (56 % for 40 minutes). This demonstrated that high reaction temperature is necessary to diminish the reaction time for the dehydration of D-xylose catalyzed by SSP under microwaves-assisted irradiation in batch reactor.

2.1.5 Effect of catalyst and substrate loading

Both effects of different initial catalyst SSP amounts varying from 5 to 20 wt % and D-xylose loading variation in a mixture of water-CPME (1:3, v/v) were respectively studied when heated at 190 °C for 40 min (Figure 2.1.4 and 2.1.5). Firstly, loading of catalyst superior to 10 % can significantly affect the D-xylose selectivity and furfural
yield (Figure 2.1.4). Higher catalyst concentration caused lower furfural yield, due to further degradation of adsorbed furfural or due to its sequestration inside the hydrophobic cavity of the catalyst. On the other hand, all D-xylose cannot be sufficiently transformed when catalyst concentration is lower than 10 %. Besides, there is no great gain for the conversion of D-xylose and for furfural yield with the increase of substrate loading (Figure 2.1.5). Thus, when D-xylose loading was superior to 0.3 g (2.0 mmol), furfural accumulated on the surface of SSP which could promote the cross-polymerization with the unreacted surrounding sugar. Therefore, these results confirmed us that the initial loading of 10 wt % and 150 mg of D-xylose in water remained the best ratio at 190 °C for 40 minutes under microwave-assisted irradiation.

Figure 2.1.4 SSP catalyst loading on the yield of furfural and xylose contents. Reaction conditions: D-xylose (1.0 mmol), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.
2.1.6 Effect of NaCl addition

Usually, sodium chloride showed significant effects on furfural formation rate by complexing with carbocation intermediates during the D-xylose dehydration. Furthermore, addition of NaCl also promoted the transfer of furfural formed in water phase into organic phase by salting-out effect. Impact of the NaCl concentration varying from 0 to 2.5 mol/L during the process was investigated while keeping constant the other previous optimized conditions (D-xylose (1.0 mmol), SSP (10 wt%), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min). With the addition of NaCl, yield of furfural increased by 10 % in average, and conversion of xylose was also slightly
enhanced (Figure 2.1.6). A maximum of yield was obtained with 1.5 mmol of NaCl with a value of 69%. Increased amount of NaCl did not change the yield of furfural and contribute to the side-reactions. In our optimized reaction (D-xylose (1.0 mmol), SSP (10 wt %) and NaCl (1.5 mmol)), the initial pH of 2.3 felt to reach a value of 1.16. In our hands, furfural was obtained with its maximum yield. These results are in accordance with the literature data showing that strong acidic medium is necessary to dehydrate xylose, for pH closed to 1.12.¹

![Graph showing the effect of NaCl dosage on furfural yield and xylose content](image)

Figure 2.1.6 Effect of NaCl addition on the furfural yield and xylose contents. Reaction conditions: D-xylose (1.0 mmol), SSP (10 wt%), water (1 mL), CPME (3 mL), MW, 190°C, 40 min.

### 2.1.7 Effect of catalysts recovery

Recycling performance is an important condition to evaluate the performance of the catalyst. In order to estimate the properties of recovered catalysts, at least ten cycles of
experiments must being carried out using the optimized conditions. Basically, after a catalytic run, the reaction medium was separated from the organic CPME phase containing the furfural. Then, D-xylose (150 mg) and fresh CPME (3 mL) were added to the recycled aqueous phase, without further treatment containing SSP before starting the next cycle. In our hands, activity of SSP was maintained during 10 consecutives tests (65–69 %) (Figure 2.1.7). Similar procedure without NaCl was realized as a blank with an average loss of 10 % of yield.

Figure 2.1.7 Reusability of the catalyst. Reaction conditions: D-xylose (1.0 mmol), SSP (10 wt%), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min.

2.1.8 Furfural production from xylan

Prior to extend the furfural production to biomass, our optimized method was transferred to xylan as a good model (Figure 2.1.8). In the optimized conditions
(xylan (1.0 mmol based on D-xylose units), SSP (10 wt%), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 190 °C, 40 min), furfural yield reached 35 %. As expected, the furfural yield was lower than from D-xylose because direct production of furfural from xylan involves a two-steps reaction: a pseudo-first order irreversible depolymerization followed by dehydration of release pentose sub-unit.\textsuperscript{24} For this reason, variation of both the temperature from 150 to 210 °C for 40 minutes (Figure 2.1.8) and the reaction time from 10 to 70 minutes at 190 °C (Figure 2.1.9) have been done to optimized furfural production from xylan.

Less than 170 °C, the temperature is not sufficient for the formation of furfural but enough to hydrolyze xylan into monomers and oligomers sub-unit (Figure 2.1.8). From 190 °C, as usual, furfural quickly formed even if few D-xylose was detectable. For temperatures higher than 190 °C, side-reactions occurred and caused the decrease of furfural yield. When heated at 190 °C, furfural yield first increased gradually from 10 to 50 minutes, then remained almost constant after 50 min (Figure 2.1.9). In regards these results, the optimized formation of furfural from xylan was obtained at 190 °C for 50 min under microwave irradiation in the presence of 10 wt % of sulfonated sporopollenin and sodium chloride (1.5 mmol) in water-CPME (1:3, v/v).
Figure 2.1.8 Furfural yield and xylose contents from xylan against temperature. Reaction conditions: xylan (1 mmol based on xylose units), SSP (10 wt%), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 40 min.

Figure 2.1.9 Furfural yield and xylose contents from xylan against reaction time. Reaction conditions: xylan (1 mmol based on xylose units), SSP (10 wt%), NaCl (1.5 mmol), water (1 mL), CPME (3 mL), MW, 190 °C.

2.1.9 Conclusions

In summary, this work reports a new efficient process using sulfonated sporopollenin in presence of NaCl for the production of furfural from D-xylose in 69 %
yield. This new composite biomaterial is an active and recyclable solid acid catalyst in a water-CPME biphasic system under microwave irradiation. Regarding these promising results, the bio-based SSP could replace a lot of synthesized materials as acid catalyst with the advantage of being less toxic and environmentally friendly.
2.2 Comprehensive study of an expeditious conversion of pre-hydrolyzed alginic acid to furfural in Cu (II) biphasic systems using microwaves

2.2.1 Introduction

Alginic acid is one of the major polysaccharide free of lignin and is easily accessible from biomass. This biopolymer is extracted from a variety of microalgae such as brown sea weeds. Structurally, it comprise a copolymer incorporating two kinds of hexuronic acids, mainly D-mannuronic acid (MnA) and L-gulucoronic acid (Gla), these elements being all linked via 1,4-glycosidic linkages. This class of carbohydrate polymers is initially deployed as starting materials for the production of ethanol or low molecular weight fatty acids via biochemical or enzymatic transformations. Recently, it has been shown that an acid-catalyzed hydrothermal treatment of alginic acid can potentially afford furfural with sufficient yields at 200 °C. This decomposition of alginic acid involved a three-step mechanism which includes sequentially (i) hydrolysis of the glycosidic linkages between each hexuronic acid subunits; (ii) decarboxylation of released sugar species and (iii) dehydration of the ensuing hexoses into furfural.

Inspired by these findings, in this present work, we described an expeditious microwave (MW)-expedited reaction that enhances both, the production and selectivity of the hydrothermal conversion of alginic acid into furfural (Scheme 2.2.1). Copper salts were employed as the main catalysts and subsequent hydrolysis of alginic acid or its related oligomers, decarboxylation of carbohydrate monomer and finally, the dehydration were investigated by varying successively temperature, residence time, volume ratios of the biphasic systems and substrate to catalyst ratio’s
in three different extractive solvents: CPME, MTHF and MIBK. Optimum conditions were then deployed to effectively produce furfural from the biopolymer.

Scheme 2.2.1 Copper-catalyzed production of furfural by means of a biphasic system under MW irradiation conditions from native alginate.

2.2.2 Preliminary experiments

Nowadays, it is well known that the type of extractive solvent has a great influence on the partition coefficient of furfural between the two layers of a biphasic system, especially exposed to an acid or a homogeneous catalyst for a longer period. It could also influence the selectivity of different reactions leading to the formation of platform chemicals through the biomass conversion. In this present work, water-CPME biphasic system was compared to water-2-methyltetrahydrofuran (MTHF) and water-methylisobutylketone (MIBK). Prior to the experiments, some attempts to determine the evolution of the partition coefficient was carried out. For
instance, when 2.0 mL of an aqueous solution of 0.7 g/L of furfural was heated up in microwave oven at 220 °C for 1 minute, in presence of 2.0 mL of fresh CPME, 30 % of the initial furfural amount was degraded. Substitution of CPME by MTHF conducted to the degradation of 50 % of the aldehyde. However, for MIBK, the stability of the furfural was proved.

Regarding the results obtained by Kim and coworkers, copper II cation (Cu (II)) was chosen for its potential to convert alginate into the desired furfural in 13 % yield. The same group reported the better furfural production (34% yield) using acidic homogeneous catalyst \( \text{H}_3\text{PW}_{12}\text{O}_{40} \) as a substitute for copper II salts in THF/H\(_2\)O co-solvent at 180°C for 30 minutes. In our hands, application of the above process in the presence of CuCl\(_2\) (0.025 g) as catalyst enhanced the degradation of furfural in CPME (40 %), in MTHF (70 %) and no degradation has been observed in MIBK. It seems that MIBK could be a better organic layer for the conversion of alginic acid to furfural in our conditions.

### 2.2.3 Conversion of D-glucuronic acid in water-CPME mixture

For the initial study, d-glucuronic acid was selected as a model starting monomer which is reportedly a component of partially oxidized cellulose. Indeed, glucuronic acid hold a carbonyl group at the C5 position instead of the hydroxymethyl group at the same position currently found for \( \alpha \)-D-glucose of cellulose. Its acidic decomposition therefore leads to the production of furfural via a similar two-steps
mechanism, i.e. successive decarboxylation of sugar and dehydration of the more sensitive pentose intermediate. In view of our own previous explorations on the production of furfural from D-xylose using aqueous CPME and MW irradiation, a classical methodology was developed (see ESI Table S2.2.1). The results of this preliminary study gave us important clues for later adaption of the entire system to alginic acid. Thus, after placing D-glucuronic acid (0.05 g, 0.25 mmol) in water-CPME biphasic system (4 mL, 3:13, v/v) and heating the resulted mixture for 1-2.5 minutes in a MW oven at 210 °C in presence of copper (II) chloride dihydrate (CuCl₂, 2 H₂O, 0.05 g, 0.29 mmol), the yield of furfural reached a maximum value of 31 % (Scheme 2.2.2). Despite our several attempts, it was difficult to increase the reaction temperature due to overpressure recorded in the vessel. It should be noted that Kim and co-workers has much lower yields (13%) using CuCl₂ with reaction times 10 times longer.

\[ \text{D-glucuronic acid} \xrightarrow{\text{CuCl}_2 \cdot 2\text{H}_2\text{O} (1.2 \text{ eq})} \xrightarrow{\text{H}_2\text{O-CPME (3:13, v/v)}} \text{furfural} \]

Scheme 2.2.2 Synthesis of furfural starting from D-glucuronic acid.

**2.2.4 Conversion of alginic acid in water-CPME mixture**

Next, the adaptation of the method starting from alginic acid at variable temperatures was undertaken (Scheme 2.2.3 and Figure 2.2.1). In our hands, a higher yield (28 %) of furfural was obtained just after one minute of MW irradiation at 220
°C. Under these reactions, but at elevated temperatures > 200 °C and for a longer duration than 2 minutes, showed no improvement in the furfural yield while at lower temperatures ~ 190 °C, the yield did not exceed 25 %, even after prolonged reaction time. Compared with the dehydration of D-glucuronic acid, the optimized temperature is higher starting from alginic acid (220 °C vs 210 °C) and yield is similar (28 % and 31 %).

Scheme 2.2.3 Synthesis of furfural starting from alginic acid.

Figure 2.2.1 Reaction profile of alginic acid conversion to furfural. Reaction conditions: alginic acid (0.05 g) (based on hexuronic acid sub-units), CuCl₂·2H₂O (0.05 g), water (0.75 mL), CPME (3.25 mL), MW.
Figure 2.2.2 depicts the possible influence of the water-CPME ratio on the furfural generation. In regards to the previous result, the temperature was set at 220 °C and the reaction mixture was then stirred under MW irradiation for one minute. Interestingly, the same ideal volume ratio water-CPME (3:13, v/v) defined for glucuronic acid was also applicable in case of the alginic acid.

![Graph showing the effect of water to CPME phase ratio (v/v) on the yield of furfural formation.](image)

Figure 2.2.2 Effect of water to CPME phase ratio (v/v) on the yield of furfural formation. Reaction conditions: alginic acid (0.05 g) (based on hexuronic acid sub-units), CuCl₂·2H₂O (0.05 g), water, CPME, 220 °C, 1 min, MW.

A more detailed analysis was necessary to determine the optimum alginic acid to copper salt ratio in spite of a very short residence time; these results obtained using
aqueous CPME are documented (see ESI, Figure S2.2.1). For a mass of alginic acid varying from 0.025 and 0.075 g in presence of CuCl$_2$.2 H$_2$O (0.025 g), dehydration in water-CPME (4 mL, 3:13, v/v) at 220 °C under MW irradiation for 1 and 1.5 minute furnished furfural with a maximal yield of 28 %. By reducing the amount of catalyst deployed in the reaction, it necessitated more time according the substrate to catalyst ratio thus emphasizing that this process could be applied in a more economical manner by preserving the copper catalyst.

A screening of various catalysts composed of Cu(II) bearing different anions types were performed in the conversion of alginic acid to furfural using the optimized method. As shown in the Figure 2.2.3, a blank was also performed and a low value of furfural yield of 6 % was obtained without catalyst, in parallel to the release of a small amount of hexuronic acid subunits and their relative generated pentose in the aqueous layer (see ESI, Figure S2.2.2).$^{34}$ In all cases, the acidic monomers and their decarboxylated counterparts were consumed just after a short time in presence of any catalyst due to the higher temperature and pressure conditions. Compared to CuCl$_2$, CuCl gave a value of 20 % by using the same molar ratio of catalyst. Notably, CuCl$_2$ remained better than the result obtained with hydrochloric acid which provided furfural with a moderate value of 23 %. Furthermore, Cl$^-$ and SO$_4^{2-}$ counter-ions are apparently more effective than nitrate (NO$_3^-$) and the use of acetylacetonate ligand (acac$^-$) shows that nature and steric hindrance of anion furnished by the copper salt have a crucial effect on the catalytic activity of Cu (II). Thus, anions could potentially participate and stabilize the ensuing Cu (II)-uronic acid complexes prior to its
decarboxylation. In case of Cu(NO$_3$)$_2$, a slight amount of nitric acid produced during the process may be responsible for the nitration of furan ring thus accounting for the reduction in yield. All hypotheses were confirmed by the difference of pH measured with the respective copper salt solutions. As an example, for equimolar solution of CuCl$_2$ and Cu(NO$_3$)$_2$, the aqueous solution of CuCl$_2$ provides more free protons than the later. However, in case of CuCl, the absence of a possible typical one electron oxidation could surely explain the reason behind a 10 % difference of furfural yield obtained in presence of CuCl$_2$.

Table 2.2.1 pH variation of the reaction medium in each stage of the reaction

<table>
<thead>
<tr>
<th>Entry</th>
<th>Times</th>
<th>Materials</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Before MW irradiation</td>
<td>water</td>
<td>6.50</td>
</tr>
<tr>
<td>2</td>
<td>Before MW irradiation</td>
<td>Water + CuCl$_2$.2 H$_2$O</td>
<td>3.38</td>
</tr>
<tr>
<td>3</td>
<td>Before MW irradiation</td>
<td>Water + alginic acid</td>
<td>2.72</td>
</tr>
<tr>
<td>4</td>
<td>Before MW irradiation</td>
<td>Water + alginic acid + CuCl$_2$.2 H$_2$O</td>
<td>1.69</td>
</tr>
<tr>
<td>5</td>
<td>After reaction</td>
<td>Water + alginic acid + CuCl$_2$.2 H$_2$O</td>
<td>1.57</td>
</tr>
</tbody>
</table>

*Reaction conditions: alginic acid (0.075 g), CuCl$_2$.2 H$_2$O (0.075 mg), water (2.25 mL), CPME (9.75 mL), MW, 1.5 min.*

In order to complete our hypothesis, the pH of the reaction medium was measured at different stages of the process (see Table 2.2.1). Before starting the experiments, just after added the alginic acid to the copper (II) chloride aqueous solution, the pH decreased from 2.72 to 1.69. This variation could be evidence for the release of a large amount of protons after complexion of Cu with carboxyl or hydroxyl groups of the sugar. Additionally, when the reaction was carried out in a water-CPME biphasic system, only a slight drop of the pH was finally observed. However, it is possible to
imagine the production of carbonic or formic acids during the complete alginic acid transformation.

Curiously, the use of CuCl$_2$ and NaCl did not show an additional positive salt-out effect usually encountered in a typical biphasic system employed for dehydrating carbohydrates like xylose into furfural;\textsuperscript{22,35} a slight reduction in the yield (24%) of furfural was noticed. It is important to bear in mind the strong tendency for the precipitation of copper salt complexes during the process (see ESI, Figure S2.2.4a). This phenomenon could be also be explained by the competition between Na$^+$ and Cu$^{2+}$ for forming complexes with the carboxylic acid moieties of the free hexuronic acids. It has been recognized that this type of organometallic dimer, incorporating the central chelated Cu (II) (as shown in Scheme 2.2.4), is subjected to a decarboxylation mechanism inhibited here by the presence of the sodium cation. The inhibition of furfural production was particularly reinforced when CuCl/NaCl and CuSO$_4$/NaCl were employed as catalysts instead of CuCl and CuSO$_4$, respectively. Based on aforementioned results, the production of furfural starting from alginic acid in a mixture of water-CPME was optimized by the use of CuCl$_2$.2H$_2$O at 220 °C for 1.5 minute.

![Scheme 2.2.4 Potential structure of a mononuclear Cu(II) glucuronoside complex. Adapted from Stapley and Bemiller.\textsuperscript{34}](image-url)
2.2.5 Conversion of alginic acid in water-MTHF mixture

The above method using water-CPME biphasic systems was compared to water-MTHF. Prior to the experiments, determining the evolution of the partition coefficient was carried out, and a constant value of 6 was finally determined according the following formula $K_p = \frac{[\text{furfural}]_{\text{water}}}{[\text{furfural}]_{\text{MTHF}}}$; the value was greater than obtained with water-CPME under the same conditions. This study was conducted by replacing CPME by MTHF using the optimized conditions: 0.075g of alginic acid (based on hexuronic acid subunits), CuCl$_2$, 2 H$_2$O (25.0 mg, 0.147 mmol), water (0.75 mL), MTHF (3.25 mL), 210 °C, 90 seconds. Notably, here the reaction temperature was kept at 210 °C vs 220 °C due to its lower boiling point of 83 °C and the associated limiting overpressure detected in the apparatus; 28% yield of furfural.
generation could be reached (see ESI, Figure S2.2.1). In parallel, additional efforts to modify the water-MTHF volume ratio were also performed. Thus, by increasing the volume of MTHF involved in the reaction, the furfural yield increased from 16 % in pure water to 23 % for a ratio of 1:7, v/v. On the other hand, a short survey of the substrate to catalyst ratio was realized, leading to the optimized conditions (Table 2.2.2).

Table 2.2.2 Influence of alginic acid-CuCl$_2$ ratio on the furfural yield in water-MeTHF $^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alginic acid (g)</th>
<th>CuCl$_2$·2H$_2$O (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.05</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.025</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>0.075</td>
<td>0.025</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>0.025</td>
<td>0.025</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>0.025</td>
<td>0.0125</td>
<td>26</td>
</tr>
</tbody>
</table>

$^a$ Reactions conditions: defined mass of alginic acid (based on hexuronic acid sub-units), defined mass of catalyst, 4.0 mL of water-MTHF (3:13, v/v), 2.5 min, 210 °C, MW.

In MTHF, at 210 °C, the maximum yield of furfural (30 %) was obtained after 2.5 minutes from 0.05 g of alginic acid in presence of 0.025 g of copper catalyst. Curiously, despite our efforts, variations of alginic acid-CuCl$_2$ ratio were not conclusive and the yield never exceeded 30 %. Based on these results, production of furfural starting from alginic acid in a mixture of water-MTHF was optimized by the use of CuCl$_2$·2H$_2$O at 210 °C for 2.5 minutes. Using this optimized method in
presence of MTHF, time required is longer and yield is similar to what was obtained in presence of CPME.

2.2.6 Conversion of alginic acid in water-MIBK mixture

In accordance with the results obtained in water-CPME and water-MeTHF, only the concentration of CuCl$_2$.2 H$_2$O was studied in water-MIBK (Table 2.2.3). It was possible to improve the yield of furfural barely after 1 minute heating but the amount of alginic acid substrate required to be reduced to 0.025 g (Table 2.2.3 and ESI Figure S2.2.1); 31% yield of furfural was attained. Despite our efforts, variations of alginic acid-CuCl$_2$ ratio were not conclusive and the yield never exceeded 31% keeping the reaction condition unchanged. Besides after a quick analysis, it appeared that under the same conditions, respectively for MIBK and MTHF, at different volume ratios, the furfural yield increased jointly with the volume of the extractive solvent until its progression reached a limit for the same volume ratio of (3:13, v/v).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alginic acid (g)</th>
<th>CuCl$_2$.2 H$_2$O (g)</th>
<th>Furfural yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>0.05</td>
<td>25</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.025</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>0.075</td>
<td>0.025</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>0.025</td>
<td>0.025</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>0.025</td>
<td>0.0125</td>
<td>24</td>
</tr>
</tbody>
</table>

*Reactions conditions: defined mass of alginic acid (based on hexuronic acid sub-units), defined mass of catalyst, water (0.75 mL), MIBK (3.25 mL), 220°C, MW, 1 min.*
2.2.7 Reusability of the aqueous phase containing CuCl$_2$

In order to estimate the properties of recovered catalysts, ten cycles of experiments were carried out using the conditions as identified in our optimized water-MIBK biphasic system (Figure 2.2.4). After a catalytic run, the aqueous layer containing carbohydrates and the catalyst was separated from the organic MIBK phase containing the furfural. Then, alginic acid (0.14 mmol) and fresh MIBK (3.25 mL) were added to the recycled aqueous phase containing both Cu (II) and Cu (I) as catalysts and the hydrozylate. Up to 5 cycles, the furfural yield measured in the organic layer remained stable and gave an average value of 26 % from the sixth. After five cycles, the yield decreased gradually to 9 % for the tenth cycle. This phenomenon is possibly attributable to the progressive formation of insoluble complexes between copper cations and organic acids such as malic, succinic or formic acids (See ESI, Figure S2.2.3). Despite our efforts, all remaining residues are undetected by mass spectrometry; a progressive disappearance of Cu(II) in favor to Cu(I) in the reaction medium was observed (See ESI, Fig. S2.2.4a). Under the current reaction conditions, the pH measurement of the aqueous layer gave a value of 1.7 before starting the experiments, however the value of pH did not change between each cycle, although CO$_2$ was supposed to be released in the mixture.
2.2.8 Comprehensive study of the furfural origin

After hydrolysis of our alginic acid substrate, starting from 10 g of the native biopolymer 8 g of an insoluble solid was recovered by filtration. In order to understand more exactly where the furfural came from, the NMR and FT-IR analysis were performed by using both soluble and insoluble oligomeric mixtures obtained from the hydrolysis of alginic acid at pH of 1.7 (see ESI Figure S2.2.5); all analysis gave clear information about their molecular compositions. At the lower pH, the cleavage of $\beta$-D-MnA-(1$\rightarrow$4)-$\alpha$-L-GIA $O$-glycosidic bonds is easier compared to those of $\alpha$-L-GIA-(1$\rightarrow$4)-$\beta$-D-MnA with a characteristic first-order rate constant.\(^{37}\) Interestingly, the higher rate value is generally observed for the cleavage of

![Figure 2.2.4 Reusability of the aqueous phase containing copperchloride for alginic acid conversion to furfural.](image-url)
β-D-MnA-(1→4)-α-L-GlA linkage. When the water soluble fraction (2.0 g from 10.0 g) was studied more attentively by $^1$H NMR, no trace of D-lyxose, formed from the decarboxylation of the hexuronic acids, was detected in the sample, explained by the lower temperature of the hydrolysis condition. Furthermore, from $^{13}$C NMR analysis, the mixture seems to be poor in α-L-GlA-(1→4)-α-L-GlA and α-L-GlA-(1→4)-β-D-MnA bonds due to the disappearance of the peak at 104 ppm although it could probably contain a few traces of GlA free subunits.38,39 According to the $^1$H NMR chart, the water soluble fraction was rich in MnA oligomers, a result corroborated by the signals observed on the FT-IR spectrum;40,41 the absence of the band usually found in alginic acid at 787 cm$^{-1}$ confirmed also the absence of large GlA oligomers in the mixture. Additionally, with the first doublet found at 5.21 ppm, a second one at 4.63 pm and another one at 4.29 ppm, it is possible to state that all signals are representative of several MnA oligomers found in the mixture displaying sometimes β-D-MnA-(1→4)-α-L-GlA terminations. On the other hand, despite our efforts, it was very difficult to solubilize and analyze the insoluble material (8.0 g from 10.0 g) isolated from the alginic acid hydrolysis by NMR spectroscopy. However, some conclusions could be made from the FT-IR analysis. Two bands located at 903 and 948 cm$^{-1}$ are generally assigned to α-L-GlA-(1→4)-β-D-MnA linkage and overall the α-L-gulopyranuronic (GlA) asymmetric ring vibration. At 894 cm$^{-1}$, the spectrum showed the characteristic band for β-anomeric CH deformation caused by β mannuronic residues. At 822 cm$^{-1}$, the typical signal confirmed here the inclusion of a small amount of MnA residue in a large structure of homopolyguluronic
In case of MnA enriched homopolymer fraction, indeed the soluble hydrolyzate, the furfural yield never exceeded 26 % under our optimized conditions (dried solid (0.025 g based on hexuronic acid sub-units), CuCl$_2$.2 H$_2$O (0.05 g), water (0.75 mL), MIBK (3.25 mL), MW, 220 °C, 1 min, MW). However, by using the fraction enriched in short GlA homopolymeric chains, under the same conditions; the final furfural yields reached a value of 35 %. This improvement in furfural yield could be explained, in part, by the lowest polymerization degree of the GlA oligomers. Despite further attempts, the furfural yield enhancement was not successful by increasing the amount of the copper catalyst.

