Carbon Catalysts in Biofuel Production: from Furfural to 2-Methylfuran

Salla Jaatinen

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Abstract

Production of bio-based chemicals, fuels and energy are essential in the current climate environment. Hydrotreatment of renewable platform chemical furfural yields many valuable products, such as furfuryl alcohol and 2-methylfuran (MF). MF has excellent properties for use as a gasoline octane booster to replace current fossil methyl tert-butyl ether and ethyl tert-butyl ether. The current CuCr-catalyst in furfural hydrotreatment is toxic and new and selective catalysts are required.

In this dissertation, noble metal free and non-toxic catalysts were prepared for production of MF. Metal catalyst options chosen for this work were copper, nickel and iron. High yields (up to 60%) of MF were achieved with the prepared catalysts in liquid phase batch reactor experiments in short reaction time (1 - 2 h). High temperature (230 °C) and high hydrogen partial pressure (40 bar) were optimal for MF production, and the most optimal metal combinations were copper-nickel and copper-iron. Active metals were tested in MF production on various activated carbon supports and a mesoporous carbon material (CMK-3). Deep characterization was performed to obtain data of beneficial catalyst characteristics for MF production. Production of MF was enhanced by small metal particle size, small pore volume and higher acidity. These enhancements suppressed the production of competitive products and side reactions, and increased the selectivity towards 2-methylfuran.

Solvents may also react in furfural hydrotreatment. The applied 2-propanol can react through catalytic transfer hydrogenation (CTH) offering hydrogen for hydrotreatment reactions and producing acetone. The solvent can also dehydrogenate to acetone and hydrogen. Acetone formation mechanisms were studied with the prepared catalysts. The acetone formation was metal dependent: with nickel and copper acetone formation occurred through CTH while with iron also dehydrogenation took place.

Hydrogen solubility in the reaction media is important for the process and especially in scaling up processes. Hydrogen solubilities in furfural and 2-propanol were measured and observed to increase as a function of temperature (50 - 200 °C) and pressure (50 - 125 bar). Hydrogen solubility in 2-propanol was observed almost three times higher to solubility in furfural. By way of example, at 200 °C and 125 bar hydrogen mole fraction in 2-propanol and furfural was measured to be 0.064 and 0.038 respectively. The solubility data was modelled with PC-SAFT model and the model predicted the hydrogen solubility data well.

This dissertation offers a MF selectivity optimized and fast noble metal free catalyst alternative for the current catalyst, new data of hydrogen solubility in the reaction media and optimized carbon support characteristics for the production of MF.

Keywords Furfural, 2-methylfuran, activated carbon, mesoporous carbon, hydrotreatment

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Kemikaalien, polttoaineiden ja energian tuottaminen uusiutuvista raaka-aineista on erittäin tärkeää jatkuvasti etenevän ilmastomuutoksen takia. Yksi vaihtoehto tuottaa kemikaaleja ja polttoaineita on vedyttää uusiutuvaa kemikaalia, furfuraalia. Furfuraalin vedytyksellä voidaan tuottaa useita tuotteita, kuten furfuryylialkoholia ja 2-metyylifuraania (MF). MF:llä on erinomaisia ominaisuuksia korvaamaan bensiinin tuotannossa oktaaniluvun nostajina toimivat fossiiliset vaihtoehdot metyylitert-butyylieetteri ja etyylitert-butyylieetteri. Tällä hetkellä prosessissa käytetty katalyytti on myrkyllinen ja uusia, selektiivisiä vaihtoehtoja tarvitaan.

Tässä väitöskirjassa tavoitteena oli tuottaa jalometallittomia ja myrkyttömiä katalyyttivaihtoehtoja MF:n tuotantoon. Katalyytin metallivaihtoehtoiksi valikoitiin siirtymämetallit kupari, nikkeli ja rauta. Reaktio-olosuhteiden optimointi osoitti korkean lämpötilan (230 °C) ja vetypaineen (40 bar) suosivan MF:n tuotantoa. Parhaat tulokset saavutettiin nestefaasissa panosreaktorissa lyhyessä reaktioajassa (1 - 2 h). Metallikatalyyttien kantajina testattiin useita aktiivihiliä ja mesohuukoista hiilimateriaalia (CMK-3). Valmistettuja katalyyttejä karakterisoitiin useilla menetelmillä, jotta niiden suotuisista ominaisuuksista MF:n valmistuksessa saataisiin tietoa katalyyttien optimointiin. MF:n tuotannon havaittiin tehostuvan pienillä metallipartikkeleilla, pienellä kantajan huokoskoolla ja happamalla kantajalla.

