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Hydrogenation of furfural to 2-methylfuran with carbon catalysts

Relatore: **Luca Lietti**
Correlatore: **Juha Lehtonen**

Tesi di Laurea Magistrale di:
Sara Castellazzi
Matr. **817321**

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ABSTRACT

2-methylfuran (2-MF) production through liquid-phase catalytic hydrogenation of furfural using 2-propanol as solvent was investigated over carbon-supported catalysts in a batch reactor. Acceptable values of 2-MF yields and selectivity were achieved using impregnated catalysts supported over activated carbon Norit® RB4C. The best results were observed using 2%/2% CuFe catalysts after 5 hours reaction time at 230°C: 42.8% yield and selectivity. Nevertheless, with some nickel-based catalysts, such as 2% and 10% Ni, almost 33% and 41% yields of 2-MF were achieved, respectively. An important outcome was that copper catalysts, historically the best catalysts suitable for 2-MF production, showed better results when used in combination with other metals, such as Fe or Ni. Moreover, it is advisable to reduce Cu before the reaction at lower temperature (~200°C) in order to improve catalytic performances. Other types of support (i.e. acid-washed Norit® RX3) and preparation techniques (i.e. atomic layer deposition) were tested, showing poor results.

ESTRATTO IN LINGUA ITALIANA

La presente tesi di Laurea Magistrale concerne la produzione del 2-metilfurano (2-MF) attraverso l'idrogenazione catalitica in fase liquida del furfurolo, condotta all'interno di un reattore batch usando 2-propanolo come solvente. A tale scopo sono inoltre stati utilizzati vari catalizzatori supportati su carboni attivi. Sono stati ottenuti buoni valori di resa e selettività in 2-MF usando catalizzatori supportati su carboni attivi Norit® RB4C preparati attraverso la tecnica dell'impregnazione. In particolare, i migliori risultati sono stati osservati con 2%/2% CuFe con una reazione condotta a 230°C per 5 ore: circa 43% sia in resa che in selettività. Tra i migliori catalizzatori si annoverano inoltre quelli a base di nickel, in particolare 2% e 10% Ni, con cui sono stati raggiunti valori di resa in 2-MF di circa 33% e 41%, rispettivamente. Un'importante scoperta riguarda i catalizzatori a base di rame, storicamente i più attivi nella produzione di 2-MF: infatti essi hanno manifestato i risultati migliori quando utilizzati in formulazioni bi-metalliche (tipo CuFe o CuNi). Tutti i catalizzatori sono stati ridotti *in situ* prima della reazione, generalmente a 250°C; quando presente il rame, è però preferibile condurre tale trattamento intorno ai 200°C, in modo da ottenere una migliore performance catalitica. Lo screening dei catalizzatori ha coinvolto anche un diverso tipo di supporto (carboni attivi Norit® RX3, pretrattati con lavaggio acido) e una diversa tecnica di preparazione (i.e. atomic layer deposition, ALD), che tuttavia hanno prodotto risultati piuttosto scarsi.

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FROM FURFURAL TO 2-METHYLFURAN

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List of abbreviation

2-MF: 2-methylfuran;
5-MF: 5-methylfuran;
2-MTHF: 2-methyltetrahydrofuran;
AC: activated carbons;
ALD: atomic layer deposition;
BDO: 1,4-butanediol;
CAPEX: capital expenditure;
CB: carbon blacks;
CHN: cyclohexanone;
CNT: carbon nanotubes;
CTH: catalytic transfer hydrogenation;
CVD: chemical vapor deposition;
DMF: 2,5-dimethylfuran;
ECH: electro catalytic hydrogenation;
EFE: ethylfurfuryl ether;
EROEI: energy returned on energy invested;
FA: furfuryl alcohol;
FCC: face-centered cubic;
FID: flame ionization detector;
GC: gas chromatograph;
HC: hydrocarbons;
HCP: hexagonal close packed;
HOPG: highly-ordered-pyrolitic graphite;
HTHP: high-temperature high-pressure;
IMEP: indicated mean effective pressure;
LC_{50}: lethal concentration;
LD_{50}: lethal dose;
LHV: lower heating value;
MON: motor octane number;
MWCNT: multiple-walls carbon nanotubes;
NOx: nitrogen oxides;
ON: octane number;
OPEX: operating expenditure;
P: pressure;
PA: 1-pentanol;
PTMEG: poly(tetramethylene)ether glycol;
PZC: point of zero charge;
RON: research octane number;
R.T.: room temperature;
SWCNT: single-wall carbon nanotubes;
T: temperature;
Tc: critic temperature;
THF: tetrahydrofuran;
THFA: tetrahydrofurfuryl alcohol.

Preface

The present Master's Thesis regards the possibility to produce a valid bio-fuel, the 2-methylfuran, starting from furfural, which is a derivative of hemicellulose-containing biomass. This perspective is very attractive: furfural in general can be converted into very high value-added chemicals, and it represents an alternative to fossil energetic sources such as oil, natural gas and coal. Although the discovery of 2-methylfuran dates back to the 1940s, it has only recently caught the attention of researchers for its use as gasoline component, both to improve engine performances (thanks to its high octane number) and to increase the "green" content of fuels. In the past, an industrial process was developed in order to produce 2-methylfuran through the catalytic hydrogenation of furfural; however, such process was based on copper-chromite supported catalysts, which have become an issue for the toxicity of chromium towards environment and human health. For this reason, new active catalysts are under examination, in order to substitute chromium-containing ones and even to improve the selectivity towards 2-methylfuran. Carbon materials represent an interesting opportunity for supporting different active metals in hydrogenation reaction, since they are not toxic and available at relatively low cost. Thus, carbon-supported catalysts were tested in this work, with the goal to reach the highest yields and selectivity in 2-methylfuran possible, evaluating the most suitable operating conditions.

This work is divided into two parts: the first part regards some theoretical aspects of the topic, while in the second part the experimental procedures and the results of the experimental work will be presented. Chapter 1 relates to furfural: properties, production technologies and main uses; Chapter 2 is about 2-methylfuran, to explain why it is important and to illustrate the state-of-the-art in its production. In conclusion, some considerations about the catalysis of hydrogenation reactions, including a focus on carbon catalysts, are made in Chapter 3. The second part includes Chapter 4, with the explanation of the experimental procedures and characterization techniques, and Chapter 5, presenting all the results of the tests in laboratory; Chapter 6 summarizes conclusions and outlook.

The experimental activity was entirely developed within the "CatBio Project" at the Department of Industrial Chemistry, Aalto Yliopisto (Finland).

LITERATURE PART:
FROM FURFURAL TO 2-METHYLFURAN

1. FURFURAL

Furfural is an organic compound, more precisely a heterocyclic aldehyde, with a ring structure. Its molecular formula is $C_5H_4O_2$ and it is known with many different names (i.e. furfuraldehyde, furan-2-carboxaldehyde, fural, 2-furaldehyde, pyromucic aldehyde). It is mostly known as "furfural", a word derived from the Latin *furfur*, which means "bran", as bran is a typical source of it, as well as corn cobs, oat and other agricultural byproducts.[1] It has many uses in the Organic Chemical Industry thanks to its versatility and to well-developed conversion technologies. It is the starting reactant also for the 2-methylfuran that will be investigated in this work, so it is convenient to illustrate the main chemical and physical properties and the ways to produce such compound, together with its derivatives.

1.1 Furfural properties

Furfural (Fig.1) is a colorless oily liquid with an almond-like odor, but when exposed to air it turns from yellow to brown and black, since the reaction with oxygen occurs; if stored under vacuum, it remains colorless.[2]

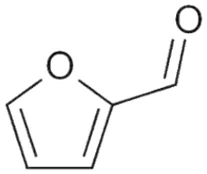


Figure 1: Furfural

Its versatility is connected to the fact that it has two strong functional groups: an aldehyde (C=O) and a conjugated double-bond system (C=C-C=C). The first one can undergo reactions such as acetalization, acylation, aldol condensation, reduction to alcohols, decarbonylation and oxidation to carboxylic acids; the furan ring system instead is mainly involved in alkylation, hydrogenation, oxidation and open ring reactions.[3] According to its spectroscopic polarity (E_T^N=0.426) it is more polar than acetone (E_T^N=0,355), thus it is completely miscible with aromatics and organic compounds, and slightly miscible with saturated hydrocarbons. This property explains why furfural itself is often used as a selective extractant.[3] Above the critical temperature of furfural (Tc=120°C), furfural and water are completely miscible, while they form an azeotrope at P=1 atm at 65% wt. of water and at a boiling point of 97.85°C. It is involved in the same reactions than other aldehydes and aromatic compounds; still, it is less aromatic than benzene. Concerning safety aspects, it must be known that heating furfural above 250 °C causes a rapid and exothermic decomposition to furan and carbon monoxide, sometimes explosively; the heating process conducted in the presence of acids leads to produce hard thermosetting resins. Moreover, it is flammable (flash point=62°C, comparable to kerosene).[1,2] Another aspect that must be taken into consideration is furfural toxicity: although it may occur in some foods and flavouring (e.g. vanilla), it has a considerable lethal dose (LD_{50}= 65mg/kg, oral, rat) and has adverse effects on eyes and skin (such as irritation) even at very low concentrations (2ppm); moreover, it is a confirmed animal carcinogen, but with unknown relevance to humans. Thus, contact with eyes, skin and respiratory system must be prevented when working with this compound by wearing a proper full-facepiece respirator (i.e. gas mask).[4,5] Other properties can be found in many references.[1-3]

1.2 Furfural production

Furfural is the dehydration product of xylose (which means “wood sugar”, from the Greek), a monosaccharide containing five atoms of carbon, with the molecular formula $C_5H_{10}O_5$. [6] Xylose (especially D-xylose stereoisomer) is a pentose sugar with three different isomers; it can be derived from hemicellulose, a polysaccharide and one of the main constituent of biomass. Hemicellulose undergoes a hydrolysis reaction if heated at high temperature (above 150°C) with an acid (e.g. sulfuric acid), giving xylose as main product; in the same conditions, xylose is involved in a dehydration reaction, losing water and becoming furfural. As shown in Figure 2, the reactions are:

$$(C_5H_8O_4)_n + n\ H_2O \rightarrow n\ C_5H_{10}O_5 \qquad \text{(eq. 1)}$$

Pentosan Pentose

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O \qquad \text{(eq. 2)}$$

Pentose Furfural

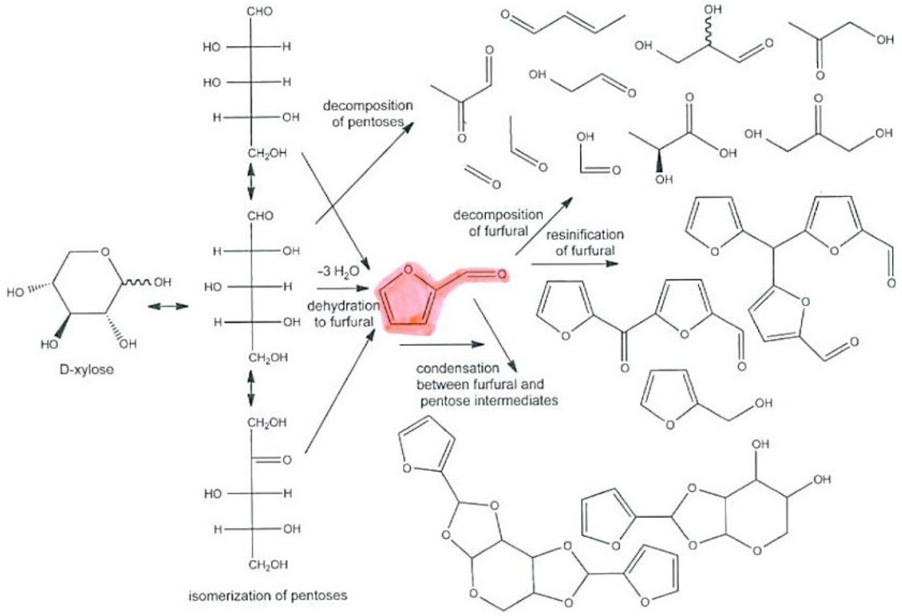
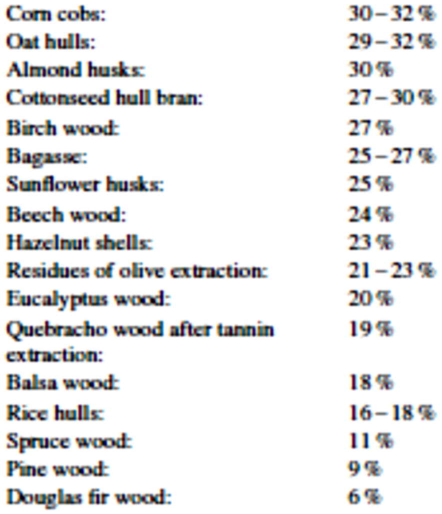


Figure 2: Reaction pathway from xylose to furfural and possible side reactions [7]

The explanation of such a mechanism can be found in many references.[2] Furfural can be produced starting from many raw materials rich in pentosan (i.e. polypentose); Table 1 shows different options: the choice can be made considering not only the pentosan content but also the economical value of the raw material (for example, using a dedicated cultivation or waste products).

Table 1: Pentosan content of various raw materials [2]



Corn cobs:	30 – 32 %
Oat hulls:	29 – 32 %
Almond husks:	30 %
Cottonseed hull bran:	27 – 30 %
Birch wood:	27 %
Bagasse:	25 – 27 %
Sunflower husks:	25 %
Beech wood:	24 %
Hazelnut shells:	23 %
Residues of olive extraction:	21 – 23 %
Eucalyptus wood:	20 %
Quebracho wood after tannin extraction:	19 %
Balsa wood:	18 %
Rice hulls:	16 – 18 %
Spruce wood:	11 %
Pine wood:	9 %
Douglas fir wood:	6 %

Furfural was commercially produced for the first time by Quaker Oats Company (Iowa) in 1921 through a batch process, using dilute sulfuric acid; since then, many other processes have been developed, both batch and continuous. [1] They typically involve reactions of homogeneous catalysis in aqueous solutions, but there are many recent studies concerning heterogeneous catalysts (see part 3.3), that would allow reducing corrosion-related problems (due to the use of homogeneous mineral acids), minimizing waste and simplifying the catalyst separation. [7] Although furfural can also be formed without any catalysts, through an auto-catalyzed mechanism (i.e. furfural turns into organic acids that act as catalysts themselves), it is advisable to use a catalyst because of many undesired side reactions that may occur; thus, it is crucial to have an effective selective catalyst.

1.2.1 Differences between the batch and the continuous process in furfural production

Taking into consideration the two Quaker Oats processes, we can discover the main differences between them.

1.2.1.1 Batch process

This was the first process used for furfural production in 1921 and it was adopted since Quaker Oats Company had many iron pressure cookers unused in the plant of Cedar Rapids previously employed for a cereal product which did not prove profitable. Thus, such cookers were used like digesters in the first attempt at large scale operation; since then, many studies about metal materials were made, since iron showed corrosion problems due to the use of acid. Moreover, the first equipment and operating conditions were not the results of an optimization, but just a pragmatic solution for using some reactors already available and it is to consider also that the kinetics of the furfural formation was not known yet. Anyway, apart from a few changes, this process (illustrated in Figure 3) is still in use nowadays.

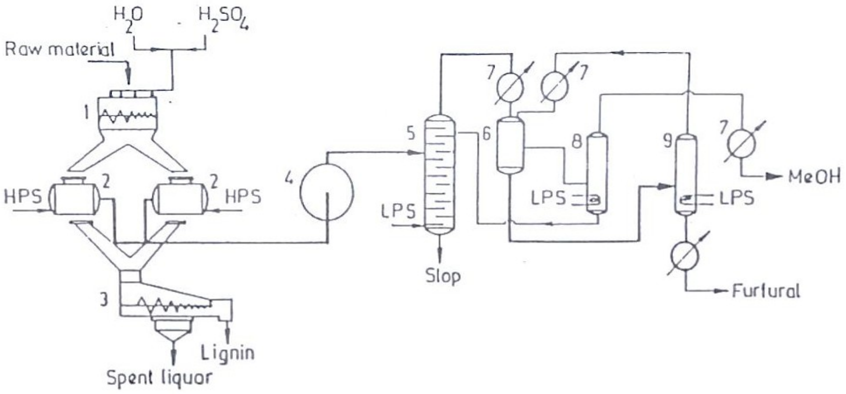


Figure 3: Quaker Oats batch process scheme.
(1) Mixer, (2)Reactors, (3)Screw press, (4)Secondary steam generator, (5)Azeotropic distillation column, (6)Decanter, (7)Condensers, (8)Recovery column for low boilers, (9)Furfural dehydration column. [1]

The feed stream, made of raw materials, is mixed with dilute sulfuric acid and sent to a spherical or cylindrical reactor (12 feet long and 8 feet of diameter) capable of rotating around the horizontal axis. In order to design the batch reactor correctly, it is important to calculate the optimal residence time, which in this case is the one required for xylose to disappear. From experimental results, the rate of such a reaction was found to be:

$$-\frac{\mathrm{d[Xy]}}{\mathrm{dt}} = \mathrm{k} \cdot \mathrm{c_H} \cdot [\mathrm{Xy}] \cdot \exp\left(-\frac{16894}{\mathrm{T}}\right) \qquad \text{(eq. 3)}$$

where [Xy] is the xylose concentration (mole/L), $k=9.306\cdot10^{15}$ (L/mole/min) is the reaction rate constant, c_H is the initial hydrogen concentration (mole/L) and T is the absolute temperature (K). We can introduce a term $k_1 = k \cdot c_H \cdot \exp(-16894/T)$; rearranging the equation, we obtain:

$$\frac{d[Xy]}{[Xy]} = -k_1 \cdot dt \qquad \text{(eq. 4)}$$

Integrating the first member from the initial to the final xylose concentration and the second member in time:

$$\frac{[Xy]}{[Xy]_0} = -\exp(-k_1 \cdot t) \qquad \text{(eq. 5)}$$

The residence time τ is typically calculated in this case as the time requested in order to decrease xylose until 1% of its original concentration; thus, for t=τ, we can arrive to the final expression:

$$\frac{[Xy]}{[Xy]_0} = 0.01 \rightarrow \exp(-k_1 \cdot \tau) = 100 \rightarrow \tau = 4.60517/k_1 \text{ (min)} \qquad \text{(eq. 6)}$$

Considering a constant and uniform hydrogen concentration, due to sulfuric acid, this is a fundamental equation for the batch-reactor design. As temperature appears inside the exponential function, even little excursions cause great differences in reaction time, and high temperatures are desired, in order to raise the rate of xylose disappearance and to reduce τ, thus the reactor size. Moreover, increasing temperature works against loss reactions, improving the furfural yield. Temperatures are upper-limited only by corrosion problems. Typically, the Quaker Oats batch process is operated at 153°C for 5 hours. Steam is used for providing heat for the reaction and for stripping (i.e. for removing furfural product before it undergoes undesired reactions); when operating furfural reactors, one of the major costs is precisely the large quantity of steam used, which can be from 30 to 50 times more the amount of furfural produced. The furfural obtained in the distillate is about 40-50% of the theoretical yield, with little losses in the residue (from 1.25 to 3.80%). Furfural has a maximum at an initial water content of 25.4%; under this value, there is a decreasing trend. This phenomenon is related to the so called “paradox of furfural yield”, which consists in significant yields losses in industrial processes that don’t occur in laboratory experiments, where a 100% yield is possible. The main reason of such a paradox is the following: xylose leads to high boiling point solutions and industrial furfural reactors are heated by steam injection, i.e. by condensation of water vapor; this vapor cannot bring to a boiling xylose solution because larger quantities of heat should be provided. Thus, in industrial processes the reaction medium is not boiling. Furfural generated can then remain in solution and can be involved in degradation reactions (especially resinification). In the laboratory process instead, where the reaction medium is kept boiling at atmospheric pressure during all the digestion period, furfural cannot dissolve into the solution because it is “rejected” in the vapor phase. To summarize, loss reactions can be completely avoided only in a boiling liquid, but in industrial processes the steam used for heating and stripping is not able to provide such a condition for a xylose solution. The laboratory-scale furfural process could be reproduced on industrial scale with a continuous plug flow reactor with raw materials entering and being discharged at the two ends of the reactor; the operating conditions include high temperature (250°C), short residence time (5-60 s), low acid concentration (0.3-2% wt.) and steam injection to rapidly remove furfural. This new method promises to produce furfural at yield of 70%, but it is still at a pilot-scale.

In conclusion, the main disadvantages connected to this batch process are:

- long residence time due to low process temperature;
- low temperature is compensate using large quantities of acid (2.25 kg of sulfuric acid for 100 kg of raw materials);
- an extremely acidic residue that must be handled;
- rotational mechanism must be kept efficient and it complicates the reactor design. [1]

1.2.1.2 Continuous process

In the 1960s, Quaker Oats realized a continuous operating plant for furfural production. Although it was abandoned in 1997, it is considered as a milestone in furfural technology. The plant consists of three different lines, with two units operating and one under maintenance at the same time. After the pre-treatment of the bagasse used as raw material (using low pressure steam to increase moisture and so decrease viscosity), the bagasse entered the horizontal reactor through an auger press with a moisture content of 45%. Each reactor (1.8m of diameter and 16m long) was made of four horizontal sections in series; it was built with mild steel lined with acid-resistant bricks, while the transport paddles were of stainless steel. At this point, steam and sulfuric acid were added through multiple nozzles. As steam was injected at 10.888 atm and superheated at 650°C, it had a drying effect and could reduce moisture level to 40%. The reaction was performed at 184°C for 1h. Thanks to a double-lock ram valve system, product vapor and residue were discharged intermittently. With this system, the furfural yield reached 55%. A separation unit (i.e. a cyclone) was located downstream to separate the solids and the vapor. The main problems connected to this kind of process were related to the possibility of having a good control especially of the pressure and moisture of feed stream. Figure 4 shows the continuous process scheme. It is important to say that the causes that led to abandon such a plant were only marginally related to technical problems, but mostly due to high costs of maintenance and administrative choices. [1]

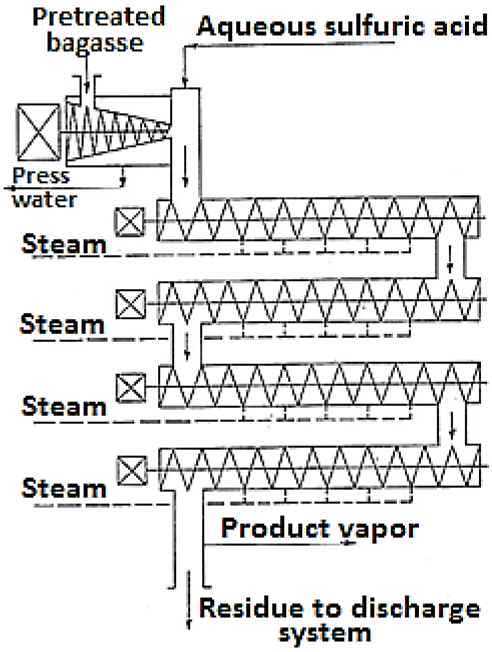


Figure 4: Quaker Oats continuous process scheme [1]

1.2.1.3 Outlook

In all more recent process proposal, [3,7] the temperature level is much higher than the one used in Quaker Oats process: at least above 200°C. This would have many benefits, as already told: especially, furfural yield increases with increasing temperature because of the "entropy effect", that works against the formation of bigger molecules. Another important aspect that must be taken into consideration is the possibility of using a suitable heterogeneous catalyst with acidic properties (in order to replace the homogeneous one) in low-cost and low-temperature liquid-phase processes: there are many proposals and recent patent applications in literature regarding that. [3,7] Another possibility is to mitigate the effect of water of accelerating consecutive reactions that consume the formed product: the use of solvents or co-solvents can help improving the selectivity of the dehydration reaction, but also technological solutions concerning the removal of water can lead to same result. Finally, even if water is the most economical and "eco-friendly" solvent known, it can be replaced in furfural production, for example with supercritical CO_2

(because it helps extracting the furfural from the pores of the catalyst and discourages secondary reactions) or with ionic liquids. [7]

1.2.2 Furfural distillation

Generally speaking, all industrial furfural reactors produce a vapor stream with the following composition: at least 90% of water, up to 6% of furfural and various by-products. Such stream is then condensed (in order to produce secondary steam), sometimes separated from solids through filtration or centrifugation, and fed into a distillation unit. [1]

As shown in Figure 5, the distillation unit typically consists of a tray azeotropic column (1) where the water/furfural azeotrope (boiling point at atmospheric pressure = 97.85°C) is collected as a side stream, cooled and sent to a decanter (2); from the top of the column a mixture of low boiling compounds (mainly methanol, but also some furfural) is obtained and it is processed into a randomly packed column (3), in order to recover furfural and water (which are sent to decanter (2) as well); finally, the bottom fraction of column (1) is a mixture of water, carboxylic acids (mostly acetic acid) and possible traces of furfural (depending on the quality of distillation column (1)) and it can undergo anaerobic digestion to produce biogas (i.e. methane) or an extraction followed by distillation to recover acetic and formic acids before discharge (if economic considerations justify such measures). In decanter (2) the separation of two liquid phases occurs: a light phase rich in water, which is recycled into the first column, and a heavy one rich in furfural (about 94%). The latter goes through a neutralizer (4) and into a randomly packed vacuum column (5) where the “raw furfural” is separated from water. The head fraction of this column is roughly the water/furfural azeotrope: it is condensed and collected in a second decanter (6) where the light phase produced is sent back to decanter (2) while the heavy phase is recycled.

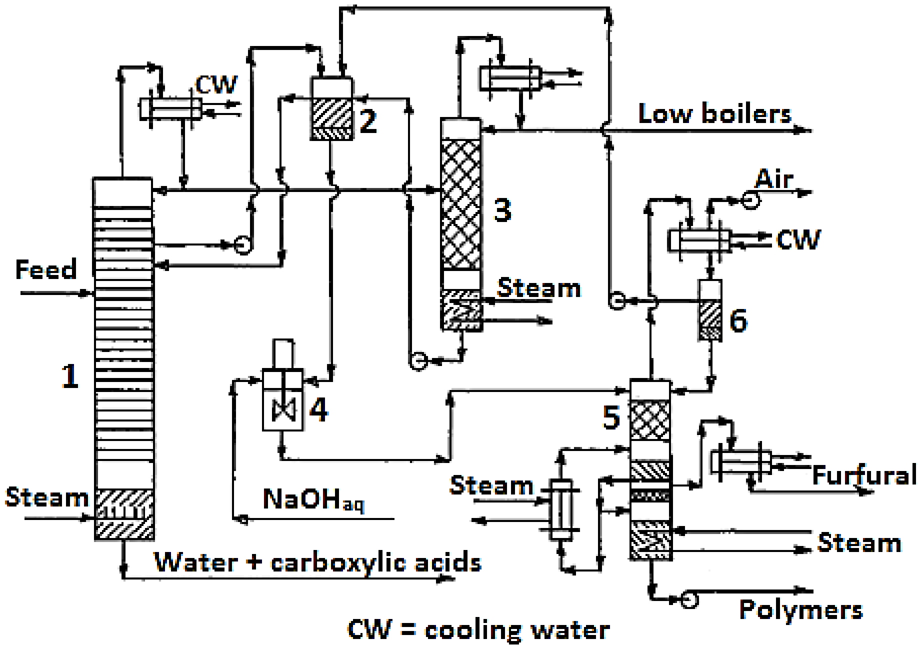


Figure 5: Simple furfural distillation scheme [1]

The bottom fraction, separated from furfural thanks to a demister, consists of polymers (discharged). The furfural vapor, withdrawn as a side stream and condensate, is the desired final product. Normally it contains between 0.5 and 1.2% of impurities (especially 5-methylfurfural and 2-furyl methyl ketone, undesired byproducts), depending on the process, but it is considered acceptable since it would be too expensive to remove such impurities. [1]

1.3 Uses of furfural

Global production capacity of furfural is about 300 000 tons/ year (2012). China is the leading producing country, together with Dominican Republic and South Africa. [1,3] More than 60% of furfural produced is converted to furfuryl alcohol (see *1.4 Derivatives of furfural*). However, furfural can be employed also as an extractant in refining process, for example to remove aromatics from lubricating oils, as improver of the relationship between viscosity and temperature in hydrocarbons (i.e. the viscosity index), to isolate unsaturated compounds from vegetable oils obtaining “drying oils” suitable for paint and varnishes, to remove aromatics from diesel fuels to improve ignition characteristics and to form cross-linked polymers. The use of furfural as an extractant is possible thanks to the so called "intermolecular conjugation": when molecules with conjugated double bonds (such as furfural) meet other double-bonded molecules, they form an enlarged conjugated double bond system and this causes the liberation of energy, similar to the one occurred when a new intramolecular bond is formed. For this reason, furfural seems "not to see" other molecules but the ones with double bonds. Moreover, furfural has a fungicide behavior, especially in the inhibition of growth of wheat smut (*Tilletis foetens*); this use of furfural allows avoiding formaldehyde solutions, which would be less efficient in the same quantity and especially more toxic. This use concerns treatments of seeds as well as growing plants and wood. Finally, it can be used as a nematocide, which means the capability to kill plant-parasitic nematodes (also called eelworms) that each year cause billions of dollars of agricultural loss, as they attack many crops e.g. potatoes, peanuts, soybeans, tomatoes, bananas, tobacco and cotton. [1-3]

1.4 Derivatives of furfural

As already mentioned, furfural is a very versatile chemical (see Figure 6) and it is considered one of the main building block for a new oil-independent chemistry. It is a valid bio-based alternative for the production of fertilizers, plastics and paints but, above all, it was recently discovered as one of the most promising compound for sustainable production of fuels and chemicals.[3] Moreover, nowadays it is the most important way to provide for example furans, furanones, furfuryl alcohol and furfuryl acetate.[2] In this chapter the most important derivatives of furfural will be presented, including a brief description of their properties and uses (2-MF is not included, since it will be discussed in details in Chapter 2).

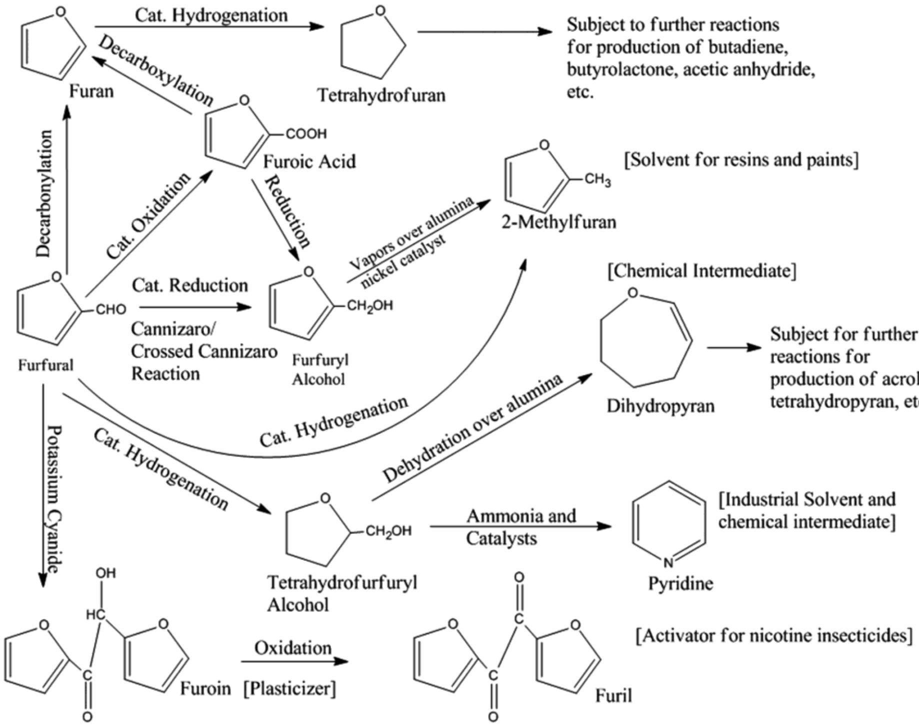


Figure 6: Conversion of furfural into many value-added chemicals and biofuels

1.4.1 Furfuryl alcohol

Furfuryl alcohol or furanol ($C_5H_6O_2$, Fig. 7) is the most important derivative of furfural and it represents at least 60% of furfural conversion. It contains a furan ring with the addition of a hydroxymethyl group.[3]

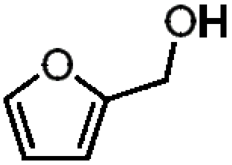


Figure 7: : Furfuryl alcohol

Like furfural, it is a colorless liquid when pure, but turns into amber-yellow when exposed to air. It has a slight burning odor, it is completely miscible with water and soluble in common organic solvents (but not into saturated hydrocarbons) and, when heated in presence of an aqueous acid solution, it can polymerize into a resin, called poly-furfuryl alcohol; this reaction is highly exothermic and potentially explosive if catalyzed by sulfuric, hydrochloric or nitric acid. Thus, furfuryl alcohol is employed especially for foundry resins, adhesive and wetting agents production and for wood treatments, but it also has many applications in the manufacture of furan fiber-reinforced plastics (for piping) and of high-performance chemicals and as a solvent.[3] The process leading to furfuryl alcohol production is a simple hydrogenation and it used to be industrially conducted using copper-chromite catalysts at high pressures (70-100 bar) and at 175°C, with very high yields in furfuryl alcohol (up to 99%).[1] The use of such a catalyst was discovered to be dangerous both for human health and for the environment, so during the last years many different types of new catalysts have been tested.[3] The aim for the future is to improve the catalyst design and to optimize the operating conditions in order to achieve the best yields possible.

1.4.2 Tetrahydrofurfuryl alcohol

Tetrahydrofurfuryl alcohol (THFA, Fig.8), with molecular formula $C_5H_{10}O_2$, is an important transparent and biodegradable solvent, completely miscible with water, characterized by high boiling point (178°C) and low toxicity. Its major use is in stripping formulations (especially employed in the automotive industry) to remove epoxy and/or protective coatings, paints and grime before final paintings; moreover, it is an intermediate in the synthesis of many pharmaceutical and fine chemicals (for example 1,5-pentanediol with an open-ring reaction).[3]

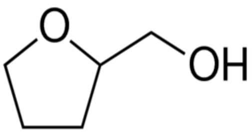


Figure 8: THFA

At laboratory scale there are two different ways of producing THFA, i.e. directly from furfural (through hydrogenation) or from furfuryl alcohol, but only the latter is typically used at industrial scale. The conversion mechanism is a vapor-phase hydrogenation of furfuryl alcohol on various nickel-supported catalysts.[1]

1.4.3 Furan

Furan (also called furfuran, Fig. 9), C_4H_4O, is the parent compound of the heterocycles with five members, one of which is oxygen. It is a colorless liquid with low boiling point (31.36°C), a strong ether odor and high flammability.