2.2.9 Conclusions

In conclusion, we have shown for the first time, that alginic acid aqueous solution in presence of copper salts and overall under subcritical conditions afforded maximum furfural yield around 30 % in a very short time (from 1 to 2.5 minutes). Similar results were obtained using water-CPME, water-MTHF and water-MIBK mixture with small changes in terms of concentrations of alginic acid, CuCl$_2$.2 H$_2$O, temperature and time. This minimal difference is due to the fact that the dehydration occurs in the aqueous layer which is the common solvent used in these three methods. Even if the boiling points and the dielectric constants of CPME, MTHF and MIBK are different and these solvents could react differently under MW irradiation, the role of the organic layer is only to realize a continuous extraction of the furfural
considering the diffusion of HCl into the organic layer. With the premise of improving the furfural yield from alginic acid, a pre-hydrolysis of the biopolymer was realized and both MnA and GlA enriched homopolymer mixture were obtained. Each fraction was processed under the optimized reaction conditions and the GlA enriched solid afforded the maximum of furfural yield of 35 %. These promising results persuade us to develop a MW-assisted continuous flow method using a more sequenced synthetic alginic acid obtained from enzymatic transformation of polymannuronic acid.\textsuperscript{37}
2.3 Microwave continuous production of furfural using heterogeneous $\text{H}_3\text{PW}_{12}\text{O}_{40}$ under atmospheric pressure

2.3.1 Introduction

To date, few works described the continuous flow dehydration of carbohydrate derivatives for the production of furfural. As a first example, two different micro-flow processes: a single-flow reactor and a pre-heated water flow in a range of temperature found between 200 and 240 °C were reported for the conversion of D-glucose into 5-HMF in association with various other compounds.\textsuperscript{42} The production of 5-HMF from D-fructose was also performed under continuous flow condition in 1,4-dioxane with DMSO traces using the commercially available Amberlyst 15 acidic resin as heterogeneous catalyst.\textsuperscript{43} As we mentioned above, continuous flow has various advantages compared with batch reactions.

The main purpose of this present work is to produce furfural from D-xylose at atmosphere pressure in continuous flow. Due to the fact that our microwave continuous flow reactor is an open system, reactions should be performed under atmosphere pressure. Thus the solvents selected should have high boiling point, for example DMSO (bp: 189 °C) which has been proved as a good solvent for carbohydrate dehydration. In this study, $\gamma$-butyrolactone (GBL, bp: 204 °C) was chose as a co-solvent to improve furfural yield, and various reaction parameters were also optimized.

2.3.2 Effect of DMSO/GBL ratio

The influence of DMSO and GBL volume ratio on the production of furfural was determined at 160 °C for 60 minutes under microwave irradiation in batch with
D-xylose (1.0 mmol) in presence of H$_3$PW$_{12}$O$_{40}$ (40 wt. %) as heteropolyacid. It seems to be obvious that both furfural yield and selectivity increase with the volume of GBL (from DMSO-GBL, 5:0, v/v to DMSO-GBL, 1:4, v/v) and then decrease with a lower quantity of DMSO. In these conditions, a minimum of DMSO (10 %) was necessary to obtain a clear monophasic solution prior to a good dehydration process.

Figure 2.3.1 Effect of DMSO-GBL volume ratio on dehydration of D-xylose to furfural. Reaction conditions:

D-xylose (1.0 mmol), HPA (0.06 g), GBL-DMSO (5 mL, v/v), MW, 160 °C, 60 minutes.

2.3.3 Effect of reaction temperature and HAP loading

Using the optimized solvent ratio with D-xylose (1.0 mmol) in presence of HPA (0.06 g), the influence of the temperature was also measured (Table S2.3.1). When the reaction temperature rose up to 170 °C, the furfural yield reached a value of 65 % for finally remaining almost constant for temperatures higher to 180 °C with a current value of 66 % yield. As expected, less concentration of D-xylose (0.33 mmol vs 1.0 mmol) and higher amount of catalyst (120 wt. % vs 40 wt. %) permitted to have a similar production of the target aldehyde (72 %) but in a shorter reaction time (40
minutes vs 60 minutes) (Figure 2.3.2 and Table S2.3.1). It is clear that with the same ration between D-xylose and HPA (40 wt. %) yield of furfural (50 %) was lower at 140 °C for 80 minutes.

Figure 2.3.2 Effect of HPA amount on dehydration of D-xylose to furfural. Reaction conditions: D-xylose (0.33 mmol), GBL (4.0 mL), DMSO (1.0 mL), MW, 170 °C, 40 minutes.

2.3.4 Furfural production using microwave continuous flow

Continuous flow chemistry and microwave irradiation as alternative technology offer separately different advantages in term of green chemistry and sustainable development. Mixing these two technics may have some interesting benefits. Starting from the optimized conditions for the production of furfural in batch (D-xylose (0.2 M), HPA (40 wt. %), DMSO-GBL (5 mL, 1:4, v/v), MW) variations of different parameters were examined in a low flow (from 0.25 mL/min to 1.0 mL/min) (Table 2.3.1). Simple transfer from batch to continuous flow showed that a flow rate of 0.5 mL min⁻¹ was better than 1.0 mL/min (62 % vs 48 % yield) (Table 2.3.1, entries 1 and 2). Increasing the amount of heterogeneous acid catalyst (58 wt. % vs 37 wt. %) and
slight decreasing of temperature furnished the target furfural in similar yield (Table 2.3.1, entries 3 and 4). Starting from higher concentration of D-xylose (0.4 M vs 0.2 M), conversion, yield and selectivity were similar even in 0.25 mL/min (Table 2.3.1, entries 5 and 6). Starting from D-xylose (0.27 M) and low amount of HPA (14 wt. %) yield of furfural was similar for a residence time two times greater (0.25 mL/min vs 0.5 mL/min) (Table 2.3.1, entry 8).

Table 2.3.1 D-Xylose dehydration into furfural in DMSO-GBL monophasic feed solution containing a small amount of HPA under microwave-aided continuous flow process

<table>
<thead>
<tr>
<th>Entry</th>
<th>D-Xylose (g)</th>
<th>HPA (g)</th>
<th>DMSO (mL)</th>
<th>GBL (mL)</th>
<th>T (°C)</th>
<th>Flow rate (mL min⁻¹)</th>
<th>C (%)</th>
<th>Y (%)</th>
<th>S (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.5</td>
<td>1.68</td>
<td>30</td>
<td>120</td>
<td>160</td>
<td>0.5</td>
<td>93</td>
<td>62</td>
<td>67</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>1.68</td>
<td>30</td>
<td>120</td>
<td>160</td>
<td>1.0</td>
<td>84</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>2.59</td>
<td>30</td>
<td>120</td>
<td>145</td>
<td>0.5</td>
<td>94</td>
<td>61</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>4.5</td>
<td>2.59</td>
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<td>120</td>
<td>150</td>
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<td>95</td>
<td>63</td>
<td>66</td>
</tr>
<tr>
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<td>9</td>
<td>1.68</td>
<td>30</td>
<td>120</td>
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<td>91</td>
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<tr>
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<td>160</td>
<td>160</td>
<td>0.5</td>
<td>87</td>
<td>55</td>
<td>63</td>
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<tr>
<td>8</td>
<td>8</td>
<td>1.12</td>
<td>40</td>
<td>160</td>
<td>160</td>
<td>0.25</td>
<td>90</td>
<td>61</td>
<td>67</td>
</tr>
</tbody>
</table>

*Reaction conditions: D-Xylose (0.2-0.4 M), HPA (14-57 wt. %), DMSO-GBL (1:4, v/v), 145-160 °C, MW, continuous flow.*

2.3.5 Conclusions

The present work showed the best of 72 % fufural yield could be obtained using heteropolyacid as catalyst under microwave batch conditions, and benefits to high
boiling points of the solvents, the reaction was successfully transferred to microwave continuous flow which offered >60% of furfural yield. And the inferior yield obtained in continuous flow was due to the relatively lower reaction temperature. One can observed that quiet similar results were achieved under identical reaction conditions in microwave batch and microwave continuous flow regimes. This indicated that a higher target compound productivity could be reached by transferring the reaction from batch to continuous flow.

In fact, the target compound of this study is 2-furonitrile, an intermediate in pharmaceutical and fine chemical synthesis. It is overall an important building-block for the production of efficient photovoltaic elements such as diketopyrrolopyrrole. We are trying to realize its production in two steps without isolating the furfural intermediate. The second step work will be introduced in furfural applications part Section 4.1.
References


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(37) Holtan, S.; Zhang, Q.; Strand, W. I.; Skjåka Bråk, G. Characterization of the


CHAPTER 3 Furfural applications

Literature review

Furfural cyanation

Organic chemicals having a nitrogen atom such as amine, amide, oxime, nitrile are key intermediates in various industrial areas such as agricultural, pharmaceutical, textile, polymer and cleaning industry. Most of them are produced from fossil resources by introduction of nitrogen atom. Recently, the synthesis of bio-based chemicals having nitrogen atom has been reported. For example, various furan derivatives with nitrogen atom could be produced from furfural (as illustrated in Figure 3.1.1). Among them, 2-furonitrile has been suggested as a potential sweetening agent, as it has about thirty times the sweetening power of sucrose, moreover, it's an important building-block for the production of efficient photovoltaic elements such as diketopyrrolopyrrole. Industrial synthesis of 2-furonitrile is based on the vapor phase ammoxidation of furfural with ammonia over bismuth molybdate catalyst at 440-480 °C. Numerous laboratory methods also exist. In this part, a brief overview of furfural cyanation will be introduced in terms of nitrogen source, such as hydroxylamine hydrochloride ($\text{H}_2\text{NOH-}\text{HCl}$), ammonia ($\text{NH}_3[\text{aq}]$), ammonium salts etc.
3.1.1 \( \text{H}_2\text{NOH-HCl} \) as N-source

For the production of nitriles from aldehydes, hydroxylamine hydrochloride is the most commonly used nitrogen source. Generally, an oxime would be formed and act as an intermediate during the conversion (as shown in Figure 3.1.1). One-pot reaction of aldehyde to nitrile have been recently reported using basic \( \text{Al}_2\text{O}_3/\text{PCl}_5 \), ionic supported triphenylphosphine and \( \text{CBr}_3 \), Bis (trichloromethyl) carbonate, copper based catalysts, \( \text{Fe}_3\text{O}_4 \)-nanoparticles, \( \text{P}_2\text{O}_5/\text{SiO}_2 \), Silica Gel, Montmorillonites K-10, and KSF, Red mud, Ru (Cl)-Salen Complex etc. Table 3.1.1 listed the results of 2-furonitrile production from fufural with or without catalysts, solvent, microwave irradiations in literatures.

![Figure 3.1.1 Production routes of furanic derivatives with nitrogen atom from fufural](image)

### Table 3.1.1 2-Furonitrile production from fufural with \( \text{H}_2\text{NOH-HCl} \)

<table>
<thead>
<tr>
<th>Entry</th>
<th>catalyst</th>
<th>solvent</th>
<th>( T(°C) )</th>
<th>time</th>
<th>FN yield(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no</td>
<td>NMP</td>
<td>110-115</td>
<td>4h</td>
<td>88</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>no</td>
<td>DMSO</td>
<td>100</td>
<td>nm</td>
<td>35</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>no</td>
<td>NMP, DMF...</td>
<td>Nm</td>
<td>Reflux</td>
<td>80</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Al}_2\text{O}_3/\text{PCl}_5 )</td>
<td>no</td>
<td>120</td>
<td>-</td>
<td>85</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Na}_2\text{CO}_3 )</td>
<td>no</td>
<td>MW 150W</td>
<td>6 min</td>
<td>80</td>
<td>16</td>
</tr>
<tr>
<td>6</td>
<td>Pyridine</td>
<td>no</td>
<td>MW,320W</td>
<td>1 min</td>
<td>80</td>
<td>17</td>
</tr>
</tbody>
</table>
What should be noted in Table 3.1.1 is that comparable 2-furonitrile yield was obtained without any catalysts (Entries 1-3). As mentioned above, 2-furonitrile production from furfural with hydroxylamine hydrochloride consists of two steps: oximation and dehydration. The first step was considered to be occurred spontaneously even without catalyst, however, the second step certainly needs catalysts to realize dehydration process. In case of Entries 1-3, the authors supposed that the solvents N-Methyl pyrrolidone (NMP) or DMSO favored the dehydration of oxime to nitrile, which could be presented in Scheme 3.1.1 (NMP as an example).

![Scheme 3.1.1 Plausible mechanism of nitrile formation with NMP. Adapted from Chakraborti et.al.](image)

NMP may serve as a base to trap H⁺ due to their cation specific solvation property, then proton exchange between the intermittently oxime formed and the protonated solvent will activate the oxime hydroxyl group. The role of the dipolar aprotic solvent may further be realized in the fact that the _naked_ Cl⁻ should attack the methine...
hydrogen for eliminating the activated hydroxyl group.\textsuperscript{15}

Concerning the cases of no solvent, some catalysts which benefit to oxime dehydration were applied, such as P\textsubscript{2}O\textsubscript{5}, basic Al\textsubscript{2}O\textsubscript{3}/PCl\textsubscript{5}, Na\textsubscript{2}CO\textsubscript{3} etc., herein, catalysts (for example PCl\textsubscript{5}) act as similar role with activated NMP (Scheme 3.1.2). Microwave, which is considered as a green heating method, significantly expedited reaction rate (1-6 min vs several hours, entries 4-9). Interestingly, 95 % of 2-furonitrile was produced at 70 °C in 1 h when using dry chitosan supported magnetic ionic liquid as catalyst (Entry 7), but the major product changed to 2-furamide when using wet chitosan supported magnetic ionic liquid.

![Scheme 3.1.2 Plausible mechanism of nitrile formation catalyzed by Al\textsubscript{2}O\textsubscript{3}/PCl\textsubscript{5}. Adapted from Niknam et al.\textsuperscript{1}](image)

Impressively, at room temperature, 99 % of 2-furonitrile was yielded in 60 h with 2-Chloro-1,3-dimethylimidazolium chloride as catalyst (Entry 10), and 3-butyl-1,2-dimethylimidazolium triphenylphosphine-m-sulfonate gave 73 % yield for overnight (Entry 11), bis(trichloromethyl)-carbonate offered 89 % 2-furonitrile yield in 5-6 h (Entry 12). However, all of these experiments were performed in addition of basic solvent Et\textsubscript{3}N. The application of reflux could also shorten reaction time (Entries 13-15), for example, 87 % of 2-furonitrile yield was achieved with Fe\textsubscript{3}O\textsubscript{4}-CTAB NPs when refluxing DMF for 1.5 h (Entry 15). However, only 10 % of 2-furonitrile was produced by refluxing the mixture of Et\textsubscript{3}N and acetonitrile for 10 min, which was quite lower than other nitriles obtained from aldehydes respectively.
3.1.2 NH\textsubscript{3} as N-sources

As we introduced, industrial synthesis of 2-furonitrile is based on the vapor phase ammoxidation of furfural with ammonia over bismuth molybdate catalyst at 440-480 °C. With ammonia as the nitrogen sources, aldehyde will first transfer to imine by dehydration, and then the hydrogen atom will be substituted in presence of the catalyst, finally nitrile formed after releasing ammonium salts (As drawn in Scheme 3.1.3).

![Scheme 3.1.3 Plausible mechanisms of nitrile formation from aldehyde and NH\textsubscript{3}. a: adapted from Bandgar et al.\textsuperscript{21} and b from Wang et al.\textsuperscript{22}](image)

With ammonia aqueous as the nitrogen resource and solvent, 90 % of 2-furonitrile yield was obtained with ceric ammonium nitrate, NBS, tetrabutylammonium iodide combined tert-butyl hydroperoxide (Table 3.1.2 entries 2-4), and 85 % with iodosobenzene diacetate (Table 3.1.2 entry 1). The addition of THF shortened reaction time to 7 min using I\textsubscript{2} as the catalyst (Table 3.1.2 entry 5), but when dissolved NH\textsubscript{3} in benzene, nickel peroxide with NaSO\textsubscript{4} only gave 58 % of 2-furonitrile yield (Table 3.1.2 entry 9). Cu based and MnO\textsubscript{2} series catalysts also showed good catalytic performance for 2-furonitrile production.
Table 3.1.2 2-Furonitrile production from furfural with NH$_3$

<table>
<thead>
<tr>
<th>Entry</th>
<th>catalyst</th>
<th>N sources/solvent</th>
<th>T(°C)</th>
<th>time</th>
<th>FN yield(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IBD</td>
<td>NH$_3$aq.</td>
<td>rt</td>
<td>4h</td>
<td>85</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>CAN</td>
<td>NH$_3$aq.</td>
<td>0</td>
<td>nm</td>
<td>90</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>NBS</td>
<td>NH$_3$aq.</td>
<td>0</td>
<td>40 min</td>
<td>90</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>TBAI/TBHP</td>
<td>NH$_3$aq.</td>
<td>80</td>
<td>12h</td>
<td>90</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>I$_2$</td>
<td>NH$_3$aq. THF</td>
<td>rt</td>
<td>7 min</td>
<td>88</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>Cu/TEMPO</td>
<td>NH$_3$aq. in air, NaOH aq. MeCN</td>
<td>25-70</td>
<td>24h</td>
<td>92</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>Cu@C/TEMPO</td>
<td>NH$_3$aq., O$_2$, DMF</td>
<td>70</td>
<td>12</td>
<td>65</td>
<td>5</td>
</tr>
<tr>
<td>8</td>
<td>u-MnO$_2$</td>
<td>NH$_3$aq., O$_2$, MeOH</td>
<td>30</td>
<td>12h</td>
<td>91</td>
<td>27</td>
</tr>
<tr>
<td>9</td>
<td>NiO$_2$/NaSO$_4$</td>
<td>NH$_3$ gas in benzene</td>
<td>nm</td>
<td>Reflux 2.5h</td>
<td>58</td>
<td>28</td>
</tr>
</tbody>
</table>

nm: not mentioned; IBD: iodosobenzene diacetate; CAN: ceric ammonium nitrate; TBAI: tetrabutylammonium iodide; TBHP: tert-butyl hydroperoxide.

3.1.3 Ammonium salts as N-source

Ammonia is also considered as an expedient method for the transformation of furfural to 2-furonitrile. However, volatile ammonia has an undesirable smell and is harmful to the environment. In addition, ammonia is a common and undesirable contaminant in waste water and biomass cultivation media and the adverse effects of ammonia have promoted the development of various techniques for its removal. Therefore, ammonium salts as good cyanide sources such as NH$_4$Cl, NH$_4$HCO$_3$ etc. have been explored in literatures, and the results were shown in Table 3.1.3.

Table 3.1.3 2-Furonitrile production from furfural with ammonium salts

<table>
<thead>
<tr>
<th>Entry</th>
<th>catalyst</th>
<th>N sources/solvent</th>
<th>T(°C)</th>
<th>time</th>
<th>FN yield(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cu(0)</td>
<td>NH$_4$Cl, O$_2$ pyridine, NH$_3$HCO$_3$</td>
<td>20(60)</td>
<td>15h(8h)</td>
<td>76</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>CuHCO$_2$/NiHCO$_2$</td>
<td>NH$_3$HCO$_3$, (n-Bu4N)$_2$S$_2$O$_8$, KOH, MeCN</td>
<td>rt</td>
<td>1.5h</td>
<td>92</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>I$_2$</td>
<td>NH$_3$OAc</td>
<td>70</td>
<td>15 min</td>
<td>86</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>HTIB</td>
<td>NH$_3$OAc, MeCN, H$_2$O</td>
<td>80</td>
<td>2h</td>
<td>90</td>
<td>31</td>
</tr>
<tr>
<td>5</td>
<td>Phil(OAc)$_2$ /SDS</td>
<td>NH$_3$OAc</td>
<td>70</td>
<td>1h</td>
<td>90</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>PBAIS</td>
<td>NH$_3$OAc</td>
<td>70</td>
<td>3h</td>
<td>83</td>
<td>33</td>
</tr>
</tbody>
</table>

HTIB: hydroxy(tosyloxy)iodo]benzene; SDS: sodium dodecylsulfate; PBAIS: Poly[4-[bis(acetoxy)iodo]] styrene.

Capdevielle et al. achieved 76 % of 2-furonitrile production with NH$_4$Cl using Cu powder as catalyst in presence of O$_2$ and pyridine (Table 3.1.3, entry 1). Combined Cu
and Ni formate as catalyst, 92 % of 2-furonitrile was produced with tetrabutylammonium peroxydisulfate in the presence of ammonium hydrogen carbonate under basic aqueous conditions (Table 3.1.3 entry 2). More simple and efficient methodology has been developed by using the inexpensive and environmentally friendly reagent I$_2$/aqueous NH$_4$OAc, and then hydroxy(tosyloxy)iodo]benzene, Poly{4-[bis(acetoxy)iodo]}styrene and PhI(OAc)$_2$ with sodium dodecylsulfate were also proved as efficient catalysts for furfural conversion to 2-furonitrile (Table 3.1.3 entries 3-5). However, more complicated system with NaNO$_2$/HNO$_3$/4-AcNH-TEMPO as catalyst gave a marginal 2-furonitrile yield of 60 % (Table 3.1.3 entry 6).

### 3.1.4 Others

Azide compounds, such as hydrazoic acid, sodium azide and trimethylsilyl azide, have been investigated as nitrogen sources for the production of nitriles by Schmidt reaction. The plausible reaction mechanism could refer to the study of Mitra et al.$^{34}$ that acid firstly activated the carbonyl carbon, afterwards nucleophilic attack done by HN$_3$ (Scheme 3.1.4). Then expulsion of water molecule followed by N$_2$ gives the desired product. When regarding to trimethylsilyl azide, the reaction mechanism was quite similar according to Nandi et al.$^{35}$ Both Lewis and Brønsted acid (Table 3.1.4 entries 1-4) were applied to catalyze the reaction, and the best yield of 97 % 2-furonitrile yield was obtained with acid ionic liquid-[BMIM(SO$_3$H)][OTf] as catalyst.

What’s more, nitrogen sources similar to hydroxylamine hydrochloride, such as o-(2-Aminobenoyl)-hydroxylamine and CH$_3$CONHOH, or similar to NH$_3$, such as H$_2$NN(CH$_3$)$_2$ and aminopyridine were also studied, and which should be noted is that
91 % of 2-furonitrile yield was achieved at 0 °C in few seconds when using H$_2$NN(CH$_3$)$_2$ as nitrogen source and catalyzed with HOF*CH$_3$CN complex (Table 3.1.4 entry 8). Das et. al employed a greener method for the transformation of aldehydes into nitriles utilizing less toxic K$_4$Fe(CN)$_6$ catalyzed by highly active AgNPs-Av.$^{36}$

![Scheme 3.1.4 Plausible mechanism for the formation of nitrile from aldehyde with hydrazoic acid. Adapted from Mitra et al.$^{34}$](image)

Table 3.1.4 2-Furonitrile production from furfural with azide compounds

<table>
<thead>
<tr>
<th>Entry</th>
<th>catalyst</th>
<th>N sources</th>
<th>T(°C)</th>
<th>time</th>
<th>FN yield(%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg(ClO$_4$)$_2$•(2-2.5)H$_2$O</td>
<td>HN$_3$</td>
<td>nm</td>
<td>Reflux 2h</td>
<td>84</td>
<td>$^{37}$</td>
</tr>
<tr>
<td>2</td>
<td>p-TsOH + silica</td>
<td>NaN$_3$</td>
<td>120</td>
<td>2h</td>
<td>79</td>
<td>$^{34}$</td>
</tr>
<tr>
<td>3</td>
<td>[BMIM(SO$_3$H)][OTf]</td>
<td>TMSN$_3$</td>
<td>50</td>
<td>nm</td>
<td>97</td>
<td>$^{35}$</td>
</tr>
<tr>
<td>4</td>
<td>ZnCl$_2$</td>
<td>TMSN$_3$</td>
<td>rt</td>
<td>4</td>
<td>61</td>
<td>$^{38}$</td>
</tr>
<tr>
<td>5</td>
<td>BF$_3$Et$_2$O</td>
<td>O-(2-Aminobenzylnyl)-Hydroxylamine</td>
<td>nm</td>
<td>Reflux 4h</td>
<td>85</td>
<td>$^{39}$</td>
</tr>
<tr>
<td>6</td>
<td>Bi(OTf)$_3$</td>
<td>CH$_3$CONHOH</td>
<td>nm</td>
<td>Reflux 16h</td>
<td>91</td>
<td>$^{40}$</td>
</tr>
<tr>
<td>7</td>
<td>m-chloroperbenzoic acid</td>
<td>H$_2$NN(CH$_3$)$_2$</td>
<td>nm</td>
<td>nm</td>
<td>93</td>
<td>$^{41}$</td>
</tr>
<tr>
<td>8</td>
<td>HOF*CH$_3$CN complex</td>
<td>H$_2$NN(CH$_3$)$_2$</td>
<td>0</td>
<td>Few seconds</td>
<td>91</td>
<td>$^{42}$</td>
</tr>
<tr>
<td>9</td>
<td>-</td>
<td>aminopyridine</td>
<td>115</td>
<td>nm</td>
<td>61</td>
<td>$^{43}$</td>
</tr>
<tr>
<td>10</td>
<td>AgNPs-Aloe vera</td>
<td>K$_4$[Fe(CN)$_6$]</td>
<td>50</td>
<td>40min</td>
<td>84</td>
<td>$^{36}$</td>
</tr>
</tbody>
</table>

TMSN$_3$: trimethylsilyl azide

3.1.5 Conclusion

As a conclusion, furfural cyanation could be achieved at relatively mild conditions with various nitrogen sources. However, most of cases cannot satisfy the rules of Green Chemistry, as toxic solvents or reactants, expensive catalysts, and excess of acid or base were used. From the authors point of view, hydroxylamine hydrochloride as nitrogen source is more compatible than NH$_3$ and ammonium salts, not only
because it’s stable and less toxic, but also the reaction mechanism goes more smoothly (hydrogenation instead of oxidation when using NH$_2$OH-HCl rather NH$_3$ and ammonium salts). Here, which worth to be noticed that considerable 2-furonitrile yield could be obtained without catalyst when using hydroxylamine hydrochloride as nitrogen source and environmental friendly NMP or DMSO as solvent. This part will be further discussed in our next work.

**Furfural hydrogenation**

As we introduced, furfural is a crucial bio-based platform molecule, and owing to this, furfural valorization is always garnering researchers' attentions. Last part, we gave a short overview of furfural cyanation, but the most important applications of furfural is its hydrogenation. Figure 3.2.1 illustrates the downstream products concerning furfural hydrogenation. Plenty of target compounds have been investigated starting from furfural, such as (tetrahydro)furfuryl alcohol$^{44-55}$, 2-methyl(tetrahydro)furan$^{56-66}$, (tetrahydro)furan$^{67}$, tetrahydrofurfural$^{68}$, lactones$^{69-72}$, levulinate$^{73,74}$, cyclopentanone(l)$^{75-86}$ or diols$^{87-90}$ etc. Among these investigations, furfural selective hydrogenation to furfuryl alcohol is the most studied subject. Furfuryl alcohol is a very important monomer for the synthesis of furan resins which are widely used in are used in thermoset polymer matrix composites, cements, adhesives, coatings and casting/foundry resins. It's also used as a non-reactive diluent for epoxy resin, a modifier for phenolic and urea resins, an oil well, and a carbon binder. Furthermore, the salt of furfuryl alcohol is used in the synthesis of lysine, vitamin C, lubricants, and plasticizers.$^{91,92}$ As reported in recently years, around 62% of furfural was industrially used for furfuryl alcohol production, and it has been oversupplied in the chemical market.$^{93,94}$
Besides, another important products from furfural is 2-methylfuran (MF), which is considered as potential alternative fuels, as MF contains the oxygen atom having better combustion performance and the higher research octane number (RON=103) than that of gasoline (RON=96.8). In other applications, MF is used as perfume intermediates, chloroquine lateral chains in medical intermediates, and as a raw material for the production of crysanthenate pesticides.

In this part, a short review concerning furfural hydrogenation to (tetrahydro)furfuryl alcohol and 2-methyl(tetrahydro)furan (Compounds 1-4: FA, MF, THFA, MTHF) in the latest five years will be discussed in terms of different kinds of metal catalysts, such as non-noble metal Cu, Ni, Co, etc., and noble metal Pd, Pt, Ru etc. And herein, the study of bio-catalytic and electro-catalytic hydrogenation of furfural will not be included.