Liuottimen sivureaktiot ovat mahdollisia furfuraalin nestefaasivedytyksessä. 2-Propanoli liuotin saattaa reagoida furfuraalin kanssa tarjoten vetyä vedytysreaktioon ja muodostamalla sivutuotteena asetonia. 2-Propanoli saattaa myös reagoida vedyn poiston kautta asetoniksi ja vedyksi. Asetonin muodostumismekanismiin havaittiin olevan metalliriippuvainen; kuparilla ja nikkelillä asetoni muodostuu reaktiossa furfuraalin kanssa, kun taas raudalla myös vedyn poistoa tapahtuu.

Vedyn liukoisuus reaktiomatriisiin vaikuttaa nestefaasiprosesseihin ja erityisesti prosessin skaalaus suurempaan mittakaavaan tarvitsee tietoa vedyn liukoisuudesta lähtöaineisiin. Vedyn liukoisuuden fur-furaaliin ja 2-propanoliin havaittiin kasvavan lämpötilan (50 - 200 °C) ja paineen (50 - 125 bar) funktiona, vedyn liukoisuus 2-propanoliin oli lähes kolme kertaa korkeampi furfuraaliin verrattuna. Vedyn mooli-osuus esimerkiksi 200 °C:ssa ja 125 bar:ssa oli 2-propanolissa 0.064 ja furfuraalissa 0.038. Liukoisuusdatat mallinnettiin PC-SAFT mallilla ja valittu malli ennusti vedyn liukoisuusdataa hyvin.

Tämän väitöskirja tuotti selektiivisen ja nopean katalyytin MF tuotantoon nykyisen katalyytin mahdolliseksi korvaajaksi, uutta dataa vedyn liukoisuudesta reaktiomatriisiin ja optimoidut hiilikantajaominaisuudet MF tuotantoon.

Avainsanat Furfuraali, 2-metyylifuraani, aktiivihili, mesohuukoinen hiili, vedytys**ISBN (painettu)** 978-952-60-8445-9**ISBN (pdf)** 978-952-60-8446-6**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Helsinki**Vuosi** 2019**Sivumäärä** 150**urn** <http://urn.fi/URN:ISBN:978-952-60-8446-6>

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Espoo, 1 February 2019
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Contents

1.	Furfural hydrotreatment to produce valuable chemicals and fuel components	11
1.1	Furfural.....	11
1.2	Furfural hydrotreatment reactions	13
1.3	Furfural hydrotreatment products	14
1.3.1	2-Methylfuran.....	15
1.3.2	Furfuryl alcohol.....	17
1.3.3	Tetrahydrofurfuryl alcohol	18
1.4	Liquid phase vs. gas phase production.....	18
1.5	Catalysts in the production of 2-Methylfuran	19
1.6	Carbon as support material in furfural hydrotreatment	20
1.7	Acetone formation in furfural hydrotreatment	22
1.8	Hydrogen solubility in furfural.....	22
1.9.	Scope of the research	23
2.	Materials and Methods	24
2.1	Chemicals and materials	24
2.2	Catalyst preparation	25
2.3	Catalyst characterization	26
2.3.1	Atomic absorption spectroscopy.....	27
2.3.2	Nitrogen physisorption.....	27
2.3.3	Temperature-programmed desorption.....	27
2.3.4	Temperature-programmed reduction	27
2.3.5	High-resolution transmission electron microscopy	27
2.3.6	X-ray diffraction	28
2.3.7	Furfural hydrotreatment experiments.....	28
2.4	Hydrogen solubility experiments	29
2.5	Product analysis and calculations	29
2.6	Uncertainty calculations.....	30
3.	Results and discussion	32