Figure 9: Furan

From a chemical point of view, furan has some aromatic character, due to the delocalized structure, but it is (as well as its derivatives) less aromatic than other heterocycles, considering the stabilization energy (96 kJ/mole vs. 155 kJ/mole of benzene), thus it is more reactive than benzene, especially in addition reactions. In presence of an aqueous acid and heat, furan undergoes a polymerization reaction. The oxygen of the furan ring can be substituted in presence of a suitable catalyst: by nitrogen, leading to pyrrole or by sulfur, yielding a thiophene; such compounds are very important for the chemical industry. [2] Furan major use concerns the conversion through catalytic hydrogenation into tetrahydrofuran (see 1.4.4). Furan is industrially derivable from furfural with a decarbonylation reaction (i.e. with the formation of a molecule of carbon monoxide) at atmospheric pressure and high temperature (158°C), typically over a noble metal catalyst (Pd) supported on microporous carbon, with potassium carbonate as co-catalyst to promote the reaction. Yields are very high (over 98%). It is important to operate the reaction under conditions with efficient mass transfer (i.e. stirring conditions) in order to promote desorption of both CO and furan from the catalyst surface. [1,3]

1.4.4 Tetrahydrofuran

Tetrahydrofuran (THF, Fig. 10) is a very important compound for polymers production (especially for poly(tetramethylene ether)glycol, PTMEG) in presence of a strong acid, and as a versatile solvent, with its polarity and its wide liquid-range. Moreover, THF has been investigated as a miscible co-solvent in aqueous solutions as a promoter of liquefaction of lignocellulosic biomass, in order to produce biofuels. [3]

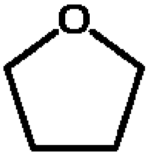


Figure 10: THF

It is made by hydrogenation of furan, so it is considered as a "second generation descendant" of furfural, as well as THFA. The process is operated typically at 100°C and 20 bar, using the same catalyst of the furfural-to-furan reaction, such as 5% of palladium on microporous carbon; nevertheless THF is not directly producible from furfural. [1]

1.4.5 2-methyltetrahydrofuran

The compound 2-methyltetrahydrofuran (2-MTHF, $C_5H_{10}O$, Fig. 11) is generally presented together with 2-methylfuran because they are both colorless liquids with high solvent power, and they have recently caught the attention of many researchers as promising biofuel components miscible with gasoline. Especially, 2-MTHF is mainly used as substitute of THF because of similar chemical properties. [2] 2-MTHF can be obtained through two different hydrogenation paths: the first one involves levulinic acid resources and the second one is made from 2-methylfuran. [6]

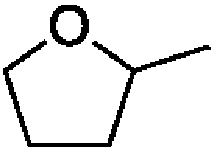


Figure 11: 2-MTHF

The hydrogenation can be either performed in a vapor-phase at atmospheric pressure, or in a liquid phase working under H_2 pressure generally with Nickel-based catalysts.[3] At present, however, none of these processes has been developed at industrial scale, but the future perspective is very promising in order to produce high-value added chemicals and especially fuels.[6]

1.4.6 Oxidation products

To have a more complete overview about furfural derivatives, it is important to say that, besides the hydrogenation reactions which produce the compounds presented so far, furfural can undergo also oxidation. Furoic acid (Fig. 12) is the first down-line (and the most important) product of furfural oxidation. It is a heterocyclic carboxylic acid and its main industrial application is in the food industry, where it is employed as a preservative (both bactericide and fungicide) and as a flavoring agent. [1]

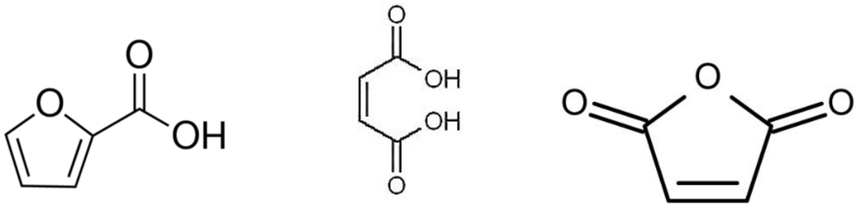


Figure 12: Furoic acid, maleic acid and maleic anhydride

When converted into furoyl chloride, it has applications in the pharmaceutical field and as insecticide. Moreover, it is a promotor in nylon production.

Another chemical produced through a vapor-phase catalytic oxidation of furfural is maleic acid, or maleic anhydride, depending on reaction temperature. Maleic acid is a di-carboxylic acid not existing in nature; as a salt, it looks like colorless prismatic crystals very soluble in water. As aqueous solution, it is a very strong organic acid (dissociation constant $K_1=1.42\cdot10^{-2}$ mole/L).[1] It is industrially used to produce alkyd resins (by heating the acid with a polyvalent alcohol) and dienes. Maleic anhydride instead is derivable from dehydration of maleic acid and it is a very important chemical in industrial production of coatings and plastics.

Oxidation reactions are exothermic; therefore it is necessary to provide the reactor with an adequate coolant system (usually with molten salts) in order to keep the temperature under control. Moreover, they can be conducted using either air or pure oxygen as reactant, but air is preferred because, at same yields, it does not raise safety issues (e.g. connected to possible explosions) and it is more easily available.

2. 2-METHYLFURAN

The goal of the present work is to investigate the production of 2-methylfuran through a liquid-phase catalytic hydrogenation of furfural on various carbon-supported catalysts. In order to understand the process better, it is necessary to know this compound, the evolution of the studies concerning its production and the main challenges for the close future, together with a focus on the processes that may be involved.

2.1 Properties

2-methylfuran (2-MF, Fig. 13) is an organic compound with molecular formula C_5H_6O. [2] It is known also as Sylvan, a word coming from the Latin *silva* (which means "forest") in order to indicate the connection between 2-methylfuran and wood, where it comes from; moreover, it is naturally present in myrtle and lavender. [8]

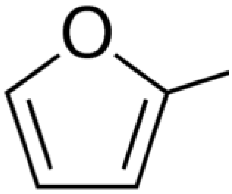


Figure 13: 2-methylfuran

For what concerns some physical and chemical properties, at room conditions it looks like a colorless and mobile liquid; it has a boiling point between 63.2 and 65.6°C and the solubility in water is very low (less than 0.3 wt %. at 25°C). The typical reactions involving 2-MF are the methyl-group substitution (especially halogenation) and ring-openings, for example the one that leads to 2-pentanol or to 2-pentanone (using Pt or Ni catalysts, respectively) through catalytic hydrogenolysis.[2] Chemical properties are actually similar to those of furan (see 1.4.3). For what concerns safety and transportation aspects, it is a flammable liquid and it can cause irritation to eyes and skin;[9] it has a lethal concentration (LC_{50}) of 1485 ppm/h (in air, rat) and overexposure-symptoms are nausea and temporary lowering of blood pressure. [1] Thus, proper protections must be taken when handling it. For more detailed properties, see Table 2.

Table 2: Properties of 2-methylfuran [1]

Molecular weight	82.098 g/mole
Boiling point (at 760 mmHg)	63.2°C
Freezing point	-88.7°C
Flash point (closed cup)	-27°C
Solubility in water (at 25°C)	< 0.3% (0.3g per 100mL of H_2O)

2.2 Historical evolution

This part will summarize the most important steps that made 2-MF growing in importance, from the first discovery to the production at industrial level.

2.2.1 First results

2-MF was discovered at first as an undesired byproduct during the vapor-phase production of furfuryl alcohol from furfural. The first researches about its production, as well as catalysts investigations and kinetics hypotheses, were conducted during the 1940s. Originally, the aim was to produce 1,3-pentadiene using an alternative reactant such as furfural, available in large quantities, because of the shortage of natural rubber reserves. [10] Apparently, such a conversion could be done through three different steps: the first one involving a catalytic hydrogenation of furfural on a copper-chromite catalyst, leading to 2-MF as intermediate; the second one was another hydrogenation on Ni catalyst giving methyltetrahydrofuran; finally, a dehydration to the desired 1,3-pentadiene. However, the process turned out to be impractical to produce rubber even at laboratory scale; the most important outcome was that 2-MF might be produced on large scale. Since then, many attempts were made in order to increase the yield of 2-MF itself, while all previous works had concentrated on furfural conversion into furfuryl alcohol (FA) or tetrahydrofurfuryl alcohol. Processes involved were catalytic vapor-phase hydrogenations at atmospheric pressure, i.e. the same way of production of FA, but the temperature range was different: under 200°C and above 300°C, the main hydrogenation product is FA, while at intermediate temperatures (~250°C) 2-MF is mostly generated. [11] It was discovered (and later confirmed by other experimental works) that the reaction involves the FA as an intermediate [3,14,15]. An important aspect that was pointed out was the considerable amount of heat generated by the reaction: $\Delta H_r = -142$ kJ/mole (at T=200°C). [10] This implies that heat must be withdrawn from the reactor in order to prevent deactivation problems of the catalyst. The experimental apparatus at laboratory scale is shown in Figure 14.

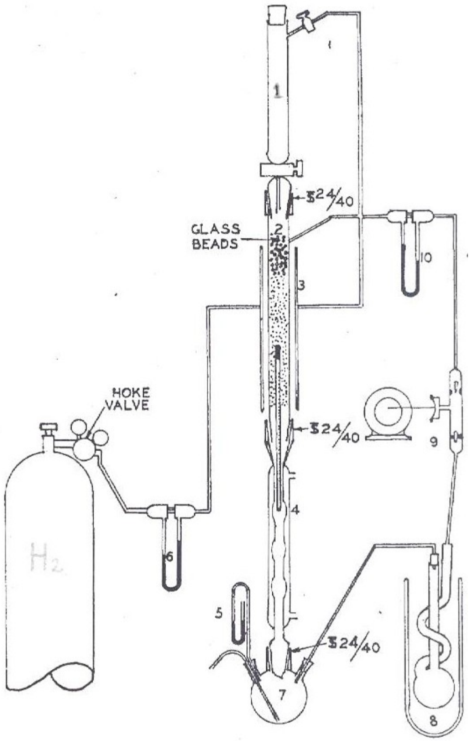


Figure 14: Experimental apparatus scheme [10]

The apparatus consisted of a Pyrex tube containing the catalyst bed with packed glass beads on top acting as vaporizer and pre-heater (2), heated at reaction temperature using an electric furnace, i.e. a wound wire (3); hydrogen, whose consumption was controlled through a manometer (6), was stocked in a cylinder and was used to dry the catalyst (before the reaction, without furfural injection). Once the catalyst had been dried (at 190-200°C), furfural was trickled from tank (1). Water and unreacted furfural were condensed from the gas stream (4) and collected in (7) under pressure control (manometer (5)), immersed in an ice bath; the gas stream instead passed into a dry ice-acetone condenser (8) to remove 2-MF (and water in traces); the remaining hydrogen was then recirculated using a diaphragm pump (9) (hydrogen recirculation was measured with another manometer, (10)). [8,13] In case of considerable heat generated by the reaction, this configuration was slightly modified, introducing a coolant system (i.e. a metal jacket filled with a suitable liquid) around the Pyrex tube in order to keep the correct reaction temperature. [11] This kind of system was used to test different types of catalysts (especially copper-based ones): the results showed that copper-chromite dispersed on active charcoal had the best performances [1,8,13,16] (with a yield in 2-MF up to 90-95%), although it suffered of deactivation at the high reaction temperature; this problem was overcome by adding an alkaline-earth element (such as calcium or barium) as stabilizer. [10] The passage to a large-scale process required first of all the patent of a reproducible catalyst (a problem that occurred during first attempts [10]) and also different reactor (shell-and-tube type). [1]

The global reaction path involved is a hydrogenation/hydrogenolysis, also described as ‘hydrodeoxygenation’ (i.e. the removal of oxygen from an oxygenated compound):

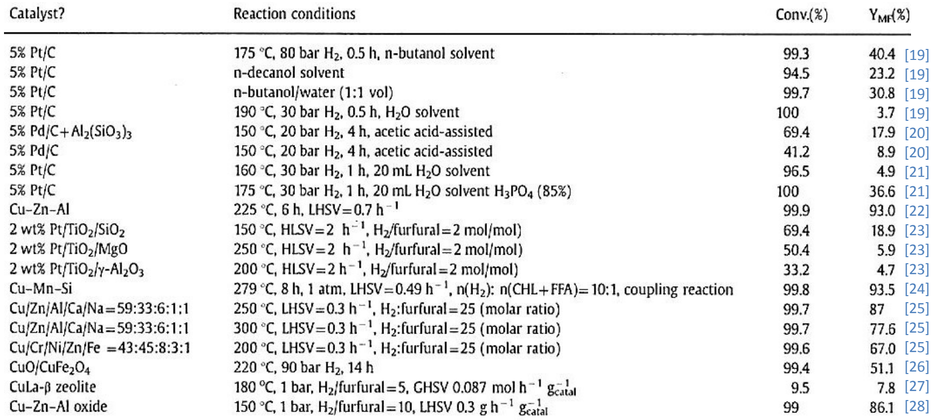
$$\underset{\text{Furfural}}{C_5H_4O_2} + 2H_2 \rightarrow \underset{\text{2-methylfuran}}{C_5H_6O} + H_2O \qquad \text{(eq. 7)}$$

Although the stoichiometric H_2/furfural ratio is 2:1, it is advisable to lead the process in excess of hydrogen (6:1 – 7:1) in order to increase 2-MF yield. [1] The main by-products are water and FA.

2.2.2 The development of 2-methylfuran

Thanks to a commercially valid production processes, 2-MF grew in importance and it was employed in many applications: still nowadays it is often used as a solvent and as an intermediate for the production of chemicals, e.g. chloroquine (i.e. an antimalarial drug), methyltetrahydrofuran (see part 1.4.5), chrysanthemate pesticides, nitrogen and sulfur heterocycles and aliphatic compounds.[3,6,17,18] However, the most valid catalyst used for the process, a copper-chromite based one, was discovered to be toxic for human and environment because of the presence of chromium. Thus, many Cr-free catalyst formulations have been proposed [3] (see Table 3) but in the best situations they have been tested only at pilot-scale. [19-28]

Table 3: Literature proposal of solid catalysts in furfural hydrogenation to 2-MF [3]



Catalyst?	Reaction conditions	Conv.(%)	Y_{MF}(%)
5% Pt/C	175 °C, 80 bar H_2, 0.5 h, n-butanol solvent	99.3	40.4 [19]
5% Pt/C	n-decanol solvent	94.5	23.2 [19]
5% Pt/C	n-butanol/water (1:1 vol)	99.7	30.8 [19]
5% Pt/C	190 °C, 30 bar H_2, 0.5 h, H_2O solvent	100	3.7 [19]
5% Pd/C+$Al_2(SiO_3)_3$	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	69.4	17.9 [20]
5% Pd/C	150 °C, 20 bar H_2, 4 h, acetic acid-assisted	41.2	8.9 [20]
5% Pt/C	160 °C, 30 bar H_2, 1 h, 20 mL H_2O solvent	96.5	4.9 [21]
5% Pt/C	175 °C, 30 bar H_2, 1 h, 20 mL H_2O solvent H_3PO_4 (85%)	100	36.6 [21]
Cu–Zn–Al	225 °C, 6 h, LHSV=0.7 h^{-1}	99.9	93.0 [22]
2 wt% $Pt/TiO_2/SiO_2$	150 °C, HLSV=2 h^{-1}, H_2/furfural=2 mol/mol)	69.4	18.9 [23]
2 wt% $Pt/TiO_2/MgO$	250 °C, HLSV=2 h^{-1}, H_2/furfural=2 mol/mol)	50.4	5.9 [23]
2 wt% $Pt/TiO_2/\gamma$-Al_2O_3	200 °C, HLSV=2 h^{-1}, H_2/furfural=2 mol/mol)	33.2	4.7 [23]
Cu–Mn–Si	279 °C, 8 h, 1 atm, LHSV=0.49 h^{-1}, n(H_2): n(CHL+FFA)= 10:1, coupling reaction	99.8	93.5 [24]
Cu/Zn/Al/Ca/Na=59:33:6:1:1	250 °C, LHSV=0.3 h^{-1}, H_2:furfural=25 (molar ratio)	99.7	87 [25]
Cu/Zn/Al/Ca/Na=59:33:6:1:1	300 °C, LHSV=0.3 h^{-1}, H_2:furfural=25 (molar ratio)	99.7	77.6 [25]
Cu/Cr/Ni/Zn/Fe =43:45:8:3:1	200 °C, LHSV=0.3 h^{-1}, H_2:furfural=25 (molar ratio)	99.6	67.0 [25]
$CuO/CuFe_2O_4$	220 °C, 90 bar H_2, 14 h	99.4	51.1 [26]
CuLa-β zeolite	180 °C, 1 bar, H_2/furfural=5, GHSV 0.087 mol h^{-1} g_{catal}^{-1}	9.5	7.8 [27]
Cu–Zn–Al oxide	150 °C, 1 bar, H_2/furfural=10, LHSV 0.3 g h^{-1} g_{catal}^{-1}	99	86.1 [28]

Commercial processes would require the optimization of the catalyst formulation and operating conditions, in order to reach the best selectivity, and the discovery of the main parameters affecting the reaction rate. Especially, the vapor-phase hydrogenation of furfural to 2-MF is operated on supported noble metal and bimetallic catalysts. For what concerns Cu-based catalysts, they generally operate at high temperatures (above 200°C) and low (i.e. atmospheric) pressure; the reaction involves the formation of FA as an intermediate, as shown in Figure 15.

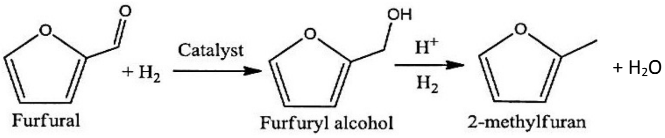


Figure 15: hydrogenation of furfural to 2-MF [3]

As a matter of fact, Cu or copper-chromite catalysts are deactivated by coking of FA (~250-300°C);[11] such deactivation is reversible by heating the catalyst in air at about 400°C and then reducing it with hydrogen.[11] It is very important not to overcome much this peak temperature (hot spots problems) because of the catalyst sintering, which leads to a permanent deactivation. In order to reach the best selectivity for 2-MF, temperature must be increased (usually gradually) over 200°C but also at this point, the catalysts undergo deactivation within a few days, mostly because of thermal polymerization and again coking at high temperatures.[3,29] Thus, limitation of deactivation processes is a great challenge; beside the optimization measurements, it is important to better understand the reaction mechanism, especially the by-product formation, to improve the selectivity through a more conscious catalyst formulation.

In literature there are very few experimental data concerning the hydrogenation of furfural; moreover, there are many debates still open about the origin of some by-products, such as carbon monoxide, ethanol and n-butanol. According to Zheng *et al.,*[23] the reaction pathway of furfural hydrogenation is the one shown in Figure 16: it was developed analyzing the product of hydrogenation over two different catalysts, a Cu-Zn (a) and a Cu-Cr (b) one. [23] The actual atomic composition was the following: Cu/Zn/Al/Ca/Na (59:33:6:1:1) and Cu/Cr/Ni/Zn/Fe (43:45:8:3:1), respectively. The catalysts were tested in a laboratory-scale tubular fixed-bed reactor between 200 and 300°C and 1atm. They both showed high activity in hydrogenation and in 2-MF selectivity (more (b) than (a), with a maximum of 87% at 250°C).

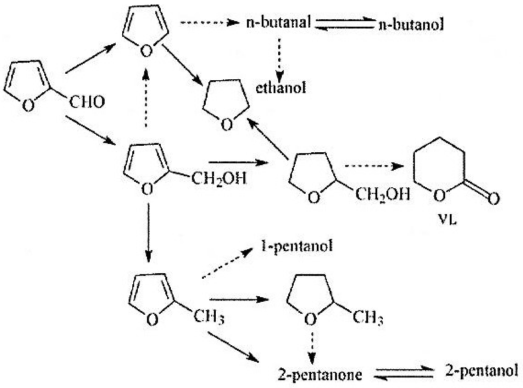


Figure 16: Reaction pathway of furfural hydrogenation involving 2-MF production [23]

The main by-products investigated were furan, n-butanol, ethanol, carbon monoxide and the hydrogenation products of 2-MF.

Furan is industrially produced through decarbonylation of furfural over noble metal catalysts (see part 1.4.3) but such conversion can be obtained also over Ni-Cu alloy over 200°C [28] and (b) produced more furan than (a) because of Ni presence. Furan can then undergo a hydrogenation reaction (with high conversion) on both (a) and (b) catalysts, yielding mostly n-butanol, n-butanal, tetrahydrofuran, ethanol and hydrocarbons. A number of reactions takes place: despite the large amount of hydrogen in the reactor, n-butanol is converted into n-butanal, which can then produce ethanol by hydrogenolysis over Cu-Cr catalyst. Theoretically, n-butanol can derive also from tetrahydrofuran, but the latter is very stable in the reaction conditions (220-300°C) so this is an unlikely reaction path.

Carbon monoxide was found as a product with both catalysts. Its presence is of key-importance because when accumulated into the system (especially in the recycling tail gases) it can deactivate Cu-based catalysts. However, there is a reaction involving CO and H_2 consumption because of their reaction with THFA to produce tetrahydrofuran, especially in presence of Ni.

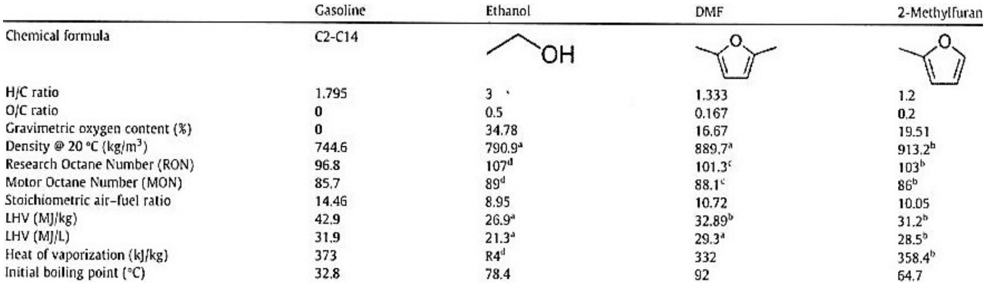
For what concerns the hydrogenation products of 2-MF, they are, in order of quantity, 2-pentanone, 1- and 2-pentanol and 2-methyltetrahydrofuran at 200-300°C; this result may indicate that the ring fission is easier than ring saturation over Cu-based catalysts.[23] Moreover, other works [31,32] over Ni-based catalysts showed that at a lower temperature (100°C) the main hydrogenation product was MTHF (86%) while at increasing temperatures, 2-pentanone increased, too, up to a maximum of 75% at 185°C.

2.3 A new perspective

Beside the applications already cited, 2-MF has been recently discovered as very promising liquid fuel, especially as an additive for gasoline, thanks to excellent energy density, boiling point, octane number and hydrophobic properties.[14,29,33] Moreover, it can subsequently hydrogenated to MTHF, which is also an excellent liquid fuel. As seen in the previous paragraph, the selectivity is strictly connected to catalyst formulation and operating conditions.

In Table 4 a comparison among bio-based gasoline components is made, based on different properties for liquid fuels suitable with current vehicles and fuel distribution network. [3,14,34]

Table 4: Comparison among properties of bio-based gasoline components [32]



	Gasoline	Ethanol	DMF	2-Methylfuran
Chemical formula	C2-C14			
H/C ratio	1.795	3	1.333	1.2
O/C ratio	0	0.5	0.167	0.2
Gravimetric oxygen content (%)	0	34.78	16.67	19.51
Density @ 20 °C (kg/m^3)	744.6	790.9^{a}	889.7^{a}	913.2^{b}
Research Octane Number (RON)	96.8	107^{d}	101.3^{c}	103^{b}
Motor Octane Number (MON)	85.7	89^{d}	88.1^{c}	86^{b}
Stoichiometric air–fuel ratio	14.46	8.95	10.72	10.05
LHV (MJ/kg)	42.9	26.9^{a}	32.89^{b}	31.2^{b}
LHV (MJ/L)	31.9	21.3^{a}	29.3^{a}	28.5^{b}
Heat of vaporization (kJ/kg)	373	R4^{d}	332	358.4^{b}
Initial boiling point (°C)	32.8	78.4	92	64.7

Ethanol is already used as transportation fuel especially in Brazil, where a production technology starting from sugar cane has been developed at industrial scale since many years; 2,5-dimethylfuran (DMF) is a heterocyclic compound derived from furan (thus from biomass) and it is considered a new biofuel for spark ignition engines.[29,34] For what concerns 2-MF, it shows some properties similar to DMF and some outstanding qualities. For example, its latent heat of vaporization is higher than for DMF (358.4 vs 332 kJ/kg), which means higher power output; the flash point instead is lower than DMF (-22°C vs. 16°C), as consequence of higher rates of vaporization and higher combustion stability, which would overcome cold-engine-start problems (usually associated with bio-ethanol). Moreover, 2-MF has high energy density (Lower Heating Value, LHV about 40% greater than ethanol) and mass density. Finally, the most interesting aspect: it has a high octane number, therefore elevate knock-suppression ability, even higher than gasoline (RON=103 vs. 96.8, MON=86 vs. 85.7).

Especially the octane number (ON) is a key-property and a quality requirement of fuel for gasoline-engine: it indicates the ability to resist knocking while burning in the combustion chamber of the engine. If the fuel/air mixture ignites spontaneously before the time, a pressure rise is rapidly generated, causing the so called “knocking” phenomenon; if repeated for a long time, knocking can seriously damage the engine. [33] The higher ON, the better the knock-suppression ability. In Table 4 two different ON are reported: the **Research Octane Number** (**RON**) and the **Motor Octane Number (MON).** The first one is the most common type of octane rating worldwide and it is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane (i.e. reference compounds with ON of 100 and 0, respectively). The MON measurement uses a similar test engine to that used for RON, but with a preheated fuel mixture, higher engine speed (900 vs. 600 rpm), and variable ignition timing to further stress the fuel's knock resistance.[34] There is no direct link between RON and MON: pump gasoline specifications typically require both a minimum RON and a minimum MON. [35,36] It is important to know that octane number depends both on chemical structure and on the combustion temperature history: branched chains have a higher ON than linear ones; the fact that 2-MF has a compact structure (unlike gasoline that is a mixture of C_4-C_8 hydrocarbons) makes it unwilling to cause knocking. Beside this, 2-MF has a higher cooling effect (i.e. the ratio between the heat of vaporization and the lower heating value, LHV) than DMF or gasoline because it needs more heat to evaporate; thus, more energy is adsorbed from the vaporization process during the in-cylinder charge and it helps to lower the ignition temperature, reducing the end-gas auto-ignition.[32] Analyzing the combustion process, 2-MF showed a faster burning rate, thus the shortest combustion duration among the four fuels reported in Table 4. This fact makes it generate the highest in-cylinder peak pressure, which means that more air and fuel are ingested: thus, more power is produced and less work is required to the engine for the air/fuel intake. 2-MF has also a high peak temperature which is closely connected to a good thermal efficiency (better than gasoline and DMF) and to a more complete (i.e. more efficient) combustion; in this sense, also the considerable oxygen content of 2-MF available during the combustion process helps increasing combustion efficiency. Moreover, the volumetric fuel consumption rate is comparable with gasoline and DMF. [32]

In conclusion, it is important to compare the emissions related to the use of 2-MF as a fuel: the main results are shown in Figure 17, where on the x-axis the Indicated Mean Effective Pressure (IMEP) is reported, indicating the average in-cylinder pressure reached during the four phases of the engine cycle (i.e. intake, compression, combustion and exhaust).[35] Because of high combustion temperature and high oxygen content, the level of hydrocarbons unreacted is lower than gasoline and DMF, as they undergo post-oxidation reactions during the exhaust stroke; unfortunately, NOx formation depends exponentially on the combustion temperature, thus 2-MF produces the highest quantity of NOx. Beside this, it tends to produce a constant amount of CO, higher than in case of gasoline. A shorter injection time and fuel spray penetration in the case of gasoline (which is more volatile, thus more incline to form a combustible mixture) causes less wet cylinder and piston walls, thus less fuel/air equivalent ratio (even if working at stoichiometric conditions) and less CO emissions. [32]

As a matter of fact, 2-MF is excellent for blending with gasoline. Blends of these components were evaluated, especially in comparison with the European EN228 standard (2004) for gasoline specification.[12] A 10% vol. 2-MF-blended gasoline was tested on road trial, using three vehicles with Direct Injection technology, for a total of 90,000 Km. As a result, the experiment showed the respect of vehicle emissions, in compliance with EURO 4/5 standards.

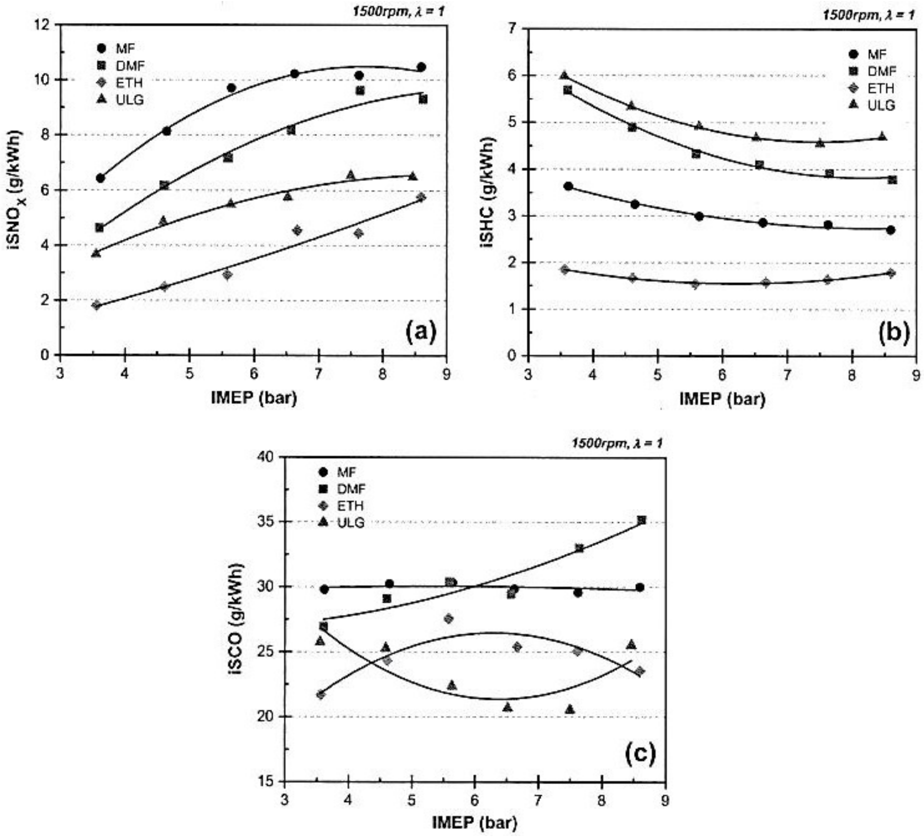


Figure 17: Comparison among different fuels of the indicated specific gaseous emission level: NOx (a), HC (b), CO (c) [32]

Moreover, penalties in fuel consumption were definitely low: the loss of fuel economy was expected to be approximately 1% (vs. 3% expected with the same blend ratio of ethanol in gasoline). Finally, there was not negative impact on the engine; however, the addition of a detergent agent is advisable in order to prevent deposits on valves and injectors. [12]

In addition to the use in gasoline-engine, there is also the possibility of producing hydrocarbon diesel fraction out of 2-MF.[14,38-40] It has only five atoms of carbon, thus it is far from the range of diesel (C_{10}-C_{20}): longer C-C chains are required, as well as their hydrodeoxygenation in order to remove oxygen and form alkanes (which have a higher thermal stability and energy density). For example, a trimer of 2-MF becomes a diesel precursor, especially a linear alkane with a branching in the middle of the chain; such compounds have desirable properties such as low pour point (which prevents fuel solidification with cold weather) and high cetane number (similarly to octane number, it is an index of fuel quality). 2-MF is likely to trimerize because the presence of the methyl group "protects" one of the two reactive α-positions and reduces the possibility of side-reactions. To obtain such a trimer, many options are possible. One of them requires first of all the hydroxyalkylation of 2-MF with an aldehyde (for example, butanal): the product of this reaction subsequently alkylates another 2-MF molecule; finally, the diesel precursor, 6-alkylundecane, results from a hydrodeoxygenation reaction (Fig. 18) conducted in a fixed-bed continuous flow reactor, at 50 bar H_2 and 350°C. [36]

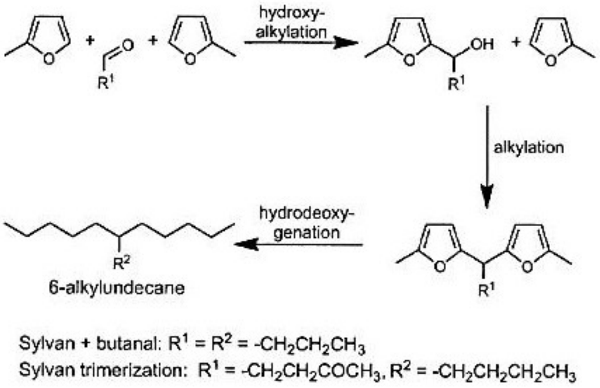


Figure 18: Diesel formation through hydroxyalkylation of 2-MF [36]

Another possible way is to synthetize the compound 5,5-bisylvyl-2-pentanone through trimerization of 2-MF in presence of an aqueous sulfuric acid (24% wt.) and heat (temperature of 60°C) under stirring conditions for 16h. Then, the 5,5-bisylvyl-2-pentanone spontaneously separates from the aqueous phase and it is hydrodeoxygenated over Pt-catalysts (at 400°C) to the hydrocarbon diesel compound shown in Fig. 19 (in 87% yield). [12]

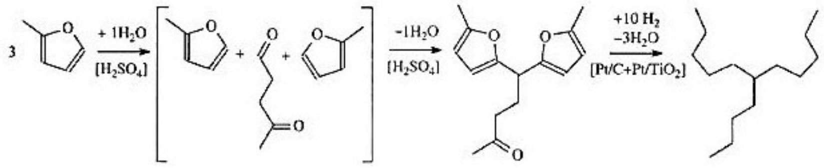


Figure 19: Trimerization of 2-MF to bisylvylpentanone and diesel formation [12]

Instead of a trimerization, it is possible to combine 2-methylfuran and 5-methylfuran (5-MF) to yield a C_{16} compound which has better properties (i.e. higher boiling point). In this case (Fig. 20), the reactants both come from biomass, as 5-MF is a cellulose-derivative. To undergo this hydroalkylation/alkylation process, an acidic catalyst is necessary: for example, a para-toluene sulfonic acid and sulfuric acid were used as catalysts (they act as Brönsted acids).[36] Other works can be found in literature. [39,40]

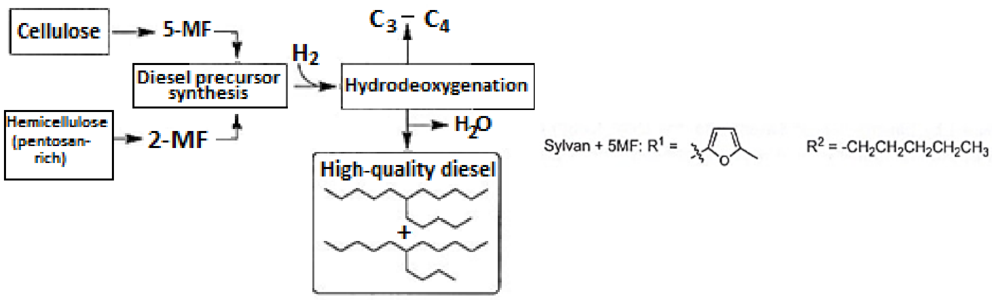


Figure 20: Diesel formation from 2-MF and 5-MF [36]

In conclusion, oligomeric components provide volatility and very high cetane number (above 70) suitable for blending in diesel fuels. However, the treatments required lead to a more expensive production and to a higher CO_2 footprint than monomeric gasoline components. [12]

2.4 The challenge

As a consequence of the growing interest towards 2-MF for fuel production, in order to make its use more affordable, it is important to develop as low-costs and eco-friendly processes as possible. In the following paragraphs some possible solutions are presented.