Figure 3.2.1 Downstream products of furfural hydrogenation
3.2.1 Non-noble metal catalysts

3.2.1.1 Cu based catalysts

Recently, Sun et al. investigated the morphological effect of non-supported copper nanocrystals on furfural hydrogenation.\textsuperscript{143} They found Cu nanowires exhibited 3 times higher TOF than Cu nanodisks, suggesting a significant morphology-dependent effect. However, without support, genuine Cu nanowires gave very limited furfural conversion (38 \%) at 200 °C, even with 30 bar H\textsubscript{2} (Table 3.2.1 entry 1). Wang et al. studied the effect of support with various acid and basic properties on Cu based catalysts performance.\textsuperscript{105} The results showed that the total acidity followed the order: Cu/ZSM-5 (687.4 μmol/g) > Cu/Al\textsubscript{2}O\textsubscript{3} (268.9 μmol/g) > Cu/SiO\textsubscript{2} (200.6 μmol/g) > Cu/ZnO (32.2 μmol/g) > Cu/MgO (0 μmol/g), and the total basicity followed: Cu/MgO (312.4 μmol/g) > Cu/Al\textsubscript{2}O\textsubscript{3} (115.2 μmol/g) > Cu/ZnO (17.2 μmol/g) > Cu/SiO\textsubscript{2} (9.4 μmol/g) > Cu/ZSM-5 (0 μmol/g). It was found that acid supported catalyst, such as Cu/ZSM-5, led to a poor mass balance and gave some oligomers as main products; however basic support, such as Cu/MgO gave a better mass balance and FA as the main product.

Hu et al. developed novel bifunctional base-metal heterogeneous catalysts (Cu/CaAlO) for the simultaneous furfural hydrogenation and 1,4-butanediol dehydrogenation under solvent-free and without external H\textsubscript{2} supply.\textsuperscript{69} Inspiringly results of 96 \% FA and 100 \% GBL yield was obtained with Cu/CaAlO (Table 3.2.1 entry 2), and it was found furfural hydrogenation accelerated 1,4-butanediol dehydrogenation to GBL. Additionally, FA selectivity greatly decreased due to the formation of MF with H\textsubscript{2}. The impressive catalytic performance of the catalyst should be ascribed to the existence of defective Cu NPs, abundant strong Lewis base sites.
and Cu\(^{+}\) species on the catalyst surface. Identically, the uniform size and well dispersed Cu nanoparticles on high surface area activated carbon with the suitable proportion of Cu\(^{2+}\), Cu\(^0\) and Cu\(^{+}\) were attributed to the superior transfer hydrogenation catalytic performance of Cu/AC catalyst, which offered 92 % of MF yield (Table 3.2.1 entry 3).\(^{144}\) Zhang et al. also proved that Cu\(^{+}\)/Cu\(^0\) are both necessary and active species for the furfural reduction reaction, and depositing a thin Al\(_2\)O\(_3\) layer on CuCr\(_2\)O\(_4\)*CuO increased the catalyst activity, simultaneously decreased the activation energy of furfural hydrogenation.\(^{145}\)

Prakruthi et al. found that Al deficient Cu-Al oxide prepared possesses higher surface area and pore volume. When loading Cu (15 wt\%) on dealuminated layered double hydroxides, the catalyst could give 77 % FA yield at 220 °C with 3.6 h\(^{-1}\) LHSV (Table 3.2.1 entry 4).\(^{146}\) The priority of the catalytic activity could be explained by new term pore occupancy hydrogenation efficiency factor.

Jiménez-Gómez et al. respectively prepared different kinds of Cu/ZnO and Cu/CeO\(_2\) catalysts, and tested their catalytic performance under gas-phase hydrogenation of furfural to FA.\(^{100,147}\) In both case, best FA yield is around 70 %, and hydrogenation products varied a little with time on stream (Table 3.2.1 entries 5 and 7). Then, they used disordered kerolitic clay formed by kerolite/stevensite mixed layer as catalytic support to disperse Cu-species, the selectivity to FA is a little poor, and the major product is MF.\(^{148}\) However, the selectivity to FA could be improved by the incorporation of Ce and Zn as promoters (Table 3.2.1 entry 8). Yang et al. improved FA yield to 94 % with Cu/ZnO (Cu/Zn = 0.8) prepared via “decrease pH” co-precipitation method (Table 3.2.1 entry 6).\(^{101}\) The excellent catalyst performance was ascribed to suitable Cu particle size (8 nm) and strong metal-support interactions. Jackson et al. supported CuO and CeO\(_2\) on \(\gamma\)-Al\(_2\)O\(_3\), and then excess CuO on the
catalyst surface was stripped with HNO$_3$.\textsuperscript{149} As shown in Table 3.2.1 entry 9, this catalyst could give 85 % FA yield at 175 °C in continuous flow regime, which showed higher intrinsic reactivity than the two control catalysts: Cu/Al$_2$O$_3$ and copper chromite.

In 2014, Vargas-Hernández studied FA production from furfural over Cu/SBA-15 as catalyst, however, limited FA yield of 52 % was obtained (Table 3.2.1 entry 12).\textsuperscript{99} Then, Srivastava et al. synthesized series Cu–Co bimetallic catalysts supported on SBA-15 for furfural hydrogenation to FA.\textsuperscript{150} They got around 80 % yield of FA with 9 % of MF and 10 % of cyclopentanol. Later, three different supported bimetallic catalysts (Cu–Co/SiO$_2$, Cu–Co/H-ZSM-5, and Cu–Co/γ-Al$_2$O$_3$) were prepared by the impregnation method, and tested for furfural selective hydrogenation to MF.\textsuperscript{56} The results indicated that the strong interaction between Cu and Co have significant influence on the catalytic performance of bi-metallic catalyst, and acidic carriers such as H-ZSM-5 and γ-Al$_2$O$_3$, are much more selective towards MF which is in line with previously study that Cu/SiO$_2$ is more effective to produce MF (~90 %, Table 3.2.1 entry 10) than Cu/ZnO and Cu/Al$_2$O$_3$ due to the synergistic effect of metal and the weak acid site.\textsuperscript{58} Srivastava et al. gave an optimization, kinetics and reaction mechanism study of furfural to MF over Cu–Co/γ-Al$_2$O$_3$.\textsuperscript{57} The experimental data could be explained using Langmuir-Hinshelwood-Hougen-Watson kinetics (As shown in scheme 3.2.1). And the data indicated that the adsorption of hydrogen and surface reaction were possibly the rate-controlling steps. Dong et al further improved MF yield to 96 % at a temperature of 200 °C using Cu/SiO$_2$ prepared by ammonia evaporation method.\textsuperscript{62} They also developed a kind of Cu-phyllosilicate-like catalyst, which could also furnish 96 % MF yield or 83 % FA.\textsuperscript{104} In case of Serivastava et al, the best MF selectivity of 78% with fully furfural conversion was achieved with Cu–
Co/γ-Al₂O₃ at 220 °C and 40 bar H₂ (Table 3.2.1 entry 16). And after optimizing with Taguchi method, they improved MF yield to 87 %. Interestingly, bimetallic catalyst Cu-Co/C-500 gave 49 % of cyclopentanone as major product with 36 % of FA at 150 °C for 3 h in presence of 5 bar H₂. But highly dispersed Cu-Co/C catalyst (Cu/Co=1/0.4) derived from Co-doped Cu-BTC metal-organic frameworks (MOFs) by thermolysis in nitrogen showed highly selectivity to FA, and the catalyst which calcined at 500 °C, attained 96 % FA yield at 140 °C with 30 bar H₂.

Romano et al. investigated furfural hydrogenation to FA under microwave irradiations over Cu/TiO₂ as catalyst. As the first example that using pressurized microwave reactors, microwave irradiations offered an unexpected enhancement in FA selectivity to 99 % and a 3–4 fold increase in conversion when compared with conventional heating method. Besides, the experiments were conducted at relatively mild conditions (125 °C) with CPME as green solvent, and the catalyst could be
Zhang et al. studied furfural transfer hydrogenation over monometallic and bimetallic Cu-Ni catalysts supported on Al$_2$O$_3$. It was found that monometallic catalyst Cu/Al$_2$O$_3$ gave furfuryl ether as major by-product, and Ni/Al$_2$O$_3$ gave ring-opening products, while the bimetallic catalysts Cu-Ni/Al$_2$O$_3$ (especially with Cu/Ni = 1/2) showed improved activity towards the production of MF and MTHF. Under optimal conditions, a 65 % yield of MF and a 18 % yield of MTHF were achieved at 230 °C for 4 h, and after 4 times reuse, MF yield decreased only 5 %. The report consistent well with the study of Srivastava et al. who reported incorporation of Ni with Cu supported on Al$_2$O$_3$ increased MF yield from 51 % to 82 %. Conversely, Pang et al. found that small amount of Ni addition on Cu/Al$_2$O$_3$ indeed improved catalytic activity, but slightly decreased the selectivity to MF. Besides, they revealed that Cu-Ni bimetallic catalyst modifying with C18 thiolate could both increase the reaction activity and hydrogenation selectivity. By adding formic acid as co-hydrogen donors, Fu et al. got 92 % of MF yield with 10% Cu-10% Ni/Al$_2$O$_3$ (Entry 20). Interestingly, CuNi alloy catalyst–Cu-Ni/MgAlO could offer 95 % of THFA yield with ethanol as solvent, and the major product will be FA when using methanol as solvent. At similar conditions, bimetallic catalyst Cu-Ni/CNTs exhibit similar catalytic performance with Cu-Ni/MgAlO, and gave 90 % yield towards THFA at mild condition of 130 °C, 40 bar hydrogen and 10 h reaction time.

The effect of Al components addition on Cu/ZnO catalytic activity was investigated by Yang et al. They found the constructed Cu/ZnO-Al$_2$O$_3$ catalyst could improve furfural conversion from 85 % to 96 % at 120 °C with high FA selectivity (96 %) when compared with Cu/ZnO catalyst. It was confirmed that the role of Al components could act as both structural and electronic promoter, thus improve the
dispersion of copper/zinc species and hinder Cu-ZnO interaction of the aurichalcite derived catalysts. Similarly, Cu/MgO-Al$_2$O$_3$ has been also proved as an efficient catalyst for furfural transfer hydrogenation to FA under near-critical isopropanol (Table 3.2.1 entry 27).\textsuperscript{98} Even at milder conditions (150 °C), Cu-Mg-Al catalyst prepared by co-precipitation method showed 100 % selectivity to FA with fully furfural conversion.\textsuperscript{102}

Zhang et al. studied selective transfer hydrogenation of furfural over hydrotalcite-derived copper catalysts using methanol as hydrogen donor.\textsuperscript{157} The copper catalyst showed excellent transfer hydrogenation selectivity towards FA by giving a FA yield of 94 % at 200 °C, and the activated catalyst with H$_2$ (Cu-Al-A, Table 3.2.1 entry 23) notably furnish 94 % MF yield at 240 °C. They stated that the valence of active Cu species, catalyst acidity and reaction temperature played an important role in product selectivity.

A series of Cu-Fe catalysts without support were prepared by Yan and Chen. and tested for furfural hydrogenation to MF.\textsuperscript{96} They got 51 % of MF yield at 220 °C for 14 h under 90 bar H$_2$ (Entry 24). The promotional effect of Fe on Cu catalyst performance was also studied by Manikandan et al.\textsuperscript{158} Cu-Fe/Al$_2$O$_3$ catalyst with 10 wt% Fe exhibited an excellent activity which led to high furfural conversion (> 93 %) and furfuryl alcohol selectivity (> 98 %) under mild reaction conditions (Table 3.2.1 entry 25), and its high activity could be attributed to the synergy between Cu and Fe, and the existence of oxygen vacancies in Fe oxide system. Notably, the bimetallic catalyst showed superior stability after 24h on stream.
### Table 3.2.1 Furfural hydrogenation over Cu-based catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H source</th>
<th>Solvent</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>P (bar)</th>
<th>Yield (%)</th>
<th>Re f.</th>
</tr>
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<td>1</td>
<td>Cu nanowire</td>
<td>H₂</td>
<td>1,4-dioxane</td>
<td>200</td>
<td>1.5</td>
<td>30</td>
<td>&gt;3/3/3</td>
<td>143</td>
</tr>
<tr>
<td>2</td>
<td>Cu/CuAlO</td>
<td>H₂</td>
<td>1,4-Butanol</td>
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<td>96</td>
</tr>
<tr>
<td>3</td>
<td>Cu/AC</td>
<td>i-PrOH</td>
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<td>5</td>
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<td>92</td>
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<td>4</td>
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<td>220</td>
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<tr>
<td>5</td>
<td>Cu/ZnO</td>
<td>H₂</td>
<td>CPME</td>
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<td>1</td>
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<td>70</td>
<td>-</td>
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<tr>
<td>6</td>
<td>Cu/ZnO</td>
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<td>-</td>
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<td>-</td>
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</tr>
<tr>
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<tr>
<td>8</td>
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<td>H₂</td>
<td>-</td>
<td>210</td>
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<td>-</td>
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<td>48</td>
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<tr>
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<td>85</td>
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<tr>
<td>10</td>
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<td>H₂</td>
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<tr>
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<td>i-PrOH</td>
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<tr>
<td>17</td>
<td>Cu-Co/C</td>
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<td>CPME</td>
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<td>3</td>
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<td>1</td>
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<td>7</td>
<td>-</td>
<td>2</td>
<td>92</td>
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<td>i-PrOH</td>
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<td>150</td>
<td>3</td>
<td>40</td>
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<td>10</td>
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<td>22</td>
<td>Cu-Ni/CNTs</td>
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<td>23</td>
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<td>Methanol</td>
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<td>51</td>
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<tr>
<td>25</td>
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<td>H₂</td>
<td>-</td>
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<td>1</td>
<td>92</td>
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<tr>
<td>26</td>
<td>Cu-Fe/Al₂O₃</td>
<td>H₂</td>
<td>-</td>
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<td>1</td>
<td>92</td>
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<td>2</td>
</tr>
<tr>
<td>27</td>
<td>Cu-Fe/Al₂O₃</td>
<td>H₂</td>
<td>-</td>
<td>150</td>
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<td>28</td>
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<td>i-PrOH</td>
<td>-</td>
<td>150</td>
<td>6</td>
<td>-</td>
<td>10</td>
<td>0</td>
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</tbody>
</table>

### 3.2.1.2 Co, Ni based catalyst

Except for Cu, Co and Ni are also cheap and high activity non-noble metal which
widely used for catalysts preparation. As we discussed in last part, they have been introduced with Cu forming bimetallic catalysts, and most of the bimetallic catalysts showed improved catalytic activities when compared with mono-ones. Previously reports suggest that sole Co based catalysts were low active at low temperature and low selective at high temperature. But recently, Audemar et al. demonstrated that monometallic Co/SBA-15 catalyst could reached 96 % of FA hydrogenation selectivity from furfural (Table 3.2.2 entry 1), however, catalyst stability study revealed that continuous Co leaching occurred which led to the loss of activity. Herein, which worthy to be noted that Lee et al. developed Co/TiO\textsubscript{2} catalyst, and they found cobalt particles were covered with a TiO\textsubscript{y} layer after high temperature calcination and reduction treatments. No leaching and cobalt particles aggregations were observed even after 105 h time-on-stream. The excellent catalytic performance (95 % FA yield, Table 3.2.2 entry 2) possibly benefits from the TiO\textsubscript{y} overcoat on cobalt and relative mild reaction conditions (80 °C). Very recently, Gong and Jiang et al. synthesized two kinds of Co based catalysts using N-doped materials as the supports. Jiang et al. synthesized Co based catalyst using nitrogen-doped porous carbon materials (CPNs) as support, comparable FA yield of 98 % was also attained, albeit with relatively higher reaction temperature (180 °C). Gong et al. developed a facile one-pot pyrolysis approach using melamine as carbon and nitrogen source to fabricate Co nanoparticles embedded in bamboo-like N-doped carbon nanotubes (named as Co/NCNTs). This catalyst showed quite high selectivity to FA at low temperature (100 % selectivity at T=60-100 °C), and when temperature was higher than 130 °C, further hydrogenation and rearrangement will occur producing cyclopentanone as main product. Interestingly, THFA with 100 % yield was detected as the final product when using Ni/NCNTs as catalyst at similar reaction conditions.
This means Ni prefers leading to deeper hydrogenation than Co. The research is consistent with the results of Su et al. who prepared carbon-embedded Ni (Ni/C) catalyst by direct thermal decomposition of Ni-MOF. And they also got 100% THFA yield at 120 °C in 2 h with 10 bar H₂ (Table 3.2.2 entry 5). As mentioned above, bimetallic catalyst Cu-Ni/CNTs has good selectivity to THFA (90%, Table 3.2.1 entry 23), in fact, Liu et al. also showed that Ni/CNTs with catalysts Ni content ≥ 10% have similar even better selectivity to THFA. Yang et al. modified Al₂O₃ with various alkaline earth metals (Mg, Ca, Sr, Ba), then used them as supports prepared a series of Ni-based catalysts, and they found Ni/Ba-Al₂O₃ was the most efficient which improved THFA selectivity from 16% (with Ni/Al₂O₃) to 99% at the same reaction conditions. The role of alkaline earth metals decreased NiAl₂O₄ species which lead to the increase in hydrogenation activity.

Notably, most of study indicated that lower reaction temperature benefit to producing FA, and higher reaction temperature will be more selective to THFA. However, in contrast thereto, Kotbagi et al. found furfural was selectively hydrogenated to FA at 200 °C over Ni supported on N-doped hierarchically porous carbon catalyst (Table 3.2.2 entry 7). Jeong et al. noticed that Ni/SiO₂ and Raney Ni have competitive selectivity to FA and THFA at 110 °C under 30 bar H₂, but they successfully developed a kind of capped Ni nanoparticles catalysts and realized furfural selective hydrogenation to FA with maximum yield of 96%. Xu et al. also noticed that Raney Ni gave various products by hydrogenation/decarboxylation or rearrangement. They conclude that the additives have great effect on the product distribution. More impressively, Gong et al. communicated that an enhanced catalytic performance for furfural selective hydrogenation could be realized using sulfonated activated carbon supported Ni catalyst. As far as we known, at a temperature of 60
100 °C, 100 % of FA yield could be considered as the best result, and 100 °C will led to THFA formation which is comparable with their previous report with Ni/NCNTs catalyst. More importantly, the conversion of transfer hydrogenation of furfural to FA also can reach almost 100 % yield under optimal conditions (140 °C, 4.0 h, Table 3.2.2 entry 9). Manikandan et al. investigated surface synergistic effect on the performance of Ni-based hydrotalcite derived catalysts with different Ni-Mg-Al ratio, and they found Ni2/MgAl could give 92 % FA yield at 180 °C. The results have demonstrated that the incorporation of Mg significantly enhances the Ni-support interaction, Ni dispersion and catalytic performance. Analogously, Sulmonetti et al. synthesized different nickel mixed metal oxides derived from layered double hydroxides containing Ni-Mg-Al and Ni-Co-Al, but maximum of 70 % FA with 10 % THFA was yielded.

On the other hand, Ni-based catalyst such as Ni/C, could be used to produce MTHF, and Ni-Fe/C bimetallic catalyst will yield MF as the main product at high pressure (Table 3.2.2 entry 11). At low pressure (1 bar), the hydrogenation selectivity of Ni/C was quite poor (furan:18%, MF:30%, MTHF:14% and THFA:30%), while Ni-Fe/C will keep its hydrogenation selectivity towards MF with 65 % yield. Commercial available nickel ferrite nanoparticles catalyst NiFe2O4 was also exploited as stable and easily separable heterogeneous catalyst for catalytic transfer hydrogenation of furfural to furfuryl alcohol which providing 94% FA yield at 180 °C for 6 h, and CoFe2O4 offering 71 % at 180 °C in 4 h.

Other metals, such as Co, Sn, In etc. were also incorporated with Ni formed bimetallic catalysts as list in Table 3.2.2 entries 13-15. When supporting Ni and Co on short channeled SBA-15, the catalyst showed superior catalytic performance (92 % FA yield) than common SBA-15 and other acidic supports, such
as MCM-48, MCF-2 and MCF-41. Unfortunately, bimetallic catalyst Ni$_3$Sn$_2$/Al$_2$O$_3$ couldn’t give a satisfiable FA yield, even in harsh conditions. Rodiansono et al. developed a method for the preparation of highly dispersed Ni-Sn alloy catalyst supported on aluminum hydroxide, and they reached a very good FA selectivity (> 90 %). Later, they prepared analogous Ni-In and Ni-Zr bimetallic catalysts. Ni-In/AlOH showed similar reaction catalytic performance with Ni-Sn/AlOH, but the hydrogenation process will go further with Ni-Zr/AlOH, which gave THFA as the final product (Table 3.2.2 entry 15).

Table 3.2.2 Furfural hydrogenation over Co,Ni-based catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H source</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>t(h)</th>
<th>P(bar)</th>
<th>Yield (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FA</td>
<td>MF</td>
</tr>
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<td>Co/SBA-15</td>
<td>H$_2$</td>
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<td>88</td>
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<tr>
<td>3</td>
<td>Co/CPNs</td>
<td>H$_2$</td>
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</table>
3.2.1.3 Zr-based and other catalysts

Unlike reduced Cu, Co and Ni based metallic catalysts, Zr-series compounds have been proved as efficient catalysts for furfural especially by the Meerwein-Ponndorf-Verley (MPV) reduction. Recently, ZrO$_2$ prepared by the microemulsion method showed excellent transfer hydrogenation selectivity to FA ($\geq 98\%$), but FA yield only achieved 53\% in 120 h which mainly due to relative lower reaction temperature (100 $^\circ$C), and as illustrated microwave irradiations could accelerate the reaction 15-30 times when compared with conventional heating method.$^{50}$ Zr(OH)$_4$ also showed almost stoichiometric FA yield when using iso-propanol as hydrogen source and solvent (Table 3.2.3 entry 2).$^{166}$ Experimental result indicated that basic centers in Zr(OH)$_4$ displayed pronounced effect for furfural transfer hydrogenation and moderate monoclinic phase content in ZrO$_{2-x}$ enhanced the conversion rate and furfuryl alcohol selectivity. The proposed mechanism for the transformation of furfural into FA catalyzed by Zr(OH)$_4$ via catalytic transfer hydrogenation with iso-propanol was illustrated in Scheme 4.2.2. Sha et al. developed a super-efficient catalyst Zr-HAs by combining Zr with humic acid. 97\% of FA yield was obtained via MPV reduction at very mild conditions (Table 3.2.3 entry 2).$^{167}$ And it really make sense that humic acid extracted from lignite could be directly applied into the preparation of the catalyst without need of further separation or treatment. Li et al. synthesized recyclable Hf-phenylphosphonate nanohybrids (PhP-Hf) via assembly of phenylphosphonate with HfCl$_4$. A FA yield of 98\% with formation rate of 9760 $\mu$mol /g/h was obtained at 120 $^\circ$C for 2 h, and the superior catalytic activity of PhP-Hf is attributed to its moderate acidity and relatively strong basicity.$^{51}$ Simultaneously, PhP-Zr showed lower activity than PhP-Hf (Table 3.2.3 entry 4), which agreed with the theoretical study that the catalytic activity followed the order:
Hf > Zr > Sn.\textsuperscript{168,169}

It is noteworthy that alumina-carbon composite catalyst (Al\textsubscript{2}O\textsubscript{3}-S) synthesized by reacting Al(NO\textsubscript{3})\textsubscript{3} with the polyether-based surfactant showed comparable FA yield (96 \%) with Zr-series catalysts though catalytic transfer hydrogenation, and they ascribed the high selectivity to the presence of acidic sites on the catalyst.\textsuperscript{170}

Unfortunately, gradually deactivation of the catalyst was observed due to the leaching of Al species. Very recently, Wu et al. presented a rapid and mild approach for the quantitative production of furfuryl alcohol in presence of KF and a liquid H-donnnor: polymethylhydrosiloxane (PMHS). It's reported that 97 \% of FA was yielded in 30 min at room temperature. To the best of our knowledge, it's the production of FA at the mildest conditions. Although supported Ir on hydrogenated MoO\textsubscript{x} catalyst could give 99 \% FA at 30 °C, the reaction time is 6 h and the experiments were performed under 20 bar H\textsubscript{2} (Table 3.2.3 entry 7).\textsuperscript{171} In presence of H\textsubscript{2}, Fe/C combined with K\textsubscript{2}CO\textsubscript{3} catalytic system also furnished 94 \% of FA yield under harsh conditions (220 °C), what’s interesting is that when the reaction performed in presence of O\textsubscript{2}, furfural will selectively convert to furan-2-acrolein.\textsuperscript{172}
In terms of furfural deep hydrogenation, Lee et al. investigated hydrodeoxygenation of furfural to MF on molybdenum carbide catalyst.\textsuperscript{66} The best MF selectivity was around 56 \%, and the conversion of furfural was less than 10 \% which possibly due to the relatively lower reaction temperature (150 °C). Grazia et al. found MgO and Mg/Fe/O catalysts were active for furfural transfer hydrogenation reaction, and MgO was selective to FA, whereas Mg/Fe/O was shown to be highly active and selective for MF production (Table 3.2.3 entry 9). Later, using FeVO\textsubscript{4} as catalyst, they got similar MF yield of 80 \% under the same system.\textsuperscript{173}

\begin{table}[h]
\centering
\begin{tabular}{|l|l|l|l|l|l|l|l|l|}
\hline
Entry & Catalyst & H source & Solvent & T(°C) & t(h) & P(bar) & Yield (%) & Ref. \\
\hline
1 & ZrO\textsubscript{2} & i-PrOH & 100 & 120 & - & 53 & - & - & 50 \\
2 & Zr(OH)\textsubscript{4} & i-PrOH & 170 & 2.5 & 10 & 99 & - & - & 166 \\
3 & Zr-HAs & i-PrOH & 50 & 15 & - & 97 & - & - & 114 \\
4 & PhP-Zr & i-PrOH & 120 & 2 & - & 78 & - & - & 51 \\
 & PhP-Hf & & & & & 98 & - & - & \\
5 & Al\textsubscript{2}O\textsubscript{3}-S & i-PrOH & 130 & 6 & - & 96 & - & - & 170 \\
6 & KF & PMHS & DMF & 25 & 0.5 & - & 97 & - & - & 174 \\
7 & Ir/H-doping MoO\textsubscript{x} & H\textsubscript{2} & Water & 30 & 6 & 20 & 99 & - & - & 171 \\
8 & Fe/C+K\textsubscript{2}CO\textsubscript{3} & H\textsubscript{2} & Ethanol & 220 & 2 & 20 & 93 & - & 3 & 172 \\
9 & MgO & Methanol & 250 & 1 & 1 & 58 & - & - & 59 \\
 & Mg/Fe/O & & 380 & 1 & 1 & - & 83 & - & \\
10 & FeVO\textsubscript{4} & Methanol & 320 & TOS=3h & 1 & - & 80 & - & 173 \\
\hline
\end{tabular}
\caption{Furfural hydrogenation over Zr-based and other catalysts}
\end{table}

\subsection{3.2.2 Noble metal catalysts}

\subsubsection{3.2.2.1 Pd based catalysts}

When compared with non-noble metal catalysts, noble metal catalysts generally result a higher reaction efficiency under relatively milder condition, especially for the production of deep hydrogenation products, such as MF, THFA etc. Taking Pd based
catalysts as an example; the group of Prof. LUQUE investigated various Pd supported catalysts for furfural hydrogenation in continuous flow.\textsuperscript{115,122,175} As listed in Table 3.2.4 entries 1-3, 76 % of MF could be attained at very mild temperature (90 °C) with Pd/C as catalyst. Interestingly, at a higher temperature of 150 °C, the major product changed to THFA. The opposite result was obtained with Pd/MAGSNC which produced THFA at 90 °C and FA at 150 °C. Here, which should be noted is that selective hydrogenation of furfural could be achieved not only by changing the temperature, but also by varying the flow rate which decided the residence time of the reactant in the catalyst. In these cases, it seems that catalytic process of furfural over Pd based catalyst prefers to furnish FA and THFA. Indeed, when support Pd on different supports, such as carbon, bio-char, TiO$_2$, Al$_2$O$_3$ etc. the catalysts would yield different amount of FA and THFA.\textsuperscript{48,119,121,176–178} Some of them exhibited excellent catalytic performance, for example, Pd supported on hydroxyapatite (HAP) and MIL-101(Cr)-NH$_2$ giving 100 % THFA yield.\textsuperscript{52,53} Noticeable difference could be found with Pd/Al$_2$O$_3$ as catalyst if one compares Table 3.2.4 entries 6-8. THFA yield severely decreased when using water rather than iso-propanol as the solvent with lower H$_2$ pressure, but more interestingly, the side-product was identified as tetrahydrofurfural with 84 % yield, which means the catalysis occurred on double bond of the furan ring rather aldehyde group in current conditions.\textsuperscript{68} Hu et al. suggest that a polar solvent facilitates furfural hydrogenation more efficiently and tended to favor the hydrogenation of the furan ring over that of the carbonyl group.\textsuperscript{176} They obtained 6 % of tetrahydrofurfural with non-polar diethyl ether as solvent when performing the experiment with Pd/C at 170 °C under 70 bar total pressure (H$_2$ pressure > 40 bar). Except for the effect of support, solvent and reaction conditions, different metal reduction methods of the catalysts also showed significantly influence
on the catalyst performance. For example, the Pd catalysts prepared via the chemical reduce method exhibited smaller particle sizes and higher metal dispersions, leading to greater conversions than those achieved using the catalysts prepared via the impregnation followed by thermal reduction method.\textsuperscript{120} Date et al. systematically investigated the effect of different particle size of Pd/C catalysts on furfural hydrogenation. They found NaBH\textsubscript{4} reduced catalyst gave smallest crystallite size of 4.8 nm due to incorporation of B into the inner lattices of Pd-Pd while formaldehyde reduced catalyst gave highest size of 22.4 nm. The catalytic results of Pd based catalysts with different supports were shown in Figure 3.2.