3.1	Optimization of laboratory scale batch reactor conditions for furfural hydrotreatment	32
3.1.1	Hydrogen addition method	32
3.1.2	Atmosphere in heating.....	33
3.1.3	Catalyst pretreatment atmosphere	35
3.1.4	Stirring speed	37
3.1.5	Metal loading.....	37
3.1.6	Reaction temperature	38
3.1.7	Hydrogen pressure.....	40
3.2	Furfural hydrotreatment with earth abundant copper, nickel and iron catalysts.....	42
3.2.1	The effect of metal in 2-methylfuran production.....	42
3.2.2	The effect of metal loading in 2-methylfuran production...	44
3.2.3	The effect of reaction temperature in 2-methylfuran production	46
3.3	Carbon as a support material in furfural hydrotreatment reactions.....	47
3.3.1	Physical characteristics of carbon materials.....	47
3.3.2	Active surface groups of carbon materials	49
3.3.3	Crystallographic structure of carbon supported catalysts ...	51
3.3.4	Metal particle size on carbon supported catalysts	52
3.3.5	Comparison of carbon support materials in the production of 2-methylfuran.....	53
3.4	Acetone formation in furfural hydrotreatment with carbon supported copper, nickel and iron catalysts.....	57
3.4.1	Effect of metal loading on acetone formation.....	59
3.4.2	Effect of temperature on acetone formation.....	59
3.4.3	Acetone formation mechanism in furfural hydrotreatment conditions	59
3.5	Hydrogen solubility in furfural hydrotreatment	61
3.5.1	Hydrogen solubility in furfural and 2-propanol	62
3.5.2	Hydrogen solubility calculations.....	63
3.5.3	Modeling the hydrogen solubility in furfural and 2-propanol	65
4.	Summary and Conclusion	68
	References	70

List of Abbreviations and Symbols

Abbreviations

AAD	Average absolute deviation
AAS	Atomic absorption spectroscopy
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CB	Carbon black
CNT	Carbon nanotubes
DISI	Direct injection spark-ignition
DMF	2,5-dimethylfuran
EDS	Energy dispersive spectroscope
EOS	Equation of state
FA	Furfuryl alcohol
FID	Flame ionization detector
FMA	Furanmethanol acetate
FUR	Furfural
GC	Gas chromatography
HF	Hydrofluoric acid
HR-TEM	High-resolution transmission electron microscopy
IWI	Incipient wetness impregnation
MF	2-Methylfuran
MIBK	Methyl isobutyl ketone
MS	Mass spectrometer
MTHF	2-Methyltetrahydrofuran
PC-SAFT	Perturbed-chain statistically associating fluid theory
PL	2-pentanol
PN	2-pentanone

PR	Peng-Robinson
RAD	Relative average deviation
RON	Research octane number
SI	Spark ignition
SRK	Soave-Redlich-Kwong
TCD	Thermal conductivity detector
THF	Tetrahydrofuran
THFA	Tetrahydrofurfuryl alcohol
TPD	Temperature-programmed desorption
TPR	Temperature-programmed reduction
WI	Wetness impregnation
XRD	X-ray diffraction

Symbols

A	Parameter for density or vapor pressure in DIPPR correlation
A_i	Area of component i
A_{std}	Area of standard
B	Parameter for density or vapor pressure in DIPPR correlation
B	Line broadening (°)
C	Parameter for density or vapor pressure in DIPPR correlation
$C_{FUR,o}$	Concentration of furfural at time 0 ($\text{mmol}\cdot\text{g}^{-1}_{\text{sample}}$)
$C_{FUR,t}$	Concentration of furfural at time t ($\text{mmol}\cdot\text{g}^{-1}_{\text{sample}}$)
C_i	Concentration of component i ($\text{mmol}\cdot\text{g}^{-1}_{\text{sample}}$)
$C_{i,t}$	Concentration of component i at time t ($\text{mmol}\cdot\text{g}^{-1}_{\text{sample}}$)
D	Parameter for density or vapor pressure in DIPPR correlation
d	Mean average metal particle size (nm)
d_i	Diameter of the particles in certain diameter range (nm)
E	Parameter for density or vapor pressure in DIPPR correlation
F_i	Response factor of component i
$H_{2, FLOW}$	Hydrogen flow ($\text{cm}^3\cdot\text{min}^{-1}$)
κ	Shape factor
λ	X-ray wavelength (nm)