2.4.1 Coupling reactions

There is the possibility to improve 2-MF yield and selectivity, as well as reducing its production costs, by coupling furfural hydrogenation with another reaction, typically a dehydrogenation. In this work only a couple of examples taken from literature will be taken into consideration.

2.4.1.1 MF and γ-Butyrolactone

γ-Butyrolactone is a versatile intermediate in fine chemical industry: it is especially employed to produce pyrrolidone, N-vinylpyrrolidone, N-methylpyrrolidone (plastics and pharmaceutical compounds), herbicides and rubber additives.[20] One of the main process to obtain γ-butyrolactone is the dehydrogenation of 1,4-butanediol (BDO).[41,42] This reaction, as well as the vapor-phase furfural hydrogenation, has some critical points, such as poor hydrogen utilization and difficulty in controlling the reaction temperature. Thus, the idea was to combine the two reactions in the same reactor: hydrogenation is an exothermic reaction (ΔH_r =-142 kJ/mole), while dehydrogenation is endothermic (ΔH_r = +62 kJ/mole).[20] As a consequence, the global process is exothermic for only 80 kJ/mole and the temperature control results definitely easier. Working at lower temperatures allows also improving 2-MF yield (up to 96.5%).[27] Beside this, there is the possibility to reduce (even to eliminate) hydrogen supply, as dehydrogenation itself produces the H_2 necessary. To improve the reaction rate, a Cu-Zn-Al catalyst was used for both reactions, with high conversions (>99%).[20] The global process is reported in Figure 21.

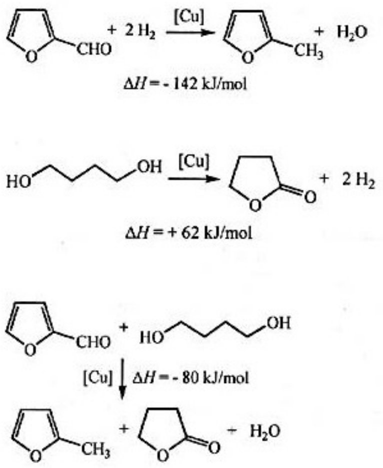


Figure 21: Coupling hydrogenation/dehydrogenation to obtain 2-MF and γ-butyrolactone [20]

2.4.1.2 *MF and Cyclohexanone*

Cyclohexanone is a very important chemical: it is used to produce caprolactone, caprolactam and adipic acid, the main precursors for polyamide (nylon 6 and nylon 6,6 respectively) production.[41] The considered reaction pathway yielding cyclohexanone (CHN) is the vapor-phase dehydrogenation of cyclohexanol, an endothermic reaction (+63.4 kJ/mole) severely constrained by thermodynamic equilibrium, thus with lower conversion.[28,43] Coupling this reaction with the strongly exothermic hydrogenation of furfural to 2-MF over Cu-based catalysts has many benefits: enhanced conversions, higher energy efficiency, better temperature control (since the reaction becomes less exothermic, -15.2 kJ/mole), higher selectivity as a consequence (up to 92.8% at 270°C), and the effective use of hydrogen obtained from the dehydrogenation process instead of the hydrocarbons-derived one. Such process was carried at 280°C and atmospheric pressure, for a total reaction time of 8h.[22] The global reaction scheme is reported in Figure 22:

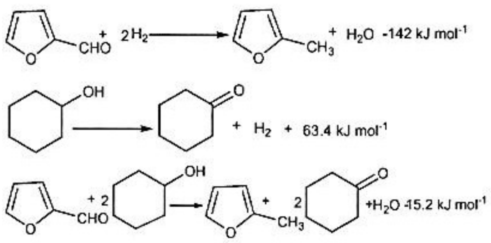


Figure 22: Coupling hydrogenation/dehydrogenation to yield 2-MF and cyclohexanone [22]

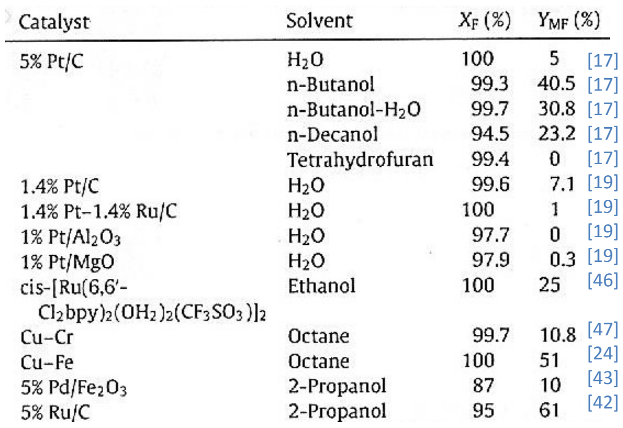
In the simple dehydrogenation, the conversion of cyclohexanol to CHN is lower than the equilibrium conversion in the temperature range of 220-300°C and many side reactions occur; instead with the coupling reactions, conversion is improved at the same temperatures: the presence of furfural "breaks" the thermodynamic conversion because it is an H_2 acceptor, thus it shifts the equilibrium by consuming H_2. Selectivity of both CHN and 2-MF is higher compared to the individual processes (for example, at 270°C on Cu-Zn-Al catalyst, CHN selectivity is raised by 8.7% and 2-MF one by 7.5%). A subsequent separation of the product mixture is necessary in order to recover the desired products, but it does not cause any problems as the boiling points are sufficiently different (63°C for MF vs. 155°C CHN).[26]

All in all, coupling reactions can considerably reduce the environmental impact, especially considering the CO_2 emissions and the dependence on petroleum resources. [24,28]

2.4.2 Liquid-phase hydrogenation

One of the main problems of furfural vapor-phase hydrogenation to 2-MF is the rapid deactivation of the catalysts occurring at high temperatures. Thus, the possibility of producing it at lower temperature, through a liquid-phase hydrogenation, has been recently taken into consideration. Precisely, due to its high vapor pressure, furfural hydrogenation can occur both in vapor and liquid phase, and the latter is even more compatible with the upstream production of furfural.[42,44] Another important aspect concerns the employment of molecular hydrogen, which raises a safety and economic issue connected to availability of resources, transportation, storage, complex reactor design. Many alternatives to molecular hydrogen have been proposed, for example using hydrogen donors (undergoing dehydrogenation) such as formic acid and alcohols, or electro catalytic hydrogenation (see 2.4.3). The employment of formic acid has advantages in storage, handling and transport compared to hydrogen, but it is corrosive, creating problems to materials and catalysts; thus, the use of alcohols, potentially both as reactants and solvents, is the best options.[43] Many catalysts have also been tested for the liquid-phase process. Common hydrogenation catalysts are Pt, Ru, Rh, Cu, Ni and Fe, generally supported on carbon, alumina or silica. [14,44,46,47] It is also possible to combine the catalytic activity of two metals in the same catalyst, i.e. in bimetallic Ni-Fe catalysts, which are likely to cleave the C=O bond in furfural molecule, probably because of a raise of metal electron density or the creation of new active sites.[42] Although palladium supported on carbon showed a good yield to 2-MF, other undesired parallel and consecutive hydrogenations (such as conversion to THFA and MTHF, respectively) occurred: this means that the choice of the catalyst alone is not enough to ensure high yields and selectivity. It is necessary to choose also a suitable solvent: the main properties required are intermediate polarity (i.e. expressed in an octanol/water partition coefficient, $-1 < \log P < +2$) and being neither acidic nor basic. Thus, effective solvents include alcohols (especially methanol and ethanol), esters and THF.[44,45] Table 5 shows some literature catalyst/solvent combination proposals and the corresponding yields in 2-MF.

Table 5: Literature catalysts and solvent proposal for furfural hydrogenation to 2-MF



Catalyst	Solvent	X_F (%)	Y_{MF} (%)	
5% Pt/C	H_2O	100	5	[17]
	n-Butanol	99.3	40.5	[17]
	n-Butanol-H_2O	99.7	30.8	[17]
	n-Decanol	94.5	23.2	[17]
	Tetrahydrofuran	99.4	0	[17]
1.4% Pt/C	H_2O	99.6	7.1	[19]
1.4% Pt–1.4% Ru/C	H_2O	100	1	[19]
1% Pt/Al_2O_3	H_2O	97.7	0	[19]
1% Pt/MgO	H_2O	97.9	0.3	[19]
cis-[Ru(6,6′-Cl_2bpy)$_2$(OH_2)$_2$](CF_3SO_3)$_2$	Ethanol	100	25	[46]
Cu–Cr	Octane	99.7	10.8	[47]
Cu–Fe	Octane	100	51	[24]
5% Pd/Fe_2O_3	2-Propanol	87	10	[43]
5% Ru/C	2-Propanol	95	61	[42]

Moreover, the catalyst is preferably a strong acid assisted by halide anions; the presence of an acidic co-catalyst, usually HCl, showed to improve the selectivity towards 2-MF. As a result, for example in [12], a yield of about 50% mol. of 2-MF was obtained at 30°C and 2.5 barH_2 over Pd/C and Pd/SiO_2 catalysts in ethanol in presence of a small amount of HCl. Changing the conditions, especially eliminating HCl, the yield of 2-MF dramatically decreased to 18% over Pd/C and 0% over Pd/SiO_2.[12] Another work [42] concerning the catalytic transfer hydrogenation produced *in situ* the hydrogen required for furfural hydrogenation, through 2-propanol dehydrogenation. The reaction was carried in a laboratory-scale batch reactor heated in a temperature-controlled oil bath, using a Ru/C catalyst. Yield in 2-MF was very high: 61% at 180°C after 10h reaction.[42] An interesting idea is using a continuous-flow reactor instead of a batch one: the main advantages are improved productivity (no idle time), enhanced heat and mass transfer and smaller reactor volumes.[45,50] The liquid feed (i.e. furfural and solvent, for example 2-propanol) is introduced into a stainless-steel tubular reactor through a pump; the reactor is packed with the catalyst (Pd/Fe_2O_3) and quartz (to improve the feed distribution). While in batch operations the main products are 2-MF and FA, in the continuous process considerable amounts of ring-hydrogenated products of 2-MF and FA are obtained; as a result, selectivity of 2-MF is 26%. As a matter of fact, when the transfer hydrogenolysis involves FA and not furfural, 2-MF yield is drastically improved, reaching a maximum of 76%, much higher than the one obtained with a batch reactor.[43]

There are a few articles available in literature, thus the testing of new catalysts and adequate operating conditions is fundamental in order to improve the selectivity of 2-MF and to reduce costs (connected for example to the use of noble metals and for hydrogen supply). The experimental activity of the present work fits into this open research field.

2.4.3 Electro catalytic hydrogenation

The electro catalytic hydrogenation (ECH) of biomass has been recently proposed in literature [51-54] as a promising and environmentally-friendly way of producing chemicals. Especially, ECH of furfural to FA and 2-MF will be taken into consideration. This method allows producing 2-MF at atmospheric pressure and at temperature below 100°C, minimizing the solvents used and especially the costs for hydrogen supply. The main difference between ECH and the vapor-phase hydrogenation process is precisely the way to generate atomic hydrogen: the latter requires an external supply of H_2 which is then split into atomic H (eq. 8); the ECH instead reduces hydronium ions to form atomic H directly on the catalytic cathode surface, using external electrons (eq. 9).[49] It is powered with electricity.[50]

$$H_2 + 2M \rightarrow 2(H)_{ads}M \qquad \text{(eq. 8)}$$

$$H_3O^+ + e^- + M \rightarrow (H)_{ads}M + H_2O \qquad \text{(eq. 9)}$$

M is the metal active site for hydrogen adsorption and $(H)_{ads}M$ is the chemisorbed hydrogen. Once hydrogen has been produced, the ECH involves the adsorption of unsaturated compounds (eq. 10), the hydrogenation reaction between such adsorbed compounds and the adsorbed hydrogen (eq. 11) and finally desorption of the hydrogenated product (eq. 12):

$(Y=Z)_{aq} + A \rightarrow (Y=Z)_{ads}A$ (eq. 10)

$2(H)_{ads}M + (Y=Z)_{ads}A \rightarrow (YH\text{-}ZH)_{ads}A + 2M$ (eq. 11)

$(YH\text{-}ZH)_{ads}A \rightarrow (YH\text{-}ZH)_{aq} + A$ (eq. 12)

In the above-mentioned equations, (Y=Z) represents an unsaturated organic compound, which can adsorb on A site for organic substrate leading to the adsorbed form, $(Y=Z)_{ads}A$. (YH-ZH) instead is the hydrogenated product. Another reaction may occur, such as the formation of molecular hydrogen, through the so called "Tafel" (eq. 13) or "Heyrovsky" (eq. 14) reaction:

$(H)_{ads}M + (H)_{ads}M \rightarrow H_2 + 2M$ (eq. 13)

$(H)_{ads}M + (H^+)_{aq} + e^- \rightarrow H_2 + M$ (eq. 14)

The hydrogen produced is not subsequently involved in the hydrogenation, thus these are competitive reactions and it negatively affects the electrochemical efficiency.[49] The ECH process takes place in an electrochemical cell, which consists of two electrodes (anode and cathode), namely catalytic sites for the reactions involved, and an electrolyte, either liquid or solid, which allows ions circulation. Such a system is also provided with an external circuit: according to the process involved (i.e. Gibbs free energy), electricity will be either developed from chemical reactions ($\Delta G<0$, i.e. galvanic cell or *battery*) or introduced in the system in order to catalyze chemical reactions ($\Delta G>0$, i.e. electrolytic cell). Precisely, Gibbs free energy can be calculated with the following expression:

$\Delta G = -n \cdot F \cdot E_{Cell}$ (eq. 15)

where n represents the number of electrons transferred, F is Faraday constant (=96485 Coulombs/mole) and E_{Cell} is the electrode potential, i.e. the electromotive force of the cell ($E_{Cell}=E_{cathode} - E_{anode}$, Volt). Table 6 shows Gibbs free energy and standard cell potentials for the hydrogenation of furfural.

Table 6: Gibbs free energy and cell potentials for hydrogenation of furfural with hydrogen gas or water electrolysis [50]

	Hydrogen gas		Water electrolysis	
Reaction	ΔG (kJ mol^{-1})	E_{cell} (V)	ΔG (kJ mol^{-1})	E_{cell} (V)
1. Furfural → FA	−35.95	0.19	200.38	−1.04
2. FA → THFA	−80.97	0.21	391.69	−1.01
3. FA → MF	−25.27	0.13	211.06	−1.09
4. MF → MTHF	104.78	−0.27	577.44	−1.50
5. THFA → MTHF	160.48	−0.83	396.81	−2.06

In the electrochemical cell, a redox-reaction occurs: the anode is the electrode where the oxidation reaction takes place, while the cathode is involved in the reduction reaction. In an electrolytic cell, the anode is identified as (+) while cathode is (-); for the galvanic cell is the opposite.

Few examples of ECH are reported in literature, especially for what concerns 2-MF production; however, two different types of electrochemical cell can be used: an undivided one (Fig. 23a) and a cell with a membrane (for example a Nafion one) dividing the anode and cathode sections (Fig. 23b).

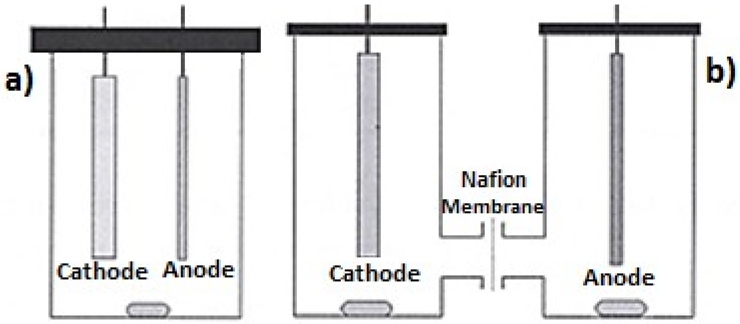


Figure 23: Undivided (a) and divided (b) laboratory-scale electrochemical cells [49]

The first configuration allows avoiding the proton exchange membrane, thus lowering electrical resistance and equipment costs. Anode and cathode can be realized in different materials: for example, sacrificial Ni anode and cathode of Al, Fe, Ni, Cu or stainless-steel [49]; Pt-Ru/C anodes and Pd/C or Pt/C cathodes [50]; TiO_2[51]. Moreover, there are many electrolytes available, from aqueous solutions to ionic liquids [51] and proton exchange membranes (PEMs)[50]. A simple representation of the reactant and product streams can be seen in Fig. 24.

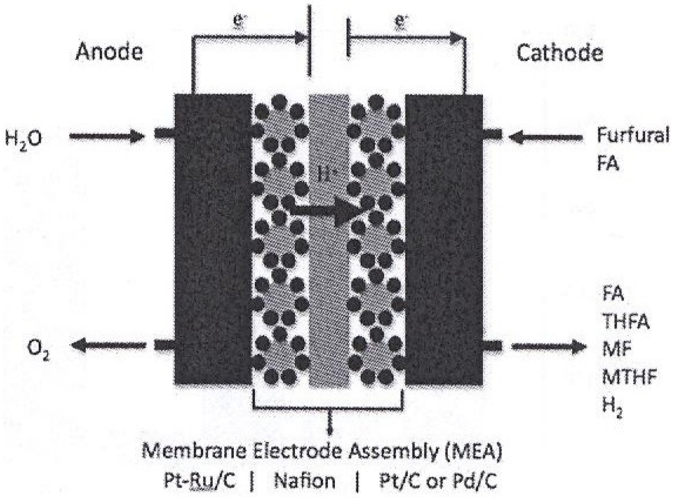


Figure 24: Electrocatalytic membrane reactor for ECH of furfural over Pd/C or Pt/C using protons derived from water electrolysis over Pt-Ru/C [50]

The development of such a technology allows changing the energy activation barrier by controlling the electrode potential; thus, reactions that usually require high temperatures and pressures to occur (even if catalyzed) could occur at atmospheric pressure and temperature; moreover, through the electrode potential control it is possible to change reaction selectivity, even to secondary or side-products (high potentials).[50] The main disadvantage is the amount of electrical power required (and its cost); although it could be a promising process for furfural upgrading, still much research has to be done before developing a competitive production process.

2.4.4 Economic considerations

The possibility to upgrade furfural to produce fuels and fuel-components is very attractive, because the raw materials could be available almost everywhere and with low cost, even zero cost if we consider using for example agricultural waste. The most important things to succeed are first of all an available and technically feasible technology (as seen in the previous paragraphs) and secondly, the production based on this technology should be economically affordable (both OPEX and CAPEX). The main problem of renewable and new sources of energy is that, since their discovery is more or less recent, they still lack of a competitive price if compared to fossil fuels. Often the expression "Energy Returned On Energy Invested" (*EROEI*) is used to describe this fact: in many cases, the energy used to produce a fuel or a chemical is more than the one obtainable from it, both in terms of power and profit. Nevertheless, the environmental impact of a new technology has also been a concern lately. It is then very important to consider the effective practicability of furfural upgrading to 2-MF in order to justify an investment in research in such direction. This paragraph tries to present a simplified analysis of it, in terms of investment costs and net CO_2 emissions. For what concerns the theoretical investment cost, it can be roughly calculated through a capital index (eq. 16) using the heat of reactions involved as a measure of the overall energy required [52]:

$$\text{Capital Index} = \frac{\sum |\Delta \mathrm{H_r}|^{0.6} \left[\frac{\mathrm{kJ}}{\mathrm{mol}}\right]}{\mathrm{LHV_{fuel}} \left[\frac{\mathrm{GJ}}{\mathrm{mol}}\right]} \qquad \text{(eq. 16)}$$

At numerator there is the sum of the heat of reaction (in absolute terms) of the steps occurring during the fuel formation, raised to the power 0.6; at denominator is reported the Lower Heating Value of the resulting fuel. This formula has been applied for several fuel and chemical production processes, especially for natural gas conversion processes, where highly endothermic or exothermic reactions overshadow other contributions to energy transfer.[12] For what concerns the evaluation of CO_2 emissions, the most critical step is the production of hydrogen (used in the hydrogenation of furfural) from fossil resources, assumed a stoichiometric H_2 consumption. In this analysis the CO_2 released during the production and transport of biomass and its conversion to furfural is not included; however it is important to remind that biomass during the plant-life converts CO_2 into oxygen through the photosynthesis, thus consuming it and reducing the global CO_2 emission. Such emission is expressed per MJ of the final biofuel. [12] The following diagram (Fig. 25) sums up the impact of different biofuels derived from furfural:

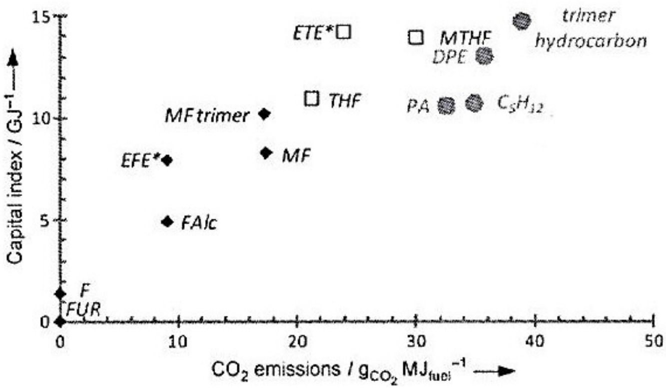


Figure 25: Capital intensity and CO_2 emission of furfural (FUR) upgrade to biofuels: dipentyl ehter (DPE), ethylfurfuryl ether (EFE), ethyltetrahydrofurfuryl ether (ETE), furan (F), furfuryl alcohol (FAlc), 2-methylfuran (MF), methyltetrahydrofuran (MTHF), 1-pentanol (PA), tetrahydrofuran (THF) [12]

It is evident that 2-MF is one of the most “sustainable” products, both in economic and environmental terms, especially considering it as a gasoline-additive. The impact of a compound increases when the furan ring is saturated (e.g. MTHF) or opened (e.g. 1-pentanol, PA); the latter process especially involves large amount of carbon dioxide released. Biofuels provided with processes characterized by high capital and CO_2 emissions have to prove excellent fuel performance and high added-value in order to justify their development and production. In conclusion, low-impact processes usually yield FA and good gasoline components, such as 2-MF and ethylfurfuryl ether (EFE); good diesel components from furfural instead are provided with higher-impact upgrading processes.

3. CATALYTIC HYDROGENATION AND CARBON CATALYSTS

This chapter presents an overview of the most important aspects of the catalysis applied to the production of 2-MF through catalytic furfural hydrogenation and mentions some catalysts used for furfural production.

3.1 Catalytic hydrogenation

Hydrogenation is the addition of hydrogen to a molecule across the π-bond, while if hydrogen is added across σ-bond, it is called hydrogenolysis. These reactions usually need the presence of a catalyst: since the hydrogen commercially available is in molecular form (H_2), its reactivity is low, especially when organic compounds are involved. Thus, the use of a catalyst decreases the activation energy of hydrogenation reaction, which can then occur at acceptable conditions (even at ambient temperature and pressure) with reasonable rate.[53] For what concerns heterogeneous catalysis (the most employed method for industrial productions), the unsaturated compound undergoes a chemisorption process over the catalyst: chemisorbed species do strong chemical bonds with the catalyst surface. The formation of hydrides (M-H) takes place at first, because of the weakening of H-H bond until its breaking; then, hydrogen is transferred to the chemisorbed substrate. According to the reactor used for the process, the catalysts are divided into two categories: the ones for fixed-bed reactors and the ones for fluidized-bed or slurry reactors. The most important difference between the two categories is particle size: for fixed-bed reactors the size is relatively large (0.8-8mm), while fluidized-bed and slurry reactors need very fine particles in order to maintain them in suspension. Transition metals and metal oxides are often used as active phase in hydrogenation catalysts, also for commercial processes: nickel, copper, cobalt, iron, chromium, zinc and metals from platinum group. [53] Metals from platinum group (i.e. platinum, palladium, rhodium and ruthenium) are very active in hydrogenation and they can reduce almost all functional groups, but they must be used under mild operating conditions in order to prevent rapid deactivation, which would also lead to considerable economic losses. Palladium is the best catalyst for hydrogenate olefins, acetylenes, C-C, C-O and C-N bonds, especially at low pressure;[53] it is usually supported on carbon: almost 75% of hydrogenation reactions are catalyzed in this way.[54] Platinum works well with all functional groups apart from esters, carboxylic acids and amides; generally the operating conditions are not severe: temperatures under 70°C and hydrogen pressures of 3-4atm. Rhodium is the catalyst involved in hydrogenation of carbonyl groups. Ruthenium is frequently used in liquid-phase hydrogenation of aromatics,[55] as it promotes hydrogenation of aromatic rings without breaking amino- and hydroxy-groups and it is also used for hydrogenation of aldehydes and ketones in aqueous solutions at low pressures; moreover, it is the only metal of platinum group able to catalyze high pressure hydrogenation of carboxylic acid, thanks to a hexagonal close packed (HCP) crystal lattice (instead of a face-centered cubic, FCC).[53] Cobalt catalysts are especially used for the hydrogenation of nitriles to primary amines; it has catalytic properties similar to nickel, thus for other reactions, nickel is rather employed.[53] Nickel is very active as hydrogenation catalyst with all functional groups; however, its major use is related to partial saturation of fat and oils, as well as hydrogenation of aromatic rings. Compared to metals like platinum, nickel can undergo more severe operating conditions thanks to its stability, but it is susceptible in acidic media (pH<5.5); moreover, it shows preferably the cleavage of C=C bond and this fact is of key importance in terms of selectivity. It can be used as supported catalyst or in a “skeletal” form (unsupported), such as

Raney nickel (i.e. very fine particles of Ni-Al alloy).[53] Copper was often used in the past in association with chromium as copper-chromite supported catalyst; the best activity was shown in hydrogenation of esters, amides and aldehydes. For the latters, the copper-based catalysts preferably cleave C-O bonds rather than C=C ones. They suffer of rapid deactivation when very reactive organic compounds are involved in the hydrogenation reaction: coking represents the major problem, but it is reversible (coke can be burned off at high temperatures). [53]

Metals and metal oxides can be used in combination to increase the effect of both activity and selectivity. Moreover, some additives can improve catalyst performance (and in this case they are called "promoters"), for example enhancing thermal and mechanical stability (physical promoters) or selectivity (chemical promoters). The choice of the catalyst is made according to its activity for the desired reaction; in this way, it is possible to operate at lower temperatures, using less catalyst and reducing residence time and thus costs. Moreover, it is important to take into account the selectivity of the process under all its declinations: chemoselectivity (i.e. the selective hydrogenation of one functional group rather than others), regioselectivity (selective hydrogenation of one functional group in presence of other identical groups in the same molecule) and stereoselectivity (obtaining a stereoisomer rather than another, e.g. *cis* or *trans*). [53]

3.2 Carbon materials in catalysis: a general overview

Carbon is a versatile material: thanks to the fact that carbon atoms can combine together in many different ways, such as linear, planar or tetrahedral configurations, a large variety of products can be obtained. As a result, physical and chemical properties (e.g. electrical conductivity), together with porosity and surface area and acidity could be adjusted according to the need.[56] Because of its versatility, carbon is employed for a wide range of technological processes, for example water and gas purification and as refractory material. Recently, carbon has raised attention also for what concerns energy production: the old technologies for burning coal have been re-examined and improved in emission reduction in order to exploit the large quantities of raw material available at competitive costs; moreover, the possibility to convert coal into liquid fuels through a Fisher-Tropsch process is very attractive. Finally, carbon nanotubes offer the possibility to store large quantities of hydrogen in very little volumes and to exploit such hydrogen for motion (e.g. hydrogen cars). Nevertheless, carbon is used in heterogeneous catalysis under different forms (such as activated carbons, carbon blacks, graphite, synthetic diamond powder, nanotubes), both as catalyst or support. [58,59] Considering especially the support-function, some properties required are high dispersion of the active phase (strictly connected to porosity and surface area), mechanical resistance, thermal resistance (high boiling point), inertness towards the reaction, affinity to the active-phase, conductivity (to spread heat homogeneously) and low cost.[57] Many carbon-based supports are thus suitable, considering such properties.

3.2.1 Activated Carbons

Activated carbons (AC) are also known as activated coal or charcoal, since they are usually derived from charcoal; there are many raw materials available, such as wood, coconut and nut shells, fruit pits.[58] AC have a porous structure due to an irregular overlapping of elementary carbon sheets at high temperatures (>700°C), after the evaporation of heteroatoms such as oxygen, hydrogen and nitrogen. The resulting interspaces can be filled with tars at first, but then they are cleaned thanks to the reactions of such tars with the gaseous phase, leaving empty pores; this is the “activation” process. Pores can be classified according to their size: micropores (< 2nm), mesopores (2-50nm) and macropores (> 50nm); adsorption reactions mostly take place at micropore level, however mesoand macropores affect the diffusion of adsorbing and desorbing species (as micropores are usually deeply hidden within the support).[57] The pore-size distribution can be changed, depending on the starting raw-material and the preparation method. Thanks to such porosity, AC show a high surface area (> 500m^2/g, see Table 7); thus, they are effective in active-phase dispersion, which allows using a smaller amount of metal phase (especially when noble metals are involved).[58-60] AC are often employed in catalysis, especially as supports in liquid-phase hydrogenation reactions.

3.2.2 Carbon Blacks

Carbon blacks (CB) are elemental carbons in very fine (10-500 nm) spherical particles which can agglomerate, with high surface area. A so called “graphitization” process can increase the order of the particles at very high temperatures (2500-3000°C), thus reducing porosity and surface area, according to the need.[58,59] They are produced through pyrolysis of hydrocarbons such as natural gas or oil fractions; thus, the final ash content is very low (<1% wt.). Surface of CB is provided with chemically-bonded oxygen in order to improve their performance; moreover, when acidic property is needed, an acid can be sprayed during the high-temperature production process. Pyrolysis occurs at very high temperatures, especially for the subtype “acetylene black” (T>2500°C) which is employed in catalysis despite it is very expensive.[56,60]

3.2.3 Graphite

Graphite is a mineral almost exclusively made of carbon atoms and it is the most stable allotrope of carbon at standard conditions. It has by a layered structure, where each layer is formed by a honeycomb lattice of covalent-bonded carbon atoms.[59] There are many types of graphite (e.g. crystalline flake, amorphous, lump [60]). It is a very conductive material, but it is rarely used in catalysis, since its surface area is low, compared to other carbons.[57]

3.2.4 Synthetic Diamond Powder

Diamond is known as the most resistant and incorruptible material; it is formed by carbon atoms arranged in a so called “diamond lattice” (i.e. FCC crystal structure) through strong covalent bonds.[59] For the high cost of natural diamond, it can be produced through synthetic processes (i.e. high-temperature high-pressure, HTHP, and chemical vapor deposition, CVD). Diamond powder is suitable for catalytic supports for inertness, mechanical resistance and high thermal stability, but it has a low surface area.[63,64]

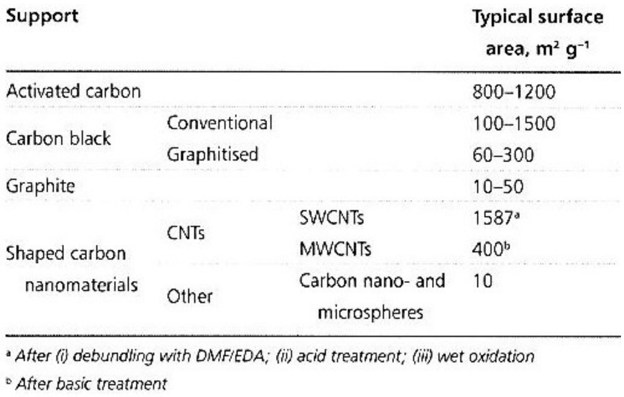
3.2.5 Carbon Nanotubes

Carbon nanotubes (CNT) represent the state-of-the-art in catalytic carbon applications; they are a subtype of fullerenes characterized by a cylindrical shape and hexagonal rings connected to each other by strong covalent bonds. According to the number of concentric cylinders, they can be classified as single-wall (SWCNT) or multiple walls (MWCNT). Single nanotubes can adhere to each other through Van der Waals interaction forces. CNT show very high mechanical resistance, thus they are suitable for supports loaded into stirred batch reactors; moreover, the surface area can be very high (see Table 7) and this allows high dispersion of active-phase metals as well as a more reproducible loading of them.[54] Many production processes for CNT have been proposed, (i.e. CVD, arc discharge and laser ablation). CNT have been lately tested for hydrogenation reactions, especially as palladium, platinum and bimetallic catalysts support [54] showing interesting results. However, their cost is still much too high for being competitive especially with AC; moreover, depositing metals on CNT is not easy, since they are not wetted by most liquids. [63]

3.2.6 Properties of Carbon Catalysts

Many advantages are related to carbon supports: for example, they show high thermal stability in reducing atmospheres (but below 400-500°C for hydrogenation reactions); they are resistant either in acidic or basic media; mechanical resistance towards attrition and crushing is considerable; many macroscopic shapes are available (e.g. powder, fibers, pellets, monoliths); usually the cost is less than other conventional supports. Moreover, simply burning the carbon support, it is possible to easily recover the metals dispersed (especially noble metals) after the catalyst has been discharged from the reactor. Most carbons are polycrystalline, and this is a desired property in catalysis because the spaces (pores) between crystallites are the actual sites where adsorption of gas and liquid reactants takes place. This porosity leads to high surface areas, and it helps dispersing metal active phase on not-specifically acidic/basic surfaces (especially noble metals in hydrogenation reactions). [56] Table 7 shows a comparison of surface areas among different carbon supports.