Bimetallic catalysts containing Pd supported on different materials have been reported recently. The selectivity is varying with metals and supports, for example, Pd-Ni/MWNT gagnering 83 % yield of THFA, Pd-Fe/SiO\textsubscript{2} offering 83 % of MF yield while Pd-Fe/Al\textsubscript{2}O\textsubscript{3} giving 43 % furan, Pd-Cu/TiO\textsubscript{2} and Pd-Pt/TiO\textsubscript{2} furnishing respectively 98 % of FA and 95 % THFA yield (Entry 5,15-18). Consistent with non-noble metal catalysts, without rigorous high temperature, the major product will be FA with Pd based catalyst via transfer hydrogenation. Herein, It is much worth point out that the transfer hydrogenation could be performed at 25 °C with NaH\textsubscript{2}PO\textsubscript{2} as H-donner, in spite of relatively poor FA yield (68 %).\textsuperscript{123}
Figure 3.2.2 Pd based catalyst screening for hydrogenation of furfural with different supports. Adapted from Date et al.179

Reaction conditions: Furfural, 5 g; Solvent, Isopropyl alcohol (95 g); Temperature, 220 °C; Pressure, 500 psi; Agitation Speed, 1000 rpm, Catalyst, 4% metal loading; loading, 0.5 g; Reaction time, 5 h

Table 3.2.4 Furfural hydrogenation over Pd-based catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H source</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>t(min)</th>
<th>P(bar)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd/C</td>
<td>H2</td>
<td>Ethyl acetate</td>
<td>90</td>
<td>TOS=20 min</td>
<td>50</td>
<td>0 (76)</td>
</tr>
<tr>
<td></td>
<td>Pd/PBSAC</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>72 (8)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>Pd/AlSBAred</td>
<td></td>
<td></td>
<td>150 (9)</td>
<td>TOS=20 min</td>
<td>50</td>
<td>74 (17)</td>
</tr>
<tr>
<td></td>
<td>Pd/MAGSNC</td>
<td></td>
<td></td>
<td>150</td>
<td>TOS=20 min</td>
<td>50</td>
<td>8 (22)</td>
</tr>
<tr>
<td></td>
<td>Pd/SBA-15</td>
<td></td>
<td></td>
<td>150</td>
<td>TOS=20 min</td>
<td>50</td>
<td>77 (58)</td>
</tr>
<tr>
<td></td>
<td>Pd/C</td>
<td></td>
<td></td>
<td></td>
<td>0 (0)</td>
<td>74 (80)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Pd/BCH</td>
<td>H2</td>
<td>-</td>
<td>110</td>
<td>265</td>
<td>4</td>
<td>65</td>
</tr>
<tr>
<td>4</td>
<td>Pd/TiO2</td>
<td>H2</td>
<td>i-PrOH</td>
<td>30</td>
<td>240</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pd-Pt/TiO2</td>
<td></td>
<td></td>
<td></td>
<td>0</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>5</td>
<td>Pd/Al2O3</td>
<td>H2</td>
<td>i-PrOH</td>
<td>25</td>
<td>480</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Pd/Al2O3</td>
<td>H2</td>
<td>water</td>
<td>30</td>
<td>240</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Pd/Al2O3</td>
<td>H2</td>
<td>water</td>
<td>90</td>
<td>120</td>
<td>20</td>
<td>28</td>
</tr>
<tr>
<td>8</td>
<td>Pd/HAP</td>
<td>H2</td>
<td>i-PrOH</td>
<td>40</td>
<td>180</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Pd/C</td>
<td>H2</td>
<td>Water-CO2</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>62</td>
</tr>
<tr>
<td>10</td>
<td>Pd/MIL-101(Cr)-NH2</td>
<td>H2</td>
<td>Water</td>
<td>40</td>
<td>240</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Pd/CB</td>
<td>H2</td>
<td>Water</td>
<td>50</td>
<td>30</td>
<td>5</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>Pd/CNT</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>39</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Pd/C</td>
<td>H2</td>
<td>Diethyl ether</td>
<td>170</td>
<td>60</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>Pd/C-TR(CR)b</td>
<td>H2</td>
<td>i-PrOH</td>
<td>180</td>
<td>300</td>
<td>20</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>34 (57)</td>
</tr>
<tr>
<td>14</td>
<td>Pd-Fe/SiO2</td>
<td>H2</td>
<td>i-PrOH</td>
<td>250</td>
<td>W/F=4.5 min</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>15</td>
<td>Pd-Fe/Al2O3</td>
<td></td>
<td></td>
<td></td>
<td>20</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>16</td>
<td>Pd-Ni/MWNT</td>
<td>H2</td>
<td>ethanol</td>
<td>130</td>
<td>300</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>17</td>
<td>Pd-Cu/TiO2</td>
<td>H2</td>
<td>water</td>
<td>110</td>
<td>80</td>
<td>6</td>
<td>98</td>
</tr>
<tr>
<td>18</td>
<td>Pd-Cu/C</td>
<td>HCOOH</td>
<td>1,4-dioxane</td>
<td>170</td>
<td>180</td>
<td>-</td>
<td>99</td>
</tr>
<tr>
<td>19</td>
<td>Pd/NPC</td>
<td>2-BuOH</td>
<td></td>
<td>120</td>
<td>600</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>20</td>
<td>Pd/Al2O3</td>
<td>NaHPO4</td>
<td>THF-water</td>
<td>25</td>
<td>60</td>
<td>-</td>
<td>68</td>
</tr>
<tr>
<td>21</td>
<td>Pd/Al2O3</td>
<td>NaHPO4</td>
<td>THF-water</td>
<td>25</td>
<td>60</td>
<td>-</td>
<td>68</td>
</tr>
</tbody>
</table>

a: Total pressure; b: TR-Thermal reduction, CR-chemical reduction; c: W/F = catalyst mass/mass flow rate of reactant;
3.2.2.2 Pt based catalysts

The hydrogenation of furfural with Pt based catalysts differs with Pd ones, as in most of cases, FA and MF or furan were formed without THFA. That is to say that reaction prefers occurring on aldehyde group via hydrogenation, hydrodeoxygenation or decarboxylation with Pt based catalyst. As an example, Pt/\(\text{SO}_4\)-ZrO\(_2\) gave 47 % of MF and 33 % furan as main products at a temperature of 240 °C (Table 3.2.5 entry 1). Interestingly, the research of Chatterjee et al. suggested that THFA could be a potential candidate of catalyst deactivation.\(^{182}\) They found that compressed \(\text{CO}_2\) has synergy effect with Pt based catalyst and it could render the generation of THFA. Besides, protic solvents, especially methanol, could improve furfural conversion, but simultaneously lead to 74 % selectivity to side-product-furfural dimethyl acetal. Using the same catalyst and solvent, Taylor et al. succeed to limit the formation of this kind of side-products with > 97 % FA selectivity by decreasing the reaction temperature and \(\text{H}_2\) pressure (Table 3.2.5 entry 3).\(^{183}\) The supports MgO and CeO\(_2\) gave similar catalytic results with \(\gamma\)-Al\(_2\)O\(_3\) which are better than SiO\(_2\) and ZnO. One of the methods to improve the support activity is modifying their surface. Castelbou et al. developed a new methodology for the synthesis of well-defined Pt nanoparticles supported on phosphine-functionalized silica.\(^{184}\) The catalytic performance of the catalyst was significantly improved (Table 3.2.5 entry 4). Modified carbon materials also showed improvement on furfural selective hydrogenation.\(^{84,185}\) For example, Liu et al. prepared porous heteroatom doped carbon materials and supported Pt on these materials. They observed more than 99 % FA yield at 100 °C, and when perform the
experiment at severe conditions, the reaction will selectively towards cyclopentane via rearrangement.\textsuperscript{84}

Table 3.2.5 Furfural hydrogenation over Pt-based catalysts

<table>
<thead>
<tr>
<th>Entri</th>
<th>Catalyst</th>
<th>H source</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>t(h)</th>
<th>P(bar)</th>
<th>Yield (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FA</td>
<td>MF</td>
<td>THF A</td>
</tr>
<tr>
<td>1</td>
<td>Pt/Al(_2)O(_3)</td>
<td>H(_2)</td>
<td>i-PrOH</td>
<td>120</td>
<td>10</td>
<td>20</td>
<td>91</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pt/SO(_2)-ZrO(_2)</td>
<td></td>
<td></td>
<td>240</td>
<td>8</td>
<td>4</td>
<td>97</td>
<td>47</td>
</tr>
<tr>
<td>2</td>
<td>Pt/Al(_2)O(_3)</td>
<td>H(_2)</td>
<td>CO(_2)</td>
<td>80</td>
<td>4</td>
<td>90(^a)</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Pt/(MgO or CeO(_2))</td>
<td>H(_2)</td>
<td>Methanol</td>
<td>50</td>
<td>7</td>
<td>1</td>
<td>77</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Pt/P-SiO(_2)</td>
<td>H(_2)</td>
<td>Heptane</td>
<td>80</td>
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<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Pt/MWNT</td>
<td>H(_2)</td>
<td>i-PrOH</td>
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<td>5</td>
<td>20</td>
<td>75</td>
<td>14</td>
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<td>Water</td>
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<td>10</td>
<td>99</td>
<td>-</td>
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<td>6</td>
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<td>H(_2)</td>
<td>Toluene</td>
<td>100</td>
<td>5</td>
<td>20</td>
<td>17</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Pt-Sn/SiO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Pt/Cu S-PNPs</td>
<td>H(_2)</td>
<td>Methanol</td>
<td>150</td>
<td>12</td>
<td>20</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Pt-Sn/SiO(_2)</td>
<td>H(_2)</td>
<td>-</td>
<td>160</td>
<td>nm</td>
<td>1</td>
<td>97</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Pt-Co/C</td>
<td>H(_2)</td>
<td>Methanol</td>
<td>130</td>
<td>8</td>
<td>50</td>
<td>96</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>Pt-Fe/MWNT</td>
<td>H(_2)</td>
<td>Ethanol</td>
<td>100</td>
<td>5</td>
<td>30</td>
<td>87</td>
<td>-</td>
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<td>11</td>
<td>Pt-Re/TiO(_2)-ZrO(_2)</td>
<td>H(_2)</td>
<td>Ethanol</td>
<td>130</td>
<td>8</td>
<td>50</td>
<td>96</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>Pt-Co/C</td>
<td>H(_2)</td>
<td>Water</td>
<td>35</td>
<td>10</td>
<td>1</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>Pt-Co/C</td>
<td>H(_2)</td>
<td>n-PrOH</td>
<td>180</td>
<td>W/F=2.5(0.5)</td>
<td>1(30)</td>
<td>0</td>
<td>88(75)</td>
</tr>
</tbody>
</table>

\(a\): 10 bar H\(_2\)+ 80 bar CO\(_2\); b: W/F means mass of catalyst divided by mass flow rate of furfural and H\(_2\).

Indeed, when support Pt on SiO\(_2\) without modification, only 17 % FA yielded with > 99 % selectivity.\textsuperscript{129} O’Driscoll found the incorporation of second metal could certainly improve furfural conversion while keeping the same FA selectivity. The order followed as: Sn>Mo>Mg>Ba>Fe>Ni, where Pt-Sn/SiO\(_2\) giving 47 % of FA yield. Later, they changed a little the ratio of Pt/Sn, and improved the yield to 63 %.\textsuperscript{186} Maligal-Ganesh et al. synthesized encapsulated intermetallic PtSn@mSiO\(_2\) nanoparticle catalysts using a ship-in-a-bottle strategy.\textsuperscript{127} In continuous regime, The
catalyst exhibited the best performance with 97% FA yield when compared with its monometallic counterparts Pt@mSiO2 and catalyst with other porous silica as support Pt-Sn/MCF-17.

Bimetallic catalyst Pt-Cu nanoparticles showed poorly furfural conversion and FA selectivity due to the formation of furfural dimethyl acetal, however, the Pt-Cu nanoparticles with hollow-core structure exhibited over 4-fold increase in catalytic activity with 100% FA selectivity, compared to Pt-Cu nanoparticles without hollow structure.126 The authors proposed that aldehyde group was adsorbed into the hollow cavities (C atoms of C=O group attached to the Pt-rich outside shell and O atoms are proposed to occur toward the Cu-rich inner shell) which prevented the activated C=O bond reacting with methanol. Comparatively, the formation of furfural diethyl acetal seems unavoidable when using other Pt based bimetallic catalysts on different supports.124 Pt-Fe supported on modified multiwalled carbon nanotubes (MWNT) showed highest FA yield of 87%, but still with 5% acetal. Chen et al. improved FA yield to 96% with 3% acetal formation with Pt-Re/TiO2-ZrO2 as catalyst.125 Impressively, Pt-Co/C bimetallic catalyst furnished 100% FA yield at quite mild conditions (Table 3.2.5 entry 12), and 86% yield for FA was observed with concentrated furfural (40 wt%) at 50 °C and under 10 bar H2 pressure.187 The characterization of catalyst revealed that the presence of electron rich Pt and ionic Co species in proximity with each other are correlated with activity of catalysts. Additionally, this type of catalyst possibly resulted in MF production at higher temperature as shown in Table 3.2.5 entry 13.162 Wang et al. observed maximum of 88%
MF yield at 1 bar H₂ flow, and slight decrease to 75 % at 33 bar H₂ due to overhydrogenation.

3.2.2.3 Ru and other noble metal based catalysts

In terms of MF production, non-noble metal catalysts, such as Cu based catalysts, seems more efficient than noble catalysts, but relatively harsh reaction conditions are required. Oppositely, noble metal catalysts could achieve the production of MF at mild conditions, especially in continuous flow regime. Recently, Vlachos et al. realized furfural catalytic transfer hydrogenation to MF with the catalyst Ru with partially oxides supported on activated carbon. With iso-propanol as solvent, they got 61 % of MF yield at 180 °C in 10 h, and later, they improved the yield to 76 % with 2-butanol or 2-pentanol as solvent. Subsequently, the mechanistic study revealed that Lewis acid-catalyzed intermolecular hydride transfer is the dominant pathway for FA formation, and further hydrogenolysis of the C–OH bond in FA to MF occurs mainly via ring-activation involving both metal and Lewis acid sites (Scheme 3.2.3). This means the bifunctional nature of a catalyst is critical in the efficient hydrodeoxygenation of furfural to MF. Possibly inspired by these findings, Wang et al. obtained 83 % of MF yield with Ru/NiFeO₄ as catalyst at similar reaction conditions. Unlike the case Vlachos et al. faced, which the catalyst easily deactivated due to the RuOₓ reduction to metallic Ru during reaction, Ru/NiFeO₄ showed excellent catalytic activity and recycling performance, possibly benefits to its relatively stable Lewis acid sites. Interestingly, Aldosari et al. found that ca. 20 % of
MF could be produced with Pd-Ru/TiO$_2$ at room temperature in 2 h, and the incorporation of Ru in Pd/TiO$_2$ decreased the catalytic activity but improved the selectivity towards 2-methylfuran and furfuryl alcohol with decreased byproduct formation.$^{134}$

![Scheme 3.2.3 Reaction mechanism for the hydrogenolysis of FA to MF over Ru/RuOx/C catalyst using isotopic lebelling. Adapted from Gilkey et al.$^{64}$](image)

With Ru based catalysts, more attentions were focused on the production of FA at mild conditions. Ru supported on activated carbon, multi-wall carbon nanotubes or carbon black have been proved to be not enough efficient for furfural hydrogenation,$^{116,130}$ but the introduction of bimetallic catalyst or other supports, such as reduced graphite or MOFs-UIO-66 and Al-MIL-53, showed significantly improvement, and $>90\%$ FA yield could be reached at 20 $^\circ$C (Table 3.2.6 entries 5-8). Importantly, homogeneous catalyst Ru/Ph$_2$P(CH$_2$)$_4$PPh$_2$ also showed high efficiency, as the reactions could be conducted without solvent and achieved 100% atom economy with a high turnover frequency of 6273 h$^{-1}$. Besides, the catalyst performance remained stable after twelve consecutive runs making it more
competitive with heterogenous catalysts. Recently, Bagnato et al. proposed an innovative ruthenium based catalytic membrane reactor.\textsuperscript{188} Under mild conditions and low H\textsubscript{2} loading, they obtained 26 % FA yield, however, the reaction turnover frequency is as high as 48 000 h\textsuperscript{-1}, 2 orders of magnitude higher than those obtained so far. Notably, when increasing H\textsubscript{2}/furfural molar ratio from 1:1 to 4:1, a >99% selectivity to THFA was obtained under the same process conditions. This means Ru based catalysts could be potentially used to reduce C=C bond. Huang et al. found Pd/\text{Al}_2\text{O}_3 prefers catalyzing C=C bond in furan ring, while Ru/\text{ZrO}_2 more inclined to C=O bond.\textsuperscript{68} When combined these two catalysts physically, an unexpected 100 % THFA yield was obtained at 30 °C in 4 h. Detailed kinetics studies suggested that firstly hydrogenation of furfural to tetrahydrofurfural over Pd/\text{Al}_2\text{O}_3 and then subsequent C=O bond hydrogenation over Ru/\text{ZrO}_2 will require lower activation energy which should be response to the superior activity of the mix-catalyst.

Other noble metal, such as Ir, Au etc. have been applied for furfural hydrogenation to MF.\textsuperscript{65,184,189} Selective TOF over Au/\text{Al}_2\text{O}_3 (at 150 °C) was proved significantly higher than the benchmark supported Cu catalysts operated at higher temperatures (180-220 °C). And the higher selective hydrogenation rate can be linked to the greater capacity of nano-sized Au to chemisorb/activate H\textsubscript{2} relative to supported Cu for Cu/C.\textsuperscript{189} Date et al. prepared various Ir supported catalysts, and they found the catlayt Ir/C with metallic (Ir\textsuperscript{0}) and oxide (IrO\textsubscript{2}) phases could give 95 % of MF yield at very low H\textsubscript{2} pressure of ~6.9 bar (Table 3.2.6 entry 12). Consistant to the research of Vlachos et al. who used partically oxide Ru supported on carbon, Date et al also
proposed an acid mediated mechanism from furfural to MF. According to these findings, a general consensus could be concluded that acidic sites on the catalyst will facilitate to furfural hydrogenation to FA, and FA further hydrogenolysis to MF.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>H source</th>
<th>Solvent</th>
<th>T(°C)</th>
<th>t(h)</th>
<th>P(bar)</th>
<th>Yield (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru/C</td>
<td>i-PrOH</td>
<td>180</td>
<td>10</td>
<td>20.4a</td>
<td>-</td>
<td>61</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ru-RuO₂/C</td>
<td>2-butanol or 2-pentanol</td>
<td>7</td>
<td>76</td>
<td>1</td>
<td>131</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ru/NiFe₂O₄</td>
<td>i-PrOH</td>
<td>180</td>
<td>10</td>
<td>21a</td>
<td>1</td>
<td>83</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>Pd-Ru/TiO₂</td>
<td>H₂</td>
<td>octane</td>
<td>RT</td>
<td>2</td>
<td>3</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Ru/C</td>
<td>H₂</td>
<td>water</td>
<td>90</td>
<td>5</td>
<td>12.5</td>
<td>40</td>
<td>130</td>
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<tr>
<td></td>
<td>Ru/Sn/C</td>
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<td>5</td>
<td>12.5</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>Ru/rGO</td>
<td>H₂</td>
<td>water</td>
<td>20</td>
<td>5</td>
<td>10</td>
<td>91</td>
<td>-</td>
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<td>H₂</td>
<td>water</td>
<td>20</td>
<td>5</td>
<td>10</td>
<td>95</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>Ru/Al-MIL-53</td>
<td>H₂</td>
<td>water</td>
<td>20</td>
<td>2</td>
<td>5</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>Ru/Ph₂P(CH₂)₄PPh₂</td>
<td>H₂</td>
<td>no</td>
<td>140</td>
<td>1.3</td>
<td>25</td>
<td>100</td>
<td>192</td>
</tr>
<tr>
<td>10</td>
<td>Ru/PES membrane</td>
<td>H₂</td>
<td>water</td>
<td>70</td>
<td>7</td>
<td>26</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>Ru/ZrO₂⁺Pd/Al₂O₃</td>
<td>H₂</td>
<td>water</td>
<td>30</td>
<td>4</td>
<td>5</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>12</td>
<td>Ir/C</td>
<td>H₂</td>
<td>i-PrOH</td>
<td>220</td>
<td>5</td>
<td>6.9</td>
<td>0</td>
<td>95</td>
</tr>
</tbody>
</table>

a: N₂ pressure; b: CF: continuous flow

### 3.2.3 Conclusions

In conclusion, furfural selective hydrogenation over non-noble and noble metal catalysts is still elusive as a high amount of variables determine the final product yield and distribution. Based on the researches in the latest five years, we can see that the selectivity to various hydrogenation products of furfural can be achieved by:

1) Controle the reaction conditions which including a) temperature (> 200 °C benifiting to MF formation from furfural with Cu based catalysts); b) H₂ pressure (high H₂ pressure will lead to deep hydrogenation, even ring-opened products); c)
time (deeper hydrogenation occurred with prolonging reaction time); d) solvents (in certain case, protic solvent leads to side-reactions) etc.

2) Change hydrogen resources. One can notice that transfer hydrogenation of furfural generally produce FA as the product or MF under harsher conditions. Almost no THFA or MTHF observed.

3) Alter active metal. For example Cu and Ru catalysts prefer resulting in hydrodeoxygenation to MF, while Co, Ni and Pd catalysts will lead to furan ring hydrogenation to THFA.

4) Incorporation of different active metal. In many cases, the synergy of bimetallic catalysts showed remarkable improvement of furfural conversion and target product yield, when compared with monometallic catalysts.

5) Vary the supports. As we reviewed, the same metal supported on different supports, the products possibly change a lot. Especially, the acidity and basicity of the supports have significant influence on the catalytic performance of the catalyst.

6) Alter reaction regime. When compare batch reaction with continuous flow, one can observe that the productivity generally improved, and sometimes the type of products varied.

More than that, the catalysts preparation methods and metal reduction methods etc. also have crucial effects on their catalytic performance. In fact, these factors make the comparison of the performance of different catalysts rather complex. In spite of this, from the author's point of view, more efficient and greener methods for furfural
selective transfer hydrogenation over non-noble metal catalysts in continuous flow regime still need to pay more attention in the future.
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CHAPTER 4

4.1 A two-steps microwave assisted continuous flow Process for direct conversion of xylose into 2-furonitrile

At the end of Chapter 2, we realized furfural production in microwave continuous flow reaction regime with high boiling points solvents: DMSO and GBL. Then for next step, we aimed to produce 2-furonitrile without separation of furfural obtained here. To achieve this goal, the conversion of furfural into 2-furonitrile needed to be investigated using similar experimental conditions, especially using DMSO-GBL mixture.

4.1.1 Effect of DMSO-GBL volume ratio on 2-furonitrile production

In the first step, the one-pot synthesis of 2-furonitrile from furfural using ammoximation followed by dehydration was carried out at 100 °C for 20 minutes under microwave activation in batch in a mixture of DMSO and GBL (5 mL, 1:4, v/v). The solvent mixture was loaded with pure furfural (1.0 mmol) in presence of \( \text{NH}_2\text{OH}*\text{HCl} \) (1.23 eq) to afford the corresponding nitrile (conversion 94 % and selectivity 97 %). It is important to note that the presence of HPA (40 wt. %) was essential for the formation of furfural in the first step. Its presence in the second step also let to the formation of the target 2-furonitrile without any significant reduction in yield. In this regards, next reactions were repeated in presence of HPA (0.06 g). Rapid
solvent volume ratio effect was investigated (Figure 4.1.1). The use of DMSO and GBL, mixed or pure, resulted in furfural conversion greater than 90%. On the other hand, it is evident that DMSO allowed the formation of 2-furonitrile even in low yield (58%) but it is indispensable since only trace of 2-furonitrile was observed. In this case, furfural furnished the corresponding oxime via ammoximation and dehydration was not detected (see ESI, Figure S4.1.1). Besides, complete $^1$H and $^{13}$C NMR analysis of each set was done after column chromatography and confirm our hypothesis: formation of furan-2-carbaldehyde oxime isomers and then 2-furonitrile during the process (see ESI, figure S4.1.2). This phenomenon could be explained by a mechanism described in the Scheme 4.1.1. Despite our efforts, even heated up at 110 °C for 20 or 30 minutes, furfural conversion and furonitrile yields were both limited to

Figure 4.1.1 Effect of DMSO-GBL volume ratio (5 mL, v/v) on 2-furonitrile production. Reaction conditions:

furfural (1.0 mmol), hydroxylamine hydrochloride (1.23 mmol), HPA (0.06 g), DMSO-GBL (5.0 mL), MW, 100 °C, 20 minutes.
87 %. Variation of the temperature showed that under 100 °C less yield and conversion were observed (see HPLC charts on ESI figure S4.1.3).

As mentioned, DMSO is indispensable; it plays the role of solvent and catalyst. Augustine et al. supposed that the interaction of HCl (associated with hydroxylamine hydrochloride) with DMSO yields an oxysulfonium salt. The ionic liquid-like _activated DMSO_ instantaneously reacts with aldoxime to produce an intermediate via electrophilic addition. Subsequent expulsion of nitrile from the intermediate regenerates DMSO and HCl (Scheme 4.1.1). Interestingly, heating hydroxylamine in GBL did not occur the ring opening of the lactone type solvent and no trace of hydroxamic acid was detected by HPLC or \(^1\)H NMR analysis.

![Scheme 4.1.1 Proposed mechanism for nitrile generation from aldehydes involving _activated DMSO_. Adapted from Augustine et al.](image_url)

Scheme 4.1.1 Proposed mechanism for nitrile generation from aldehydes involving _activated DMSO_. Adapted from Augustine et al.\(^1\)
4.1.2 Impact of the hydroxylamine hydrochloride concentration on the furonitrile yield and selectivity

Variation of the ratio between furfural and hydroxylamine was studied (Figure 4.1.2). By increasing the excess of the hydroxylamine, furfural conversion (96 %) and 2-furonitrile yields (94 %) increased together until the amount of the salt reached 1.6 equivalents. In our hands, increase amount of HPA gave similar yield (95 %) and selectivity (97 %).

![Figure 4.1.2 Impact of the hydroxylamine hydrochloride concentration on the furonitrile yield and selectivity.](image)

Reaction conditions: furfural (1.0 mmol), HPA (0.06 g), DMSO (2 mL), GBL (3 mL), MW, 100 °C, 20 minutes.
4.1.3 2-Furonitrile production using two step microwave continuous flow

For the next step, 150 mL of a furfural solution (0.25 M) obtained from the optimized condition (Table 2.3.1 entry 6) was used as starting material. A solution of NH₂OH.HCl in DMSO-GBL (100 mL, 1:4, v/v) was injected with a flow rate of 0.25 mL/min and mixed with the existing stream of furfural at a T-shape mixer. The mixed stream was introduced to the second microwave-aided continuous flow reactor at 100 °C with a residence time of 40 minutes (Scheme 4.1.2). Any comparison being equal, the yield of 2-furonitrile under microwave irradiation in batch reactor was 56 % yield in two steps (2 times 20 minutes) without isolation and purification of the furfural, while in the continuous process the target nitrile was obtained in 49 % yield (two steps) for 80 minutes without furfural. The conversion of furfural was 97 % and HPLC analysis of the crude mixture showed that the presence of the corresponding oxime (∼ 50 %). This result could be explained by the nature of the microwave continuous flow system which is currently an open type machine. Thus, when the solution was heated, a large part of the HCl contents diffuse in the atmosphere before to be able to dehydrate the oxime derivative into its cyano counterparts.
Scheme 4.1.2 Dehydration/ammoniation sequence for the synthesis of 2-furonitrile under two successive microwave-aided continuous flow systems

4.1.4 2-Furonitrile production using microwave continuous flow + continuous flow by conventional heating

Unlike dehydration process of D-xylose, the ammoniation can be carried out in continuous flow with conventional heating (the reactor is a closed system). After dehydration of D-xylose using the same protocol described above, the stream of furfural was introduced to a batch reactor containing NH$_2$OH.HCl and the combined mixture was introduced to a second reactor at 100 °C with a residence time of 20 minutes. Under a lower residence time (20 min vs 40 min) and with a slight excess of hydroxylamine hydrochloride, yield of 2-furonitrile was improved and reached a value of 56 % (two steps) with a furfural conversion of 97 % (Table 4.1.1). Variation of the amount of nitrogen-containing reagent gave similar results. Regarding the productivity of both processes, successive dehydration under microwave continuous flow and ammoniation under conventional heating appeared to be higher than that
obtained with two successive microwave continuous flows (0.78 mmol/s/L vs 0.31 mmol/s/L).

Table 4.1.1 Furfural conversion into 2-furonitrile in DMSO-GBL monophasic feed solution containing a small amount of HPA and hydroxylamine hydrochloride under conventionally heated continuous flow process

<table>
<thead>
<tr>
<th>Entry</th>
<th>NH$_2$OH, HCl (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.404</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>0.53</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>0.46</td>
<td>55</td>
</tr>
</tbody>
</table>

Reactions conditions: D-Xylose (0.4 M), HPA(19 wt. %), DMSO-GBL (1:4, v/v), 150 °C, 40 min, MW, continuous flow then NH$_2$OH.HCl (0.29-0.38 wt. %), 100°C, 20 min, continuous flow.

4.1.5 Conclusion

This work reports successfully transfer of a two-steps batch conversion of D-xylose into 2-furonitrile as valuable furanic compound. Dehydration of D-xylose in the presence of HPA in a mixture of DMSO-GBL under microwave irradiation was a novel procedure giving furfural in 65 % yield. Ammoniation of furfural with NH$_2$OH.HCl and HPA gave the 2-furonitrile in 87 % yield (56 % in two steps). Despite our efforts, it seems to be impossible to produce 2-furonitrile directly from the sugar with one pot two-steps batch reaction. However using a two stages
continuous flow system, the target compound was obtained in good yield and selectivity. The use of one microwave continuous flow for the dehydration and then one thermic continuous flow for the ammoximation permitted to have a better yield and a higher volumetric productivity of 0.78 mmol/s/L than that obtained by using two successive microwave continuous flow reactors (0.31 mmol/s/L). These promising results convince us to try more experiences to convert directly xylan or hemicellulose into furonitrile. Currently, the complete bio-based continuous-flow process is also studied.
4.2 On the catalytic performance of carbon supported metal catalysts for liquid phase furfural hydrogenation: batch vs. continuous flow

4.2.1 Introduction

As we known, furfural hydrogenation is the most important application way of furfural, and literatures review indicated that most of the research on catalytic reduction of furfural aims to attain high selectivity to FA and/or MF. FA can be applied in the synthesis of renewable materials such as polymers, resins and carbons, but it can also be further hydrogenated to other compounds. MF in particular is an attractive chemical. It can be applied as an additive in gasoline fuels or it can be coupled with cyclopentanone and subsequently hydrotreated for the synthesis of diesel or jet fuel range cycloalkanes. Many catalysts have been proposed for the liquid phase hydrogenation of furfural. The generally accepted reaction pathway is illustrated in Scheme 4.2.1. The majority of the catalysts consist of metal particles, mostly Cu, Pd, Ni and Pt. In many cases their corresponding bimetallic systems (also with other metals such as Ru and Ir) have shown positive effects on the selectivity and/or stability of the catalyst. Most of these studies are based on batch reactor experiments, although recently studies on continuous flow hydrogenation are also reported. Only Biradar et al. compared the catalyst performance between batch and continuous flow.
The type of support also plays an important role. Supports often include Lewis acids ($\gamma$-Al$_2$O$_3$, TiO$_2$, ZrO$_2$, CeO$_2$, SiO$_2$ and SBA-15), basic metal oxides (MgO and ZnO) and base metal carbonates (CaCO$_3$), which assist in polarizing the furfural carbonyl bond. More neutral supports such as (doped) carbons were also used in some studies. Molecular hydrogen (H$_2$) is used as the hydrogen donor in the majority of these studies, either prior to the hydrogenation experiment in a catalyst activation step (typically 1-4 h) or either during the furfural hydrogenation itself. In these cases where H$_2$ was used for catalyst activation only, protic solvents were used as the hydrogen donor through catalytic hydrogen transfer reactions to furfural. The use of protic solvents has important implications for the catalytic performance. Whereas methanol, ethanol and...
isopropanol\textsuperscript{7–9,11,16,18,20} are good solvents to achieve high catalytic activity, they often lead to lower product selectivity due to the formation of side products, e.g. (hemi)acetals.\textsuperscript{14,19,21,23} Other side products include polymeric compounds\textsuperscript{14} (e.g. humins), especially in acidic aqueous media. Aqueous phase hydrogenation is therefore reported in only few cases.\textsuperscript{12,17,20} Non-protic organic solvents such as ethyl acetate,\textsuperscript{10,15} toluene,\textsuperscript{14,16,19,20} dichloroethane,\textsuperscript{14} dioxane,\textsuperscript{16} n-octane\textsuperscript{14} and supercritical CO\textsubscript{2}\textsuperscript{13} have also shown to suit well for furfural hydrogenation. Operational parameters such as temperature, reaction time, flow rate and (hydrogen) pressure also imply important effects on the catalytic performance.

In conclusion, a high amount of variables determine the final product yield and distribution in the catalytic hydrogenation of furfural, which makes the comparison of the performance of different catalysts rather complex. In this work, we compared the catalytic performance of various monometallic catalysts supported on a commercial micro/mesoporous activated carbon (Cu/AC, Pd/AC, Ni/AC and Pt/AC) for the hydrogenation of furfural, both in batch and in continuous flow and using molecular hydrogen or isopropanol as the hydrogen donor. Whereas 5\% Ni/AC performs better in batch experiments (in terms of selectivity to 2-methylfuran), better results are obtained with Pt/AC in continuous flow regime. Re-utilization of the spent 5\% Ni/AC catalyst by simple filtration after batch experiments changes the selectivity drastically from 2-methylfuran to furfuryl alcohol. High selectivity to 2-methylfuran is also demonstrated for a bimetallic Ni-W catalyst in continuous flow at higher temperatures using isopropanol as the hydrogen donor, however with low stability. In general, the
hydrogenation reactions highly depended on the organic solvent used. Metal leaching was the main cause of catalyst deactivation.

4.2.2 Catalyst characterization

A series of monometallic catalysts supported on commercial activated carbon were prepared via wet impregnation (10% Cu/AC, 10% Ni/AC, 5% Ni/AC, 3% Pd/AC and 3% Pt/AC) followed by thermal treatment in both inert and H₂ atmosphere. The corresponding bimetallic Ni catalysts (5% Ni-15% W/AC and 10%Ni-15% W/AC) were prepared similarly. The porosity characteristics (from N₂ sorption experiments) of the parent commercial activated carbon (AC) and the AC supported metal catalysts are shown in Table 4.2.1. The parent AC support is a microporous carbon (< 2 nm) with high contribution of meso/macroporosity. About 65 % of its total surface area and 36 % of its total pore volume is attributed to micropores, the rest being mainly due to meso/macropores and external surface area, as revealed from the N₂ isotherm shapes shown in Figure S4.2.1 (see Supporting Information), where a progressive increase of adsorbed N₂ can be observed over the whole P/P₀ range, indicating the presence of a relatively disordered network of meso- and macropores. Due to this size inhomogeneity, a distinct peak in the BJH pore size distribution curves was not observed, while only a weak peak was identified in the DFT pore size distribution curve with an average diameter of 3.4 nm. The total and micropore surface area, as well as the pore volumes of the monometallic loaded AC catalysts were essentially unchanged compared to those of the AC (decrease of max. 10 %). The porosity
characteristics of the bimetallic catalysts decreased by ca. 30 %, as determined for the 10% Ni-15% W/AC catalyst.

Table 4.2.1 Porosity and crystal size data of the mono- and bi-metallic catalysts supported on activated carbon (AC).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total SSA (m²/g)ᵃ</th>
<th>Total pore volume (cc/g)ᵇ</th>
<th>Micropore area (m²/g) and volume (cc/g)ᶜ</th>
<th>Meso/macropore &amp; external area (m²/g) and volume (cc/g)ᵈ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated carbon (AC)</td>
<td>1280</td>
<td>0.95</td>
<td>840 / 0.34</td>
<td>440 / 0.60</td>
</tr>
<tr>
<td>10%Cu/AC</td>
<td>1170</td>
<td>0.83</td>
<td>770 / 0.31</td>
<td>400 / 0.52</td>
</tr>
<tr>
<td>3%Pd/AC</td>
<td>1340</td>
<td>0.95</td>
<td>890 / 0.36</td>
<td>450 / 0.59</td>
</tr>
<tr>
<td>3%Pt/AC</td>
<td>1180</td>
<td>0.85</td>
<td>760 / 0.31</td>
<td>420 / 0.54</td>
</tr>
<tr>
<td>5%Ni/AC</td>
<td>1250</td>
<td>0.88</td>
<td>830 / 0.34</td>
<td>420 / 0.54</td>
</tr>
<tr>
<td>10%Ni/AC</td>
<td>1250</td>
<td>0.90</td>
<td>810 / 0.33</td>
<td>440 / 0.57</td>
</tr>
<tr>
<td>5%Ni-15%W/AC</td>
<td>1020</td>
<td>0.72</td>
<td>680 / 0.28</td>
<td>350 / 0.44</td>
</tr>
<tr>
<td>10%Ni-15%W/AC</td>
<td>920</td>
<td>0.64</td>
<td>610 / 0.25</td>
<td>310 / 0.39</td>
</tr>
</tbody>
</table>

ᵃ SSA: specific surface area from N₂ sorption at -196 °C (multi-point BET method); ᵇ Total pore volume at P/P₀ = 0.99 ; ᶜ t-plot method; ᵈ Meso/macropore & external area = Total SSA - Micropore area;

Meso/macropore volume = Total pore volume - Micropore volume (t-plot);

The catalysts were also characterized using powder XRD and the respective patterns spectra are shown in Figure S4.2.2 (see Supporting Information). The 5% Ni/AC catalyst consisted essentially of metallic Ni(0) nanoparticles with average crystal size of 6.8 nm while as the Ni content increases to 10 %, the Ni(0) crystal size increases to 23.2 nm and a small but XRD visible NiO phase appears with crystal size of 6.1 nm. In the case of the bimetallic catalysts, and more specifically in 5% Ni-15% W/AC the crystalline phases of tungsten oxide (WO₂) and nickel tungsten oxide (NiWO₄) prevail with average crystal sizes of 9.9 and 15.5 nm, respectively. However,
for the 10% Ni-15% W/AC catalyst, the dominant peak in the XRD pattern is again that of Ni(0) corresponding to crystal size of 10.7 nm, being markedly lower than the Ni(0) crystal size in the monometallic 10% Ni/AC catalyst. The crystal sizes of 10% Cu/AC, 3% Pt/AC and 3% Pd/AC were 23.2 nm (a Cu$_2$O phase was also detected with a crystal size of 16.6 nm), 13.6 nm and 16.6 nm, respectively.

### 4.2.3 Batch hydrogenation experiments

The experiments were carried out with 30 bars H$_2$ (total pressure around 100 bars) at 200 °C for 5 h. Table 4.2.2 shows the results obtained with the different monometallic catalysts (entries 2-5), as well with the bimetallic Ni catalysts (entries 11-14). The blank experiment (entry 1) gave almost negligible conversion of furfural. High selectivity to FA was seen for the 10% Cu/AC catalyst, but only at low conversion (entry 2). Using the 3% Pd/AC catalyst (entry 3), the conversion reached 47 %, but with only 43 % selectivity to FA, below the values reported in previous works with Pd catalysts.$^9$–$^{16}$ Much higher conversions were observed with the 3% Pt/AC and 5% Ni/AC catalysts (entries 4 and 5, respectively). Whereas 3% Pt/AC was more selective to FA, high selectivity to MF was achieved with the 5% Ni/AC catalyst (78 %). The high hydrogenation activity from 5% Ni/AC is also demonstrated by comparing the residual H$_2$ pressure after the experiments (Figure 4.2.1), as it takes more hydrogen to fully remove the oxygen functionality in furfural. In the absence of molecular hydrogen (entry 9), only 10 % conversion was observed. At 260 °C (entry 10), in contrast, almost full conversion was reached, albeit with lower selectivity to
MF (53 %). When using the spent 5% Ni/AC catalyst (entry 8), the selectivity changed quite drastically from MF to FA. The bimetallic Ni-W catalysts (entries 11 and 13) gave lower conversions (ca. 50 %) and lower selectivity to MF (30-39 %).

Again, in the absence of molecular H\(_2\) and at 260 °C, higher conversion was observed, but with incomplete mass balances (entries 12 and 14), similar to the monometallic 5% Ni/AC catalyst (entry 10). Most of the missing balance was covered by the presence of some unidentified compounds, eluting at different times depending on in function the solvent type (methanol, ethanol and isopropanol).

Table 4.2.2 Conversion and products yield in batch hydrogenation experiments of 0.35 M furfural in 60 mL solvent (FA: furfuryl alcohol, MF: 2-methylfuran, MTHF: 2-methyltetrahydrofuran and iPrO-MF: 2-(isopropoxy)-methylfuran.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>T (°C)</th>
<th>H(_2) (bar)</th>
<th>Solvent</th>
<th>t (h)</th>
<th>Con. (%)</th>
<th>Yield (%)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FA</td>
<td>THFA</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>1</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10%Cu/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>24</td>
<td>22</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3%Pd/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>47</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>3%Pt/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>93</td>
<td>47</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>5%Ni/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>85</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>5%Ni/AC</td>
<td>200</td>
<td>30</td>
<td>MeOH</td>
<td>5</td>
<td>87</td>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>5%Ni/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>7</td>
<td>95</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>5%Ni/AC(^a)</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>67</td>
<td>38</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>5%Ni/AC</td>
<td>200</td>
<td>0</td>
<td>i-PrOH</td>
<td>5</td>
<td>10</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>5%Ni/AC</td>
<td>260</td>
<td>0</td>
<td>i-PrOH</td>
<td>5</td>
<td>95</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>11</td>
<td>5%Ni-15%W/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>50</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>12</td>
<td>5%Ni-15%W/AC</td>
<td>260</td>
<td>0</td>
<td>i-PrOH</td>
<td>5</td>
<td>83</td>
<td>16</td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>10%Ni-15%W/AC</td>
<td>200</td>
<td>30</td>
<td>i-PrOH</td>
<td>5</td>
<td>51</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>10%Ni-15%W/AC</td>
<td>260</td>
<td>0</td>
<td>i-PrOH</td>
<td>5</td>
<td>83</td>
<td>25</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{a}\) Unknown compound U2 eluting at 3.9 min. in GC-FID analysis not included (48 % of total peak area); \(^{b}\) Spent catalyst from entry 5; \(^{c}\) Unknown compounds U3 and U4 eluting at 10.4 and 12.0 min in GC-FID.
analysis not included (39 % of total peak area). Unknown compounds U3 and U4 accounted for 21 % of total peak area.

4.2.4 Continuous flow hydrogenation experiments using molecular hydrogen (H₂) as the hydrogen donor

The experiments were conducted using a continuous H₂ flow and a continuous liquid flow of a furfural feedstock in H-Cube Pro (ThalesNanoTM) equipment. As no kinetic data were available from the batch experiments, the reaction conditions for the continuous flow experiments required optimization. The same solvent (i-PrOH) was used as in the batch experiments. Initially, we studied the effect of temperature, hydrodynamic pressure and flow rate on the conversion and product yield over time (Figure 4.2.2). The conversion and product yield increased with higher temperature (Figure 4.2.2a,b), pressure (Figure 4.2.2c,d,e) and residence time (Figure 4.2.2f,g,h). At time zero, all the conversions were close to 100 %, except when the flow rate was
too high (0.5 mL/min) or the pressure in the reaction column too low (30 bar, Figure 4.2.2c). Then, after measuring the collected samples during 2 h on stream, all the conversions gradually decreased. A linear correlation fitted the decrease rate well, showing the catalyst deactivation effect of in time. Only in optimized conditions of 150 °C, 50 bar and 0.2 mL/min (Figure 4.2.2f), the conversion remained constant (1 % less conversion after 2 h). It was also under similar conditions that the MF yield remained the highest (20 %) and quasi constant. In contrast to the batch hydrogenation, significant amounts of MTHF and THFA were produced, however with decreasing trend (hydrogenation stops at the formation of FA).

Figure 4.2.2 Conversion, product yield and mass balance in continuous flow hydrogenation of 0.2 M furfural in i-PrOH with 5%Ni/AC using H₂ (H-Cube reactor) at increasing (a-b) temperature (50 bar, 0.3 mL/min), (c-e) pressurization (150 °C, 0.3 mL min⁻¹) and (f-h) flow rate (150 °C, 50 bar).
Next, using optimized conditions, different solvents such as ethanol, ethyl acetate, isobutyl methyl ketone, cyclopentyl methyl ether were tested (Figure 4.2.3). Whereas the hydrogenation in protic solvents such as iso-propanol and ethanol (Figures 4.2.3a-3b), gave almost full conversion without significant decrease during 2-3 h on stream. The conversions achieved with non-protic organic solvents were substantially lower (50-75 %) and decreased 3-8 % after 2 h, with cyclopentyl methyl ether offering the most interesting result (Figure 4.2.2e) in terms of selectivity (only FA and MTHF ). Higher conversion and MTHF yield was obtained by using a 0.1 instead of 0.2 M feedstock (Figure 4.2.3f). In our hands, the highest MF yields were produced

Figure 4.2.3 Conversion, product yield and mass balance in the continuous flow hydrogenation of 0.2 M furfural with 5%Ni/AC using H\textsubscript{2} (H-Cube reactor), operating at 0.2 mL/min, 150 °C and 50 bars in (a) iso-propanol, (b) ethanol, (c) ethyl acetate, (d) methyl isobutyl ketone, (e) cyclopentyl methyl ether (0.2 M furfural) and (f) cyclopentyl methyl ether (0.1 M furfural).

with protic solvents. But, the mass balance for protic solvents reached only 40-50 %,
whereas they were quasi complete (90-100 %) when using non-protic solvents.

When looking closer to the chromatogram of the hydrogenation product obtained in i-PrOH (Figure 4.2.4a), one can observe two additional peaks at higher retention times. These were also present in the chromatogram of the hydrogenation product obtained in EtOH, but at lower retention times, while these were absent in the chromatograms of the products collected using non-protic solvents (see Figure S4.2.8 in the Supporting Information). After evaporation of the solvent under reduced pressure, only traces of MF were detected in the hydrogenation product when analyzed by 1H-NMR (Figure 4.2.4b) and 13C-NMR (Figure 4.2.4c), as MF is the only hydrogenation product with lower boiling point than i-PrOH. Analysis of both spectra revealed the presence of 2-(isopropoxy)-methylfuran (iPrO-MF) in agreement with previous works which also proposed the presence of (hemi)acetal side products when using EtOH or i-PrOH, however without explicit experimental evidence. Next to iPrO-MF, the corresponding ring hydrogenated product 2-(isopropoxy)-methyltetrahydrofuran (iPrO-MTHF) was also identified. At first sight, the incorporation of solvent molecules in the hydrogenation product is an undesired side reaction and should therefore be suppressed. Gilkey et al. recently demonstrated that this etherification is reversible.

24
Figure 4.2.4 (a) GC-FID chromatogram of the hydrogenation product obtained after 2 h at 0.2 mL min$^{-1}$, 150 °C and 50 bars of 0.2 M furfural in i-PrOH, (b) corresponding $^1$H-NMR spectrum and (c) corresponding $^{13}$C-NMR spectrum of the hydrogenation product after removal of MF and i-PrOH by rotavaporation.

Next, under optimized conditions (furfural 0.2 M in CPME, H$_2$ 50 bar, 150 °C, 0.2
ml/min flow rate), different catalysts (3% Pd/AC, 3% Pt/AC, 10% Ni/AC, 5% Ni-15% W/AC and 10% Ni-15% W/AC) were tested. Figure 4.2.5 shows that indeed, in contrast with protic solvents, mass balances were near to 100 % and kept constant during all experiments. With 10% Cu/AC no significant amounts of products were detected. Whereas with 3% Pd/AC and 5% Ni/AC the main products were FA and THFA, the 3% Pt/AC yielded mostly FA and MF. Thus, the high selectivity to MF observed with 5% Ni/AC catalyst in batch conditions were not observed in continuous flow. This is also the result of the lower hydrogenation temperature (150 instead of 200 °C). THFA was produced in all experiments conducted in continuous flow using 3% Pd/AC or 5% Ni/AC, but it was only produced in trace amounts in batch conditions. The percentages of conversion lost per h namely the deactivation rates, were 2, 8 and 12 for the 3% Pt/AC, 5% Ni/AC and 3% Pd/AC catalysts, respectively. The bimetallic Ni-W catalysts (Figure 4.2.5e-f) gave lower conversion (intercept) and lower stability. When the experiments with 5% Ni/AC and 3% Pt/AC were repeated at 42 h⁻¹ weight hourly pace velocity (WHSV) instead of 98 h⁻¹ (by using 280 instead of 120 mg of packed catalyst at equal flow rate), the deactivation rates were minimal (< 1%), with conversions near 100 % for the 5% Ni/AC catalyst and 92 % for the 3% Pt/AC catalyst. Initially (after 25 min. on stream, t = 0), the selectivity to THFA reached 90 % with the Ni/AC catalyst, but then dropped very fast to only 22 % after 2 h, as the hydrogenation stopped at FA as the main product. The 3% Pt/AC catalyst in contrast yielded mostly MF with 83 % selectivity, which remained still 71 % after 2 h.
Figure 4.2.5 Conversion, product yield and mass balance in the continuous flow hydrogenation of 0.2 M furfural in cyclopentyl methyl ether using H₂ (H-Cube reactor), operating at 0.2 mL min⁻¹, 150 °C and 50 bars with 30 mm packed beds containing 120 mg of (a) 5%Pd/AC, (b) 3%Pt/AC, (c) 5%Ni/AC, (d) 5%Ni-15%W/AC (e) 10%Ni/AC and (f) 10%Ni-15%W/AC, and with 70 mm packed beds containing 280 mg of (g) 5%Ni/C and (h) 3%Pt/AC.

4.2.5 Continuous flow hydrogenation experiments using isopropanol (i-PrOH) as the hydrogen donor

The use of i-PrOH as both hydrogen donor and as solvent for the catalytic transfer hydrogenation of furfural was considered, as it affects important techno-economic aspects of the process technology related to the fixed and
operational costs associated with the use of \textit{i}-PrOH (liquid) and H$_2$ (gas).

Batch experiments in the absence of H$_2$ (Table 4.2.2, entries 9, 10, 12 and 14) showed important differences in furfural conversion and MF yield between hydrogenation at 200 °C (MF yield 1 %) and 260 °C (MF yield 50 %). These results indicated that high temperatures were required for catalytic hydrogen transfer. Therefore, in the continuous flow experiments using only \textit{i}-PrOH as the hydrogen donor, we first studied the effect of temperature (200 °C, 230 °C and 260 °C, Figure 4.2.6a). Similar effects were observed as in batch, but the highest MF yield was observed at 200 °C instead of 260 °C.

Among different catalyst tested under identical conditions (Figure 4.2.6b), 5% Ni/AC provided the highest conversion at low flow rate (0.1 mL/min) while 10% Ni/AC gave higher conversion at higher flow rate (0.2-0.4 mL/min). These monometallic catalysts were more active (better conversion) than bimetallic 5% Ni-15% W/AC and 5% Raney-Ni, but with lower selectivity to MF. Interestingly, the selectivity to MF with bimetallic Ni-W reached 98 % at 0.1 mL/min. These findings are also demonstrated in Figure 4.2.6c, where 5% Ni/AC gave the highest conversion, while 5% Ni-15% W/AC gave the highest selectivity to MF, but only with significant conversion levels at low flow rate.
Further experiments were carried out with monometallic Ni and bimetallic Ni-W to study their operational stability using 0.1 M furfural in i-PrOH, 100 mg catalyst at 230 °C with 30 bar dynamic pressure. The 5% Ni/AC (Figure 4.2.7a) showed significant higher stability than the 10% Ni/AC catalyst (Figure 4.2.7b). The operational stability of bimetallic catalysts (Figure 4.2.7c and 4.2.7d) was significantly lower compared to the monometallic ones with a drastic decrease of furfural conversion. A significant amount of the mass...
balance lacked, especially with the monometallic Ni/AC catalysts, most probably due to the formation of side products such as iPrO-MF and iPrO-MTHF (these products were not detected in our GC conditions used for these experiments). The higher activity provided by monometallic Ni/AC catalyst was not translated to higher MF yield, in contrast, more FA and side products were formed.