Table 7: Typical surface areas of different carbon supports [54]



Support			Typical surface area, m^2 g^{-1}
Activated carbon			800–1200
Carbon black	Conventional		100–1500
	Graphitised		60–300
Graphite			10–50
Shaped carbon nanomaterials	CNTs	SWCNTs	1587[a]
		MWCNTs	400[b]
	Other	Carbon nano- and microspheres	10

[a] *After (i) debundling with DMF/EDA; (ii) acid treatment; (iii) wet oxidation*

[b] *After basic treatment*

Nevertheless, reactivity is also important: defects in the structure can interact with heteroatoms (e.g. oxygen, hydrogen, nitrogen, sulfur) through chemisorption. As a result, stable surface compounds (also called functional groups) are obtained and they affect the chemical reactivity, (even of the active phase). For example, oxygenated groups, simply formed by exposure of carbon to air (but also using some acids or bases), are very common and require large amount of heat to be removed. They can affect acidity/basicity of the surface;[56] a specific parameter called “Point of Zero Charge” (i.e. the value of pH at which the surface charge is globally zero, PZC) is used to evaluate the acidic or basic behavior of a surface: if pH<PZC, the adsorbent surface is positively charged (i.e. it attracts anions), while if pH>PZC the surface is negatively charged (attracting cations).[64] Hydrogen can make strong bonds with carbon, breakable above 1000°C, affecting for example electrical resistance. Nitrogen-groups are not spontaneously formed onto carbon surface, but their presence is of key importance for carbon acidity/basicity and for its performances as adsorbent. Sulfur (usually in elemental state) is typically a concern with catalysts, because it represents a common cause of deactivation; also with carbons, it affects surface reactivity, and it is removable by heating at high temperature (1000°C), as C-S complexes are very stable. Thus, surface modifications can occur spontaneously or intentionally, depending on the type of carbon and on the properties needed.[56] Apart from functional groups, whose presence can lead to active phase-support interactions, carbon can be considered almost as an inert support, at least less reactive than others (i.e. alumina); this is especially useful in preparation of bimetallic catalysts and also with iron, which is otherwise unlikely to remain in zero-valence form.[56,58] Carbons are commonly used as support for noble metal slurry catalysts. Despite the advantages seen so far are important, a problem is related to the reproducibility of the catalyst that may occur since the development of an accurate knowledge of this material is still in progress.[56]

3.3 Catalytic production of furfural

This paragraph focuses on heterogeneous catalysts proposed for producing furfural starting from hemicellulose. Since the dehydration of monosaccharides needs an acid to take place, many catalysts with this property have been studied in order to replace the corrosive acids used for commercial homogenous-phase reactions. Among them there are zeolites, heteropolyacids, zirconias, ion-exchange resins and solid cation exchangers.[7] A brief explanation of what they are and how they are applicable to furfural production is reported.

3.3.1 Zeolites

Zeolites have grown in importance in catalysis because of their versatility. They are alumino-silicate compounds with the addition of (metal) cations, which represent the actual active phase. The general structure is made of a combination of regular crystalline elementary cells, which form many "tunnels" (or cages); according to the size of such tunnels (usually the pore radius is between 3.6 and 7.4 Å), the zeolite acts as a "molecular sieve", allowing only compounds with adequate dimensions passing.[53] This has important consequences on the selectivity of the process, and very different zeolites can be synthesized according to the needs. Another advantage of zeolites is that, simply varying the Si/Al ratio, many properties can be regulated, such as the acidity of their surface, the thermal stability, hydrophilic/hydrophobic behavior, stability to acidic and basic media.[65] Table 8 summarizes the effects of Si/Al ratio. For what concerns furfural production, especially faujasite and mordenite showed high selectivity (up to 80%) and yield (43% and 34%, respectively) towards furfural.[7] Also silico-alumino phosphates (SAPOs) have been tested for furfural production; the best solutions are SAPO-5 and SAPO-11: because of their pore dimensions (0.73x0.73 nm and 0.64x0.44 nm respectively), they are selective towards the passage of xylose (molecular diameter=0.68 nm) and furfural (molecular diameter=0.57 nm), preventing side reactions because of spatial hindrance. The yields were approximately 65% (after 24h at 170°C) for SAPO-5 and 50% (after 4h at 180°C) for SAPO-11.[7]

Table 8: Effect of Si/Al ratio on zeolites properties [65]

Si/Al atomic ratio	Zeolites	Properties
Low (1-1.5)	A,X	Relatively low stability of framework, low stability in acid, high stability in base, high concentration of acid groups with moderate acid strength, hydrophilicity.
Intermediate (2-5)	Erionite, Chabazite, Clinoptilolite, Mordenite, Y	
High (~10 to ∞)	ZSM-5, Erionite, Mordenite, Y	Relatively high stability of framework, high stability in acid, low stability in base, low concentration of acid groups with high acid strength, hydrophobicity.

3.3.2 Heteropolyacids

Heteropolyacids (HPA) are acids usable both in homogeneous and heterogeneous catalysis. In their chemical structure hydrogen and oxygen are combined to a central "hetero" atom (i.e. S, P or Ar) and surrounded by metal "addenda" atoms (such as W, Mo, V, Ta, Nb), linked by oxygen.[53] Many different combinations of addenda and hetero atoms are possible, but especially two structures are known: Keggin's ($H_nXM_{12}O_{40}$, where X=hetero atoms and M=metal addenda atoms) and Dawson's ($H_nX_2M_{18}O_{62}$), reported in Figure 26. The surface area of HPA is low (5 m^2/g); thus they are usually supported on oxides (e.g. mesoporous silica), whose pore size is regulated according to xylose and furfural dimension, in order to prevent undesired side reactions.[53] Only a few experiments were conducted using HPA as catalysts for furfural production.[7]

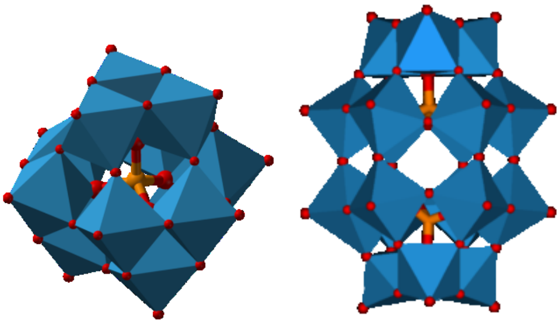


Figure 26: Heteropolyacids structures – Keggin's (left) and Dawson's (right) [66]

3.3.3 Zirconias

ZrO_2 (zirconium oxide, or zirconia) is a crystalline compound, in appearance a white powder, characterized by the so called "polymorphism": it means that its crystal phase can change according to temperature.[53] Especially, there are three different crystalline structures for zirconia: monoclinic up to 1170°C, tetragonal between 1170°C and 2370°C and cubic above 2370°C (Fig. 27).

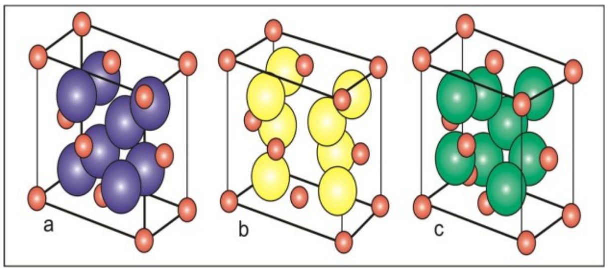


Figure 27: Zirconia crystalline structures- a) monoclinic; b) tetragonal; c) cubic [67]

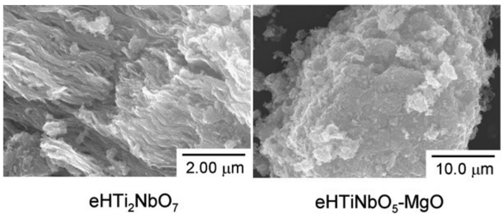
Usually, the form employed in catalysis (as well as the most thermodynamically favored) is the monoclinic one; although it has a very weak acidity (thus leading to low furfural yields, under 10%), zirconia can be sulfated. In this way, by increasing the acidic behavior, the catalytic activity in dehydration of monosaccharides is improved, providing furfural yields between 22% and 45% (at 160°C), higher than the values reachable with ordinary homogeneous H_2SO_4. Mesoporous sulfated zirconia and sulfated zirconia promoted with Al and supported on silica showed the best results. Deactivation problems of such catalysts are related to the loss of sulfate groups (especially when the catalyst is recycled) and worsened by the presence of water.[7]

3.3.4 Ion-exchange resins

The employment of ion-exchange resins (IER) is usually connected to water treatment or to separation of undesired ions from a solution. In general, the materials are insoluble polymers, which can exchange some ions present in the polymer with ions in the solution when they come in contact. Such exchanges do not modify the ion-exchange material.[68] The acidity of some sulfonated materials can be exploited to act as active site for dehydration of monosaccharides. IER used for this purpose need to show acidic behavior, thus the materials involved are co-polymers of styrene and divinyl benzene as cation exchangers, where sulfonic groups are the acidic active sites.[68] IER work stably in furfural production up to 130-150°C and they show an increase in both furfural yield and selectivity when temperature increases. Sulfonic acids can also work as active group on other supports: the best options are MCM-41 (a mesoporous silica) and Amberlyst-15 (a polymer), with furfural yields approximately of 75% and 60% at 140°C, respectively.[7]

3.3.5 Metal cation exchangers

Layered structures of cation-exchangeable metal oxides can be prepared as solid acid catalysts for dehydration of xylose into furfural; in this case, the advantage is a higher water-tolerability, thus a longer catalyst lifetime. The most studied compounds are layered niobates, titanates and titano-niobates.[7,71] In order to improve the catalytic activity, it is advisable to "exfoliate" the material in aqueous solution, obtaining colloidal single-crystal anionic nanosheets with increased surface area and number of acid sites (see Fig. 28).[69] Using a batch process, furfural selectivity showed a dependency from xylose conversion; the best result was 55% of furfural yield with xylose conversion of 92% at 160°C in aqueous phase over exfoliated e-$HTiNbO_5$-MgO after 4 hours. Increasing the temperature to 180°C allows obtaining same results with much lower residence time.[7,70] The outcome is promising, as this method appears more effective than homogeneous acids and some zeolites.



$eHTi_2NbO_7$ $eHTiNbO_5$-MgO

Figure 28: examples of exfoliated nanosheets [69]

3.3.6 The choice of the solvent

Apart from the choice of the catalyst, the solvent used is very important, as well. Water is the most economical and eco-friendly solvent, but it shows to rapidly deactivate heterogeneous acid catalysts.[7] Removing it from the reaction media can improve furfural selectivity. The use of organic solvents as water substitutes or co-solvents requires a quick removal of furfural as it is formed; otherwise, an energy-demanding separation process is needed. Suitable (co-)solvents are toluene, DMSO, MIBK and acetone, but they can create selectivity problems with catalysts affine to organic phase (such as hydrophobic ones). On the contrary, catalysts with hydrophilic surface may have lower activity in furfural production within aqueous solutions, as water might be preferably adsorbed on them. Thus, new solvents have lately been tested, such as supercritical CO_2, which is able to concentrate a furfural-rich phase above 95% wt. and to avoid coking (because it may help "cleaning" the catalyst pores from coke precursors). Another option is using ionic liquids, both as solvents and homogeneous catalysts. They are salts in a liquid phase: they contain at least an organic component and a delocalized-charged-ion, which prevents the formation of a stable crystalline lattice; thus, ions are poorly coordinated and such salts result as liquids below 100°C.[70] Although they are suitable for dehydration of xylose (as they show low vapor pressure and high thermal and chemical stability), they are expensive. Alternatively, the prompt removal of either furfural or water from the reaction environment can be helpful: for example, boiling furfural to a gas-phase prevents it from further reactions since no catalysts or intermediates are volatile.

3.4 Catalytic production of 2-methylfuran

This chapter concerns the production of 2-methylfuran focusing especially on liquid-phase hydrogenation of furfural, used for the experimental part.

3.4.1 Metal catalysts

As already cited in part 2.2.2, many different catalysts have been tested for the catalytic hydrogenation of furfural to 2-methylfuran, both in vapor- and liquid-phase hydrogenation reactions. It is convenient to briefly summarize the effects of different metal catalysts tested for this purpose: first of all, the goal when hydrogenating furfural is primarily to activate hydrogen molecules, which will subsequently reduce the active double bonds of furfural. Furfural contains three reducible double bonds: two C=C bonds on the furan ring and a C=O carboxyl bond. Different metals show different selectivity in reducing double bonds; however, in order to produce 2-MF, the purpose is to selectively hydrogenate C=O bond. Copper and nickel are the most active catalyst in this sense, yielding FA and 2-MF as main products. [45,65,73] Nickel especially exhibits too high activity in furfural hydrogenation (i.e. it tends to break molecules), showing poor selectivity towards the desired product; thus it is better not to use it in a skeletal form but to disperse it on suitable supports.[71] There is also the possibility to increase catalyst performances in C=O breaking by addition of oxophilic metals (such as Ti, Ni, W, Sn, which are likely to form oxides by hydrolysis or abstraction of oxygen from organic compounds) as promoters or using bimetallic systems. This second option is often applied: Ni- or Co-based catalysts showed high activity in furfural hydrogenation when used with Cu, Fe or Ce, reaching very high conversions (almost 100%).[71] However, the main product is FA (up to 90-95% selectivity), while the amount of 2-MF produced is acceptable only with Cu-Fe catalysts (probably because of the high electronegativity of Fe).[72] For example, a very good result, such as 51% yield of 2-MF, was obtained (together with 99% furfural conversion) on Cu-Fe catalyst (in the form of $CuO-CuFe_2O_4$) with liquid-phase hydrogenation at 220°C and 90 bar after 14 hours (under stirring condition, 1000 rpm), using octane as solvent.[24] Also silver is able to selectively brake C=O bond especially at high temperatures (>200°C), but it preferably yields FA (80% selectivity of Ag/SiO_2 [73]). Finally, large-particle-sized Pt catalysts are able to reduce selectively C=O bond.[74] Also Ruthenium was proved to be suitable for 2-MF production, reaching a 61% yield (which is the highest result reported in literature for liquid-phase hydrogenation) when supported on carbon. Operating conditions consisted in 10 hours reaction at 180°C, using 2-propanol both as solvent and hydrogen donor.[42]

3.4.2 Structure sensitivity and support effects

Together with the desired furfural hydrogenation reaction, many side reactions take place, such as further hydrogenation of 2-MF to MTHF, hydrogenation of furanyl ring to THFA and decarbonylation of furfural to furan. If working at high temperatures and pressure allows producing 2-MF more selectively (while at low T and P furfuryl alcohol is predominant), on the other hand these conditions favor side reactions as well. Thus, in order to improve the selectivity and the yields of the process it is important to understand which are the main factors influencing the reaction, such as operating conditions and especially interaction between reactants and catalyst. In literature there are many examples of how the microstructure (both of the active phase and the support) can affect the reaction. For example there are so called “structure-sensitive” (or “demanding”) reactions, where the catalyst activity depends on the atomic structure of the surface; thus, for what concerns supported catalysts, the reaction rate is strictly connected to the size and shape of the supported metal crystallites. On the contrary, reactions that do not depend on size or shape of metal crystallites are not affected by the preparation procedure of the catalysts and they are called “structure insensitive” (or “facile”) reactions. Some catalytic hydrogenation reactions are “structure sensitive”, including furfural hydrogenation[76-78]: using Pt nanoparticles, it resulted that small-sized particles (~1 nm) yielded mainly furan, while increasing the size (~10 nm) furfuryl alcohol was predominant.[74] Many other factors can affect the selectivity of the process, such as composition, oxidation state, adsorbate mobility, intermediate compounds, charge transport and metal-support interaction.[76] For what concerns furfural hydrogenation made with the purpose to produce 2-MF, according to many researches mesoporous oxides are not able to induce appreciable changes in selectivity. [76] However, a different nature of carbon supports can (but not always) affect the catalytic properties of the catalyst, acting on the metal-phase dispersion. For example, CB and CNT differ in surface acidity (PZC= 6.1 and 7.7 respectively) and area (lower specific area and large average pore size for CNT). As a consequence, especially in the aqueous-phase hydrogenation of furfural over noble active-phase metals (e.g. Pd and Ru), CB-supported catalysts showed high activity and selectivity towards FA even at mild conditions (50°C, 0.5MPa) while CNT, with lower amount of hydrophilic functional groups, needed more severe temperatures and pressures (90°C, 2MPa) to be active.[75] On the contrary, when using copper dispersed over carbon supports, such as AC, diamond and graphitized fibers, furfural hydrogenation is not affected by the support: all three materials show similar behaviors. Especially, reducing the catalyst at lower temperature (300°C instead of 400°C) increases its activity, probably because copper is very sensitive to sintering at high temperatures; moreover, the reaction is structure-insensitive: the support affects the crystallite size, but this parameter is not as important as the amount of active sites (with oxidation state Cu^0 and Cu^+). The same result is obtained when Cu is used in association with other elements (for example Ni or Fe).[24] In general, Cu-based catalysts show very low hydrogenation of double C=C bond, yielding mainly furfuryl alcohol and 2-methylfuran.[77] The selectivity of these products is also connected to the acidic strength of the active sites of the catalyst, which can be measured through temperature programmed desorption analysis (NH_3-TPD) and which is adjustable by choosing a different kind of support (to produce new active sites). [78] Sometimes the catalytic activity can be increased adding some additives or using bimetallic systems: increased activity is probably related to an increase of metal electron density or to the production of new active sites.[42]

3.4.3 Solvent effects

Support and catalyst formulation are not the only relevant factors for controlling the reaction: also the choice of the solvent is of key importance, since it represents a potential participant in the reaction. Moreover, in heterogeneous catalysis the solvent can help controlling the reaction rates, dissipating heat in exothermic reactions and cleaning the catalyst surface from occurring site blockers.[79] Finally, when C=O bond hydrogenation is required, the solvent can suppress side reactions (such as ring hydrogenation or etherification). Especially, liquid-phase hydrogenation studies showed that both catalytic activity and product distribution are influenced mainly by the type of solvent used, more than what the nature of the catalyst and the initial amount of furfural can do.[42] It is already known that using water as a solvent can reduce the costs and the risks for the environment, but it actually worsens furfural hydrogenation reaction; moreover, aqueous solvents lead to the production of cyclopentanol and cyclopentanone, products out of this work purpose. Thus, liquid-phase furfural hydrogenation is usually performed using organic solvents, such as alcohols; they mainly produce FA, THFA and 2-MF and they can be used either merely as solvents or as hydrogen donor through dehydrogenation (catalytic transfer hydrogenation process, CTH). Figure 29 summarizes the furfural conversion and products yields in liquid-phase catalytic hydrogenation of furfural using different alcohols as both solvents and donors (CTH) over Ru/RuO_2/C catalyst. The reaction was carried at 180°C and 2.04MPa N_2 for 5h.[42]

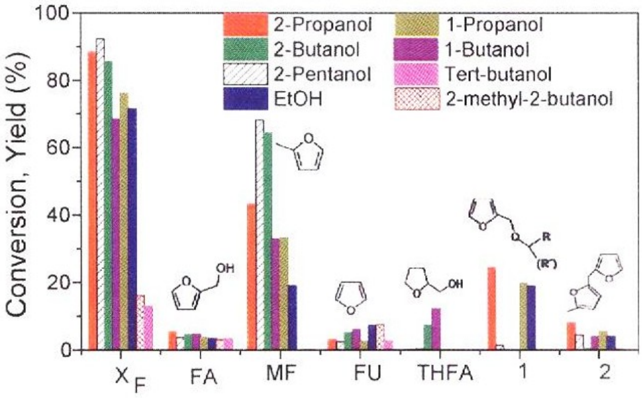


Figure 29: Furfural conversion and main products yield using different alcohols as hydrogen donors: F=furfural, FA=furfuryl alcohol, MF=2-methylfuran, FU=furan, THFA=tetrahydrofurfuryl alcohol, 1=ether of FA and alcohol, 2=2-(2-furanylmethyl)-5-methyl furan [80]

Still, little is known about solvents effects, since liquid-phase hydrogenation studies seldom focus on this aspect. However, it seems ascertained that polar solvents (e.g. 2-propanol, ethanol) enhance the adsorption of non-polar reactant and vice versa. As a result, 2-MF yield decreases when alcohol polarity increases. In corroboration of that, Fig. 30 illustrates that, at lower dielectric constant (i.e. an indicator widely used in literature to characterize solvent either as polar or not) values, 2-MF yield can reach very high values (68%) with 2-pentanol.[80]

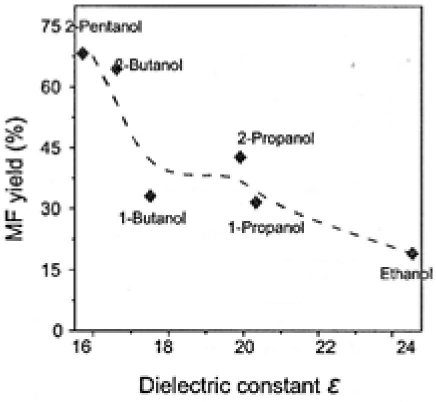


Figure 30: Effect of dielectric constant of different solvents on 2-MF yield [80]

Moreover, it was found that 2-MF yield is the result of a complex interaction among the etherification of the alcohol with FA (yielding 2-(isopropoxyl)methyl furan), the likelihood of the alcohol to dehydrogenate and the possible FA dimerization.[80] At low temperatures FA etherification is predominant, reaching a peak around 140-180°C, according to the solvent used (Fig. 31B). At higher temperatures instead, since the etherification reaction is not favored, dehydrogenation mainly occurs and 2-MF yield grows (Fig. 31A).

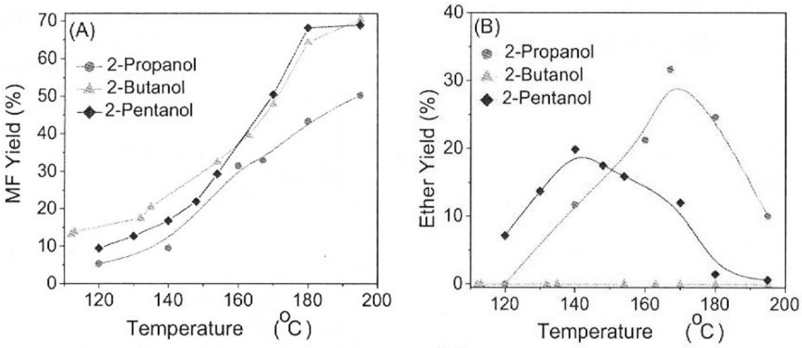


Figure 31: Effect of temperature on 2-MF production (A) and etherification (B) reactions with various solvents. [80]

Concluding, furfural conversion is strictly connected to the alcohol chosen: tertiary alcohols (i.e. with three alkyl groups bonded to C-OH) are totally inactive (due to their little dehydrogenation); secondary alcohols (i.e. with two alkyl groups) are more effective than primary ones (because short chain alcohols favor the etherification with FA which is competitive with hydrogenolysis to 2-MF). As a consequence, 2-MF yield is higher when the dehydrogenation activity is higher. [44,82]

EXPERIMENTAL PART

The present experimental part has been developed within the CatBio project at the Industrial Chemistry Department of Aalto University. CatBio project concerns the hydrogenation of furfural using carbon-based catalysts in order to produce value-added chemicals. In this work, the catalytic liquid-phase hydrogenation of furfural was mainly performed over activated carbon Norit® RB4C supports with the addition of various metal active phases. The goal was to evaluate the effectiveness of such catalysts in the production of 2-methylfuran.

4. MATERIALS AND METHODS

This chapter illustrates materials, instrumentation and working procedure used during the experiments.

4.1 Materials

All the reactants were purchased from Sigma-Aldrich without undergoing further purification: furfural (99%), furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (99%), furan (≥ 99%), 2-methylfuran (99%), 2-methyltetrahydrofuran (≥ 99%, anhydrous, inhibitor free), 2-propanol (ACS reagent, ≥ 99.5%) and 2-butanol (99%). For what concerns the catalyst support, steam-activated Norit® RB4C and acid-washed Norit® RX3 Extra granulated activated carbon were used. Supported catalysts were either prepared with incipient wetness impregnation method or with atomic layer deposition (ALD) technique see part 4.2. The catalysts were calcined at 300°C for four hours in synthetic air flow (4 l/h); however, some of them required calcination in N_2 flow (12 l/h) in order to avoid decomposing of carbon particles to powder. 2-propanol was used as solvent, since it is often employed in furfural hydrogenation;[45,91] it is a secondary alcohol, which enhances furfural hydrogenation and its polarity (dielectric constant=20,18 [82]) is suitable for 2-MF production (see part 3.4.3). Although it is not completely inert in reaction conditions (i.e. it reacts with furfural to produce acetone[43]), it has been chosen as solvent since it has little impact for environmental pollution and human health (if compared to toluene, hexane and methanol) and it has a reasonable cost. Also water-ethanol mixture was tested as solvent, but it produced unwanted solid by-products (i.e. organic compounds insoluble in water at every pH, called "humins") and it altered the obtained products into unwanted direction.

The reactor used for the experiments is an Autoclave Engineers Mini-Reactor, with a volume of 50mL and a Robinson-Mahoney catalyst basket (Fig. 32).

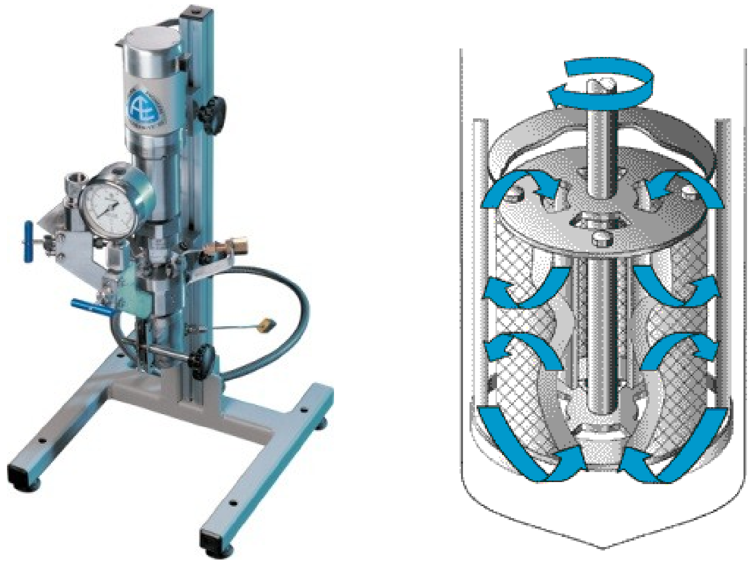


Figure 32: Autoclave Engineers Mini-Reactor and Robinson-Mahoney catalyst basket [83]

The hydrogenation reaction was carried under stirring conditions (1000rpm) in order to avoid external diffusion limitations, at high temperature (230°C) and high hydrogen pressure (i.e. hydrogen cold pressure 40 bar, increasing to 65-70 bar with mixture vapor pressure at 230°C reaction temperature), thus maintaining the liquid phase. The samples withdrawn from the reactor were analyzed through a gas chromatograph (GC) Hewlett-Packard 6890 Series connected to a flame ionization detector (FID); the column used by the GC is a Zebron ZB-wax Plus Column. Three injections were made for each sample, to avoid analytical errors: an average of the measured values was used for calculations. Injection volume was 0.5µL and injection temperature was set at 230°C while the column has a temperature ramp of 5°C/min from 40°C to 100°C and of 20°C/min from 100°C to 230°C, with final 4 minutes hold. A gas-phase sample was also withdrawn at the end of the experiment and analyzed through Agilent Technologies 6890N Network GC system, with three columns (HP-AL/KCL, HP-PLOT/Q and HP-MOLESIEVE) and both a FID (flame-ionized detector) and a TCD (thermal conductivity detector). The temperature ramp was of 9.5°C/min between 0-40°C and of 10°C/min in the range 40-200°C.

4.2 Catalysts preparation

The procedure of catalysts preparation is of key importance, since it considerably affects the catalyst properties and performance. There are many methods available for this purpose. However, for what concerns supported catalysts, it is possible to classify them in two macro-categories: the first one involves a physical interaction between support and active phase and it includes atomic layer deposition (ALD), precipitation (and co-precipitation) and impregnation techniques; the second category requires a chemical interaction, allowing a better dispersion of the active phase, like in adsorption and ionic-exchange methods. In this work, the supported catalysts were prepared through impregnation and ALD techniques, thus only such methods will be taken into consideration.

4.2.1 Impregnation

Impregnated catalysts are generally obtained starting from preformed supports, on which the active phase is then deposited in the form of a precursor. It is a typical method for preparing hydrogenation catalysts, especially for furfural hydrogenation. The support is put in contact with a certain volume of solution containing a precursor of the active element of the catalyst; according to the amount of solution used it is called either "wet" impregnation (i.e. with excess of solution) or "dry" impregnation (a volume of solution is less than support pore-volume). It also exists the "incipient wetness" impregnation if the volume of solution is equal to the pore-volume: this option was used to prepare the catalysts. It is possible to control the loading of the active phase by modifying the solution concentration when using a dry impregnation technique. The contact between support and solution must be adequate to provide a good dispersion of the active-phase precursor; in this sense, temperature is definitely the main operating variable, since it affects both solution viscosity and the precursor stability, thus the "wetting time".[84] Subsequently, the support must be dried to remove any liquid and finally it is calcined and/or reduced, according to the active-phase element; the reduction can also be performed directly inside the hydrogenation reactor (i.e. *in situ*, as in our experiments).

4.2.2 ALD

Atomic layer deposition, or ALD, is a valid method to deposit nano-sized metal particles on porous supports. It consists of exposing the surface of the support to alternate gaseous precursors in order to create a thin film. Also in this case, some suitable precursors are used. The precursors react separately with the surface (i.e. they are not simultaneously present inside the reactor, as in chemical vapor deposition) when sent on it through sequential pulses. Each exposure lasts until all the reactive sites available are consumed, thus a very uniform layer can be produced over almost every type of support; this is called "ALD cycle". The loading of active element can be regulated by changing the number of depositing cycles, and, in addition, it is possible to grow the film uniformly. Compared to impregnation, it allows reaching very high dispersion levels and the particle size is more controllable, as well. When using carbon as support, ALD is more complicated since carbon does not present many active sites, which are indispensable for anchoring metal particles on the surface. Thus, some pretreatments could be necessary, for example thermal oxidation. [85]

4.3 Catalysts characterization

Catalysts characterization is of key importance in order to understand which phenomena occur during a catalytic reaction. Thus, some of the tested catalysts underwent characterization before the experiments.

4.3.1 Characterization methods

In the following part, the main techniques used (physisorption, TPD, TPR and TEM) will be presented.

4.3.1.1 Physisorption

In order to characterize the surface of heterogeneous catalysts in terms of surface area and porosity (i.e. pores size and volume), the most used method is physisorption. It is a type of adsorption, which is the adhesion of atoms, ions or molecules from a bulk phase to a surface. This phenomenon is strictly connected to the nature of the surface: the type of bonding created during this process can be either a weak Van der Waals force (and in this case a physisorption occurs) or a strong covalent bond (leading to chemisorption).

Physisorption is used to measure the distribution and the total volume of micro and meso-pores (respectively 0-2nm and 2-50nm of diameter); for a complete characterization of macro-pores (> 50nm), a mercury intrusion porosimetry should be used as well. An inert gas, typically nitrogen, is used for the purpose; in some cases, for example for zeolites or activated carbons, argon and CO_2 are preferred to accurately identify the smallest micropores. This inert gas is adsorbed on the surface of the solid material and, in case of porous materials, on the surface of pores, as well. Adsorption of nitrogen at 77K leads to what is called “adsorption isotherm”, generally described as BET (from the names of its inventors: Brunauer, Emmett and Teller). According to this model, it is possible to calculate the specific surface area (S_{BET}, m^2/g) with the following equation:

$$S_{BET} = n_M \cdot A_M \cdot N_A \qquad \text{(eq. 17)}$$

where N_A is the Avogadro constant (~$6.022 \cdot 10^{23}$ molecules/mole), n_M is the monolayer coverage (mol/g) and A_M is the space occupied by each adsorbed molecule of nitrogen, which is known (16.2 $Å^2$). Measuring the quantity of N_2 molecules adsorbed at a monolayer coverage it is possible to calculate the internal surface area; on the other hand, the quantity of gas condensed into the pores returns the pore size.[86] It is important to pre-treat the sample at high temperature in vacuum or in flowing gas, in order to remove occurring contaminants. The analysis returns an isotherm curve similar to the one showed in Figure 33 (many differences may occur, according to the type of surface investigated); the range of P/P_0 ratio analyzed for S_{BET} calculation is between 0.05 and 0.3. For what concerns pore volume measurement instead, the range of condensation must be considered. It is remarkable that, if the curves of adsorption and desorption are compared, they are not perfectly superimposable, since the mechanisms involved in pore filling and emptying are not the same (i.e. capillary condensation); the resulting discrepancy is called "hysteresis".

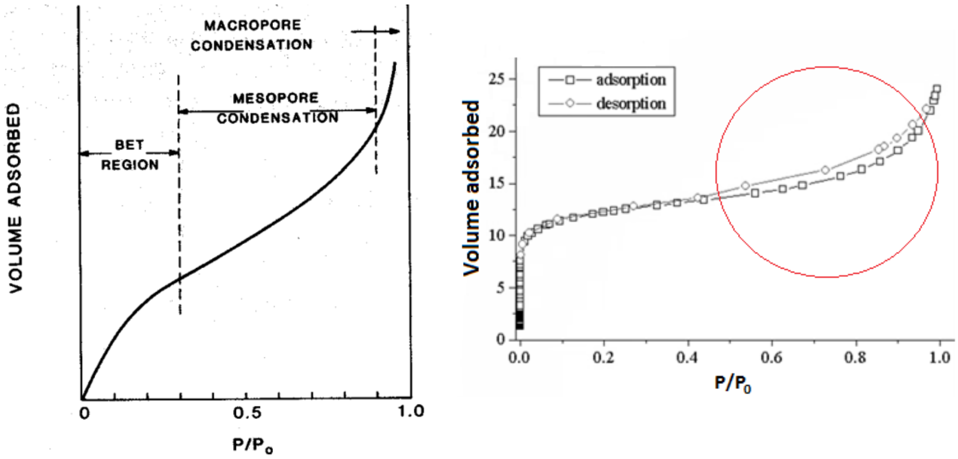


Figure 33: Typical isotherm curve for physisorption (left) and hysteresis (right)

4.3.1.2 TPD

The temperature programmed desorption (TPD) is a technique which allows studying the surface groups of the catalyst (together with adsorption mechanism, kinetic and thermodynamic parameters of desorption process. It is very important in heterogeneous catalysis, as it gives information about the amount of adsorbed species, the adsorption properties and the presence of acidic/basic sites on catalyst surface. The analysis consists of heating a sample with a temperature program within an inert atmosphere in order to cause the opposite mechanism of adsorption, such as desorption. In this way, the sample releases some molecules previously adsorbed; such molecules are then detected and measured (for example with mass spectrometry). Desorption temperature is strictly connected to the adsorption energy of different compounds over the sample: molecules with high adsorption energy are released at high temperature. Two different kinds of adsorption are possible, that is physisorption (when weak electrostatic interactions such as Van der Waals forces are predominant) and chemisorption (when chemical bonds are formed); as a consequence of the different forces involved, the physisorbed species are released at lower temperature and usually they are removed from the sample before the actual temperature-programmed analysis starts. Each compound found results in a desorption-curve as the types shown in Figure 34; especially the right-side picture shows the half and three-quarter width peaks, which are important parameters for a rough-estimated analysis. The area under the peak is proportional to the adsorbed amount of a certain compound, while position and shape of the peaks indicate some properties of the adsorption process (such as desorption energy and heterogeneity).