![Graphs showing conversion, product yield, and mass balance](image)

Figure 4.2.7 Conversion, product yield and mass balance over 6-10 h continuous flow hydrogenation at 0.2 mL/min using 0.1 M furfural in i-PrOH without H₂ (Phoenix reactor) at 230 °C and 30 bar using 100 mg of (a) 5 % Ni/AC, (b) 10% Ni/AC, (c) (5% Ni-15% W)/AC and (d) (10% Ni-15% W)/AC

As the bimetallic Ni-W contained more Lewis acid sites (WO₂ and WO₄) compared with monometallic ones, this result is surprising. Based on previous reports, the role of Lewis acid sites in zeolites to reduce the carbonyl group on furfural²⁵–²⁷ and the etherification of alcohols were significant.²⁵,²⁸
Different mechanisms for the reduction of furfural and FA to MF were described in the literature. More recently, it was found that the transfer of hydrides from $i$-PrOH to furfural mainly occurs through formation of a complex between furfural, ROH and Lewis acid sites (Scheme 4.2.2a), rather than production of $H_2$ from ROH on the metal surface (Scheme 4.2.2b). Koehle and Lobo showed the role of Lewis acid sites in zeolites in the formation of the corresponding hemiacetal ($i$PrO-MF) by catalytic hydrogen transfer from alcohols to furfural (Meerwein-Ponndorf-Verley or MPV reduction).23 The results of the present study are more in line with the findings reported by Gilkey et al.,24 who demonstrated experimentally that when starting from FA the hydrogenolysis via ring activation (remove carbonyl groups as $H_2O$ to form MF
Scheme 4.2.2c) was predominant over direct metal-mediated hydrogenolysis (Scheme 4.2.2d). Apart from facilitating the reduction and maintaining the reduced state of Ni species in bimetallic Ni-W catalysts, WO$_2$ and WO$_4$ species also served as Lewis sites in the present study, which improved the selectivity to MF, according to Gilkey’s findings. Based on tedious experimental work, the authors concluded that strong adsorption of furfural retards the metal catalyzed pathway but does not affect the MPV pathway because of its concerted bulky nature in which i-PrOH bonds its hydrogen directly to the furfural (no site competition). The fact that acetone was not detected in the present GC conditions used in any of the experiments conducted in i-PrOH as the solvent, supports Gilkey’s conclusion that hydrogenation of the carbonyl group in furfural to a hydroxymethyl group proceeds via intermolecular hydride transfer. Whether this step is catalyzed by Lewis acid sites (as they stated) remains unclear, as the present study shows clearly that intermolecular hydride transfer from i-PrOH is also possible on monometallic surfaces. Further studies of the Lewis acidity of the AC support may reveal this.

Currently, most of the work published on furfural hydrogenation reported catalysts highly selective to furfuryl alcohol (FA). Other works which reported also further hydrogenation to other products, including MF, proposed reduction of the alcohol group in FA as the first step of the mechanism. Also, Koehle and Lobo found that FA and FA polymerization side products deactivated the catalyst active sites in zeolites.$^{23}$ Therefore, experiments using FA instead of
furfural feedstocks were also considered in the present work, under identical conditions (Table 4.2.3).

Table 4.2.3 Conversion and products yield in batch hydrogenation experiments of 0.35 M furfuryl alcohol with 30 bar H₂ in 60 mL i-PrOH at 200 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Yield (%)</th>
<th>Mass balance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>THFA</td>
<td>MF</td>
</tr>
<tr>
<td>1</td>
<td>10%Cu/C</td>
<td>15</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>5%Ni/C</td>
<td>97</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>3%Pt/C</td>
<td>97</td>
<td>18</td>
<td>50</td>
</tr>
</tbody>
</table>

In line with the results on furfural batch hydrogenation, low conversion was seen for the 10% Cu/C catalyst (entry 1) while 5% Ni/C and 3% Pt/C gave high conversion (entries 2 and 3). The selectivity in contrast, changed drastically, with significant higher yields of THFA and MTHF when using 5% Ni/C. In these conditions, reduction of the furan core was possible. Lower amounts of iPrO-MF were detected, in line with the kinetic observations reported by Gilkey et al.²⁴ The lacking compounds in the mass balance may correspond to FA derived oligomerization products which are not detected in our conditions. However, in continuous flow regime (Figure 4.2.8), near to 100 % mass balance was observed during more than 1 h on stream, at 100 % conversion level and with ca. 50 % yields to MTHF for 3% Pd/C and near to 80 % yields to THFA for 5% Ni/C, respectively. These results show that the present catalyst are more reactive towards FA than furfural and produce much more ring-hydrogenated products, in line with the findings of Gilkey et al. who showed that the
reduction of the carbonyl group in furfural is kinetically constrained compared to further hydrogenation steps. We believe that this is related to the difference in the coordination of the furan ring on the catalyst surface and consequently on the different ring activation and product desorption characteristics.

![Graph showing conversion, product yield, and mass balance over 1 h continuous flow hydrogenation at 0.2 mL/min using 0.2 M furfuryl alcohol in i-PrOH with H₂ (H-Cube reactor) at 150 °C and 50 bar using 120 mg of (a) 3%Pd/AC and (b) 5%Ni/AC.]

Importantly, Gilkey et al. demonstrated experimentally that hydrogenolysis of FA to MF proceeds mostly via ring-activation (reformation of the furan double bonds via H abstraction from C-3 of the furan ring and H donation to the C-1 atoms) and subsequent scission of the C-OH bond, rather than direct C-OH scission via double hydride transfer. They hypothesized that after scission the OH is bonded to a Lewis acid site as a result of the high coverage of oxygenates on the metal surface itself. As the bimetallic Ni-W catalyst did contain Lewis acid sites (WO₂ and NiWO₄) and the monometallic catalyst only few (NiO), Gilkey’s findings can explain the different
behavior observed in Figure 4.2.7, where the MF yield and the mass balance with monometallic Ni was considerably lower than with Ni-W. At first sight it looked that the operational stability of these bimetallic Ni-W catalysts may be limited due to the saturation of the Lewis acid sites, but the same was observed for the monometallic analogues, which changed the direction of the hypothesis for catalyst deactivation, as described hereafter.

### 4.2.6 Effect of process conditions on catalyst deactivation

In contrast to all the previous works reported on liquid phase furfural hydrogenation, the catalysts in the present work were not activated with H$_2$ prior to the catalytic hydrogenation experiments (H$_2$ was only used for purging the batch reactor during ca. 1 min.). Despite the promising results described above in terms of conversion and selectivity, significant effects were observed on catalyst deactivation (stability). Changes in metal dispersion and metal leaching are among the main causes for catalyst deactivation in many occasions. The effect of process conditions on the metal dispersion were studied by analyzing the change in mean crystal size, as seen from XRD analysis (Figure 4.2.9), using the Scherrer equation. A higher crystallize size indicates that the metal dispersion has been affected negatively. However, caution must be taken for the interpretation of these results, especially when metal leaching occurs. The effect of the process conditions on the Pd(0) and Pt(0) crystal sizes were minimal, and no obvious aggregation of metal particles was observed. The general trend was that smoother conditions (130-150 °C using H$_2$ in H-Cube equipment)
resulted in smaller changes of the mean crystal size. Note that for the fresh Ni/AC and Ni-W/AC catalysts, much higher crystal sizes were observed when increasing the Ni load during their synthesis, which can explain their worse performance in catalytic activity.

At 260 °C using i-PrOH as hydrogen donor, most of the Ni(0) may have been leached or oxidized, as very low intensity peaks at 44° and 51° were detected for the spent Ni-W/AC catalyst. The fresh monometallic (5% Ni/AC) and bimetallic (5% Ni-15% W/AC) catalysts and the corresponding spent catalysts from batch and
continuous flow experiments (collected by simple filtration and drying) were also analyzed with XPS (Figure 4.2.10) and ICP-MS after acid digestion (Table 4.2.4) to study the effect of the process conditions on the amount of metal leaching from the carbon support.

Table 4.2.4 C, O, Ni and W content as determined by XPS analysis and by ICP-MS analysis in fresh and spent mono- and bimetallic Ni/AC catalysts (B: batch and CF: continuous flow).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>XPS (wt%)</th>
<th>ICP-MS (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>1</td>
<td>5% Ni/AC – Fresh</td>
<td>86.8</td>
<td>12.3</td>
</tr>
<tr>
<td>2</td>
<td>5%Ni/AC – Spent (B, 200 °C, 30 bar H₂)</td>
<td>79.1</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>5%Ni/AC – Spent (B, 260 °C, 0 bar H₂)</td>
<td>86.6</td>
<td>12.3</td>
</tr>
<tr>
<td>4</td>
<td>5%Ni/AC – Spent (CF, 150 °C, 50 bar, with H₂)</td>
<td>86.0</td>
<td>13.4</td>
</tr>
<tr>
<td>5</td>
<td>5%Ni/AC – Spent (CF, 260 °C, 30 bar, without H₂)</td>
<td>82.5</td>
<td>16.7</td>
</tr>
<tr>
<td>6</td>
<td>5%Ni-15%W/AC – Fresh</td>
<td>67.4</td>
<td>15.4</td>
</tr>
<tr>
<td>7</td>
<td>5%Ni-15 %W/AC – Spent (B, 260 °C, 0 bar H₂)</td>
<td>75.4</td>
<td>18.8</td>
</tr>
<tr>
<td>8</td>
<td>5%Ni-15%W/AC – Spent (CF, 260 °C, 30 bar, without H₂)</td>
<td>69.6</td>
<td>14.3</td>
</tr>
</tbody>
</table>

a C (1s), O (1s), Ni(0)(2p3/2), NiO (2p3/2) and W(4f) signals

b Not quantitative (only small amounts of W were solubilized in the acid digest due to complex formation)

These results show the relative elemental composition on the surface (XPS) and in the whole catalyst materials (ICP-MS). The metal loads were slightly lower than their theoretical loads used in their synthesis (5 wt%). Surprisingly, based on the ICP-MS analysis, substantial higher leaching was observed in batch conditions compared to continuous flow, independent from being mono or bimetallic and independent from the reaction temperature. We believe that the high stirring rate in the batch experiments promoted the leaching. Anyhow, these results play in favour of continuous flow vs. batch hydrogenation. The XPS analysis showed that the catalyst
surface layer was much more enriched in metal oxide (NiO), even in the fresh Ni catalyst, which is not surprising as the catalysts were stored under air atmosphere. The spent catalysts from batch experiments contained less NiO compared to the spent catalysts from continuous flow and instead presented more oxygen functionalities on the carbon support. However, this does not mean that in batch conditions more Ni(0) was retained on the catalyst surface, because in batch more profound leaching (40-41 %) occurred than in continuous flow conditions (5-26 %).

Figure 4.2.10 (Left) Full and (Right) zoomed XPS spectra of (a) 5%Ni/AC, (b) spent 5%Ni/AC (batch, 0 bar H\textsubscript{2}, 260 °C), (c) 5%Ni-10%W/AC and (d) spent 5%Ni-10%W/AC (batch, 0 bar H\textsubscript{2}, 260 °C) catalysts.
4.2.7 Conclusions

High selectivity (78%) to 2-methylfuran (MF) at high furfural conversion level (85%) was demonstrated for a monometallic 5% Ni catalyst supported on commercial activated carbon (AC) in batch hydrogenation experiments after 5 hours using 30 bar molecular hydrogen (H₂) in isopropanol (i-PrOH) at 200 °C. Re-utilization of the spent catalyst recovered by simple filtration changed the selectivity to 57% furfuryl alcohol (FA) at 67% conversion. In continuous flow experiments at 130-150 °C, the 5% Ni/AC catalyst was not that selective to MF (14-20% at 100% conversion), with FA and tetrahydrofurfuryl alcohol (THFA) being the other main products. The catalytic performance of the catalysts in continuous flow highly depended on the operational conditions, including flow rate, temperature, pressurization and especially the solvent type. When using protic solvents such as i-PrOH, important amounts of methylfuran ether side products were formed, as observed experimentally by ¹H-NMR and by the lacking mass balances. Aprotic solvents did not lead to the formation of side products; cyclopentyl methyl ether showed the best catalytic activity and selectivity at optimized conditions. Under these conditions 3% Pt/AC catalyst showed superior performance with 41-64% selectivity to MF at 52-53% conversion at 42 h⁻¹ weight hourly pace velocity (WHSV) and 71-82% selectivity at 91-92% conversion at 98 h⁻¹ WHSV. Experiments without H₂ showed that i-PrOH can act as hydrogen donor for the hydrogenation of furfural, but high temperatures (min. 230 °C) are required for significant conversion. Significant higher amounts of methylfuran ether side products were obtained in the absence of H₂, both in batch as in continuous flow. In the
absence of H\textsubscript{2}, a bimetallic 5\% Ni-15\% W/AC catalyst showed a remarkable near to 100 \% selectivity to MF starting from 0.2 M furfural, but only in continuous flow at low flow rates (0.1 mL/min). For higher flow rates (0.2-0.4 mL/min) the feedstock concentration was limited to 0.1 M to attain ca. 80 \% selectivity to MF. In agreement with the literature, this effect was attributed to the presence of Lewis acid sites (WO\textsubscript{2} and NiWO\textsubscript{4}) which acted as receptor sites for the OH formed upon hydrogenolysis of the C–OH bond in FA. However, the operational stability of the bimetallic catalyst was limited, as seen from the decreasing conversion and MF yield after 10 h on stream at 230 °C. XPS and elemental analysis showed that leaching was the main cause of catalyst deactivation when using high surface area carbon supports, at least for Ni based catalysts and for the catalyst preparation method used in this work. The leaching was found to be more profound in batch regime than in continuous flow rate systems. Additional experiments with FA instead of furfural as the feedstock showed that the catalysts were more reactive towards FA than furfural and that ring hydrogenated product such as THFA and MTHF were the main products formed instead of MF, showing the important role of the carbonyl group in the positioning of furfural on the catalyst surface.
4.3 Microwave-assisted catalytic upgrading of bio-based furfuryl alcohol to alkyl levulinate over commercial activated carbon

4.3.1 Introduction

Alkyl levulimates (ALs), which have been identified as one of top ten biorefinery candidates, are a kind of promising renewable fuel additives and platform chemicals for the synthesis of angelica lactone, GVL, valerates, as well as good building blocks. Generally, ALs were produced by direct esterification of levulinic acid over acidic catalysts or enzymatic methods, however, in the production of levulinic acid, its separation and purification are costly, which made it unsuitable for as the raw material for this purpose. Recently, great efforts were devoted to develop new methods to produce ALs from various feedstock, such as raw biomass, carbohydrates, 5-hydroxymethyl furfural or furfural, and furfuryl alcohol. Among them, furfuryl alcohol is a promising starting material due to its easy accessibility from furfural by reduction of its aldehyde function. Besides, each year around 62 % of furfural was used for furfuryl alcohol production, however, it’s not fully utilized and is oversupplied in the chemical market. Thus, the development of a feasible and competitive pathway for furfuryl alcohol upgrading is strongly demanded.

It has been reported that acidic catalysts are crucial to the alcohololysis of furfuryl alcohol to ALs. Based on this point of view, various homogeneous catalysts such as mineral acids, salts, ionic liquids, and also
heterogeneous catalysts, such as ion-exchanged resins, oxides and zeolites, have been concretely investigated. Due to the advantages of less corrosion, easy handle and separation, the exploration of heterogeneous catalysts is progressing satisfactorily in recent years. For example, Song et al. have synthesised a series of arylsulfonic acid functionalized hollow mesoporous carbon spheres catalysts, and successfully applied them into the ethanolysis of furfuryl alcohol, which gave the best ethyl levulinate yield of ca.80 % at 120 °C for 2 h. Furthermore, they fabricated some ethane-bridged organosilica nanotubes functionalized catalysts (labeled as ArSO3H-Si(Et)Si-Ph-NTs), which furnished a good ethyl levulinate yield of 84 % and reusability. However, several defects of these above-mentioned catalysts, such as the complex preparation process, the cost, environment concerns, limited their applications to some extent. Additionally, microwave-irradiations have been recognized as an efficient and green method to facilitate chemical reactions to achieve higher yield and selectivity in shorter reaction times. Recent study has shown that microwave heating could improve the reaction rate of furfuryl alcohol methanolysis to methyl levulinate 6 times when compared to conventional heating method. Combining these two aspects, it’s appealing to explore some cheaper, greener, more efficient and accessible catalysts for upgrading furfuryl alcohol to ALs under microwave irradiations.

In the present paper, we report an efficient catalytic approach for the conversion of furfuryl alcohol to alkyl levulinates over commercial available activated carbon under the assistance of microwave irradiation (as shown in Scheme 4.3.1). The catalyst loading and reaction temperature have great influence on methyl levulinate yield and the formation rate. Control experiments and different spectroscopic techniques were
also conducted to better understand the catalyst performance.

![Scheme 4.3.1 Alcoholysis of furfuryl alcohol to alkyl levulinates over activated carbon (AC).](image)

4.3.2 Catalyst screening

Firstly, the effect of different kinds of acidic catalysts on the alcoholysis of FA was studied at 150 °C for 5 min in methanol while keeping the same amount of catalyst (50 mg) under batch microwave irradiation. As figure 4.3.1 shown, the conversion of FA without catalyst was very low (18 %), and no desired product ML was formed, however, FA achieved fully conversion with other catalysts, even with commercial AC. Surprisingly, AC gave a comparable ML yield (36 %) with zeolite catalysts HY5.2 (41 %) and HY60 (30 %). More interestingly, lots of methoxymethyl furan (MmF) which was considered as the intermediate from FA to ALs, has been produced. This means a higher ML yield could be reached with AC as the catalyst by optimizing the reaction conditions appropriately. Pleasingly, 55 % of ML was obtained with 100 mg AC while MmF yield relatively decreased to 22 % from 39 %. In this case, ML yield is even higher than HZSM-5-30 (50 mg) and slightly lower than HZSM-5-50 (50 mg) which gave 54 % and 60 % ML yield respectively. It should be noted that HZSM catalysts gave quite amount of α-angelica lactone as the major
side-product which has been identified by GC-MS (see Figure S4.3.1). In spite of the home-made sulfonated carbon (SC) presented the best catalytic performance on ML production (77 % yield), the results with commercial AC seems more attractive as its commercial accessible. Therefore, these results underline that commercial AC could be a substitute of the common acidic catalysts for AL production, which convinced us further to optimise the reaction parameters.

![Graph](image)

Figure 4.3.1 Alcoholysis of furfuryl alcohol with different catalysts. Reaction conditions: 0.2 M FA 3 mL, catalyst loading 50 mg, MW, 150 °C, 5 min (exclude ramping time 2 min). a:100 mg of activated carbon

### 4.3.3 Effect of catalyst loading variation

The influence of catalyst dosage on the alcoholysis of FA in dependence of time was also investigated (Table 4.3.1). In all cases, FA reached more than 98 % conversion in 2.5 min, in the meantime, MmF was the major product which is in line with literatures which reported that the formation rate of alkoxydimethylfuran was much higher than that of alkyl levulinate. The results summarized in Table 4.3.1
indicated that the increase of reaction time and catalyst loading facilitate the conversion of methoxymethylfuran (MmF) to ML, and the best 72% ML was yielded with 100 mg AC for 20 min. Experiments were also carried out at 150 °C for 5 min to study the effect of water addition on ML formation. The results showed that ML yield gradually decreased from 36% to 24% with the water loading increasing to 2 eq. This effect was out of accord with the results from Zhang et al.\textsuperscript{30} who proved that the addition of water has a positive effect on furfuryl alcohol and 2-butoxymethylfuran conversion to butyl levulinate. Our results seem more agree with the findings from Maldonado et al.\textsuperscript{66} who demonstrated that water does not participate in the mechanism for conversion of FA to ethyl EL, as EL yield decreased with the addition of water.

Table 4.3.1 The effect of catalyst loading on the alcoholysis of furfuryl alcohol

<table>
<thead>
<tr>
<th>Time /min</th>
<th>Catalyst loading</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 mg</td>
</tr>
<tr>
<td></td>
<td>FA con.%</td>
</tr>
<tr>
<td>0</td>
<td>66</td>
</tr>
<tr>
<td>2.5</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>99</td>
</tr>
<tr>
<td>10</td>
<td>99</td>
</tr>
<tr>
<td>20</td>
<td>99</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.2 M FA 3 mL, desired activated carbon loading and time, MW, 150 °C. a: 1 eq and b: 2 eq of water (corresponding to FA)
4.3.4 Effect of reaction temperature

The influence of temperature on the alcoholysis of furfuryl alcohol was studied in a range from 130 to 170 °C under batch microwave irradiations with 100 mg AC and 3 mL FA feedstock (0.2 M) loading (Figure 4.3.2). Almost complete conversion was achieved as the temperature increased from 130 °C to 170 °C at time 0, which means FA was fully consumed when heating process finished. This could be attributed to the effect of microwave irradiations that significantly accelerate the reaction rate. When compared the results obtained at 150 °C (Table 4.3.1), we can conclude that higher reaction temperature benefits to higher ML yield, and simultaneously shortened reaction time. For example, a relative stable ML yield of 78 % was achieved in 5 min at 170 °C, which is higher than that of 67 % at 150 °C for 10 min and 36 % at 130 °C for 30 min. Moreover, lower reaction temperature would limit the consumption rate of MmF to ML. Therefore, in order to diminish the
reaction time the temperature was fixed at 170 °C for further investigation.

### 4.3.5 Effect of FA loading variation

The concentration of substrate (FA) is a key factor with great influence on most of chemical reactions. Actually, FA polymerization or polycondensation could be easily occurred in acidic environment. Thus, the effect of FA concentration at 0.1 M and 0.4 M were investigated within various reaction time periods (0-10 min). With a lower concentration of FA (0.1 M), the yield of ML increased to 83 % in 7.5 min. It's notable that better ML yield was obtained is a short reaction time when a higher concentration of FA was used (0.4 M vs 0.1 M at t=0 min and 2.5 min). MmF yield was higher in lower concentration of FA. It seems that higher FA loading did a favour to convert MmF to ML more rapidly, but gave lower ML yield when prolonged reaction time to 10 min. Generally, the polymerization of FA to oligomeric compounds at a high concentration should response to the decrease of ML yield.

![Figure 4.3.3 Influence of the reactant concentration on the alcoholysis of furfuryl alcohol. Reaction conditions: 0.1 or 0.4 M FA 3 mL, 100 mg activated carbon, 170 °C, MW, desired time.](image-url)
4.3.6 Alcohol screening

Under optimized conditions (0.2 M FA 3 mL, 100 mg AC, MW, 170 °C, 5 min), we next tested the alcoholysis of FA in different alkyl alcohols. As Figure 4.3.4 depicted, with the increase of the alcohol chain length, the yield of ALs slightly decreased from 78 % to 64 % with methanol and n-butanol, respectively. With branch alcohol iso-propanol, 39 % of iso-propyl levulinate yield was relatively lower than that with linear alcohol n-propanol (66 %). One can notice that more intermediate was left with iso-propanol. That is to say that its conversion to iso-propyl levulinate is more difficult, which was probably caused by steric effects. The tendency is consistent with the literatures, and these results suggest that AC has a universal catalytic ability for the alcoholysis of FA, and the high activity is comparable with Al_2(SO_4)_3 which

![Figure 4.3.4 Influence of the solvent on the alcoholysis of furfuryl alcohol. Reaction conditions: 0.2 M FA 3 mL, 100 mg activated carbon, 170 °C, MW, 5 min.](image)

49, 53, 70
gave 65 % butyl levulinate yield in 40 min when heated to 150 °C by microwave.58

4.3.7 Catalyst reusability

Recycling of the catalyst is an important step for a sustainable and economically feasible catalytic system. Therefore, the recycle experiments for AC catalyst were also carried out at 170 °C for 5 min in ethanol. After each reaction the catalyst was separated by centrifugation, washed thoroughly with ethanol for three times and dried at 100 °C for the next catalytic reaction. The results obtained by recycling the catalyst are shown in Figure 5. Evidently, the catalyst activity severely decreased at the second run, as FA conversion decreased from 99 % to 62 % and EL yield dropped to 12 % from 74 %. To understand the deactivation of the catalyst, two control experiments were performed. Firstly, one experiment was conducted without FA under optimized conditions. When the reaction was finished, the solution was separated by centrifugation and filtration, and recharged with 0.6 mmol FA and 0.015 g decane, and then MW heated to 170 °C for 5 min (control test 1). The control test 2 was performed with the recovered AC (after 3 times washing and dry). The high EL yield of 61 % from control test 1 indicated that some active species in AC were extracted into ethanol phase, and the leaching of these active species caused to its poor reusability. Furthermore, the comparison between control test 2 and run 2 probably implied that some other factors may
attribute to the catalyst decay, for example, oligomeric compounds formed by
FA polymerization covered some acidic groups etc. From this point of view, the
AC seems more like homogeneous catalyst.

To better understand the catalytic activity of this kind of commercial
activated carbon, BET, EDS, ICP-MS and acid-base properties of the AC and
spent ACs were measured. The results were show in Table 4.3.2. No big
changes in the porosity and surface area of the carbons were observed by BET.
However, EDS gave us a clear clue that species containing ‘sulphur‘ possibly
attribute to the activity, and ca. 42 % of average atomic ‘s‘ was leached after
first run. Rigorously, EDS analysis couldn‘t give a very accurate result,
therefore, we also titrated the acidic and basic groups on these samples
following the literature. The results are in line well with EDS analysis as ~ 0.7
mmol/g acidic groups were lost after first run. Besides, no apparently basic
groups leaching were observed. Further treating AC with ethanol and water in
presence of 0.2 M furfuryl alcohol at 170 °C for 1 h without MW offered 0.6
mmol/g and 0.9 mmol/g acidic groups leaching respectively, which agreed with
our results with microwave. Simultaneously, when treating 1.5 g AC with 20
ml water at 170 °C for 1 h, ICP-MS analysis of the filtrate showed that no
significant amounts of metals leached to water, only Ni is at about 300 ppm.

Table 4.3.2 BET, EDS and acid-base properties of the AC and spent AC

277 / 342
<table>
<thead>
<tr>
<th>Sample</th>
<th>BET total SSA (m²/g)²</th>
<th>Micropore /External area [(m²/g)/ (m²/g)]</th>
<th>Total pore volume (cc/g)b</th>
<th>EDS average atomic _s‘(%)c</th>
<th>Acidic groups (mmol/g)</th>
<th>Basic groups (mmol/g)</th>
<th>Total content of surface oxides [mmol/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>702</td>
<td>412/289</td>
<td>0.546</td>
<td>43.58</td>
<td>2.585</td>
<td>1.100</td>
<td>3.685</td>
</tr>
<tr>
<td>Spent AC¹</td>
<td>710</td>
<td>392/318</td>
<td>0.579</td>
<td>25.34</td>
<td>1.877</td>
<td>1.079</td>
<td>2.296</td>
</tr>
<tr>
<td>Spent AC²</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.997</td>
<td>1.089</td>
<td>3.086</td>
</tr>
<tr>
<td>Spent AC³</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.650</td>
<td>1.040</td>
<td>2.690</td>
</tr>
</tbody>
</table>

Spent AC¹ is the sample recycled from run 1 in Figure 5. Spent AC² and AC³ are samples treated in ethanol and water in presence of 0.2 M furfuryl alcohol at 170 °C for 1 h without microwave irradiations. a

SSA: specific surface area from N₂ sorption at -196 °C (multi-point BET method); b Total pore volume at P/P₀ = 0.99; c Si, P, S, K, and Ca were measured, total atomic Si+P+S+K+Ca= 100 %.

4.3.8 Reaction pathway and possible mechanism

According to literatures, multiple pathways have been proposed for the formation of alkyl levulinate from furfuryl alcohol, including some key intermediates, such as methoxymethylfuran (MmF) and 4,5,5-trimethoxypentan-2-one (TMP). Besides, one possible mechanism was regarding to aldehydration of furfuryl alcohol to a-angelica lactone, which was in turn readily attacked by alcohols to form alkyl levulinates. However, in our case, we proposed a plausible mechanism concerning MmF as the key intermediate (Scheme 4.3.2). Because one can obviously notice that MmF is the major intermediate (Identified by GC-MS, see ESI Figure S4.3.1), which token
77 % yield at 0 min with 100mg AC (Table 4.3.1), and this routes seems more reasonable as lower energy was needed for the formation of alkoxyethylfurans. Then, species A could be formed in the presence of methanol and acidic sites. The following * step for the formation of Specie B exists a competition between water and methanol according to the study of Maldonado et al. (Scheme 4.3.3)\textsuperscript{66}, and the reaction barrier with water (from A to B\textsubscript{0}) was higher than that without water (from A to B). This could explain why the yield of ML decreased and MmF yield increased when additional water was introduced (Table 4.3.1). Then, B\textsubscript{0} was formed from B by releasing a molecule methoxymethane, and after the addition with 3 eq. methanol, the most important intermediate TMP could be produced. However, no peak of TMP was found in GC or GC-MS in present work, but some species (C and D) with similar structure to TMP were identified by GC-MS (Figure S4.3.1 X2 and X3). However, the species X1 and X4 in Figure S4.3.1 may suggest that complex multiple pathways of FA alcoholsysis are possible.
Scheme 4.3.2 Plausible reaction mechanism for furfuryl alcohol alcoholysis to alkyl levulinates.

Scheme 4.3.3 Likely reaction pathway for the formation of species B and B₀ from A. Adapted from Maldonado et al.⁶⁶

4.3.9 Conclusions

Commercial activated carbon was proved as an efficient catalyst for the production of alkyl levulinates by alcoholysis of furfuryl alcohol under microwave irradiations. Upon the optimization, 78 % of methyl levulinate yield was obtained in 5 min, which
is comparable to the results of most literatures. The study of catalyst reusability indicated that acidic groups containing 'sulphur' on AC could be easily extracted. Regardless of its poor stability, this method is environmentally benign and economical for the conversion of biomass-based derivates into fine chemicals, because the catalyst is quite cheap and commercially available.
References


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(49) Peng, L.; Gao, X.; Chen, K. Catalytic Upgrading of Renewable Furfuryl Alcohol to Alkyl


(68) Choura, M.; Belgacem, N. M.; Gandini, A. Acid-Catalyzed Polycondensation of Furfuryl


General conclusions

The aim of this PhD work was to explore green methods for the synthesis of furfural, and further apply furfural to produce high added value molecules, such as furfuryl alcohol, 2-methylfuran, alkyl levulinates and GVL etc. Briefly, in terms of furfural synthesis, we tested different catalysts (heterogeneous bio-based SSP and homogenous heteropolyacid HAP) and starting materials (the main sugar unit of hemicellulose- D-xylose and abundant polysaccharide free of lignin-alginic acid) in batch microwave and continuous flow MW reaction regimes. For the applications of furfural, we compared furfural selectively hydrogenation in batch and continuous flow over various metals supported on activated carbon. Moreover, expeditious upgrading of furfuryl alcohol to alkyl levulinates was realized with commercial activated carbon. In all studies, the optimization of green production processes was focused on several key points: solvents, activation method, catalysts and reaction regime.

**Solvents.** For the production of furfural, subcritical water (100 °C < T < 374 °C, P < 22.1 MPa) was proved as a suitable medium for the hydrolysis and dehydration processes, however, a co-solvent was needed to limit side-reactions by extracting the target chemicals. According to previous studies of our group and the experimental results of this work, we confirmed that eco-friendly solvent cyclopentyl methyl ether (CPME) is very promising when acts as an extracting solvent. And methyl isobutyl ketone (MIBK) exhibited to be more suitable to protect furfural at high operating
temperature (> 200 °C). Interestingly, in monophasic system, a co-solvent GBL into DMSO also showed certainly improvement in furfural yield (more than 7 %).

For the conversion of furfural, the effect of solvent on furfural hydrogenation is especially obvious, as big difference in hydrogenation products was observed when changed protic solvent to non-protic ones. More interestingly, DMSO not only acts as an excellent solvent to dissolve catalyst and all reagents, but also participate into the cyanation of furfural which leading to the formation of 2-furonitrile, and only oxime produced without DMSO. In the study of FA alcoholyis, the alcohols showed a significant effect on alkyl levulinates yield, as they also performed as the reactant.

**Activation method.** Microwave irradiation was found to be a good alternative to conventional heating. Thanks to MW, we achieved more than 30 % of furfural yield in 1 minute using alginic acid as starting material, and got 78 % of methyl levulinate yield in 5 minutes over commercially available activated carbon.

**Catalysts.** During this PhD study, we were tried to develop greener catalysts (such as bio-based SSP and bio-char catalyst\(^1\) (not shown in this thesis)), and more efficient catalysts (UIO-66 collaborated with Weiyi et al.,\(^2\) Ni-W bimetallic catalysts, Zr-based catalyst for transfer hydrogenation which haven’t finished etc.). Some of them are quite efficiency, for example, SSP can be reused for ten consecutive reactions without a loss of activity.

**Reaction regime.** In parallel, as an alternative to batch reactions, continuous flow reactors, such as H-Cube Pro, Pheonix, Microwave continuous flow etc. were also tested. Generally, continuous flow reactions are more efficiency than batch reactions.
Take an example, furfural hydrogenation experiments were conducted for 5 h in batch, however, in continuous flow, the residence time of the reactant was only several minutes, which significantly improved the target compound productivity. Besides, the hydrogenation selectivity could be controlled by tuning the flow rate, and side reactions could be suppressed.\(^3\)

Benefit to the exploration of these key points, the advanced results obtained during this PhD study could be summarized as follows:

**Furfural synthesis:**

**MW batch**

\[
\text{Cat. (16 wt%), NaCl (1.5 mmol)} \\
\text{D-xylene} \\
\rightarrow \\
\text{Water-CPME (1:3, v/v)} \\
\text{MW, 190 °C, 40 min} \\
\text{FF yield: \~70 %}
\]

\[
\text{Alginic acid} \\
\rightarrow \\
\text{CuCl\textsubscript{2}} \\
\text{H\textsubscript{2}O-CPME (3:13, v/v)} \\
\text{220 °C, 1.5 min} \\
\text{FF yield: \~30 %}
\]

\[
\text{D-xylene} \\
\rightarrow \\
\text{H\textsubscript{2}PW\textsubscript{12}O\textsubscript{40}} \\
\text{DMSO-GBL (1:4, v/v)} \\
\text{MW, 179°C, 40 min} \\
\text{FF yield: \~70 %}
\]

**MW Continuous flow**

\[
\text{D-xylene} \\
\rightarrow \\
\text{H\textsubscript{2}PW\textsubscript{12}O\textsubscript{40}} \\
\text{DMSO-GBL (1:4, v/v)} \\
\text{MW, 160°C, 40 min} \\
\text{FF yield: \~65 %}
\]
It's worthy to note that in furfural hydrogenation experiments, Ni catalyst exhibited the best performance to produce MF in batch, but noble metal catalysts, such as Pt supported on activated carbon, gave better MF yield than Ni, and Pd/C has similar catalytic performance with Ni/C in continuous flow regime. If compared literatures with our experimental results of alginic acid to furfural or FA alcoholsysis to levulinates etc., one can find that our results will give a relatively higher target compound productivity, which is mainly attributed to the methodology applied in our experiments (MW, continuous flow etc.).

In spite of these promising results and advantages, several prospects can be suggested in order to continue the work undertaken in this PhD: a) additional research can be done to find alternative catalysts, preferably heterogeneous ones when using continuous flow. As shown, the catalysts we prepared have a poor stability, thus, finding an active, efficient and stable catalyst is still a challenge; b) From the view of economy, non-noble metal catalysts should be developed as lots of them have showed
comparable results with noble catalysts; c) Multi-step reactions should be tried by tandem of multifunctional catalysts in continuous flow; d) Microwave continuous flow reactors which could bear certain pressure, could be designed as a more efficient catalytic system.
References


Achievements during PhD study

Publications


continuous flow, ACS Sustainable Chemistry & Engineering, 2018, 6(8): 9831-9844.


**Oral communications**

1. Y. Wang, T. Len, Y. Huang, A. D. Tabaoda, A. N. Boa, C. Ceballos, F. Delbecq, G.


**Poster communications**


Scientific research

COST Action: FP1306 (20/03/2017-30/04/2017 worked in Spain)

STSM Applicant: Yantao Wang

Host: Rafael LUQUE, Universidad de Córdoba, Córdoba (Spain)

STSM Topic: Stability of the conversion and selectivity of monometallic Ni and bimetallic Ni-M catalysts in continuous flow hydrogenation of furfural to 2-methylfuran and in the hydrogenation of furonitrile to furfuryl amine and/or derivatives
EXPERIMENTAL PART

2.1 Sulfonated sporopollenin as an efficient and recyclable heterogeneous catalyst for dehydration of D-xylose and xylan into furfural

2.1.1 Reagents

Substrates were purchased from Acros Organic (D-xylose ≥ 99%, xylan from Beechwood ≥ 90%). Solvents were purchased from Acros (cyclopentyl methyl ether, ethanol, and acetone) and Fisher Scientific (acetonitrile). Furfural (99%) for use as a reference was obtained from Acros. All materials were used without further purification. The water used in all experiments was a Millipore Milli-Q grade.

2.1.2 Catalyst preparation and characterization

2.1.2.1 Preparation of sulfonated sporopollenin

Raw spores of *L. clavatum* (100 g) were added to acetone (450 mL) and stirred for 4 h at 60 °C. The mixture was filtered and the solid dried under a vacuum overnight. The solid was stirred and heated at 80 °C in aqueous 6 % KOH for 6 h. The KOH solution was refreshed and the mixture was heated for a further 6 h. The mixture was recovered by filtration and washed with deionized water (6 × 200 mL). After drying under vacuum overnight, the solid was heated at 80 °C in 700 mL of orthophosphoric acid (700 mL) for 8 days. The mixture was filtered and washed successively with hot
water (2 L), 2.5 M NaOH (2 × 125 mL), hot water (6 × 250 mL), phosphate buffered saline (2 × 125 mL), hot water (2 × 250 mL), ethanol (2 × 125 mL). The resulting exines were refluxed in 450 mL ethanol for 4 h, filtered and washed with ethanol (2 × 125 mL) and then acetone (2 × 125 mL). The solid was suspended in acetone (600 mL) and sonicated for 30 min, filtered and dried under vacuum overnight to afford the desired extracted sporopollenin microcapsules. A sample of this isolated material (2.0 g) was added to dry dichloromethane (150 mL). The solution was cooled in an ice bath and chlorosulfonic acid (4 mL) was added slowly. The mixture was stirred 4 h at room temperature. Then, the mixture was filtered, washed with dichloromethane (50 mL) and water (6 × 50 mL) and dried under reduced pressure. The sulfonated sporopollenin was treated with 2 M sodium hydroxide (50 mL) for 24 h at room temperature. The mixture was filtered and washed with water (2 × 50 mL). The solid was added to 2 M hydrochloric acid (50 mL) and stirred for 4 h. The mixture was then filtered, washed with water (2 × 50 mL) and kept under reduced pressure. The enhanced acidity of the material was measured as follow. A sample (0.1 g) was added to a conical flask with a solution of sodium bicarbonate (0.1 M, 20 mL) and stirred for 16 hours. After filtration through Celite®, the filtrate was collected then titrated against a solution of hydrochloric acid (0.1 M) using methyl orange as the indicator.

2.1.2.2 Preparation of sulfonated carbon

Miscanthus x giganteus was the source of biomass for the production of char by carbonization in the process of slow pyrolysis. This form of pyrolysis utilizes a long
vapor residence time in order to maximize char yields. Char was produced in tubular furnace at temperature of 600°C. To achieve anaerobic conditions, a nitrogen pressure of 1.6 atm was maintained in the reactor. Once the char were collected, they were ground and sieved between 180 and 600 µm and underwent sulfonation. In order to produce the catalytic acid materials, 20.0 g of char was placed in a 500 mL flask with 200 mL of concentrated (95-97 %) sulfuric acid. The mixtures were heated at 150°C for 24 h on magnetic hotplate stirrers, fitted with J-type PTFE coated thermocouples. The slurries were then filtered and washed several times with distilled water until the pH became neutral, and sulfonated char based catalyst (SCh) was obtained [23].

2.1.2.3 Catalyst characterization

Elemental analysis was performed using an EA-1108 CHNS Elemental Analyzer (Fisons). SEM (Scanning Electron Microscopy)-EDX (Energy Dispersive X-ray Diffraction) analysis of native and recovered sulfonated sporopollenin at different stage of the experiments was performed on a Quanta FEG 250 (FEI) equipped with a microanalysis detector for EDX (Brucker). SEM micrographs acquired in secondary electron mode were obtained at low vacuum, 15 kV of accelerating voltage with a 10 mm working distance. EDX spectra were collected at 30° angle, 15 kV accelerating voltage and 10 mm working distance. FTIR spectra were recorded on a Perkin-Elmer SPECTRUM 2000 FTIR instrument in the range of 400-3700 cm⁻¹. XPS measurements were performed in an ultra-high vacuum (UHV) multipurpose surface analysis system (SpecsTM model, Germany) operating at pressures of <10-10 mbar
using a conventional X-ray source (XR-50, Specs, Mg K, 1253.6 eV) in a « stop-and-go » mode to reduce potential damage due to sample irradiation. The survey and detailed Fe and Cu high-resolution spectra (pass energy 25 and 10 eV, step size 1 and 0.1 eV, respectively) were recorded at room temperature with a Phoibos 150-MCD energy analyser. Powdered samples were deposited on a sample holder using double-sided adhesive tape and subsequently evacuated under vacuum (<10-6 Torr) overnight. Eventually, the sample holder containing the degassed sample was transferred to the analysis chamber for XPS studies. A survey spectra were firstly recorded after which detailed element XPS (typically C, O and S) were recorded. Data were processed using the program Casa XPS.

XRD experiments were recorded on a PanAnalytic/Philips X'pert MRD diffractometer (40 kV, 30 mA) using Cu Kα (λ= 0.15418 nm) radiation. Scans were performed over a 2θ range from 10 to 80, at step size of 0.018° with a counting time per step of 5 s. Nitrogen adsorption measurements were carried out at 77 K using an ASAP 2000 volumetric adsorption analyzer from Micromeritics. The samples were outgassed for 24 h at 100 °C under vacuum (po 10-2 Pa) and subsequently analysed. The linear part of the BET equation (relative pressure between 0.05 and 0.30) was used for the determination of the specific surface area. Mean pore size diameter (DBJH) and pore volumes (VBJH) were obtained from porosimetry data.
2.1.3 Typical procedure for the production of furfural

2.1.3.1 General procedure for the synthesis of furfural in water-CPME as biphasic media from D-xylose or xylan

In a typical experiment, a 10 mL glass vessel was charged with water (1 mL), CPME (3 mL), D-xylose or xylan (150.0 mg, 1.0 mmol), sulfonated sporopollenin (SSP) (10 wt%) and 0-2.50 mmol of NaCl. The vessel was sealed with a septum, placed in the microwave apparatus (Anton Paar Monowave 300) and heated to the desired temperature under magnetic stirring (600 rpm) for the desired time. Temperature in the vessel was measured by means of an IR sensor. At the end of the reaction, the vessel was cooled down to 40 °C using compressed air. Then, the two phases were separated. The aqueous phase was diluted in 200 mL of distilled water and filtered prior to analysis through a filter paper (10-20 µm, VWR). The organic phase was diluted in 100 mL of acetonitrile and filtered prior to analysis through a syringe filter (PTFE, 0.45 µm, VWR). All experiments were repeated at least three times, and the deviation was lower than 5%.

An identical procedure was followed using 0.15 g of xylan in place of the xylose.

2.1.3.2 Products analysis

Each sample of the reaction mixture was analyzed separately by means of a Shimadzu Prominence HPLC. Xylose was detected with a low temperature evaporative light scattering detector (ELSD-LTII) and the products were detected with
a UV-Vis detector (SPD-M20A) at a wavelength of 275 nm. The column used was a Grace Prevail C18 column (250 x 4,6 mm 5 m). The mobile phase was MeOH-H$_2$O (9:1) solution flowing at rate of 0.5 mL.min$^{-1}$. The column oven was set at 40 °C. D-xylose conversion ($X$), furfural yield ($Y_i$) and furfural selectivity ($S_i$) were calculated by the following eq 1-3:

$$X = \frac{(\text{Initial xylose amount (mol)} - \text{Final xylose amount (mol)})}{\text{Initial xylose amount (mol)}} \times 100 \quad (1)$$

$$Y_i = \frac{\text{Final furfural amount (mol)}}{\text{Initial xylose amount (mol)}} \times 100 \quad (2)$$

$$S_i = \frac{\text{Furfural yield}}{\text{Conversion of xylose}} \times 100 \quad (3)$$

The calibration curve was checked regularly, in order to avoid eventual experimental errors associated with all measurements reported below.
2.2 Comprehensive study of an expeditious conversion of pre-hydrolyzed alginic acid to furfural in Cu(II) biphasic systems using microwaves

2.2.1 Reagents

Substrates (alginic acid >95% and glucuronic acid 98%) and the catalysts (CuCl₂, 
2H₂O, CuSO₄, Cu(NO₃)₂ and Cu(acac)₂ ≥ 99%) were purchased from Acros Organics. 
NaCl were obtained from Carlo Erba. Solvents were purchased from 
Acros(cyclopentylmethylene), Carlo Erba (dimethylsulfoxide) and Fisher Scientific 
(2-methyltetrahydrofuran, methylisobutylketone, tetrahydrofuran and acetonitrile ≥ 
99%). Standard (furfural 99%) was obtained from Acros. All materials were used 
without further purification. Distilled H₂O was used for preparation of all aqueous 
solutions.

2.2.2 Typical procedure for conversion of alginic acid into furfural

In a typical experiment, a 10-mL glass vessel was charged with water (0.75 mL), 
MIBK (3.25 mL), alginic acid or an oligomer rich fraction generated by incubation in 
an HCl solution (25.0 mg, 0.140 mmol in average based on hexuronic acid units), 
CuCl₂.H₂O (25.0 mg, 0.147 mmol). The vessel was sealed with a septum, placed in the 
MW cavity (AntonPaar Monowave 300) and heated at 220 °C for 1 min via a resonant 
single mode under magnetic stirring (600 rpm). The reaction temperature in the vessel 
was monitored by means of an IR sensor. At the end of the reaction, the vessel was
cooled down to 40 °C using compressed air. Then, the two phases were separated. The aqueous phase was diluted with 200 mL of distilled water and filtered prior to analysis through a filter paper (10–20 µm, VWR, Fontenay-sous-Bois, France). The organic phase was diluted with 200 mL of acetonitrile and filtered prior to analysis through a syringe filter (PTFE, 0.45 µm, VWR). All experiments were repeated at least three times, and the deviation was lower than 5%.

2.2.3 Biopolymer hydrolysis in large batch scale

The partial hydrolysis of alginic acid was conducted as follow: a solution of 0.25 wt % of the polyhexuronic acid was treated with an HCl aqueous solution. The pH was adjusted to 1.7 and the resulted solution was incubated at 95 °C for 20 hours. Then, an insoluble material was filtrated and the recovered filtrate was freeze-dried to afford a clear yellow solid.

2.2.4 Analytical method

Each sample of the reaction mixture was analyzed separately by means of Shimadzu Prominence HPLC. After reaction, the possible hexose and hexuronic traces were detected with a low temperature evaporative light scattering detector (ELSD-LTII) and the furfural concentration was quantified with a UV-Vis detector (SPD-H20A) at 280 nm; Grace C18 column (250x4.6 nm 5µm) was used. The mobile phase used was MeOH-H₂O (1:1) solution flowing at a rate of 0.5 mL.min⁻¹. The column oven was set at 40 °C. The calibration was regularly checked in order to avoid eventual experimental errors associated with all measurements reported below. Both
materials produced by acidic bath incubation of alginic acid were analyzed by $^1$H NMR or FT-IR. The $^1$H and $^{13}$C NMR spectra of freeze-dried water soluble hydrozylate were recorded in D$_2$O and DMSO-$d_6$ on a Bruker Avance 400 spectrometer. The insoluble fraction was only analyzed by FT-IR.
2.3 Microwave continuous production of furfural using heterogeneous H3PW12O40 under atmospheric pressure

2.3.1 Reagents

Substrates were purchased from Acros Organics (D-xylose≥99 %, hydroxylamine hydrochloride 97 %). Solvants were purchased from Acros (γ-butyrolactone ≥ 99 % GBL) and Carlo Erba (dimethyl sulfoxide ≥ 99 %). Furfural (99 %) and 2-furonitrile (99 %) for use as reference in HPLC were obtained from Acros. Heteropolyacid H₃PW₁₂O₄₀ (HPA) was obtained from Aldrich Chemical Co. All materials were used without further purification.

2.3.2 Catalytic reactions

2.3.2.1 General procedure for the synthesis of furfural from D-xylose in batch

D-Xylose (150 mg, 1.0 mmol) and H₃PW₁₂O₄₀ (0.06 g, 40 wt/ %) in a mixture of DMSO-GBL (5 mL, 1:4, v/v) were introduced in a vial (10 mL) closed with a septum. Dehydration were carried out by way of microwave heating apparatus (AntonPaar Monowave 300) and stirred under magnetic stirring (600 rpm) for 40 minutes at 170 °C. Temperature in the reaction vessel was measured by means of an IR sensor and the vial was pressurized due to the normal vapor pressure. At the end of the reaction, the sample was cooled down at 40 °C, diluted with acetonitrile (200 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45μm, VWR).
2.3.2.2 General procedure for the synthesis of furfural from D-xylose using a microwave flow device

An Erlenmeyer flask (250 mL) was charged with D-Xylose (9.0 g, 60 mmol) and \( \text{H}_3\text{PW}_{12}\text{O}_{40} \) (1.68 g, 19 wt%) in a mixture of DMSO-GBL (150 mL, 1:4, v/v). The mixture was stirred at room temperature for 5 minutes and was pumped at 0.25 mL min\(^{-1}\) (residence time 40 minutes) in a microwave reactor (Sayrem Miniflow 200 SS, 200 W, 2450 MHz) at 150 °C. Temperature in the reaction vessel was measured by means of an IR sensor at atmospheric pressure. The effluent from the reactor was condensed at room temperature in a separator, diluted with acetonitrile (200 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR).

2.3.3 Products analysis

All product concentrations were monitored by HPLC for each sample. The column used was a GRACE Prevail C18. The detectors used are a SPD-M20A photodiode array detector (Shimadzu) and an ELSD-LTII (Shimadzu). The mobile phase is a mixture of water and MeOH (1:9, v/v) for the analysis of furfural and furonitrile and a mixture of water and MeOH (1:1, v/v) for the analysis of the sugar. The concentration of reactants and products were calculated based on calibration curves obtained from commercial standards. D-Xylose conversion (\( X_i \)), furfural yield (\( Y_i \)) and furfural selectivity (\( S_i \)) were calculated by the following equations:

\[
X_i = \frac{(\text{Initial xylose amount (mol)} - \text{final xylose amount (mol)})}{\text{Initial xylose amount (mol)}}
\]
\[ Y_i = \frac{\text{Final furfural amount (mol)}}{\text{Initial furfural amount (mol)}} \]

\[ S_i = \frac{Y_i \times 100 \, (\%)}{X_i} \]
4.1 A two-steps microwave assisted continuous flow Process for direct conversion of xylose into 2-furonitrile

4.1.1 Reagents

Substrates were purchased from Acros Organics (D-xylose $\geq 99\%$, hydroxylamine hydrochloride 97 %). Solvants were purchased from Acros ($\gamma$-butyrolactone $\geq 99\%$ GBL) and Carlo Erba (dimethyl sulfoxide $\geq 99\%$). Furfural (99 %) and 2-furonitrile (99 %) for use as reference in HPLC were obtained from Acros. Heteropolyacid $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPA) was obtained from Aldrich Chemical Co. All materials were used without further purification.

4.1.2 Catalytic reactions

4.1.2.1 General procedure for the synthesis of 2-furonitrile from furfural in batch

Furfural (96 mg, 1.0 mmol) and NH$_2$OH.HCl (86 mg, 1.23 mmol)) in a mixture of DMSO-GBL (5 mL, 2:3, v/v) were introduced in a vial (10 mL) closed with a septum. Dehydration were carried out by way of microwave heating apparatus (AntonPaar Monowave 300) and stirred under magnetic stirring (600 rpm) for 20 minutes at 100 °C. Temperature in the reaction vessel was measured by means of an IR sensor and the vial was pressurized due to the normal vapor pressure. At the end of the reaction, the sample was cooled down at 40 °C, diluted with acetonitrile (100 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45μm, VWR).
4.1.2.2 General procedure for the synthesis of 2-furonitrile from D-xylose using two successive microwave flow devices

An Erlenmeyer flask (250 mL) was charged with D-Xylose (9.0 g, 60 mmol) and H3PW12O40 (1.68 g, 19 wt/%) in a mixture of DMSO-GBL (150 mL, 1:4, v/v). The mixture was stirred at room temperature for 5 minutes and was pumped at 0.25 mL min-1 in a microwave reactor (Sayrem Miniflow 200 SS, 200 W, 2450 MHz) (residence time 40 minutes) at 150 °C. Temperature in the reaction vessel was measured by means of an IR sensor at atmospheric pressure. A solution of NH2OH.HCl (2.02 g, 29.3 mmol) in a mixture of DMSO-GBL (100 mL, 1:4, v/v) was loaded in the process with a second pump at 0.25 mL min-1 and the resulting flow stream went through the second microwave reactor (Sayrem Miniflow 200 SS, 200 W, 2450 MHz) (residence time 40 minutes) at 100 °C. The effluent from the reactor was condensed at room temperature in a separator, diluted with acetonitrile (200 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR).

4.1.2.3 General procedure for the synthesis of furfural from D-xylose using a microwave flow device

An Erlenmeyer flask (250 mL) was charged with D-Xylose (9.0 g, 60 mmol) and H3PW12O40 (1.68 g, 19 wt/%) in a mixture of DMSO-GBL (150 mL, 1:4, v/v). The mixture was stirred at room temperature for 5 minutes and was pumped at 0.25 mL min-1 (residence time 40 minutes) in a microwave reactor (Sayrem Miniflow 200 SS, 200 W, 2450 MHz) at 150 °C. Temperature in the reaction vessel was measured by
means of an IR sensor at atmospheric pressure. The effluent from the reactor was condensed at room temperature in a separator, diluted with acetonitrile (200 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR).