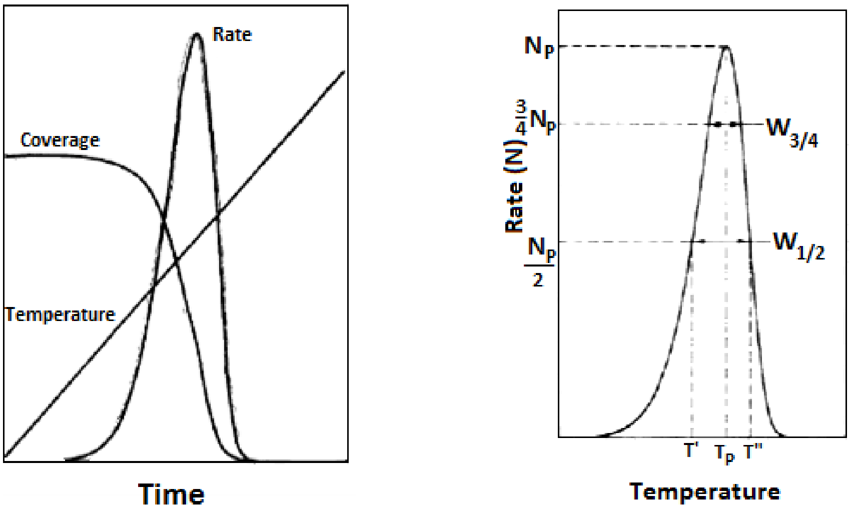


Figure 34: Temperature programmed curve-types

For what concerns single-crystalline samples or well-defined surfaces, another technique is often used, that is called continuously-pumped ultra-high vacuum (UHV) technique, also called thermal desorption spectroscopy (TDS). [87] Finally, to investigate the density of acidic (or basic) sites, adsorption and desorption processes of so called “probe compounds” are analyzed.

4.3.1.3 TPR

Temperature programmed reduction (TPR) is a technique to identify the most efficient reduction conditions. An oxidized catalyst precursor undergoes a programmed-temperature rise (generally a linear ramp) under the flow of a reducing gas mixture, usually hydrogen and an inert gas such as nitrogen or argon. If a reduction takes places, the amount of hydrogen in the effluent gases is reducing as the reaction proceeds, and such amount is measured with suitable detectors (e.g. mass spectrometer). In this way it is possible to estimate the reduction temperature needed for certain metal-containing catalysts and the reduction kinetics, as well as the influence of the support on reducibility. Each analysis returns some peaks and it is possible to evaluate the temperature at which H_2 consumption rate is maximum.[86]

4.3.1.4 TEM

The transmission electron microscopy (TEM) is a local method of analysis which results in very high-resolution images of samples, with magnification of even 1 million times (vs. 1200x of optic microscopes). Unlike the common optic microscopes, it doesn’t use light as source of power, but it is based on the interaction between the surface and a beam of electrons; the image produced is the result of the properties (for example trajectory deviation and energy) of sensor-detected electrons (Fig. 35).

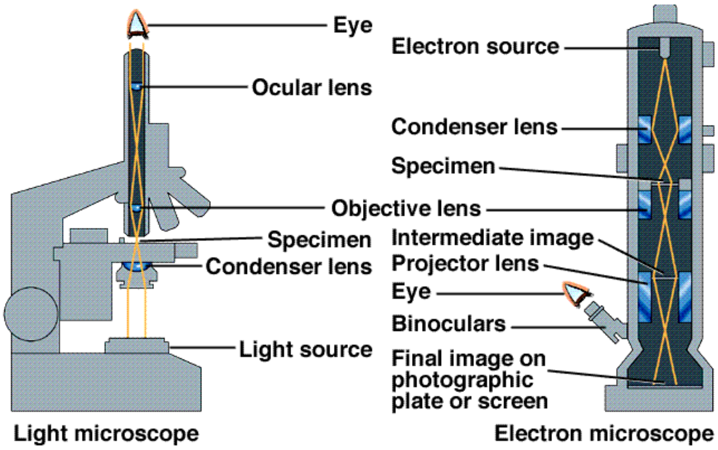


Figure 35: Comparison between light optical microscope (left) and transmission electron microscope (right) [88]

The sample has to undergo some pre-treatments in order to be analyzed, such as it must be a very thin layer (< 0.1 µm); it is very important that the sample does not emit any gases during the analysis, therefore it is analyzed under high vacuum environment (in order to prevent any deviation of the electrons caused by air molecules). It is very useful for studying the surface of metals and supports used in catalysis, for what concerns not only the morphology (i.e. shape and size of metal dispersed particles) but also for crystallography (i.e. how the atoms are disposed onto the sample surface, lattice parameters and eventual defects) and surface composition (which means identifying elements and compounds occurring onto the surface, TEM-EDS).

4.3.2 Characterization results

4.3.2.1 Type of support

Comparing the datasheets of the two Norit® supports, the main difference is the quantity of adsorbed butane (20 and 28 g/100g for RB4C and RX3, respectively, at $p/p_0=0.1$). Moreover, from titration experiments, the amount of acid sites measured was 0.20 mmol/g_{cat} for RB4C and 0.22 mmol/g_{cat} for RX3; hence, the higher RX3 acidity (due to an acidic wash) seems to be confirmed. The supports also underwent a TPD analysis, both before and after the calcination. Using a mass spectrometer to analyze the species desorbing from the surface, the main basic groups detected on the uncalcined supports were anhydride/phenol groups and phenol/carbonyl/quinone groups, while acidic groups were carboxylic acid, carboxylanhydride and lactone groups. After the calcination, only phenol/carbonyl/quinone and lactone groups remained. The presence of groups on the catalyst surface is useful, since they represent possible attaching sites for the metal deposited onto the catalyst itself. Still, it remains unclear how the differences between the two supports can affect furfural hydrogenation.

4.3.2.2 Impregnation vs. ALD

Some catalysts (supported on Norit® RB4C) were investigated through TEM in order to better understand the experimental results. Especially, many tests compared impregnated and ALD catalysts.

Impregnated 2% Ni showed particles between 2 and 4 nm, while same ALD catalyst had some particles even an order of magnitude bigger (~20 nm), together with 2-4 nm-sized particles. Similar results occurred when analyzing 2% Cu: the metal formations are sufficiently small (10-30 nm) with impregnation, bigger (25-100 nm) with ALD. However, in both cases, some particles aggregated; this is undesirable, since clustering lowers the metal dispersion, thus the catalytic activity. For what concerns impregnated Ni-containing catalysts, such as 2%/2% CuNi and NiFe, no nickel was detected during the analysis (probably because mixed together with the other metals); the other single metal particles were small (a few nm) but found together in clusters over 100 nm wide. ALD 2%/2% NiFe had both Ni and Fe particles between 5 and 40 nm. Finally, also 2%/2% impregnated CuFe was tested, showing aggregated particles of 20-100 nm; also single iron particles were detected (50-250 nm).

4.4 Experimental procedure

The catalyst (0.2g in the form of pellets with size between 1.68 and 2mm) was loaded into the catalyst basket and reduced *in situ* at 250°C (or 200°C) with 40 bar hydrogen cold pressure for 1.5 hours. All lines were flushed with nitrogen before both the reduction and the hydrogenation reaction, in order to avoid any traces of air. The reactant mixture, made of 15mL of solvent (2-propanol) and 1mL of furfural was introduced into a feeding tank; once the temperature in the reactor had reached 230°C, the mixture was introduced into the reactor with 40bar hydrogen pressure. A simple scheme of the experimental apparatus is reported in Figure 36.

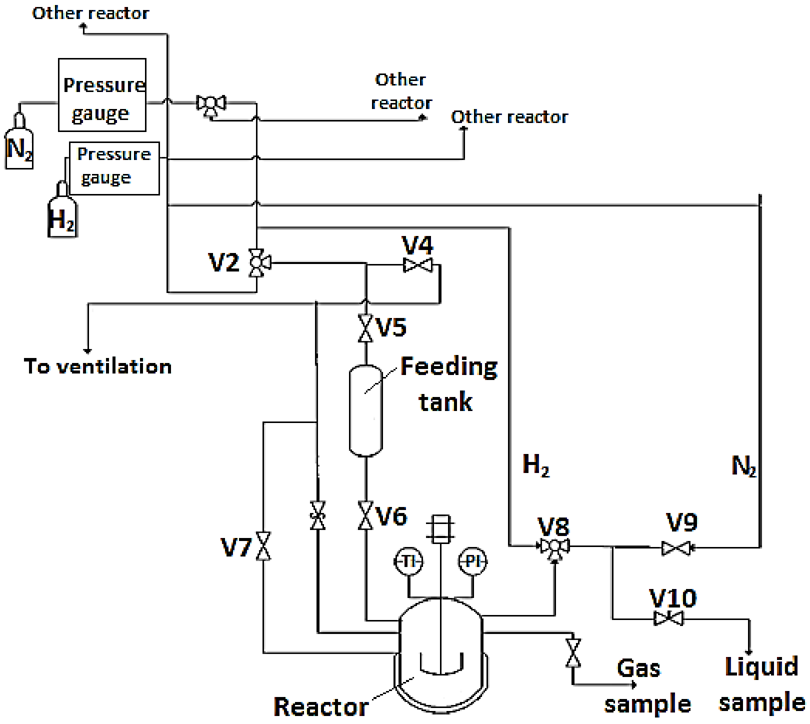


Figure 36: Experimental apparatus scheme

Samples of the reaction mixture were taken at 0, 15, 30, 60, 120 and 300 minutes; each sample was cooled in an ice-bath, while still inside the sample loop, in order to ensure its liquid phase. Then, samples were filtered from occurring impurities (with 0.45µm-meshed filters), stored in sealed vials (using 2-butanol as external standard) and analyzed through gas-chromatography. Two days were required for each catalyst to be tested.

4.5 Gas chromatography analysis

Chromatography can return both qualitative and quantitative results, since each compound present in the sample is eluted in the column at different times, thus returning different peaks. According to the retention time it is possible to distinguish the components of a mixture that are expected to be in that mixture; for identifying other unknown compounds, a mass spectrometer can be applied. By measuring the area under the peak, it is also possible to calculate the amount of a certain compound, giving an evaluation of its concentration in the original sample using calibration curves. Calibration was done for several liquid compounds: furfural, furfuryl alcohol (both calibrated in the range 0.5-25m%), 2-methylfuran, THFA and furan (all calibrated in a range between 0.5 and 15m%), since they represent the most common products of furfural hydrogenation. Also 2-butanol was calibrated, as the external standard (in the range 0.5-25m%). The m% of each compound was plotted together with the peak area measured through GC analysis; as a result, a linear function was obtained (linear regression of data). The model is described by the following equation:

$$y = mx + y_0 \qquad \text{(eq. 18)}$$

where y is the instrument response, m is the slope and y_0 is a constant (describing the background). The slope of the lines was determined and the response factor (F) was calculated: the latter is very important when analyzing the results. It can be calculated as follows:

$$F = \frac{Slope_{STD}}{Slope_i} \qquad \text{(eq. 19)}$$

where subscript i represents each of the compounds (i.e. furfural, FA, 2-MF, THFA, furan, 2-propanol and 2-butanol).

Figure 37 presents an example of chromatogram. Three main peaks are visible: the numbers written on top of them are the measured retention times; it is possible, knowing the typical retention times, to identify such compounds as 2-propanol (5.806), 2-butanol (7.356) and furfural (16.003).

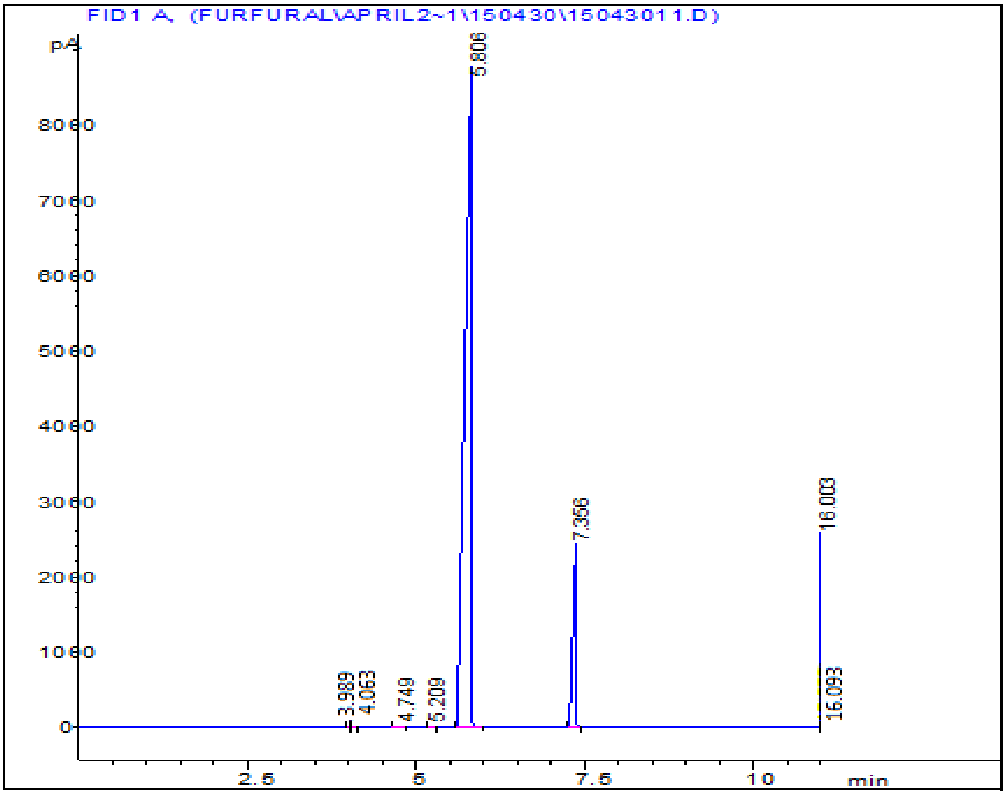


Figure 37: Example of a calibration chromatogram

The chromatograms and especially the values of the retention times were compared among the injections (three for each sample) to prove the reliability of the test. In addition, the software measured some peak features, such as height (y-coordinate) and area.

Table 9 reports the retention times of the most-likely-occurring products in the reaction mixture during furfural hydrogenation. They can vary according to the oven temperature profile, and also during the experiments some slight differences were noticed among the measured retention times of same compounds; this could mean that columns utilization rate, age and used gas flow have an effect on the retention times. However, it does not affect the results of the experimental part, since all the following compounds were easily individuated.

Table 9: Retention times of main products of furfural hydrogenation

Compound	Retention time
Di-isopropyl ether	3,63
Furan	4,24
Acetone	4,40
2-methylfuran	4,91
2-methyltetrahydrofuran	4,96
2-propanol	5,77
2-pentanone	6,55
MIBK	7,00
2-butanol	7,40
2-pentanol	9,53
1-butanol	10,14
2-pentanol, 4-methyl	10,56
2-furan methanol acetate	13,79
Furfural	16,08
THFA	16,48
Furfuryl alcohol	17,76
Trans-furfurylidene acetone	19,47

The values of area peak measured through GC were used to calculate the mass of a certain compound in each sample, according to eq. 20:

$$m_i^{SAMPLE} = \frac{F_i \cdot A_i \cdot m_{STD}}{A_{STD}} \qquad \text{(eq. 20)}$$

F_i is the response factor, A_i is the peak area, m_{STD} is the mass of the standard (2-butanol) contained in the vial sample and A_{STD} is the peak area of the standard. From such mass (expressed in grams) it is possible to calculate the corresponding concentration per gram of sample (mmol/g, eq. 21).

$$C_i = \frac{1000 \cdot m_i^{SAMPLE}}{MW_i \cdot m_{SAMPLE}} \qquad \text{(eq. 21)}$$

In this equation, MW stands for molecular weight and m_{SAMPLE} is the measured mass inside the GC-vial before the introduction of the standard.

4.6 Conversion, selectivity and yield

Calculating the concentration for the various samples taken at different times, it is possible to draw the conversion curve of a component; the conversion of furfural, χ_{FURF} , is calculated with equation 22:

$$\chi_{FURF} = \frac{C^0_{FURF} - C^t_{FURF}}{C^0_{FURF}} \cdot 100 \qquad \text{(eq. 22)}$$

The goal is to convert as much furfural as possible, since it is the main reactant and the main source of 2-MF. But conversion alone is not enough: also a high selectivity must be achieved, which means that the reactant has been transformed into the desired product. Selectivity (S) can be calculated with the following expression:

$$S_i = \frac{C^t_i}{(C^0_{FURF} - C^t_{FURF})} \cdot 100 \qquad \text{(eq. 23)}$$

By multiplying conversion and selectivity, yield (Y) is obtained:

$$Y_i = \frac{\chi_{FURF} \cdot S_i}{100} \qquad \text{(eq. 24)}$$

4.7 Tested catalysts

Many combinations of different metals and supports where tested in order to analyze their performances in furfural hydrogenation towards 2-MF. However, the choice of the metals was made according to studies available in literature where valuable and selective hydrogenation properties were pointed out. These catalysts were all prepared within the CatBio research group through either impregnation or ALD methods. Table 10 reports the catalysts tested during the experiments.

Table 10: Tested catalysts

Metal	Support	Notice
-	Norit RB4C	only support, not calcined
2% Cu	Norit RB4C	
5% Cu	Norit RB4C	
2% Ni	Norit RB4C	
5% Ni	Norit RB4C	
10% Ni	Norit RB4C	calcined with N2
2% Ni	Norit RX3	
2%/2% CuNi	Norit RB4C	
2%/2% CuNi	Norit RX3	
2%/2% CuFe	Norit RB4C	calcined with N2
2%/2% NiFe	Norit RB4C	
2%/2% NiFe	Norit RB4C	calcined with N2
5%/2% NiFe	Norit RB4C	
5%/5% NiFe	Norit RB4C	
Cu	Norit RB4C	ALD calcined with N2
Ni	Norit RB4C	ALD calcined with N2
CuFe	Norit RB4C	ALD calcined with N2
NiFe	Norit RB4C	ALD calcined with N2
Co	Norit RB4C	ALD calcined with N2

5. RESULTS OF THE EXPERIMENTS

In this chapter, the results of the experiments will be presented making comparisons among different catalysts' performances as well as analyzing the consequences of changing some operating conditions.

In a typical test, the selectivity towards the desired product (2-MF) is always below 50% despite furfural often reaches almost perfect conversion. The reason is that during furfural hydrogenation several reactions take place: undesired products come not only from furfural itself, but also from FA (which is the intermediate of 2-MF) and from consecutive hydrogenations of 2-MF. Figure 38 summarizes some of such reactions.

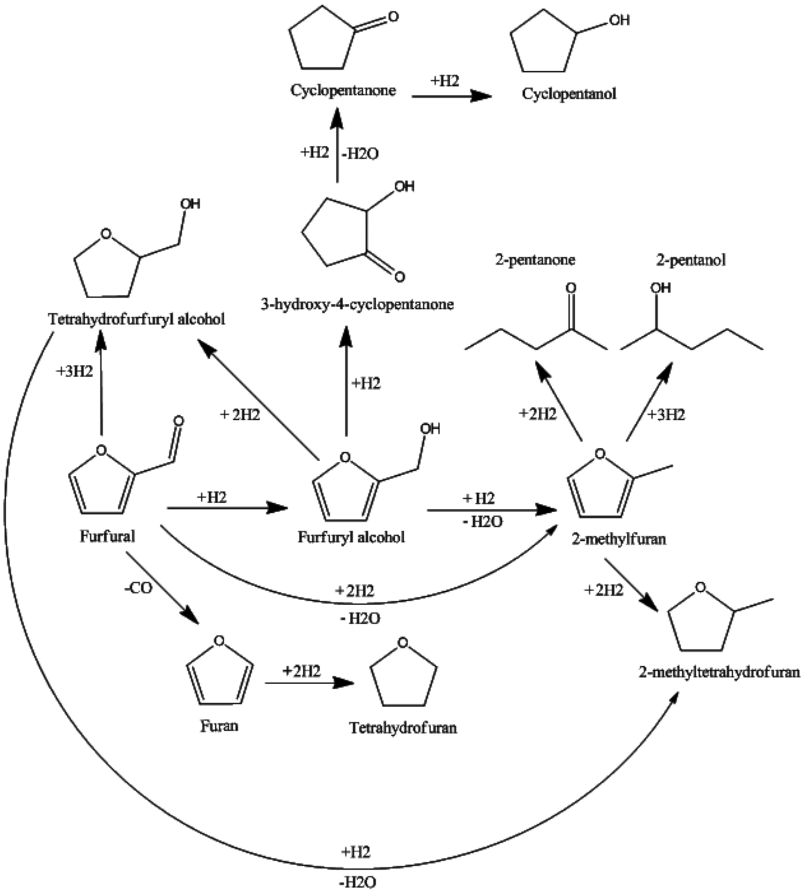


Figure 38: Reaction paths during furfural hydrogenation

As a confirm of the fact that a high number of products is obtained through catalytic hydrogenation of furfural, the mass balance for some catalysts (i.e. the most active) was calculated, in order to estimate the amount of unidentified compounds. Carbon balance is the most significant: starting from the initial amount of carbon contained in the reactant (i.e. furfural), the carbon content in the products was evaluated during the reaction time. As shown in Fig. 39, 100% mass balance could not be reached because not all the compounds have been identified yet. Unidentified compounds represent a significant part of the product mixture, especially because there is the tendency to form aggregates (such as polymers) containing numerous carbon atoms. Moreover, coke formation is very likely to happen; thus, significant carbon losses can occur. Finally, some compounds can turn into gases (see part 5.9), but such amount is relatively insignificant.

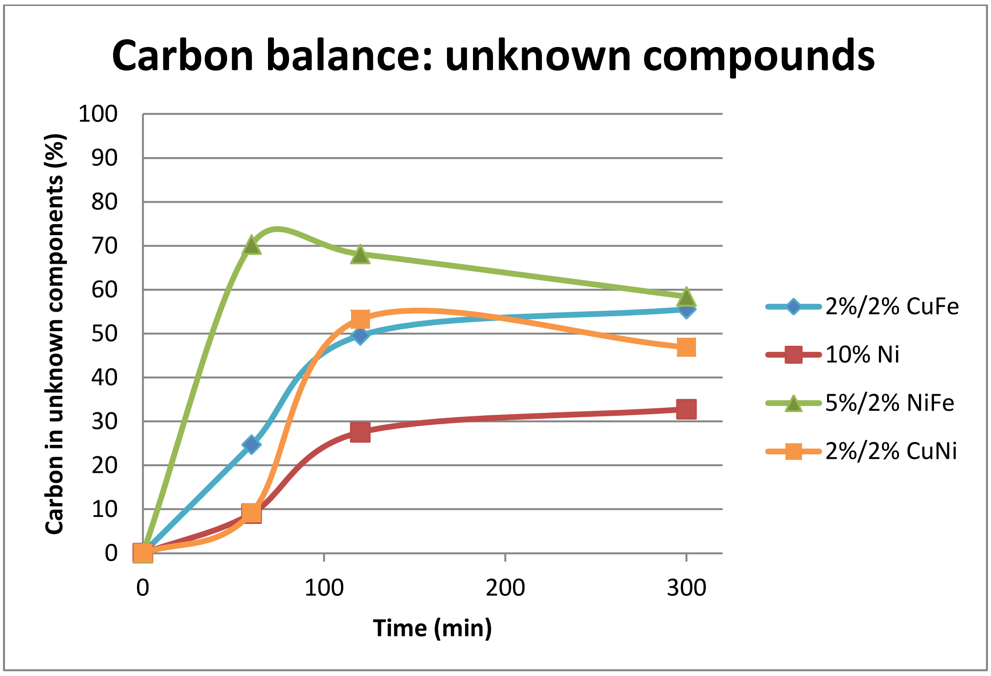


Figure 39: Carbon content in unknown products of furfural hydrogenation with different catalysts

5.1 Effect of the carbon support

5.1.1 Experiment with only carbon support

In order to check the reactivity of the materials involved, an experiment without any metal phase, but just with RB4C support was performed. The result is very interesting: as shown in Figures 40-42, the support is not inert for this reaction, but shows furfural conversion and production of FA.

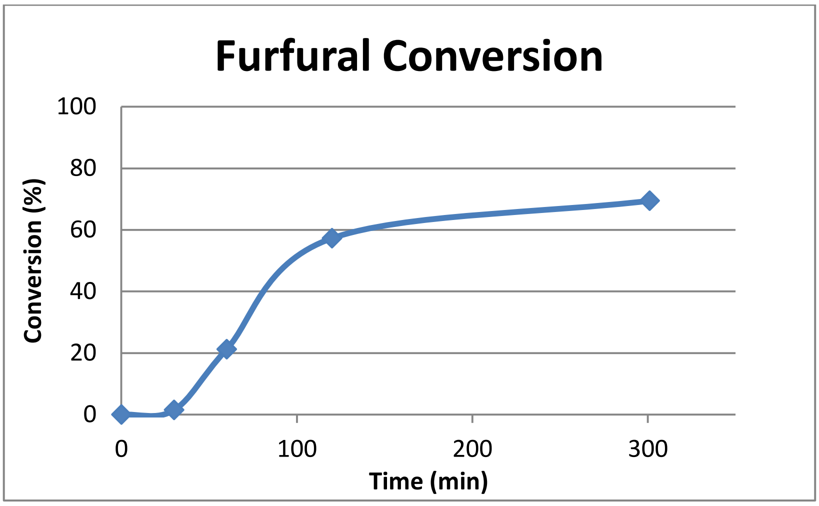


Figure 40: Furfural conversion with only support Norit®RB4C

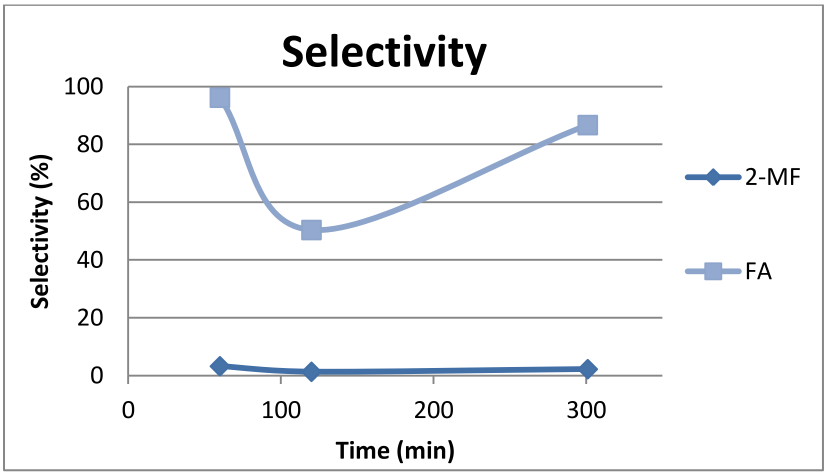


Figure 41: Selectivity towards 2-MF and FA with only support Norit®RB4C

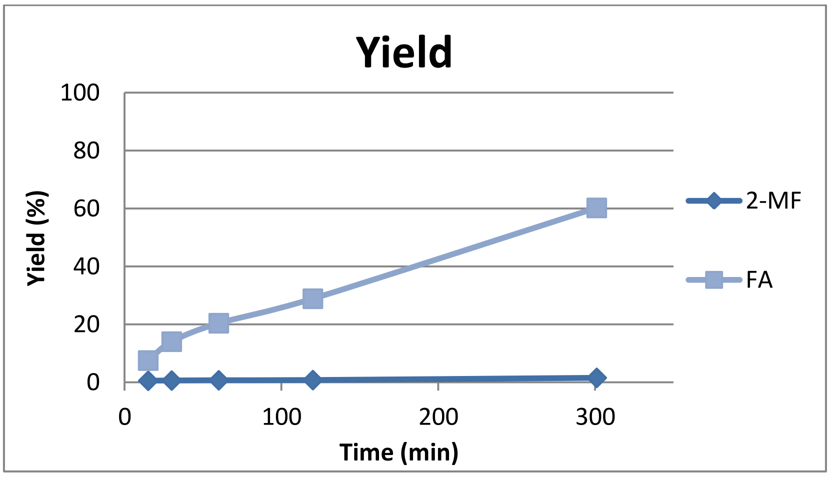


Figure 42: Yield towards 2-MF and FA with only support Norit®RB4C

Although 2-MF is practically absent, it is significant that the support contributes to produce the intermediate product FA. The trend of FA selectivity shown in Fig. 42 may result from an outlier value, since no other products were detected in significant amounts.

5.1.2 RB4C vs. RX3

During the experiments, two different types of AC-support were tested: steam-activated carbon Norit® RB4C and acid-washed activated carbon Norit® RX3. As explained in part 4.3.2, the main difference between the two supports is their acidity: RX3 is more acidic compared to RB4C. The diagrams below show the results in furfural conversion, 2-MF yield and selectivity. This kind of comparison was made for 2% Ni (Fig. 43-45) and 2%/2% CuNi (Fig. 46-48) catalysts.

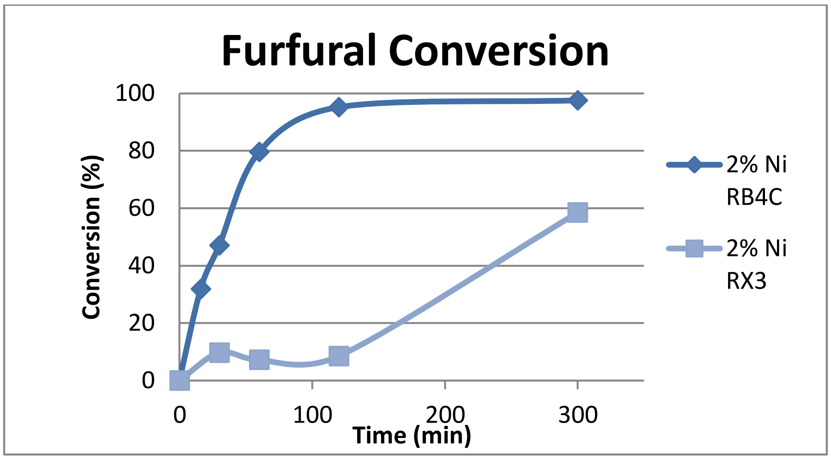


Figure 43: Furfural conversion with 2% Ni over Norit®RB4C and RX3

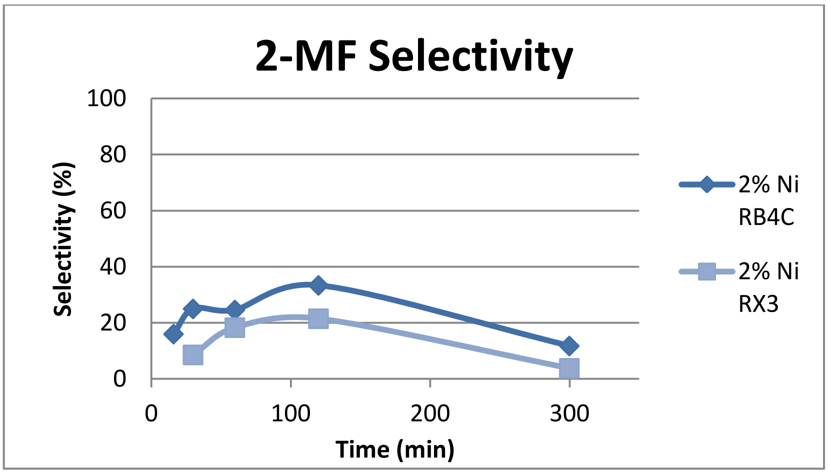


Figure 44: 2-MF selectivity with 2% Ni over Norit®RB4C and RX3

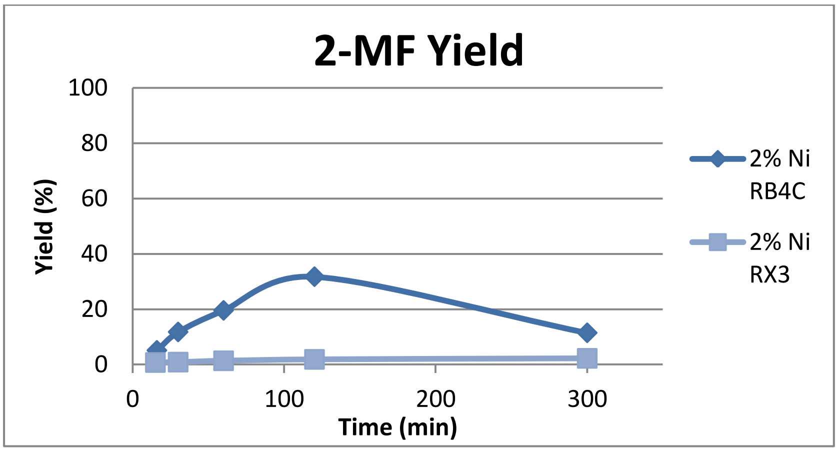


Figure 45: 2-MF yield with 2% Ni over Norit®RB4C and RX3

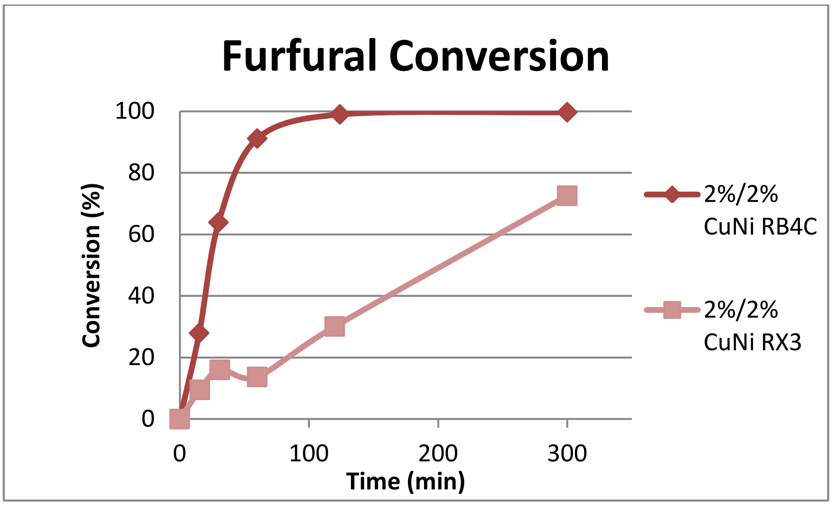


Figure 46: Furfural conversion with 2%/2% CuNi over Norit® RB4C and RX3

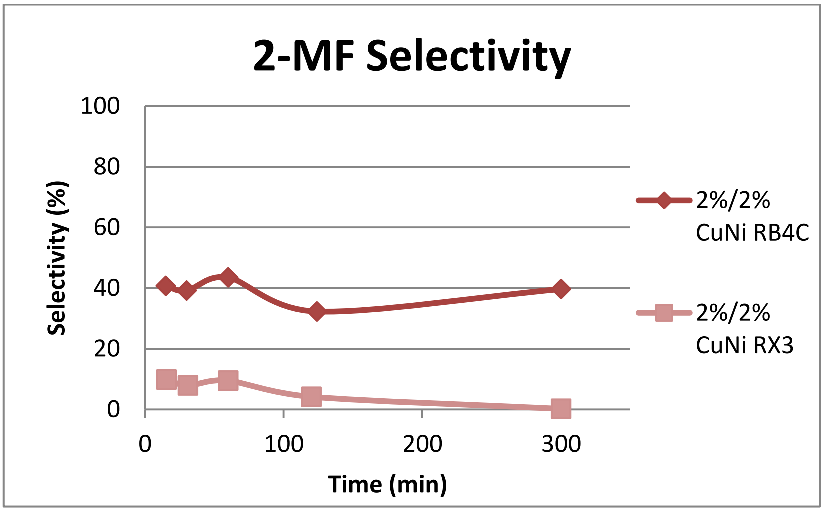


Figure 47: 2-MF selectivity with 2%/2% CuNi over Norit® RB4C and RX3

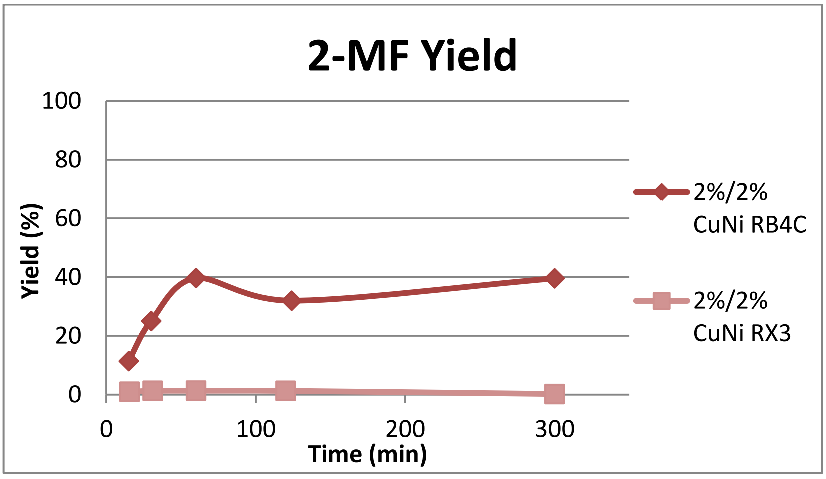


Figure 48: 2-MF yield with 2%/2% CuNi over Norit® RB4C and RX3

For both catalysts, RB4C supports achieved higher conversion of furfural and higher yield and selectivity of 2-MF than RX3 ones. Because of the poor performances, other RX3 catalysts were not further investigated. However, such behavior is not clear: some characterization is required for finding a possible explanation. For example, it is important to check whether the metal was effectively dispersed and anchored to the carbon surface and if the pore structure and size may cause internal mass transfer limitations.

5.2 Metal loading

Focusing only on Norit® RB4C as support, many tests were made changing the amount of metal active-phase on the catalyst, especially for Cu, Ni and Fe (the latter used in bi-metallic catalysts together with Ni).

5.2.1 Effect of copper loading on catalytic activity

Impregnated copper catalysts were tested with 2% and 5% loading; as shown in Fig. 49-51, the increasing amount of metal leads to higher conversion of the reactant, but also improves the production of 2-MF. Moreover, 5% Cu was reduced at two different temperatures: 250 and 200°C. As a matter of fact, a lower reduction temperature shows better results; this is probably due to a sintering of the metal occurring at higher temperatures, which brings to lower metal dispersion, thus to a lower activity. Cu-only catalysts reach the highest selectivity in 2-MF after 120 min, while with all the other Cu-based catalysts tested, selectivity continues increasing throughout 300 min reaction time (see following parts).

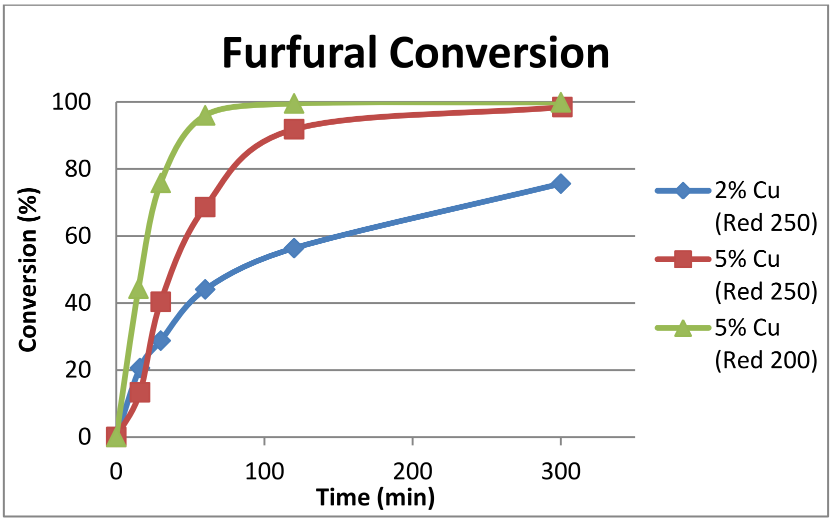


Figure 49: Cu-load and reduction temperature effects on furfural conversion

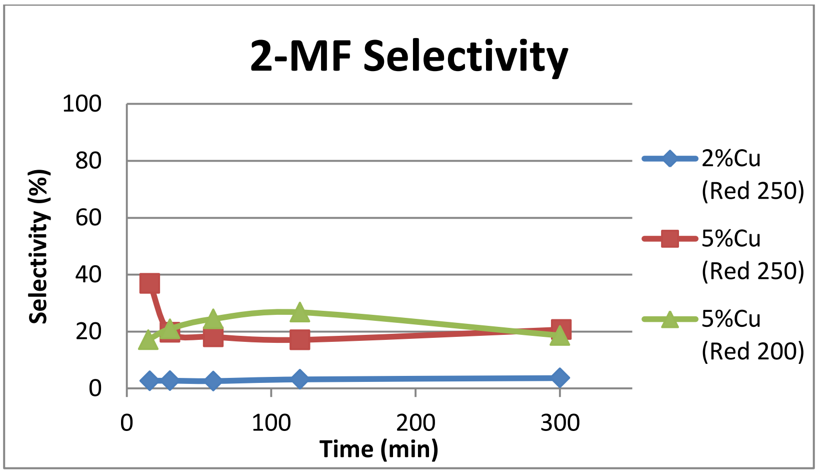


Figure 50: Cu-load and reduction temperature effects on 2-MF selectivity

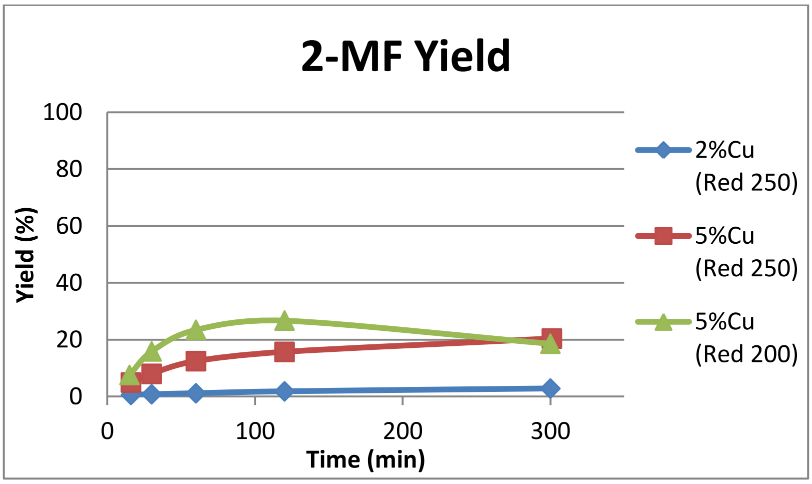


Figure 51: Cu-load and reduction temperature effects on 2-MF yield

5.2.2 Effect of nickel loading on catalytic activity

The analysis of the effect of Ni load dispersed on the catalyst showed interesting results; 2%, 5% and 10% Ni were tested, always reducing them at the same temperature (i.e. 250°C). The results are presented in Figures 52-54.

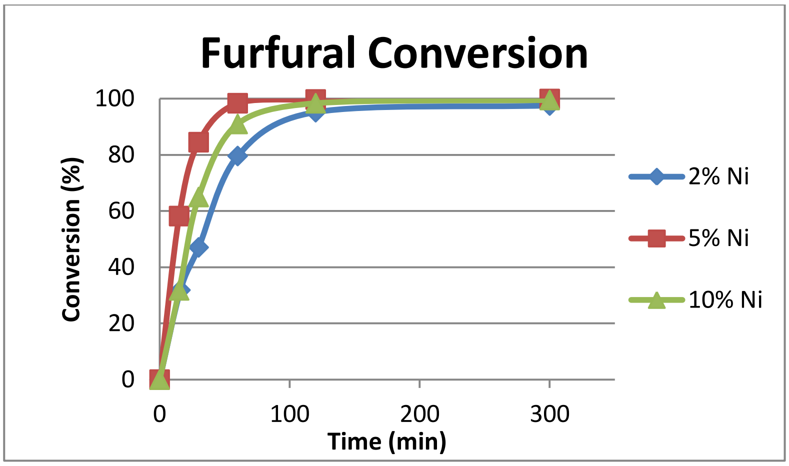


Figure 52: Ni-load effect on furfural conversion

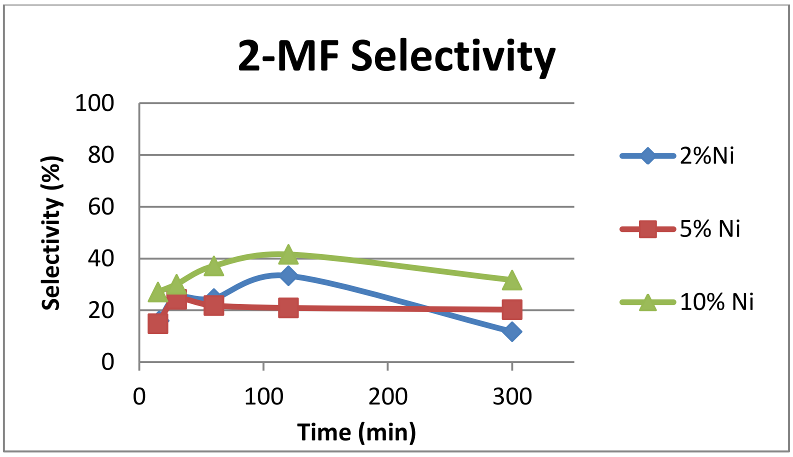


Figure 53: Ni-load effect on 2-MF selectivity

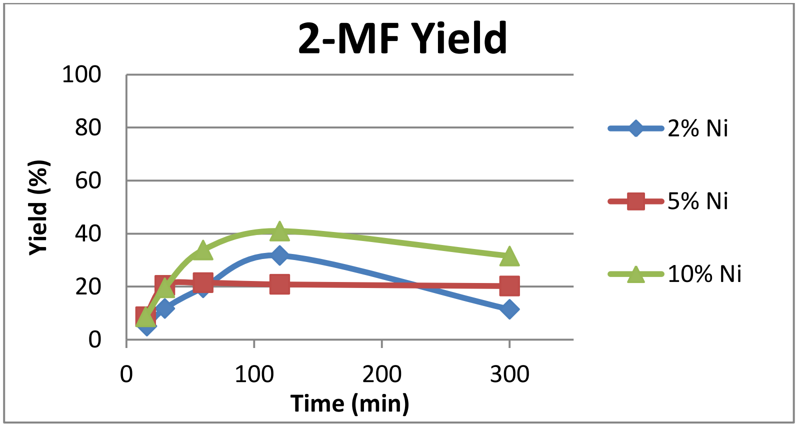


Figure 54: Ni-load effect on 2-MF yield

The intermediate load leads to the highest and the fastest conversion: lower dispersion corresponds to a lower metal load, while a higher load can cause particles aggregation. Though, the intermediate load shows the lowest selectivity for 2-MF production, almost constant around 20%; as a matter of fact, 2-MF preferably requires a larger amount of metal to be produced. However, the relationship existing between 2-MF yield (and selectivity) and the loading of Ni is not linear. Therefore, this result is the exact opposite of what was found out for Cu. The reason of that might be related to a different reaction mechanism involved.

5.2.3 Effect of iron loading on catalytic activity of Ni catalysts

A bi-metallic NiFe catalyst was tested, changing either iron or nickel amount in the following ratios: 2%/2%, 5%/2% and 5%/5% NiFe; also 5% Ni was reported to see the effect of Fe addition (Fig. 55-57). Iron is often used to improve the hydrogenation of furfural, but its amount should be carefully evaluated. Comparing 2%/2% and 5%/2%, it is interesting to notice that, for what concerns furfural conversion, the result obtained for nickel-only catalysts is maintained, i.e. 5% Ni is more active than 2%; however, the discrepancy between the two curves is much less when iron is added as a promoter. The 5%/5% NiFe curve is basically perfectly superimposable to 5%/2% NiFe one, confirming that the actual active phase in furfural hydrogenation is Ni; Fe is just a promoter.

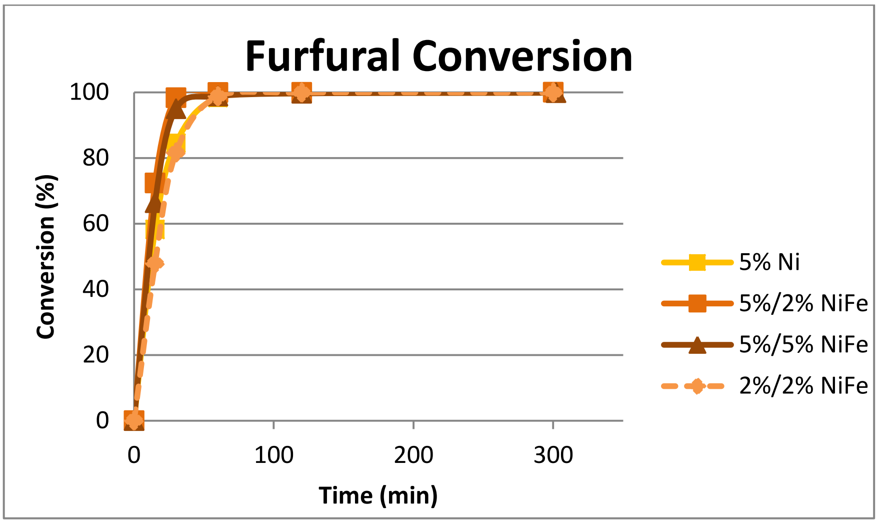


Figure 55: Effect of metal loading in bi-metallic NiFe catalysts on furfural conversion

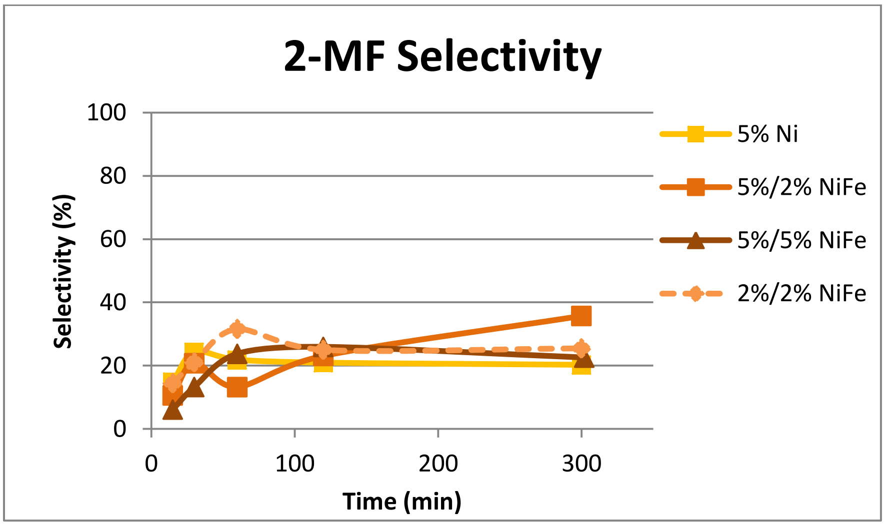


Figure 56: Effect of metal loading in bi-metallic NiFe catalysts on 2-MF selectivity

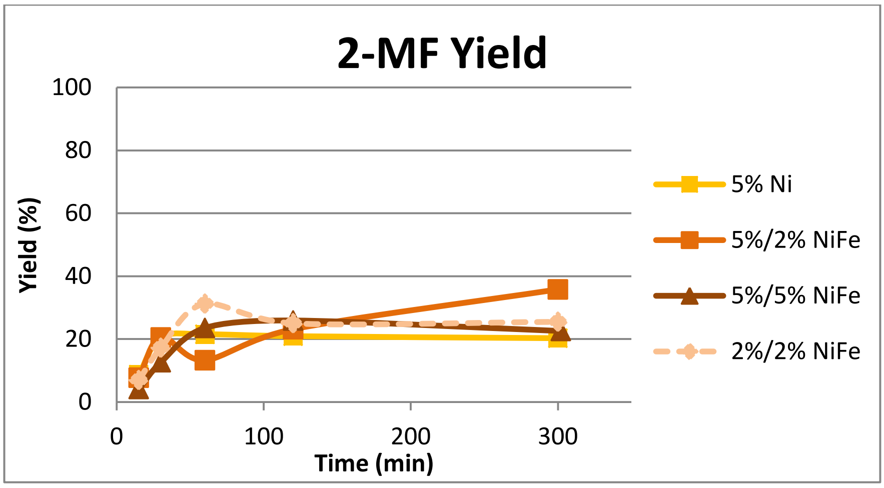


Figure 57: Effect of metal loading in bi-metallic NiFe catalysts on 2-MF yield

In terms of 2-MF production, both selectivity and yield show that for short residence times (< 100 minutes) 2%/2% NiFe is better than 5%/2% NiFe, with a peak of 31.2% and 31.6% of yield and selectivity, respectively, after one hour. For t > 100 min instead there is a trend-inversion: the 2-MF produced over 2%/2% NiFe decreases; on the other hand, 5%/2% NiFe curve grows, reaching 35.7% of both yield and selectivity after 5 hours. Moreover, the lower peak should be better considered as an outlier value. 5%/5% NiFe has an intermediate behavior: the trend is smoother and the maximum value in 2-MF yield and selectivity is lower than for the other catalysts. Therefore, an excessive amount of metals on the catalyst surface should be avoided. Moreover, for short-time reactions 2%/2% NiFe is preferable, while for long-time reactions 5%/2% NiFe is the best.

5.3 Bi-metallic copper catalysts

According to literature, copper-chromite was the first effective catalyst discovered for 2-MF production. Though, the amount of 2-MF obtained in our experiments with pure Cu is still low (below 30%); therefore, associating it with other metals can be a solution to improve the selectivity towards 2-MF. As a matter of fact, bimetallic CuNi and CuFe showed the best catalytic performances towards the desired product 2-MF among all tested catalysts.

5.3.1 CuNi alloy

Copper and nickel are the most active metals in furfural hydrogenation; thus, the obvious thing to do is to combine them, in order to get the best out of each. A 2%/2% CuNi catalyst was prepared (using Norit®RB4C as support); the results are reported in Figures 58-60, comparing CuNi with single-metal 2%Cu and 2%Ni catalysts. At same metal loading and operating conditions (both in reaction and reduction processes), the bimetallic catalyst has the highest activity: probably the high Ni activity is “guided” preferably towards 2-MF because of the presence of copper. In this way, almost 40% yield and 43.5% selectivity were achieved.

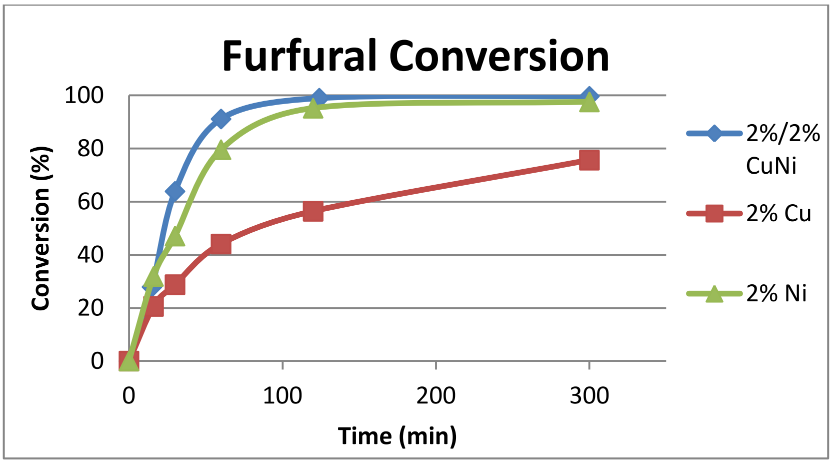


Figure 58: Single-metal Cu and Ni catalysts and bimetallic CuNi performance in furfural conversion

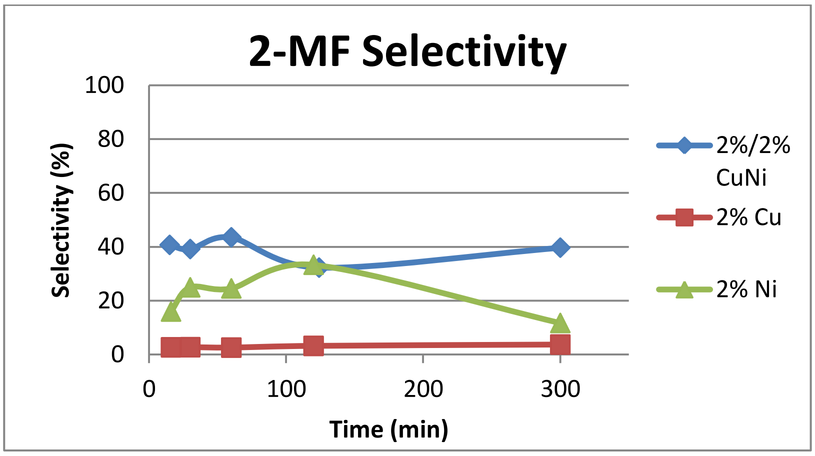


Figure 59: Single-metal Cu and Ni catalysts and bimetallic CuNi performance in 2-MF selectivity

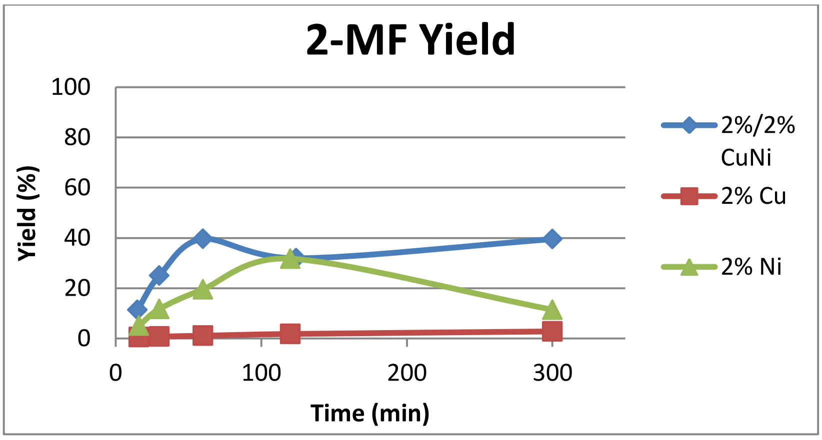


Figure 60: Single-metal Cu and Ni catalysts and bimetallic CuNi performance in 2-MF yield

5.3.2 CuFe alloy

A 2%/2% CuFe catalyst was also tested, showing very good results. The addition of iron to copper catalysts is reported in literature as a way to improve the hydrogenation activity; though, its action is not completely clear yet. The load of Fe suitable for hydrogenation catalysts varies in a range between 2 and 25%; however, the optimum amount should be chosen according to the support and the operating conditions. Figures 61-63 report the results, showing the increasing performances in 2-MF production (and in furfural conversion) due to iron presence (if compared to copper catalyst).

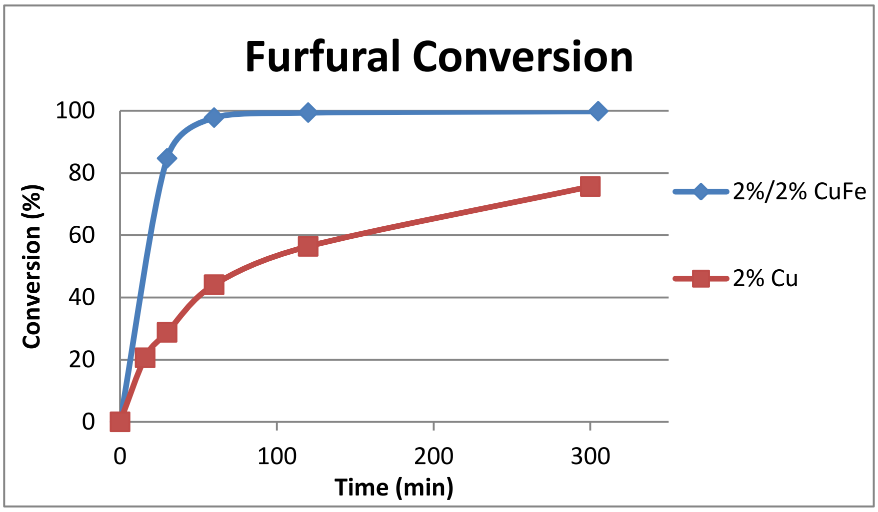


Figure 61: Furfural higher conversion over 2%/2% CuFe vs. 2% Cu

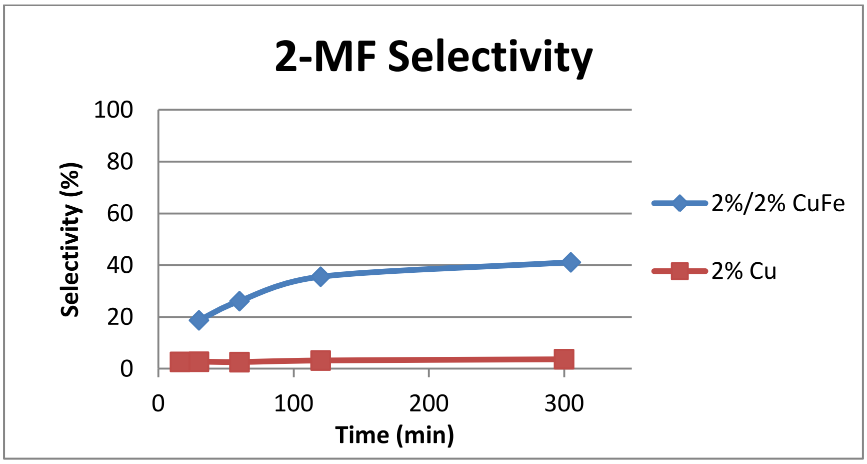


Figure 62: Higher 2-MF selectivity over 2%/2% CuFe vs. 2% Cu

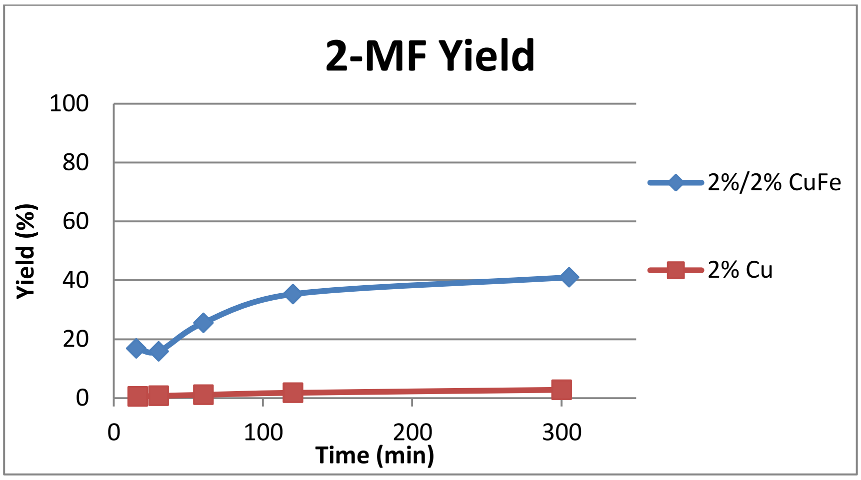


Figure 63: Higher 2-MF yield over 2%/2% CuFe vs. 2% Cu

Unfortunately, for this bi-metallic system only a ratio of 2%/2% CuFe could be prepared, since increasing the amount of iron causes serious problems for what concerns the mechanical resistance, leading to pellets powdering. Nevertheless, acceptable 41% of yield and selectivity were achieved; in literature only one study has proved to get a better result over a Cu-Fe catalyst (i.e. 51%), but only after 14h reactions, almost three times more than our experiment duration.

5.4 Effect of catalyst preparation method

The results presented so far only concerned impregnated catalysts. However, two different techniques were used for catalyst preparation: impregnation and ALD. In the following part a comparison between the two techniques will be made.

5.4.1 Nickel catalysts

For what concerns Ni catalysts, Fig. 64-66 compare a 5% Ni catalyst prepared through impregnation and an ALD-prepared 5.6% Ni one.

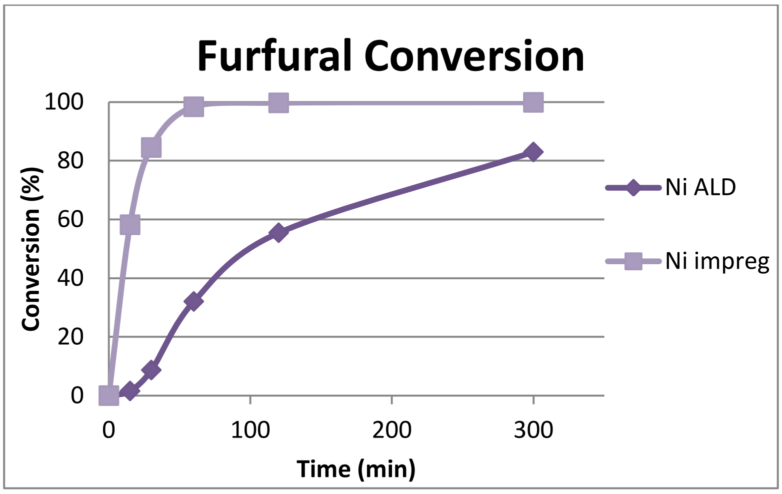


Figure 64: Furfural conversion with impregnated 5% Ni vs. ALD 5.6% Ni

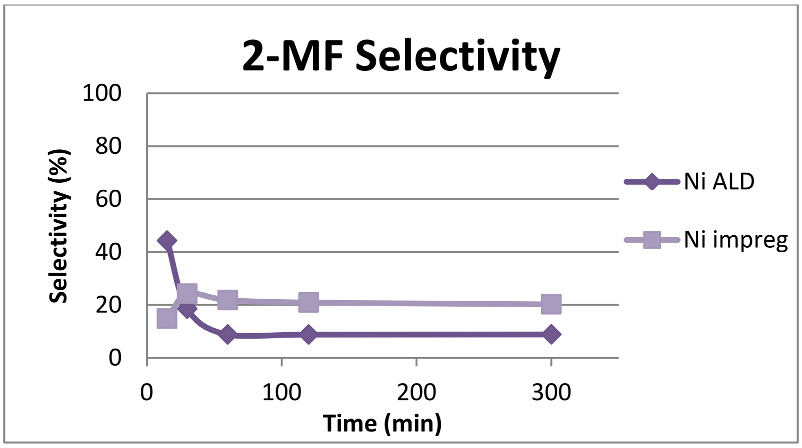


Figure 65: 2-MF selectivity with impregnated 5% Ni vs. ALD 5.6% Ni

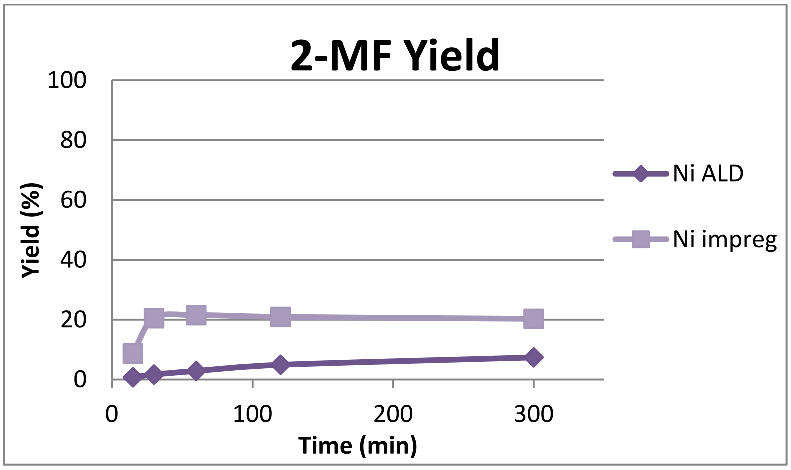


Figure 66: 2-MF yield with impregnated 5% Ni vs. ALD 5.6% Ni

In this case, the metal loading is very similar; however the ALD catalyst shows lower and slower furfural conversion, as well as lower values of 2-MF selectivity and yield (the 44% selectivity at the beginning of the reaction occurs at very low furfural conversion and it could be affected by inaccuracy).

5.4.2 Copper catalysts

Copper catalysts prepared with different methods are compared in Figures 67-69: the metal loading is not comparable, since the ALD led to a 14.38% Cu; a 5% Cu reduced at 200°C was chosen to represent the impregnated catalysts (since it was the best impregnated Cu-catalyst). As discussed in part 5.2.1, Cu seems to have a linear relationship between metal load and furfural conversion, as well as 2-MF production; thus, a better activity would be expected in the case of ALD catalyst. However, the results prove the exact opposite: final furfural conversion is lower with the ALD catalyst and the reaction is definitely slower than in the case of impregnated catalyst. Same considerations can be extended to 2-MF selectivity and yield. A possible reason to explain this phenomenon is that over a certain metal loading, its dispersion is not high enough anymore (e.g. clustering).