4.1.3 Products analysis

All product concentrations were monitored by HPLC for each sample. The column used was a GRACE Prevail C18. The detectors used are a SPD-M20A photodiode array detector (Shimadzu) and an ELSD-LTII (Shimadzu). The mobile phase is a mixture of water and MeOH (1:9, v/v) for the analysis of furfural and furonitrile and a mixture of water and MeOH (1:1, v/v) for the analysis of the sugar. The concentration of reactants and products were calculated based on calibration curves obtained from commercial standards. D-Xylose conversion ($X_i$), furfural yield ($Y_i$) and furfural selectivity ($S_i$) were calculated by the following equations:

$$X_i = \frac{\text{Initial xylose amount (mol)} - \text{final xylose amount (mol)}}{\text{Initial xylose amount (mol)}}$$

$$Y_i = \frac{\text{Final furfural amount (mol)}}{\text{Initial furfural amount (mol)}}$$

$$S_i = \frac{Y_i \times 100}{X_i}$$

Similar equations were employed for determination of furfural conversion, furonitrile yield and selectivity.
4.2 On the catalytic performance of carbon supported metal catalysts for liquid phase furfural hydrogenation: batch vs. continuous flow

4.2.1 Reagents

Furfural (99 % purity), furfuryl alcohol (FA, 98 % purity), 2-methylfuran (MF, 99 % purity), tetrahydrofurfuryl alcohol (THFA, 99 % purity), 2-methyltetrahydrofuran (MTHF, 99 % purity), tetrahydrofuran (THF, 99.5 % purity), 1,4-pentanediol (PD, 99 % purity) and n-octane (99 % purity) were purchased from Sigma-Aldrich and further used without purification. The metal precursor salts were purchased from Alfa Aesar (H2PtCl6.xH2O), Strem (PdCl2 and Ni(NO3)2.6H2O), Merck (CuCl2.2H2O), and Fluka (H26N6O40W12.xH2O). The commercial carbon SX-Plus was purchased from Norit®.

4.2.2 Catalyst synthesis and characterization.

The 10%Cu/AC, 5% Ni/AC, 10%Ni/AC, 5%Ni-15%W/AC, 10%Ni-15%W/AC, 3%Pd/AC and 3%Pt/AC catalysts were prepared by the classic wet impregnation method. First, Norit® SX-Plus carbon was activated via thermal treatment at 500 °C under N2 flow for 3 h (activated carbon, AC). In a typical preparation procedure, the required amount of the metal salt precursor (CuCl2.2H2O, Ni(NO3)2.6H2O, H26N6O40W12.xH2O, PdCl2 and H2PtCl6.xH2O), was dissolved in 20 mL of deionized water and the solution was added dropwise to a suspension of 10 g AC in
100 mL water under stirring (300 rpm). Stirring was kept for 1 h before the water was removed in a rotary evaporator. The resulting catalysts were dried overnight at 100 °C and were then calcined in air followed by calcination at 500 °C for 3 h under He flow (50 mL min.-1), followed by treatment at 350 °C (Pt), 400 °C (Pd) and 450 °C (Cu, Ni and Ni-W) for 3 h under H2 flow (50 mL min.-1). The catalysts were characterized by X-ray Diffraction (XRD) and N2 porosimetry ity analysis (see Supporting Information). The crystal size of the metal nanoparticles was estimated by the Scherrer equation based on the characteristic peaks (2θ) at 43.3° for Cu(0) and 36.3° for Cu2O, 40.1° for Pd(0), 39.7° for Pt(0), 44.3° for Ni(0) and 43.2° for NiO, 26.1° for WO2 and 31.1° for NiWO4. Fresh and spent 5%Ni/AC and 5%Ni-15%W/AC catalysts were also analyzed by X-ray Photo-emission Spectrometry (XPS). The metal content of the same set of samples was determined via inductively coupled plasma optical emission mass spectrometry (ICP-MS, Perkin Elmer, NexION 350X) using the corresponding acid digests. Acid digestions were performed with nitric acid in individual N2 pressurized (40 bar) reaction chambers in microwave equipment (Milestone, UltraWave), with the temperature raising during 25 min. until reaching 220 °C, which was hold during 15 min. The total digestion time was 50 min. and the final HNO3 concentration was 2 %. Finally, a set of spent catalysts also characterized for comparison.

4.2.3 Procedure for batch hydrogenation experiments

The experiments in batch were carried out in a stainless steel autoclave with
magnetic stirring (800 rpm), using 25 mmol furfural/furfuryl alcohol, 12 mmol n-octane (external standard, ES) and 300 mg catalyst in 60 mL solvent. This amount of catalyst (10%Cu, 10%Ni, 5%Ni, 3%Pd and 3%Pt) corresponds with a theoretical metal catalyst content of 1.9, 2.0, 1.0, 0.3 and 0.2 mol%, respectively. The hydrogenation experiments were performed with 30 bar molecular hydrogen (H2) or with isopropanol (i-PrOH) as the hydrogen donor (without H2). Further details are available in the Supporting Information (Figure S4.2.3). All results are expressed in molar percentages.

4.2.4 Procedure for continuous flow experiments using molecular hydrogen as the hydrogen donor

The experiments with H2 were carried out in a H-Cube Pro Flow Reactor (ThalesNanoTM, Hungary), which supplied a continuous H2 gas flow produced from the electrolysis of water to the central reactor module in which a 30 or 70 mm CatCart was installed, packed with 120 or 280 mg catalyst, respectively. The total flow through volume (including feed, reactor and product sections) for the 30 and 70 mm installed CatCarts were 5.0 and 5.5 mL, respectively. First, pure solvent was pumped through the system before reaching the set temperature (130-150 °C) and pressurization (0-50 bar). Once the reaction conditions were settled, the pure solvent feed was changed to the furfural/furfuryl alcohol feedstock (0.1-0.2 M). Then, in function of the flow rate (0.1-0.5 mL min.-1), the reaction proceeded during a certain time (20-100 min.) before collecting the first sample (time zero). More product
samples were collected in regular time intervals. More details are available in the Supporting Information (Figure S4.2.4). All results are expressed in molar percentages.

**Procedure for continuous flow experiments using isopropanol as the hydrogen donor.**

The experiments using i-PrOH as the hydrogen donor (without H2) were conducted in a high-temperature high-pressure Phoenix Flow Reactor (ThalesNanoTM, Hungary), connected to a HPLC pump to supply a continuous feed of a 0.1-0.2 M furfural feedstock in i-PrOH. A 30 mm CatCart cartridge was packed with 100 mg catalyst and placed in the reactor module. The total flow through volume (including feed, reactor and product sections) was ca. 14 mL. First pure i-PrOH was pumped through the system and then the feed was changed to the furfural feedstock. The initial zero time was set when the temperature (200-260 °C) and pressurization (0-70 bar) of the reactor module were reached. Then, in function of the flow rate (0.1-0.4 mL min.-1), the reaction proceeded during a certain time (20-80 min.) before collecting the first sample (time zero). Further samples were collected after regular time intervals (20-40 min.). Further details are available in the Supporting Information (Figure S4.2.5). All results are expressed in molar percentages.

**4.2.5 Products analysis**

For the batch experiments, after dropping the autoclave temperature below 35 °C and after depressurization, while keeping the mixture stirred, the lid was opened and 2
mL of the product was filtered over a 0.22 µm syringe filter and analysed by GC-FID. For the continuous flow experiments, samples were directly taken from the different product fractions (1 mL in all experiments) produced in time and subsequently analysed by GC-FID. Further details on product analysis, including calibration of furfural and all the products, are available in the Supporting Information (Figures S4.2.6 and S4.2.7).
4.3 Microwave-assisted catalytic upgrading of bio-based furfuryl alcohol to alkyl levulinate over commercial activated carbon

4.3.1 Reagents

Furfuryl alcohol (≥ 98 %), methanol (≥ 99.9 %), ethanol (≥ 99.5%), n-propanol (≥ 99.5%), iso-propanol (≥ 99.5%), n-butanol (≥ 99.5%), methyl levulinate (99 %), n-decane (≥ 99 %) were purchased from Sigma-Aldrich and further used without purification. The catalysts HY5.2, HY60, HZSM-5-30 and HZSM-5-50 were purchased from Zeolytes International (USA). The zeolite materials were calcined at 600 °C during 24 h prior to use. Activated carbon (Charcoal activated power, technical grade) was purchased from Panreac (Spain), and sulfonated carbon was prepared according to literature.422

4.3.2 Catalytic reaction

In a typical experiment, 3 ml 0.2 M FA feedstock solution and 100 mg AC were introduced in a 10 mL vial closed with a septum. 2 min ramping time was settled to reach desired reaction temperature. All of the experiments were performed in a microwave reactor (CEM discover) and stirred under magnetic stirring (600 rpm) for the desired time. The reaction temperature was measured by means of IR sensor. At the end of the reaction, the solution was filtered prior to analysis through a syringe filter (PTFE, 0.22 µm, VWR).
4.3.3 Product analysis

First, calibration curves for furfuryl alcohol (FA) and methyl levulinate were determined in the 0–100 mg mL⁻¹ range, using n-decane (5.0 mg mL⁻¹) as the internal standard (Figure S1). The GC-FID analyses were performed on a gas chromatograph (HP, 14009 Arcade, New York, United States) coupled with a FID detector equipped with a Supelco 2-8047-U (60 m x 25 m x 25 μm, Alltech Part No.31163-01). N₂ was used as carrier gas at a rate of 1 mL min⁻¹. The samples were injected directly onto the column using septum-equipped programmable injector (SPI) system. The temperature of the injector was set 250 °C and the oven started at 80 °C, held for 5 min., raised to 100°C at a rate of 10°C min⁻¹, held for 5 min and then raised to 120°C at a rate of 10°C min⁻¹ and held for 10 min at 120 °C. The ionisation mode was FID (70 eV, 300 μA, 250 °C). The identification of the compounds was performed by comparison of the retention times with pure standards.

The yield of alkyl levulinates (ALs) were calculated on the basis of the following equation:

\[
\text{Conversion } \text{FA (mol\%)} = \frac{[\text{MolFA}_{\text{initial}} - \text{MolFA}_{\text{final}}]}{\text{MolFA}_{\text{initial}}} \times 100
\]

\[
\text{Yield AL (mol\%)} = \frac{[\text{MolAL}]}{\text{MolFA}_{\text{initial}}} \times 100
\]
SUPPORTING INFORMATION

2.1 Sulfonated Sporopollenin as an Efficient and Recyclable Heterogeneous Catalyst for Dehydration of D-Xylose and Xylan into Furfural

Figure S2.1.1 SEM observation of a: native sporopollenin and b: sulfonated sporopollenin.

Figure S2.1.2 FT-IR spectrum of a: native sporopollenin and b: sulfonated sporopollenin (SSP).
Figure S2.1.3 SEM picture of SSP recovered by humin after reaction in presence of 1.5 mmol of NaCl.

Figure S2.1.4 XRD spectrums of a:native sporopollenin and b: sulfonated sporopollenin.
2.2 Comprehensive study of anon expeditious conversion of pre-hydrolyzed alginic acid to furfural in Cu(II) biphasic systems using microwaves

Table S2.2.1 Investigations for finding the optimum conditions for transformation of glucuronic acid to furfural in water-CPME biphasic system under MW irradiation.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Gluronic acid/g</th>
<th>FeCl3/g</th>
<th>Water/CPME</th>
<th>Temperature/°C</th>
<th>Time/min</th>
<th>Yield/Furfural/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TT110</td>
<td>0.2</td>
<td>0.05</td>
<td>1/5</td>
<td>280</td>
<td>10</td>
<td>18.45</td>
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<tr>
<td>TT114</td>
<td>0.2</td>
<td>0.05</td>
<td>1/5</td>
<td>190</td>
<td>6</td>
<td>18.01</td>
</tr>
<tr>
<td>TT115</td>
<td>0.2</td>
<td>0.05</td>
<td>1/5</td>
<td>190</td>
<td>10</td>
<td>18.04</td>
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<tr>
<td>TT116</td>
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<td>0.05</td>
<td>1/5</td>
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<td>18.07</td>
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<tr>
<td>TT117</td>
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<td>9.90</td>
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<tr>
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<td>1/5</td>
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<td>11.28</td>
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<td>0.05</td>
<td>1/5</td>
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<td>60</td>
<td>18.98</td>
</tr>
<tr>
<td>Error</td>
<td></td>
<td></td>
<td>1/5</td>
<td>330 ±2°C, 190 ±4°C</td>
<td>30</td>
<td>11.28</td>
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</table>

Table S2.2.2: Investigations for finding the optimum conditions for transformation of glucuronic acid to furfural in water-CPME biphasic system under MW irradiation.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Gluronic acid/g</th>
<th>FeCl3/g</th>
<th>Water/CPME</th>
<th>Temperature/°C</th>
<th>Time/min</th>
<th>Furfural yield/%</th>
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<tr>
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<td>0.05</td>
<td>1/5</td>
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<tr>
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<td>0.05</td>
<td>1/5</td>
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<tr>
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<td>0.2</td>
<td>0.05</td>
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<td>1/5</td>
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<td>1/5</td>
<td>200</td>
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<tr>
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<td>0.05</td>
<td>1/5</td>
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<tr>
<td>Error</td>
<td></td>
<td></td>
<td>1/5</td>
<td>330 ±2°C, 190 ±4°C</td>
<td>30</td>
<td>11.28</td>
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Figure S2.2.1 Various reaction profiles for alginic acid conversion into furfural in 4.0 mL of organic solvent (3:13, v/v), MW, 220°C in CPME and MIBK, 210°C in MeTHF: a) 0.05 g of alginic acid, 0.025 g of CuCl$_2$; b) 0.05 g of alginic acid, 0.0125 g of CuCl$_2$; c) 0.025 g of alginic acid, 0.025 g of CuCl$_2$; c) 0.075 g of alginic acid, 0.025 g of CuCl$_2$. 

CuCl$_2$. 

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Figure S2.2.2 Chromatogram of aqueous layer containing released uronic acids and pentoses in water. Reaction condition: 0.075 g of alginic acid, 0.025 g of CuCl$_2$, 4.0 mL of water-CPME (3:13, v/v), 1.5 min, 220 °C, MW.

Figure S2.2.3 HPLC chromatogram of aqueous phase: by-products produced during alginic acid conversion into furfural; reaction condition: 0.025 g of alginic acid, 0.025 g of CuCl$_2$, 4.0 mL of water-MIBK (3:13, v/v), 1.0 min,
by-products produced during alginic acid conversion into furfural; reaction condition: 0.1 g of alginic acid, 0.1 g of CuCl₂, 16.0 mL of water-MIBK (3:13, v/v), 1.0 min, 220 °C, MW.
Figure S2.2.5 a) and b) $^1$H NMR spectra of soluble oligomers of alginic acid in D$_2$O and DMSO-d$_6$ respectively; c) $^{13}$C NMR of soluble oligomers in DMSO-d$_6$; d) and e) are FT-IR spectra of soluble and insoluble fractions of hydrolyzed alginic acid.
2.3 Microwave continuous production of furfural using heterogeneous H$_3$PW$_{12}$O$_{40}$ under atmospheric pressure

Table S2.3.1 Effect of temperature and time on furfural yield$^a$

<table>
<thead>
<tr>
<th>Entry</th>
<th>T(°C)</th>
<th>T(min)</th>
<th>Xylose con. (%)</th>
<th>FF yield (%)</th>
<th>FF sele (%)</th>
</tr>
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<td>80</td>
<td>35</td>
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<td>9</td>
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<td>13$^b$</td>
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<td>180</td>
<td>20</td>
<td>97</td>
<td>66</td>
<td>68</td>
</tr>
</tbody>
</table>

Reaction conditions: $^a$0.15 g D-xylose, HAP 0.056g, DMSO/GBL=1/4 (ml/ml, v/v); $^b$ 0.05 g D-xylose, HAP 0.084g, DMSO/GBL=1/4 (ml/ml, v/v).
4.1 A two-steps microwave assisted continuous flow Process for direct conversion of xylose into 2-furonitrile

Figure S4.1.1 2-furonitrile production in different solvents.

Figure S4.1.2 $^{13}$C and $^1$H NMR spectra of the products: furonitrile produced in GBL (a and b) and furan-2-carbaldehyde obtained in DMSO (c and d).
Figure S4.1.3 2-furonitrile production at different temperature.
4.2 On the catalytic performance of carbon supported metal catalysts for liquid phase furfural hydrogenation: batch vs. continuous flow

![Graph of nitrogen adsorption-desorption isotherms](image)

Figure S4.2.1 $N_2$ adsorption-desorption isotherms of the parent calcined activated carbon (AC) and the supported mono- and bi-metallic catalysts.

**XRD analysis**

Powder XRD experiments were conducted on a Shimadzu X-ray 7000 diffractometer using a CuKα X-ray radiation operating at 45 kV and 100 mA; counts were accumulated in the range of 5-75° with 0.02° steps (20) with counting time 2 s per step. Figure S2 shows the spectra of the fresh catalysts.
Figure S4.2.2 XRD patterns of the supported mono- and bi-metallic catalysts (after treatment at 500 °C in He followed by reduction with H₂ at 350-450 °C depending on the catalyst, as described in the experimental section). Symbols indicate the respective crystalline phase: (*) for Ni(0) and (●) for NiO, (■) for Cu(0) and (□) for Cu₂O, (●) for Pt(0), (○) for Pd(0), (▲) for WO₂, and (∆) for NiWO₄.

**XPS**

The XPS measurements were carried out with a Phi Quantera Scanning X-ray Microprobe instrument using Al Kα (h∙ν=1486.7 eV) radiation at Chevron Energy Technology Company in Richmond (CA), USA. The instrument is equipped with a hemispherical energy analyzer with multichannel detection and an energy resolution of 1.1 eV. The catalysts were mounted on double-sticky tape confining an area of approximately 0.8 cm x 0.8 cm. The tape was completely covered by the catalyst powder and the sample surface was carefully smoothed. Spectra were collected for C-1s, O-1s, Ni-2p3 and W-4f photoelectron peaks. Total spectral accumulation times were 100 minutes per analysis area while irradiating with 100 W of X-ray irradiation. The binding energies (BE) were referenced to the C-1s peak (284.8 eV) to account for charging effects. The XPS spectra were deconvoluted using Gaussian/Lorentzian shaped curves and an iterative least
square algorithm provided in Phi Multipak software. The peak areas were computed according to the fitting
to quantify the W and Ni species contents.

**Batch hydrogenation experiments**

All the experiments were carried out in a 100 mL stainless steel autoclave equipped with a thermocouple and
magnetic stirring (800 rpm), as illustrated in Figure S4.2.3. First, 300 mg of catalyst was added, followed by
25 mmol furfural and 12 mmol n-octane (internal standard IS) were dissolved in 60 mL i-PrOH. After 3 times
purging, 30 bar of H₂ was added. The reaction mixture was stirred and heated to 200 °C (ca. 60 bar). The
target temperature was reached after ca. 45 min. at which time was set to zero. Additional experiments were
carried out without the addition of H₂, both at 200 °C (30 bar) and 260 °C (92 bar). After the reaction, the
stirring was stopped and the autoclave was cooled in an ice-batch until reaching a temperature below 35 °C.

The residual pressure was read off before releasing the remaining gas and opening the autoclave lit.

![Figure S4.2.3 Schematic illustration of the batch hydrogenation experiments.](image-url)
Continuous flow experiments using molecular hydrogen as the hydrogen donor

Continuous flow experiments using molecular hydrogen gas (H₂) as the hydrogen donor were carried out in a H-Cube Pro Flow Reactor (ThalesNano™, Hungary, Figure S4.2.4), which supplied a continuous H₂ flow produced from the electrolysis of water to the central reactor module in which a 30 or 70 mm CatCart was installed, packed with ca. 120 and 280 mg catalyst, corresponding with reactor volumes of 0.38 and 0.88 mL, respectively. The corresponding reactor volumes packed with catalyst were 0.21 and 0.48 mL, respectively. The corresponding total flow through volumes (including feed lines, reactor and product lines) were 5.0 and 5.5 mL, respectively. Full hydrogen mode was used, which corresponds to a hydrogen production capacity reaching 60 mL min⁻¹ in the H-Cube Pro. A filter was installed in the entrance of the pump to avoid undissolved compounds entering the system. First, pure solvent was pumped through the system before reaching the set temperature (130-150 °C) and pressurization (0-50 bar). Once the reaction conditions were stable, the pure solvent feed was changed to the furfural feedstock. Then, in function of the flow rate (0.1-0.5 mL min⁻¹), the reaction proceeded during a certain time (20-100 min.) before collecting the first sample (time zero). Further samples were collected after regular time intervals (20-40 min.).
Figure S4.2.4 Illustration of the ThalesNano™ H-Cube Pro equipment for continuous flow hydrogenation experiments using H₂ as the hydrogen donor.

**Continuous flow experiments using isopropanol as the hydrogen donor**

The experiments in i-PrOH (without H₂) were conducted in a high-temperature high-pressure Phoenix Flow Reactor (ThalesNano™, Hungary, Figure S4.2.5), connected to a HPLC pump to supply a continuous feed of a 0.1-0.2 M furfural feedstock in i-PrOH. A 30 mm CatCart cartridge was packed with 100 mg catalyst and placed in the reactor module. The total flow through volume (including feed, reactor and product sections) was ca. 14 mL. First pure i-PrOH was pumped through the system and then the feed was changed to the furfural feedstock. The flow was continued until the temperature (200-260 °C) and pressurization (0-70 bar) of the reactor module were reached. Then, in function of the flow rate (0.1-0.4 mL min⁻¹), the reaction proceeded during a certain time (20-80 min.) before collecting the first sample (time zero). Further samples were collected after regular time intervals (20-40 min.).

Figure S4.2.5 Illustration of the ThalesNano™ Phoenix equipment for continuous flow hydrogenation experiments using i-PrOH as the hydrogen donor.
Product analysis

The furfural (F) conversion and the selectivity and the yield of each hydrogenation product (P) in batch experiments were calculated as the following:

\[
Conversion_F (\text{mol\%}) = \frac{[\text{Mol}_F^{\text{Initial}} - \text{Mol}_F^{\text{Final}}]}{\text{Mol}_F^{\text{Initial}}} \times 100
\]

\[
Yield_P (\text{mol\%}) = \frac{\text{Mol}_P}{\text{Mol}_F^{\text{Initial}}} \times 100
\]

\[
Selectivity (\%) = \frac{Yield_P}{Conversion_F} \times 100
\]

The amount of moles was calculated from the corresponding concentration (mg mL\(^{-1}\)), the molecular weight of F and P and the reaction volume in batch experiments (64 mL).

The furfural (F) conversion and the selectivity and the yield of each hydrogenation product (P) in continuous flow experiments were calculated as the following:

\[
Conversion_F (\text{mol\%}) = \frac{[\text{CF}_F^{\text{Initial}} - \text{CF}_F^{\text{Final}}]}{\text{CF}_F^{\text{Initial}}} \times 100
\]

\[
Yield_P (\text{mol\%}) = \frac{\text{CP}}{\text{CF}_F^{\text{Initial}}} \times 100
\]

\[
Selectivity (\%) = \frac{Yield_P}{Conversion_F} \times 100
\]

CF and CP are the concentrations of furfural and hydrogenation product (mol mL\(^{-1}\)). We have assumed that the total volume in the flow experiments kept constant (no evaporation loss).

The concentrations of furfural and hydrogenation products were determined by GC-FID. The experiments in batch and continuous flow using H\(_2\) as the hydrogen donor (H-Cube Pro Flow Reactor) were carried out at Université de Technologie de Compiègne (UTC, France), while the continuous flow experiments using
\( i\text{-PrOH} \) as the hydrogen donor were carried out at Universidad de Cordoba (UCO, Spain). The GC-FID analysis equipment were therefore different and are described in the following paragraph.

a) GC-FID: batch experiments and continuous flow experiments using \( \text{H}_2 \) (H-Cube Pro Flow Reactor)

First, calibration curves for furfural, furfuryl alcohol (FA), tetrahydrofurfuryl alcohol THFA, 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF) were determined in the 0–25 mg mL\(^{-1}\) range, using \( n \)-octane (8.1 mg mL\(^{-1}\)) as the internal standard (Figure S4.2.6). The GC-FID analyses were performed on a AutoSystem XL gas chromatograph (PerkinElmer, Norwalk, CT 06859, United States) coupled with a FID detector equipped with a AT™-1HT GC CAPILLARY COLUMNS (30m × 0.25mm i.d. and 0.1 μm film thickness; Alltech Part No.16368). \( \text{N}_2 \) was used as carrier gas at a rate of 1 mL min\(^{-1}\). The samples were injected with an auto-injector directly onto the column using septum-equipped programmable injector (SPI) system in split mode (20.8:1 ratio). The temperature of the injector was set 350 °C and the oven started at 50 °C, held for 6 min., raised to 130°C at a rate of 10°C min\(^{-1}\) and then raised to 250°C at a rate of 30°C min\(^{-1}\) and held for 2 min. at 250 °C. The ionisation mode was FID (70 eV, 300 μA, 300 °C). The identification of the compounds was performed by comparison of the retention times with pure standards.
Figure S4.2.6 GC-FID calibration curves of a) furfural, b) FA, c) MF, d) MTHF and e) THFA for GC-FID analysis of the hydrogenation products obtained in batch experiments and in continuous flow experiments using H₂ (H-Cube Pro Flow Reactor).

b) GC-FID: continuous flow experiments without H₂ (Phoenix Flow Reactor)

First, calibration curves for furfural, furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF) were determined in the 0–40 mg mL⁻¹ range, using n-octane (3.0 mg mL⁻¹) as the internal standard (Figure S4.2.7). The GC-FID analyses were performed on a gas chromatograph (HP, 14009 Arcade, New York, United States) coupled with a FID detector equipped with a Supelco 2-8047-U capillary column (60 m x 25 m x 25 µm, Alltech Part No.31163-01). N₂ was used as carrier gas at a rate of 1 mL min⁻¹. The temperature of the injector was set 250 °C and the oven started at
80 °C, held for 5 min., raised to 100°C at a rate of 10°C min.\(^{-1}\), held for 5 min. and then raised to 120°C at a rate of 10°C min.\(^{-1}\) and held for 10 min. at 120 °C. The ionisation mode was FID (70 eV, 300 μA, 250 °C).

The identification of the compounds was performed by comparison of the retention times with pure standards.

Figure S4.2.7 GC-FID calibration curves of a) furfural, b) FA, c) MF, d) MTHF and e) THFA for GC-FID analysis of the hydrogenation products obtained in continuous flow experiments using \(i\)-PrOH as the hydrogen donor (Phoenix Flow Reactor).
Figure S4.2.8 GC-FID chromatograms of the hydrogenation products collected after 0 min. in continuous flow experiments with H₂ (H-Cube) and 120 mg 5 % Ni/AC at 150 °C, 50 bar, 0.2 mL min⁻¹ using 0.2 M furfural in (a) i-PrOH, (b) EtOH, (c) ethyl acetate, (d) methyl isobutyl ketone and (e) cyclopentyl methyl ether.
4.3 Microwave-assisted catalytic upgrading of bio-based furfuryl alcohol to alkyl levulinate over commercial activated carbon

Figure S4.3.1 GC and GC-MS chromatography for possible intermediates