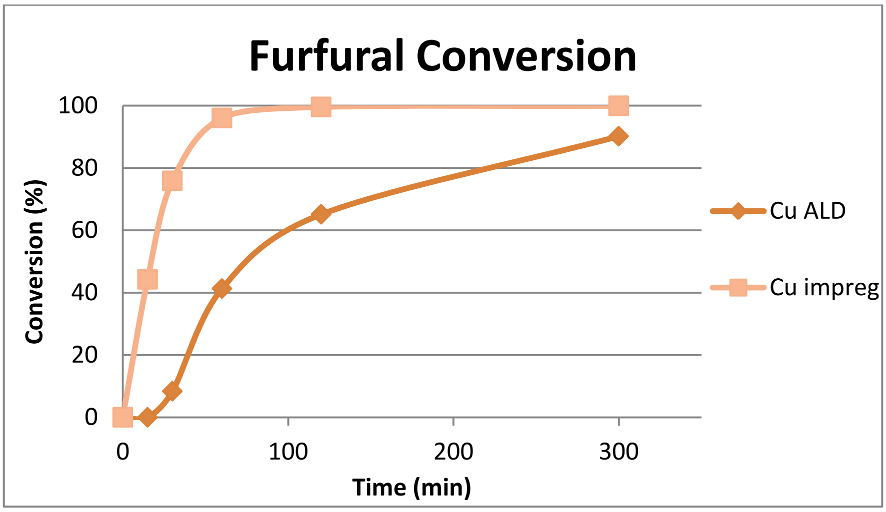


Figure 67: Furfural conversion with impregnated 5% Cu vs. ALD 14.38% Cu

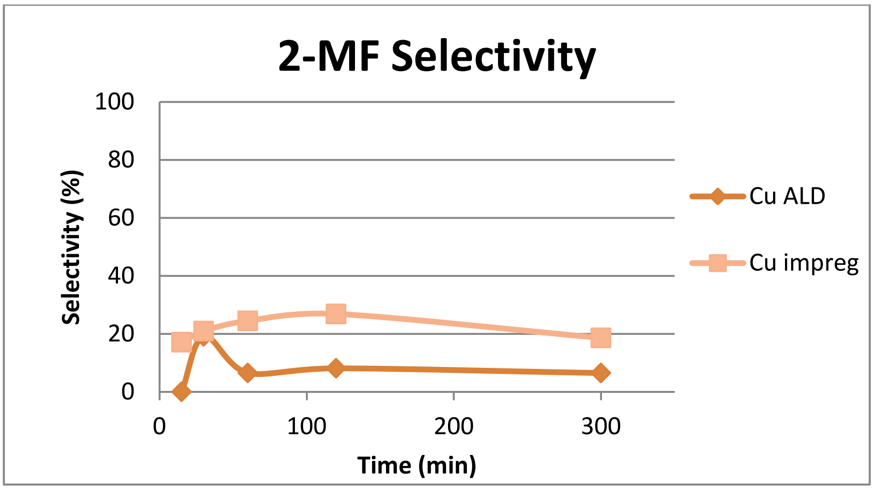


Figure 68: 2-MF selectivity with impregnated 5% Cu vs. ALD 14.38% Cu

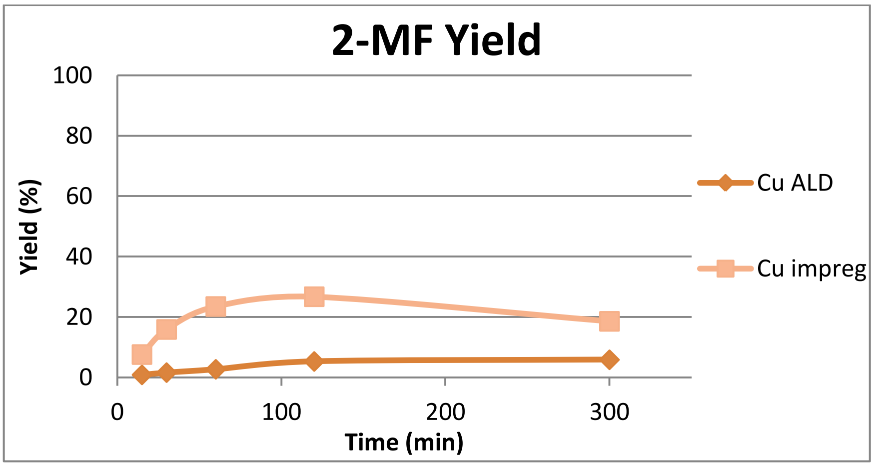


Figure 69: 2-MF yield with impregnated 5% Cu vs. ALD 14.38% Cu

5.4.3 Copper-iron catalysts

Also some bimetallic catalysts, such as CuFe and NiFe (see 5.4.4), were prepared with ALD method. In the following plots (Fig. 70-72), CuFe results are reported; the curves related to impregnated 2% Cu were also inserted for a comparison.

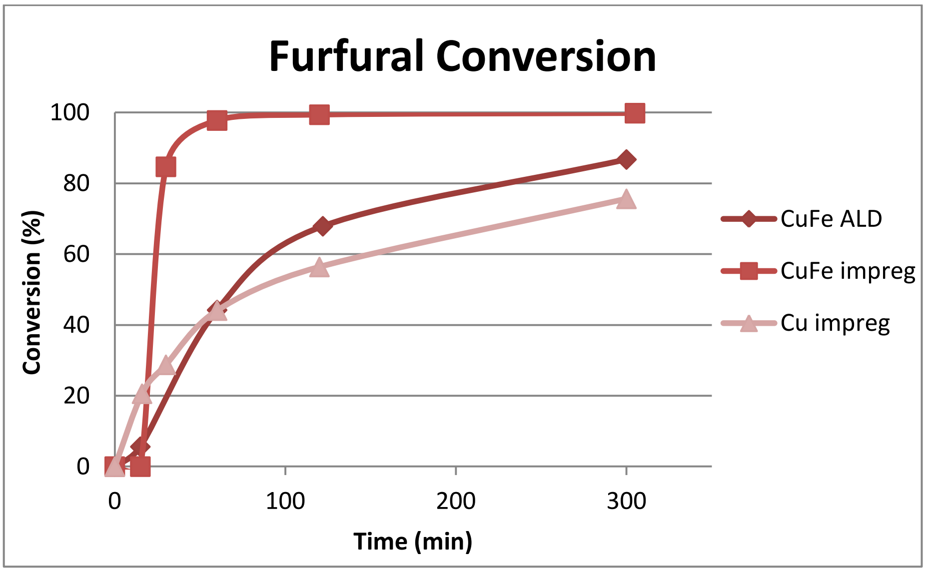


Figure 70: Furfural conversion with impregnated 2%/2% CuFe and 2% Cu vs. ALD 2.2%/7% CuFe

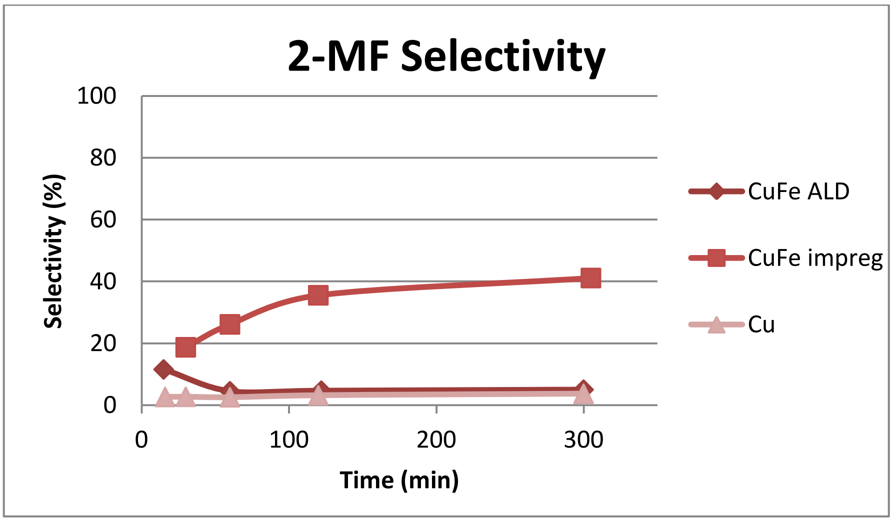


Figure 71: 2-MF selectivity with impregnated 2%/2% CuFe and 2% Cu vs. ALD 2.2%/7% CuFe

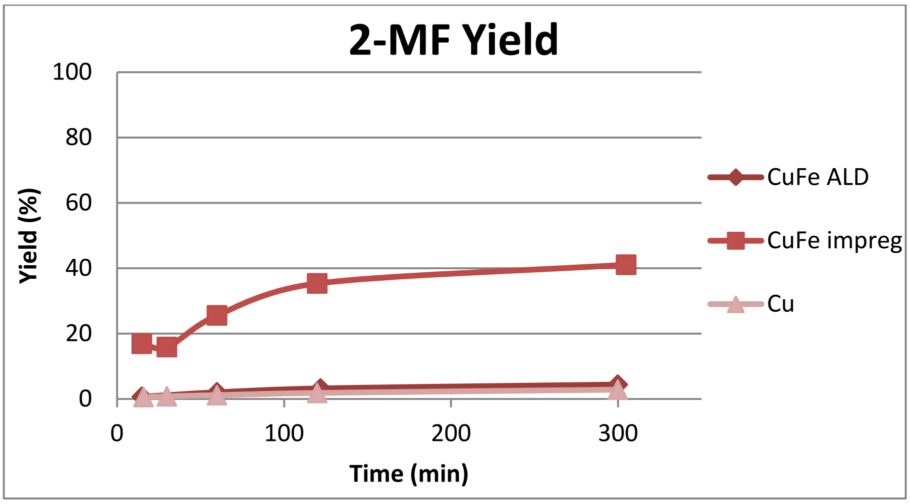


Figure 72: 2-MF yield with impregnated 2%/2% CuFe and 2% Cu vs. ALD 2.2%/7% CuFe

Although very good results were obtained with CuFe impregnated catalyst, the catalysts prepared through ALD showed a different behavior, definitely less active and not selective towards 2-MF. It must be said that the loading of iron in the ALD catalyst is higher than in the impregnated one (7% vs. 2%); also with NiFe impregnated catalysts (see part 5.2.3) the increase of iron over a certain amount lowered the catalytic activity. Therefore, it is possible to suppose that for 2-MF production the 5% loading of iron should not be exceeded. When using ALD-prepared CuFe, furfural conversion is better than with only copper, meaning that iron promotion occurred; however, 2-MF selectivity and yield are practically superimposable. This could mean same aggregation problems of the metal on the support.

5.4.4 Nickel-iron catalysts

NiFe catalysts prepared with impregnation and ALD methods and compared here had a metal ratio of 5%/2% and 3.8%/1.6%, respectively. Although the amount of metal is similar, the results presented (Fig. 73-75) show again some differences.

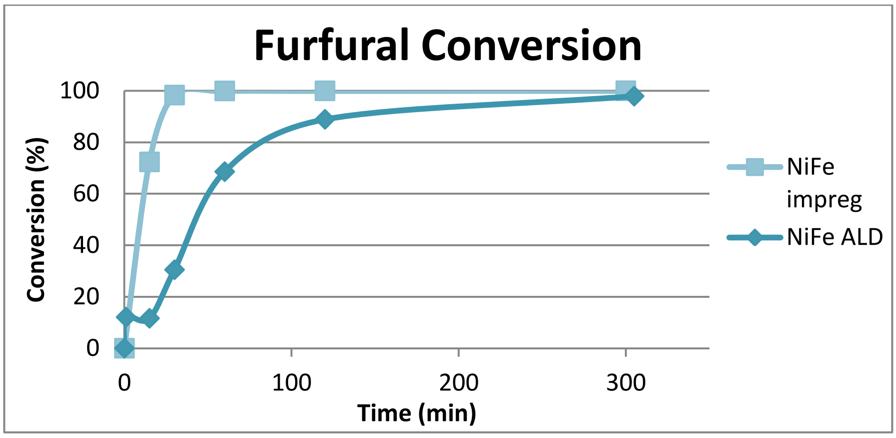


Figure 73: Furfural conversion over impregnated 5%/2% NiFe vs. ALD 3.8%/1.6% NiFe catalyst

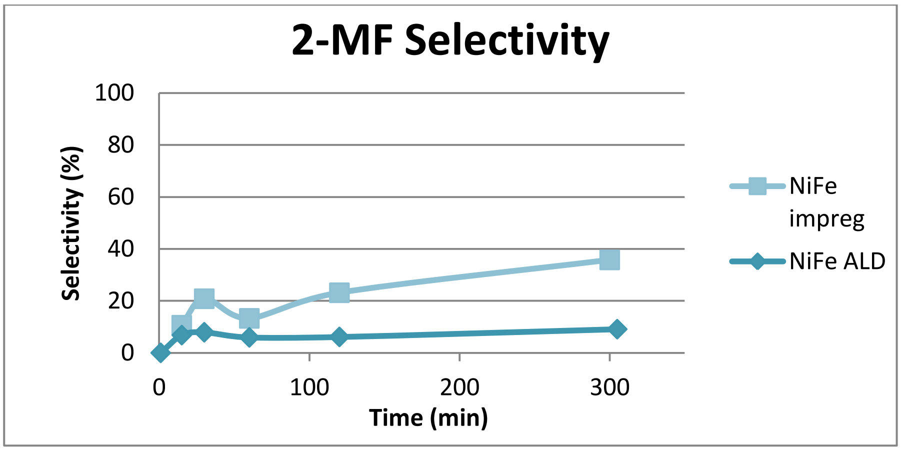


Figure 74: 2-MF selectivity over impregnated 5%/2% NiFe vs. ALD 3.8%/1.6% NiFe catalyst

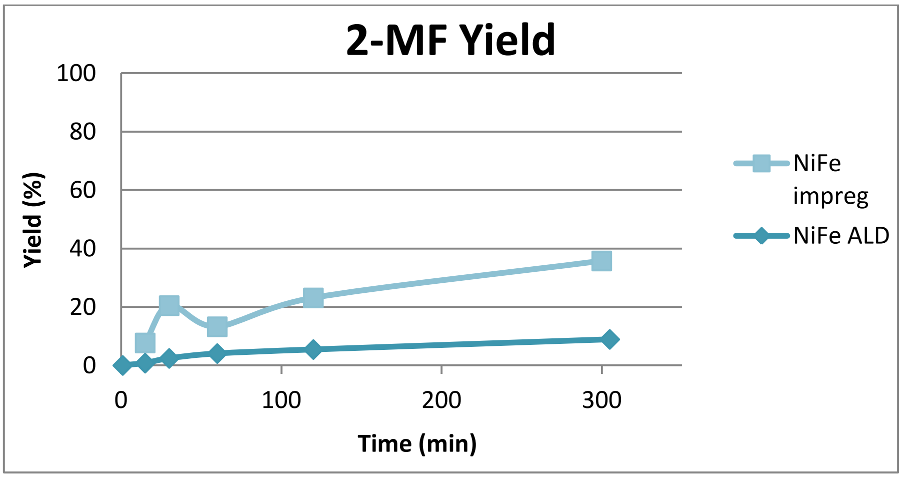


Figure 75: 2-MF yield over impregnated 5%/2% NiFe vs. ALD 3.8%/1.6% NiFe catalyst

Especially, 2-MF selectivity and yield achieved with ALD catalyst are low, while the global furfural conversion is good, though lower than the one obtained with impregnated catalyst. It is noteworthy that with ALD-prepared NiFe a considerable amount furan, THFA and 2-MTHF were detected since the beginning of reaction, which is unusual when Fe is present (see main products distribution, part 5.6).

To conclude the overview of ALD catalysts, the results were always poorer than impregnated catalysts, both in terms of furfural hydrogenation and 2-MF production. This could be imputed to bigger metal particles and their aggregation, as confirmed by TEM characterization, which leads to lower metal dispersion and catalytic activity.

5.5 Cobalt catalyst

Finally, a completely different metal was tested as active-phase: cobalt. It is known in literature for having good hydrogenation properties; however, when dispersed on a carbon support through ALD, it shows good activity in furfural hydrogenation, but very poor selectivity towards 2-MF, as shown in Fig. 76. Actually, it is noteworthy that cobalt would require a higher reduction temperature (300-400°C vs. 250°C), impossible to achieve with the present experimental instrumentation.

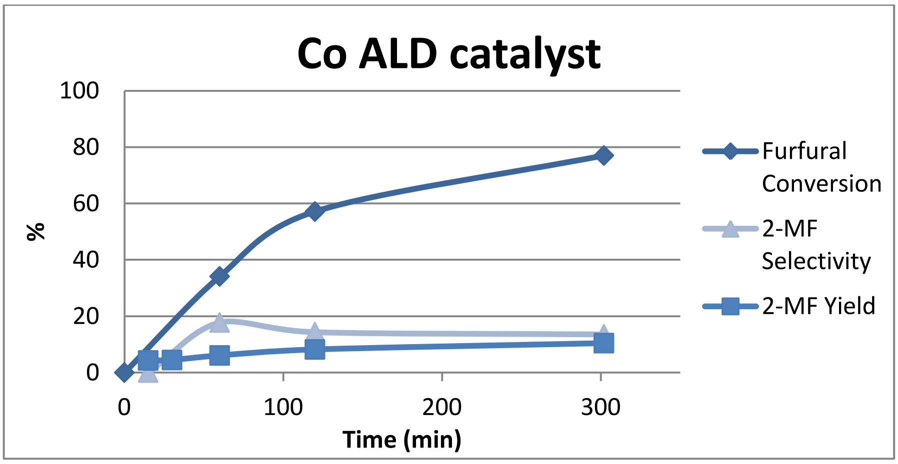


Figure 76: Furfural conversion, 2-MF selectivity and yield over Co/Norit®RB4C ALD catalyst

5.6 Distribution of main products

The results presented so far were focused on furfural conversion and 2-MF produced during the experiments. In the following part, a comparison among the most active and selective catalysts (such as 10% Ni, 2%/2% CuNi, 2%/2% CuFe and 5%/2% NiFe) is done in terms of yields for the most important products of furfural hydrogenation: 2-MF, FA, 2-MTHF, THFA and furan. Moreover, yields are presented at different reaction times, such as after 60, 120 and 300 minutes, in order to better understand products evolution and reactions involved. These considerations are essential in order to optimize 2-MF production. Figures 77-79 summarize these results.

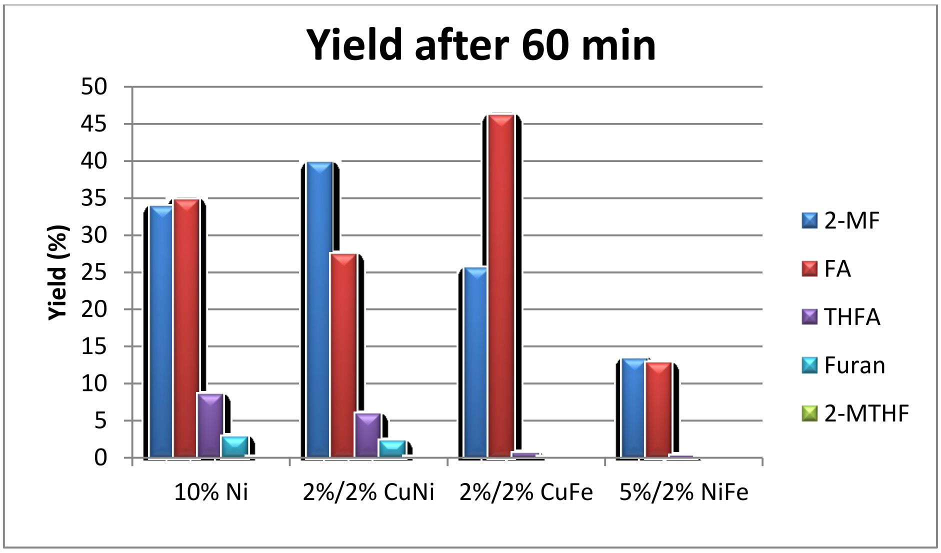


Figure 77: Yield of main furfural hydrogenation products after 60 min reaction

After 60-minutes reaction, 2-MF and FA are produced in variable amounts, based on the catalyst used. For example, 2%/2% CuNi is very selective towards 2-MF, yielding almost 40% of it; moreover, at this point furfural conversion was already very high (91%). Therefore, this could be an interesting option to be developed at industrial level, since short reaction time increases the productivity and with such a high conversion the reactant recirculation is probably unnecessary. It is interesting to notice that after 60 min, apparently 2-MF is not undergoing any further reaction (i.e. further hydrogenation) over any of these catalysts yet, since no traces of 2-MTHF (nor open-ring products) were detected. Another very important aspect concerns furan production: using iron-containing catalysts usually prevents furan formation during the whole reaction time and also reduces the likelihood of furan ring hydrogenation. Therefore, little amounts of THFA and 2-MTHF were produced.

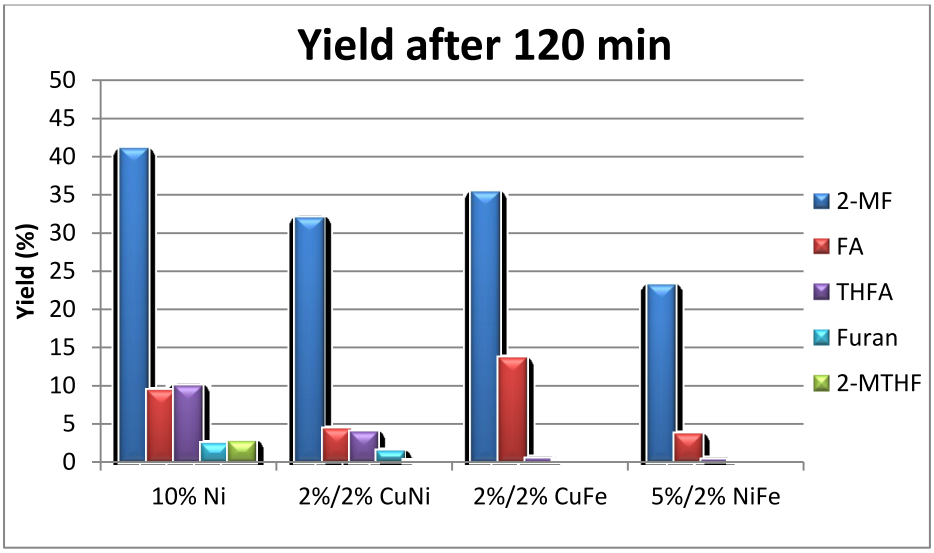


Figure 78: Yield of main furfural hydrogenation products after 120 min reaction

After 120 min, 10% Ni achieves almost 41% in 2-MF yield. However, it is noticeable the high activity of nickel in furfural hydrogenation: all main hydrogenation products are present. Especially, 2-MTHF is formed, meaning that after this time 2-MF amount is going to decrease (confirmed by next plot, Fig. 79). Since 2-MTHF is only originated from 2-MF, an hypothesis could be that the actual peak in 2-MF production was reached a little before the two hours; therefore, 2-MF highest yield would probably be 41% plus the 2.7% of 2-MTHF yield, for a total of 43.7%. However, this is not necessarily true, since it is possible that MTHF production occurs at the same time with 2-MF production and that a higher 2-MF peak is never achieved. Another observation is the fact that FA yield dramatically decreases between 60 and 120 minutes but no other products presented in Fig. 77 are significantly formed. FA is the intermediate of 2-MF, but not all of it is converted to 2-MF: other reaction pathways lead to other products (apart from 5%/2% NiFe), most of them still unknown (see Fig. 39).

Finally, the yields at the end of the reaction are reported in Fig. 79.

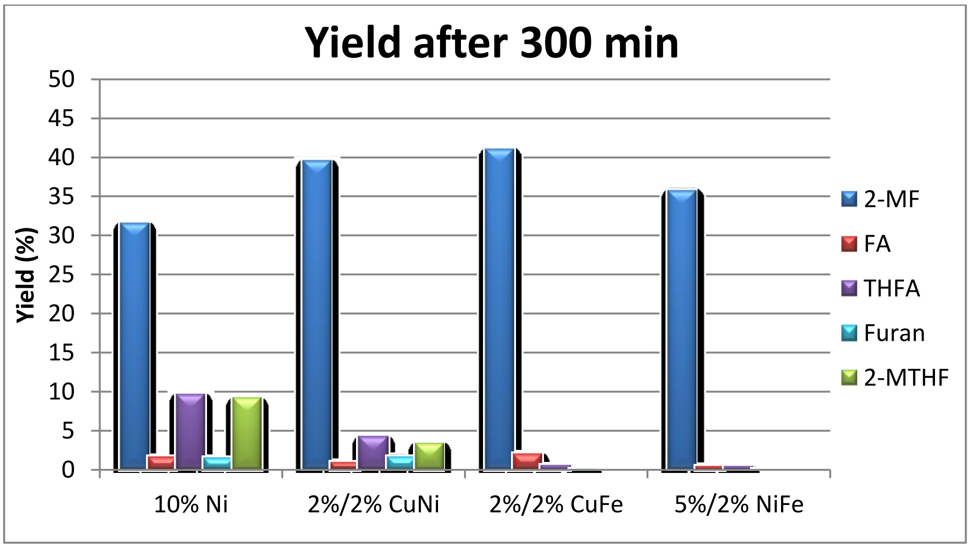


Figure 79: Yield of main furfural hydrogenation products after 300 min reaction

The two copper-based catalysts, as well as NiFe one, are more selective towards 2-MF at this point; their yields are acceptable: 39.6% for CuNi, 41% for CuFe and 35.75% for NiFe. For what concerns 10% Ni, the amount of 2-MTHF produced is almost 10% and the yield of 2-MF decreased exactly from 41% to 31%; this proves the fact that 2-MTHF derives from further hydrogenation of 2-MF. As a matter of fact, some 2-MTHF is produced also over CuNi after 300 min (～3.4%); therefore, same considerations previously made for 10% Ni are valid in this case, and finding the optimum reaction time would possibly lead to a 43% yield.

Finally, the results in furfural conversion over the above-mentioned catalysts are reported in Fig. 80. All of them are very good, varying between 99.5 and 100% after 5 hours.

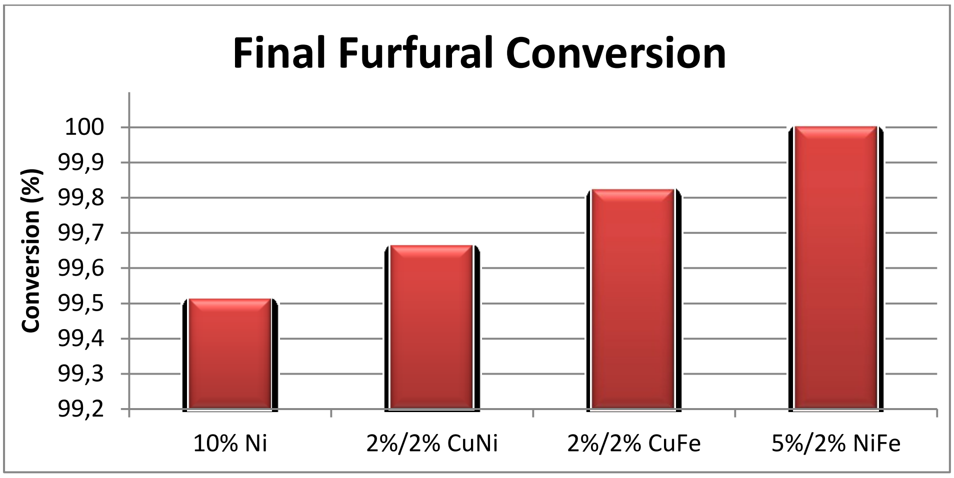


Figure 80: Comparison of furfural conversion over different catalysts after 5 hours

5.6.1 Acetone production

A remark can be made also for acetone production. Acetone is included among the products of furfural hydrogenation since it is the main side-product due to the reaction between furfural and the solvent (i.e. 2-propanol). The reaction involved is shown in Fig. 81, where 2-propanol acts as a hydrogen donor. [43]

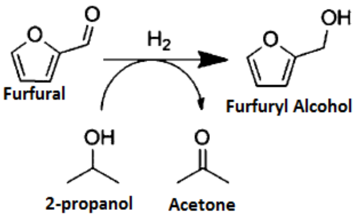


Figure 81: Production of acetone from 2-propanol and furfural

However, this is not the only possible reaction pathway: 2-propanol can also turn into acetone through either a catalytic dehydrogenation (eq. 25) or a catalytic oxidation (eq. 26); however, in reaction conditions only the first one takes place. [89]

$$\underset{\text{2-propanol}}{CH_3CH(OH)CH_3} \rightarrow \underset{\text{Acetone}}{CH_3COCH_3} + H_2 \qquad \text{(eq. 25)}$$

$$\underset{\text{2-propanol}}{CH_3CH(OH)CH_3} + \frac{1}{2}O_2 \rightarrow \underset{\text{Acetone}}{CH_3COCH_3} + H_2O \qquad \text{(eq. 26)}$$

After one hour reaction, with almost all the catalysts a certain amount of acetone is already present; with 10% Ni catalyst the amount of acetone remains practically constant (about 0.3mmol/g) from the beginning until the end of the reaction time. Instead, both CuFe and NiFe continue producing acetone, up to 0.8 and 0.7 mmol/g respectively after 5 hours (probably the presence of Fe catalyzes furfural reaction with 2-propanol). CuNi catalyst is producing less acetone, with a peak of 0.25mmol/g after one hour. These results are shown in Figure 82.

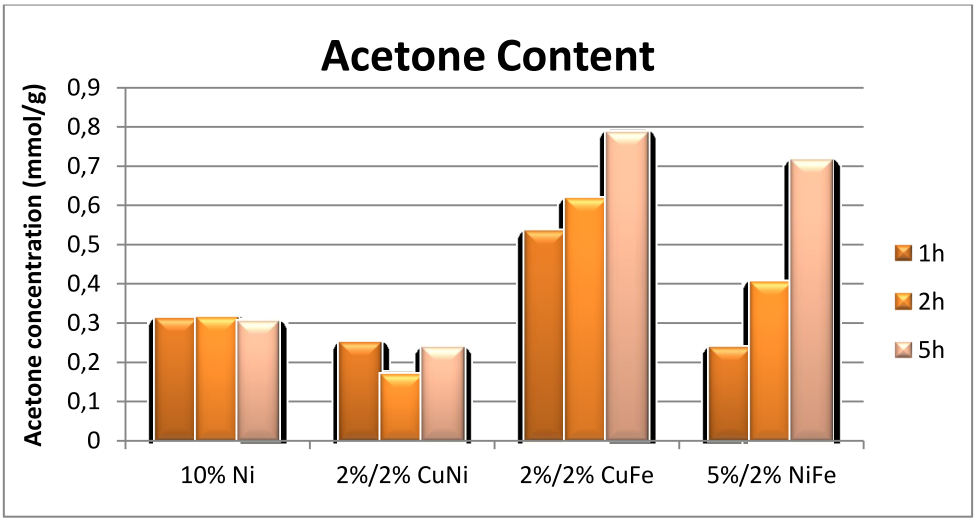


Figure 82: Acetone yield over different catalysts during hydrogenation reaction

5.7 Changes in operation conditions

After all catalysts had been tested, some changes were made concerning the operating conditions with selected catalysts. Some examples are reported in the following paragraphs, such as increasing both reaction and reduction time and lowering reaction temperature.

5.7.1 Longer reaction time

Since from previous experiment the trend of 2-MF yield and selectivity resulted growing in the end of reaction (see part 5.3.2), the reaction time of 2%/2% CuFe catalyst was extended to 7 hours instead of 5, to check whether it was possible to reach a higher selectivity. Moreover, as already done with monometallic Cu-catalysts, reduction temperature was decreased from 250 to 200°C also for CuFe catalyst. The plots presented below (Fig. 83-85) show that also for CuFe catalyst a lower reduction temperature improves, but only slightly, the results.

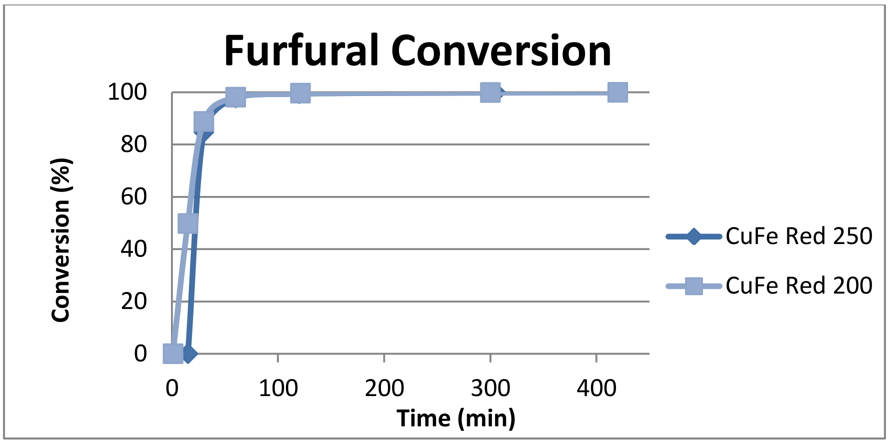


Figure 83: Furfural conversion over impregnated 2%/2% CuFe reduced at different temperatures

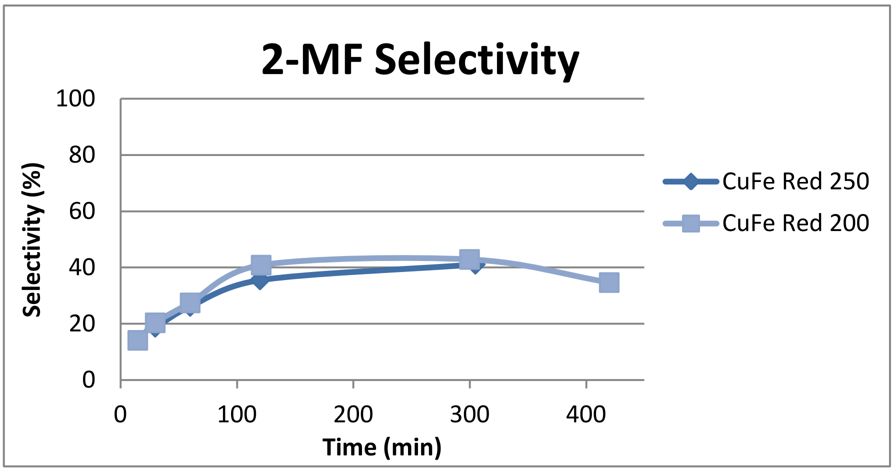


Figure 84: 2-MF selectivity over impregnated 2%/2% CuFe reduced at different temperatures

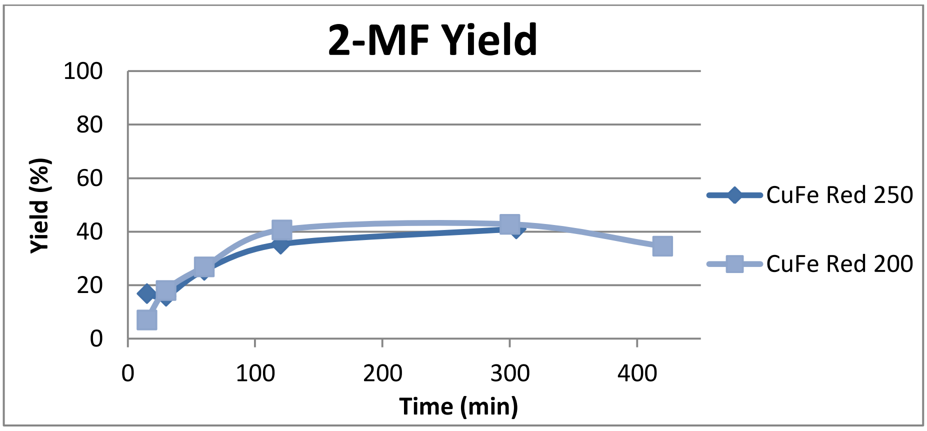


Figure 85: 2-MF yield over impregnated 2%/2% CuFe reduced at different temperatures

Especially the peak in 2-MF production achieves 42.8% both in selectivity and yield after 300 min, with practically complete furfural conversion (99.84%). After that time, the amount of 2-MF decreases, reaching 34.6% of both yield and selectivity (Fig. 84-85); however, no 2-MTHF was detected and, among the other known side products of 2-MF, only a minimum amount of 2-pentanone was produced. Therefore, many other reactions could lead to 2-MF degradation (for example, combinations with furfural or polymerization-type reactions).

5.7.2 Longer reduction time

Usually catalyst reduction process was carried at 250°C (or 200°C for Cu-based ones) and 40 bar of H_2 for 90 minutes. An experiment was also done using an impregnated 2% Ni catalyst previously reduced for 3h (double time) at 250°C.

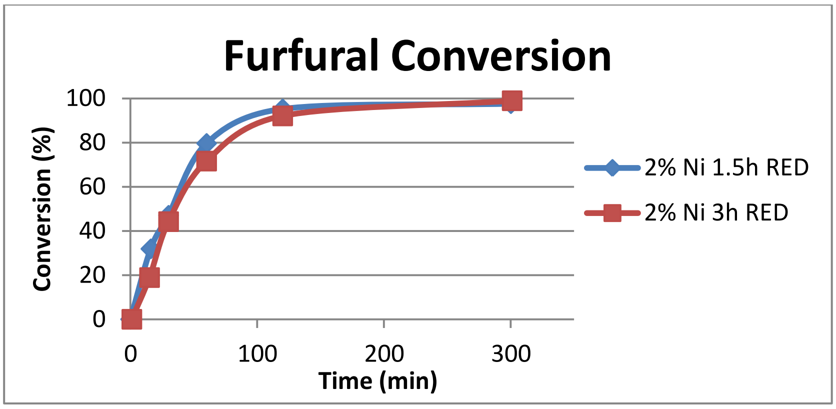


Figure 86: Effect of reduction time on furfural conversion with 2% Ni catalyst

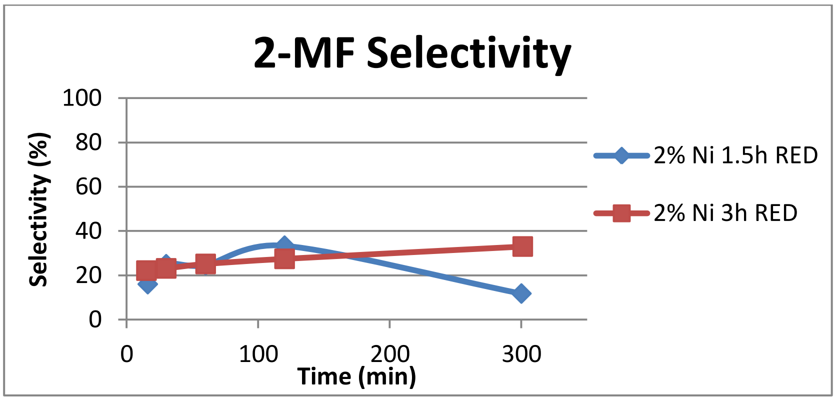


Figure 87: Effect of reduction time on 2-MF selectivity with 2% Ni catalyst

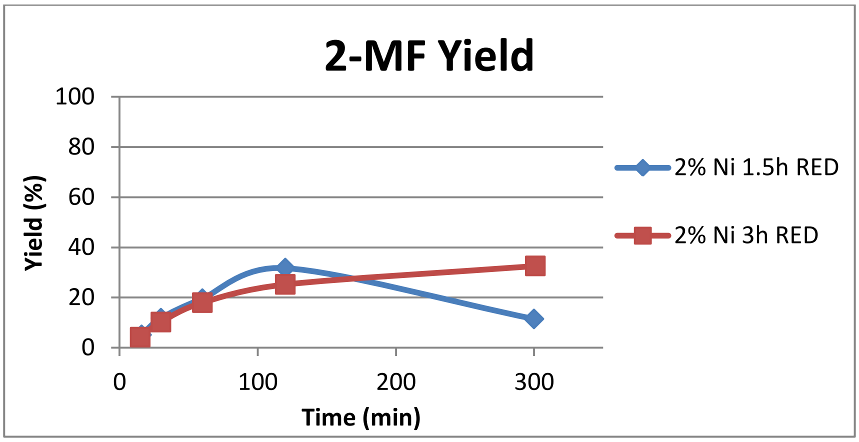


Figure 88: Effect of reduction time on 2-MF yield with 2% Ni catalyst

The results (Fig. 86-88) show that the influence on furfural conversion is almost negligible (curves almost superimposable); however, yield improved from 31.7% (with 1.5h reduction) to 32.6% (with 3h reduction) while selectivity slightly decreased from 33.35% to 32.95%. Moreover, the usual peak showed by Ni catalysts is replaced by a growing trend; therefore, the best selectivity is achieved only after a longer reaction time. However, during the reduction process the temperature did not exceed 238°C due to some problems with the heating system; thus, milder reduction conditions (Ni would require reduction temperatures even higher than 250°C) could have caused a lower activity, thus a slower reaction rate. On the other hand, a longer reduction time could somehow “compensate”, allowing reaching acceptable results.

5.7.3 Lower reaction temperature

Finally, the influence of the reaction temperature on products selectivity was evaluated: the hydrogenation of furfural was performed at 200°C instead of 230°C over 2% Ni and 2%/2% CuFe (i.e. two among the most valuable catalysts tested at 230°C).

5.7.3.1 2% Ni catalyst

Figures 89-91 summarize the results obtained using a 2% Ni catalyst.

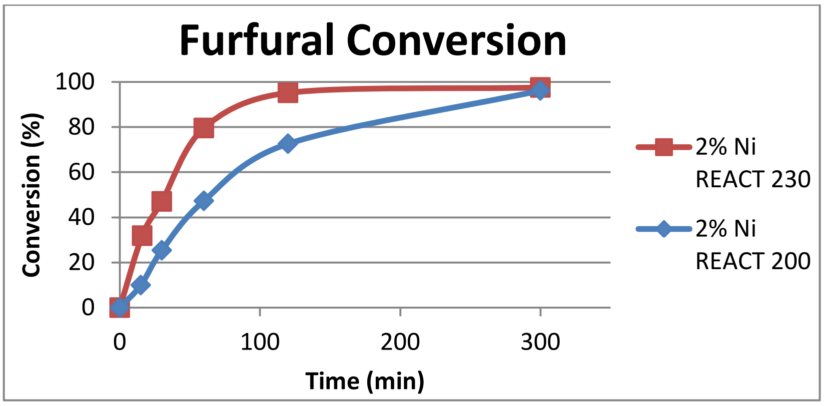


Figure 89: Influence of reaction temperature on furfural conversion with 2% Ni catalyst

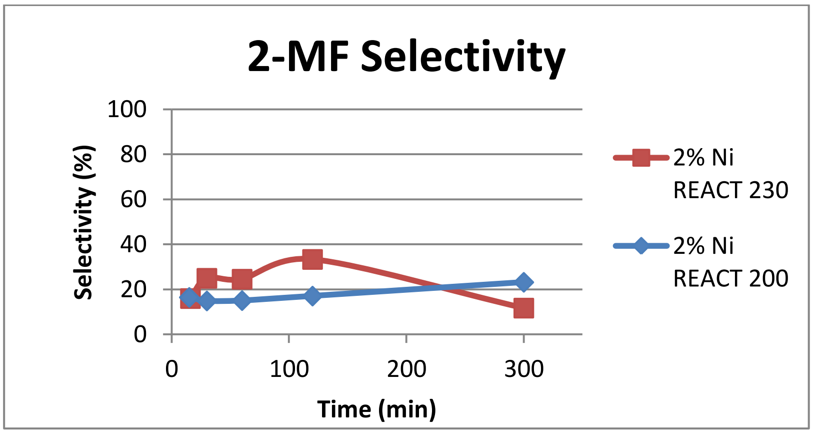


Figure 90: Influence of reaction temperature on 2-MF selectivity with 2% Ni catalyst

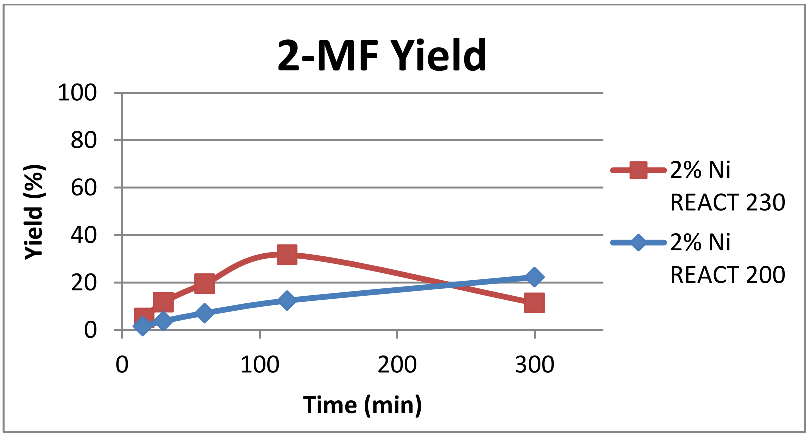


Figure 91: Influence of reaction temperature on 2-MF yield with 2% Ni catalyst

It is evident that furfural conversion is slower when the reaction is performed at a lower temperature; however, the final conversion is only slightly different (96.2% vs. 97.5%). At 200°C, 2-MF selectivity and yield decreased because of a slower hydrogenation reaction, reaching a maximum of 22.3% and 23.2% respectively. Such values were achieved after 300 min, although little amount of consecutive reaction products (such as 2-MTHF and 2-pentanone) were detected. As a matter of fact, at lower reaction temperature a longer reaction time could be tested, in order to see an occurring maximum for 2-MF yield.

5.7.3.2 2%/2% CuFe catalyst

CuFe was also tested at lower reaction temperature (Fig. 92-94).

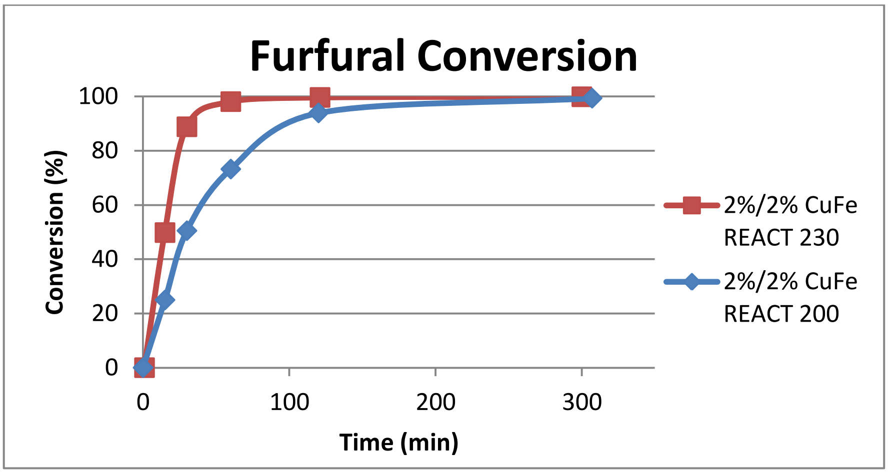


Figure 92: Furfural conversion over 2%/2% CuFe catalyst at 230°C and 200°C

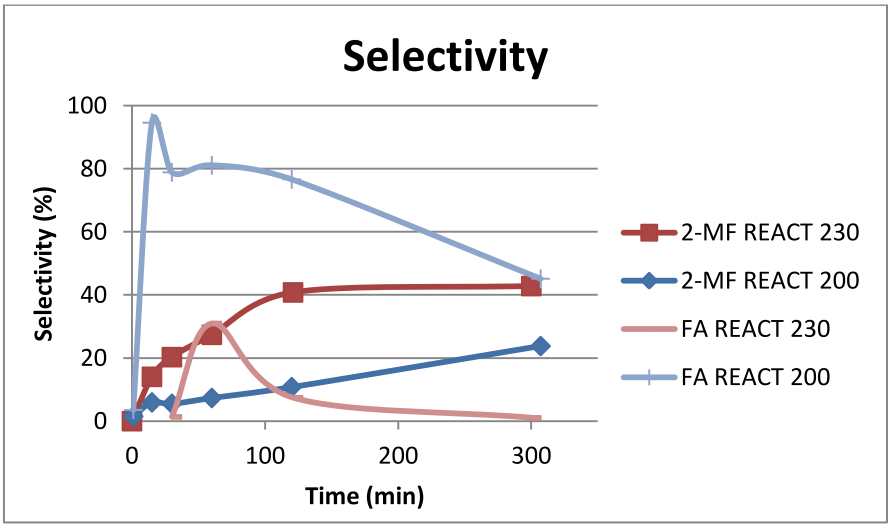


Figure 93: 2-MF and FA selectivity over 2%/2% CuFe catalyst at 230°C and 200°C

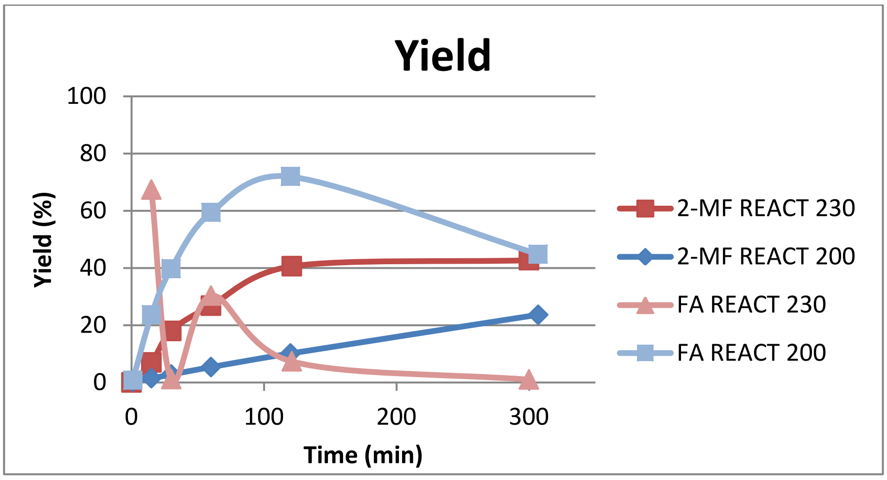


Figure 94: 2-MF and furfuryl alcohol (FA) yield over 2%/2% CuFe catalyst at 230°C and 200°C

Although furfural conversion is lower at the beginning of the reaction, it reaches a final value over 99%. However, the main product at lower temperature is furfuryl alcohol, whose selectivity and yield are clearly improved; FA consumption due to further hydrogenation towards 2-MF is slower. As a result, 2-MF selectivity and yield dramatically decreased to almost 24% (instead of ~43% when the reaction was performed at 230°C). This is a confirm of what is reported in literature about vapor-phase hydrogenation (see part 2.2.1), that is to say at low temperatures (≤ 200°C) FA is the main hydrogenation product.

5.8 Catalyst life cycle

An important property required for a catalyst employed at industrial scale is its life, that is to say how long does it last before undergoing significant deactivation and loss of activity. For this reason, some of the best catalysts in 2-MF production (i.e. 2%/2% CuFe and 2%/2% CuNi) were re-used in order to compare the results and to evaluate occurring changes in activity (referable to some kind of deactivation). The catalysts used for consecutive experiments were washed with water after the reaction and dried in oven at about 80°C. Reduction processes were also repeated in same conditions.

5.8.1 CuFe

Results of life-cycle test over 2%/2% CuFe are reported in Fig. 95-97. In both the experiments, the catalyst was reduced at 200°C while reaction was performed at 230°C.

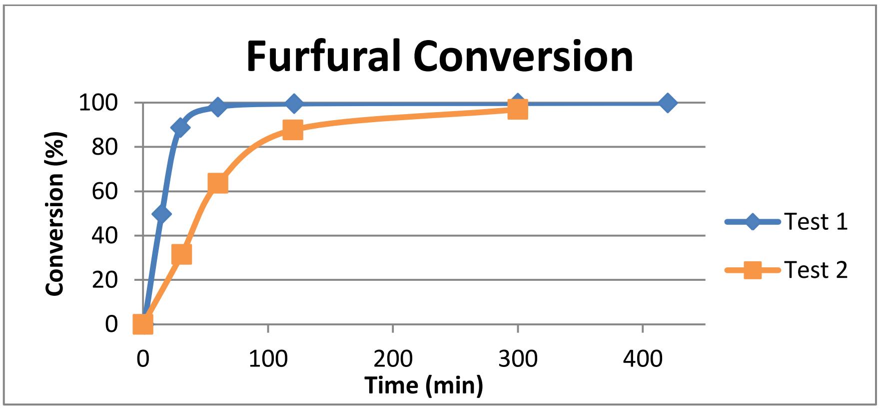


Figure 95: Furfural conversion in two consecutive experiments over 2%/2% CuFe

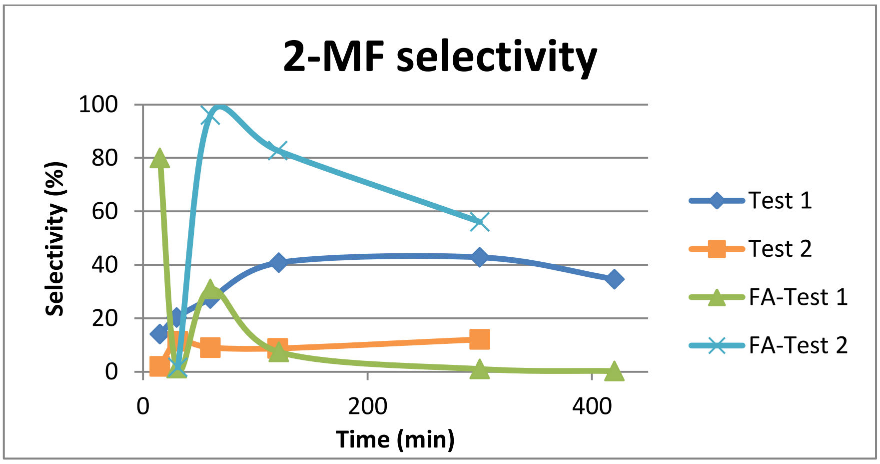


Figure 96: Selectivity of 2-MF and FA in consecutive experiments over 2%/2% CuFe catalyst

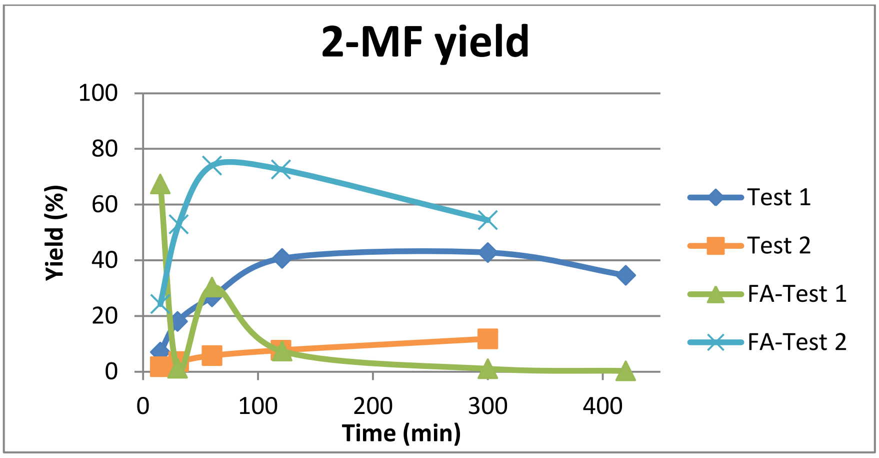


Figure 97: Yield of 2-MF and FA in consecutive experiments over 2%/2% CuFe catalyst

The first experiment lasted 420 min and already after 300 min, 2-MF production showed a decreasing trend. Apparently, also during the second experiment the catalyst underwent some deactivation, since in same reaction conditions furfural conversion was slower, although in the end it was still acceptable (97% vs. 99.84%, Fig. 99). For what concerns 2-MF production, in Figures 96 and 97 selectivity and yield of 2-MF are showed. In fact, 2-MF production dramatically decreased in the second experiment, but since furfural conversion was still acceptable, also the production of the intermediate FA was reported in the plots. It is evident that the catalyst had not completely lost its hydrogenation activity, but the main product results FA, indicating the difficulty in undergoing further hydrogenation towards 2-MF.

It is known from literature that the hydrogenation of furfural leads to the production of coke, so it is likely to be the main responsible of the reduction in catalytic activity for all the catalysts. In corroboration of that, after the experiments the weight of the tested catalysts showed an increase (usually about 10-15%), reasonably due to coke deposition on the catalyst surface.

5.8.2 CuNi

A test to evaluate the life of the catalyst was also performed re-using 2%/2% CuNi catalyst. As a result, furfural conversion decreased after the first experiment from 99.7% to 92.6% (Fig. 98); 2-MF selectivity dropped from 39.56 to 23% (Fig. 99) and yield from 39.7% to 21% (Fig. 100). Selectivity reached a high value at very low furfural conversion, thus it should not be taken into consideration.

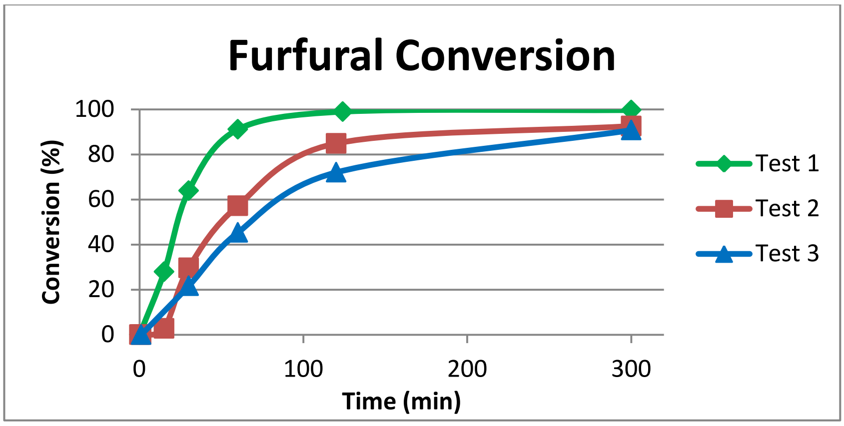


Figure 98: Furfural conversion in three consecutive experiments over 2%/2% CuNi catalyst

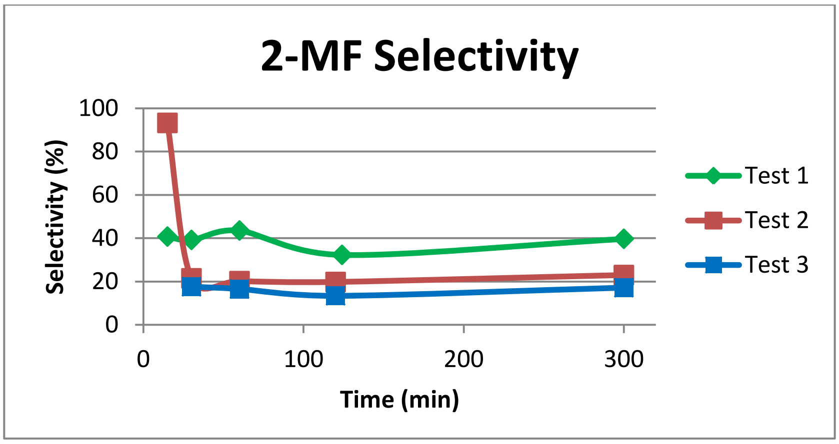


Figure 99: 2-MF selectivity in three consecutive experiments over 2%/2% CuNi catalyst

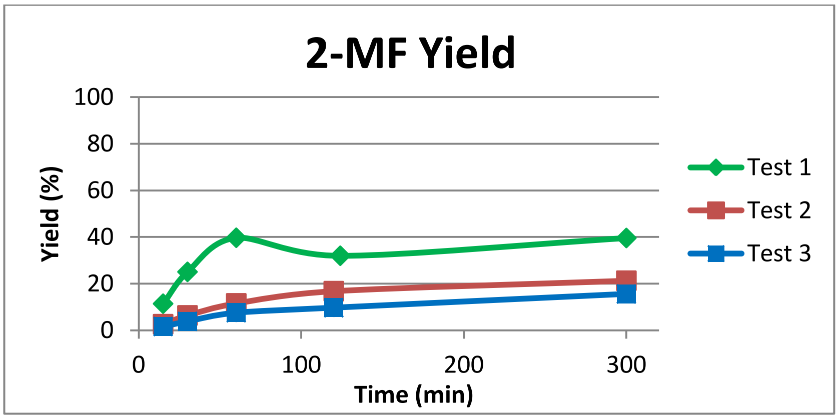


Figure 100: 2-MF yield in three consecutive experiments over 2%/2% CuNi catalyst

It is interesting to consider also the results in terms of FA production (Fig. 101-102): the activity of the catalyst definitely decreased, even if almost the same trend is maintained (especially for the selectivity); moreover, the reconversion of FA is clearly slower than in the first experiment, as expected, since the global activity was worse. Comparing second and third tests however, the discrepancy between the curves is slightly remarkable: almost the same value of final conversion (90.81%), similar trend in 2-MF production (highest values of yield and selectivity: 15.5% and 17% respectively) and superimposable curves for FA production.

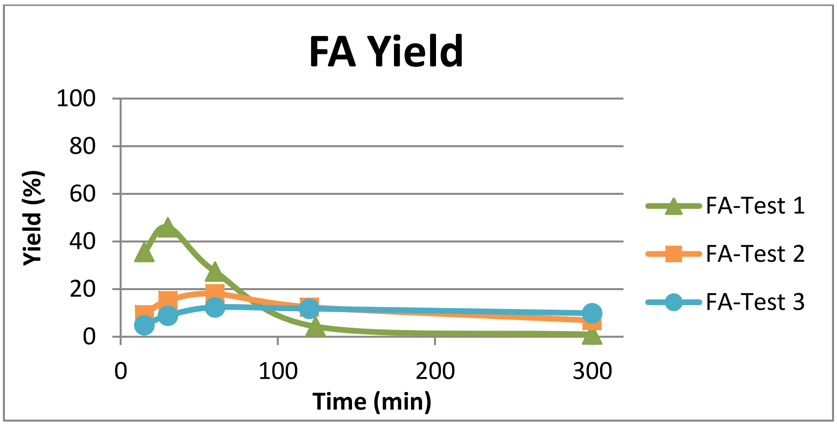


Figure 101: FA yield in three consecutive experiments over 2%/2% CuNi catalyst

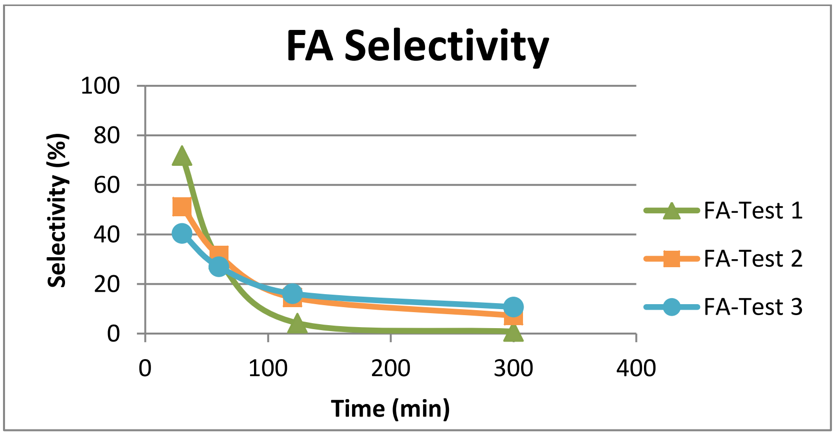


Figure 102: FA selectivity in three consecutive experiments over 2%/2% CuNi catalyst

Differently from the case of CuFe catalyst, here not only the second step of the reaction is compromised (i.e. from FA to 2-MF), but FA itself is not the most selectively produced compound, even if the conversion curves of the second experiments over CuFe and CuNi are practically superimposable, while the amount of FA produced is definitely different. Thus, a different products distribution is achieved. However, after the second experiment, there are not evident differences with the following experiment, as if the relevant deactivation already occurred previously.

5.9 Gas phase analysis

Gas samples were withdrawn from the reactor (at low pressure, 7-8 bar) into a vacuumed gas bomb. The samples were analyzed through gas-chromatography. Gas phase composition is shown in Fig. 103: the main component (~85%) is hydrogen, as expected, since it was used for performing the hydrogenation reaction. For what concerns oxygen, its amount is about 10% and it may result as impurity when the gas sample is transferred to the GC, together with nitrogen (7-8%), which is also used to flush all the lines before the reaction and to clean the feeding tank from any air after the introduction of furfural solution. Finally, little amounts of CH_4 (0.1-0.5%) were detected, as well as CO_2 (0.02-0.05%) and CO (0.01-0.02%). Usually, also four unknown peaks are measured by the GC, probably hydrocarbons; they could hypothetically be propane, propene, 2-propanol and furan.

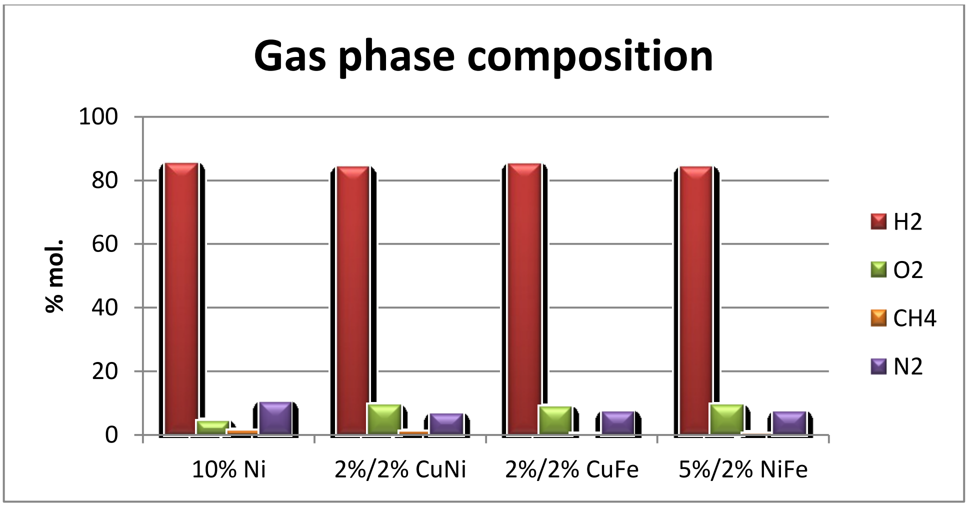


Figure 103: Low-pressure gas-phase composition with different catalysts

6. CONCLUSIONS

The screening test for finding a suitable carbon-supported catalyst for 2-MF production from furfural resulted as follows (Table 11):

Table 11: Results in 2-MF production of tested catalysts

Catalyst	2-MF Yield %	2-MF Selectivity %	Notice
2%/2% CuFe/RB4C	42.8	42.8	Reduction at 200°C
2%/2% CuFe/RB4C	41.1	41.1	
10% Ni/RB4C	40.9	41.6	Problematic preparation
2%/2% CuNi/RB4C	39.7	43.5	
5%/2% NiFe/RB4C	35.7	35.8	
2% Ni/RB4C	32.6	32.9	3h reduction
2% Ni/RB4C	31.7	33.4	1.5h reduction
2%/2% NiFe/RB4C	31.2	31.6	
5% Cu/ RB4C	26.7	26.8	Reduction at 200°C
5%/5% NiFe/RB4C	25.9	25.9	
2%/2% CuFe	23.6	23.8	Reaction at 200°C
2% Ni	22.3	23.2	Reaction at 200°C
5% Ni/RB4C	21.5	21.8	
5% Cu/RB4C	15.7	17.1	
4.2% Co/RB4C	10.4	17.8	ALD
5.6% Ni/RB4C	10.6	11.9	ALD
3.8%/1.6% NiFe/RB4C	8.9	9.1	ALD
14.38% Cu/RB4C	5.8	8.1	ALD
2.2%/7% CuFe/RB4C	4.3	5.1	ALD
2% Ni/RX3	2.2	21.5	
2%/2% CuNi/RX3	1.3	9.5	

The presented values of yield and selectivity are the highest achieved during each experiment. As a matter of fact, nickel is the most active metal in furfural hydrogenation, and also the yield of 2-MF is acceptable (up to 40% with 10% Ni). For what concerns copper, which was the metal used for first industrial applications, it showed very poor selectivity itself, and achieved the best results when used in combination with either iron or nickel.

5 hours is the optimum reaction time for 2-MF production for almost all bi-metallic catalysts, while Ni shows highest selectivity after 2 hours (apart from 3-hours-reduced 2%Ni, which worked better after 5 hours), since its activity leads to further 2-MF conversion to 2-MTHF and 2-pentanone.

Moreover, it was discovered that reducing copper catalysts at lower temperature increases their activity (probably because of less sintering). On the other hand, it is advisable to reduce nickel catalysts (and also cobalt) at higher temperatures (up to 300-350°C); however, with the actual heating system, such result is impossible to achieve. Temperature has been proved to influence the reaction. Especially, a decrease in the reaction temperature from 230°C to 200°C caused lower furfural conversion and selectivity towards 2-MF when using both 2% Ni catalyst and 2%/2% CuFe, despite the best literature results were achieved at lower T (2-MF yield of 51% at 220°C and 61% at 180°C).

It is remarkable that steam-activated carbons Norit® RB4C performed as the best support; however, acid-washed AC (RX3) will have to be tested again, checking the effective dispersion of the metal after the preparation.

Impregnated catalysts gave better results; probably the low selectivity of ALD catalysts in this work is due to a low metal dispersion (bigger metal particles, often aggregated, were detected through TEM) and to high coke formation (since the weight of such catalysts at the end of the reaction increased up to 60%).

Finally, catalyst lifetime tests showed that deactivation rapidly occurs, after less than 10hours reactions, leading to a significant decrease in 2-MF production; however, the hydrogenation capability is not totally lost: furfural conversion still reaches high values (over 90%). What happens over

CuFe is that more FA is produced during the second experiment and its further conversion to 2-MF is slower when increasing the reaction time. The main reason is probably coke formation, but it has to be verified through characterization (TEM). Over CuNi instead, the deactivation leads to a different products distribution, with poor selectivity towards FA and 2-MF.

6.1 Future Experiments

Other promising catalysts, such as 5%/2% NiFe and 2% Ni (10% Ni if possible) supported on RB4C should be tested at lower reaction temperatures. Moreover, the life of such catalysts should be estimated, evaluating the catalytic performance after some cycles of reaction. A new catalyst basket can be provided in order to check occurring internal diffusion limitations (at present it is impossible to reduce pellets size without undergoing a loss since they slip out of the catalyst basket). Finally, an improved heating system would allow achieving higher temperatures, suitable for reduction processes of some catalysts such as Ni and Co; therefore, better performances in 2-MF production could be reasonably expected. In general, catalysts characterization procedure before and after the reaction is of key importance, in order to understand not only the actual metal content and dispersion over the support, but also reaction mechanisms and possible deactivation causes.

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"Stay hungry, stay foolish" (S. Jobs).

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