L_{FLOW}	Volumetric liquid flow ($\text{cm}^3 \cdot \text{min}^{-1}$)
m_{sample}	Mass of sample (g)
m_{std}	Mass of standard (g)
$M_{W,i}$	Molar weight of component i ($\text{g} \cdot \text{mol}^{-1}$)
N_{Ao}	Concentration of component A at time 0
N_A	Concentration of component A at time t
n_i	Amount of particles
$N_{i,t}$	Concentration of component i at time t
k_{ij}	Binary interaction parameter
P	Pressure (bar)
P_c	Critical pressure (bar)
P_i	Mass fraction of component i
ρ_L	Liquid density ($\text{mol} \cdot \text{cm}^{-3}$)
P_{std}	Mass fraction of standard
S_i	Selectivity of component i (%)
θ	Bragg angle ($^\circ$)
T	Mean size ordered domains (nm)
T	Temperature (K)
T_c	Critical temperature ($^\circ C$)
V_m	Ideal gas molar volume NTP ($22\,414 \text{ cm}^3 \cdot \text{mol}^{-1}$)
x_{H_2}	Hydrogen mole fraction
X_i	Conversion of component i (%)
Y_i	Yield of component i (%)

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

I Jaatinen, Salla; Karinen, Reetta; Lehtonen, Juha. 2016. Liquid Phase Furfural Hydrotreatment to 2-Methylfuran with Carbon Supported Nickel Catalyst – the Effect of Process Conditions, *ChemistrySelect*, volume 1, issue 16, pages 5363-5373. ISSN 2365-6549. DOI [10.1002/slct.201601333](https://doi.org/10.1002/slct.201601333).

II Jaatinen, Salla; Karinen, Reetta; Lehtonen, Juha. 2017. Liquid Phase Furfural Hydrotreatment to 2-Methylfuran with Carbon Supported Copper, Nickel, and Iron Catalysts, *ChemistrySelect*, volume 2, issue 1, pages 51-60. ISSN 2365-6549. DOI [10.1002/slct.201601947](https://doi.org/10.1002/slct.201601947).

III Jaatinen, Salla; Karinen, Reetta. 2017. Furfural Hydrotreatment Applying Isopropanol as a Solvent – the Case of Acetone Formation, *Topics in Catalysis*, volume 60, issue 17, pages 1473-1481. ISSN 0972-4508. 1572-9028 DOI [10.1007/s11244-017-0828-7](https://doi.org/10.1007/s11244-017-0828-7).

IV Jaatinen, Salla; Touronen, Jouni; Karinen, Reetta; Uusi-Kyyny, Petri; Alopaeus, Ville. 2017. Hydrogen Solubility in Furfural and 2-Propanol: Experiments and Modeling, *Journal of Chemical Thermodynamics*, volume 112, pages 1-6. ISSN 0021-9614. DOI [10.1016/j.jct.2017.04.004](https://doi.org/10.1016/j.jct.2017.04.004).

V Jaatinen, Salla; Stekrova, Martina; Karinen, Reetta. 2017. Ni- and CuNi-modified activated carbons and ordered mesoporous CMK-3 for furfural hydrotreatment, *Journal of Porous Materials*, volume 25, issue 4, pages 1147-1160. ISSN 1380-2224. DOI [10.1007/s10934-017-0526-7](https://doi.org/10.1007/s10934-017-0526-7).

Author's Contribution

Publication 1: Liquid Phase Furfural Hydrotreatment to 2-Methylfuran with Carbon Supported Nickel Catalyst – the Effect of Process Conditions.

and

Publication 2: Liquid Phase Furfural Hydrotreatment to 2-Methylfuran with Carbon Supported Copper, Nickel, and Iron Catalysts.

Author prepared the catalysts, planned the experimental work together with RK and JL, characterized the catalysts excluding atomic adsorption spectroscopy, performed the planned experiments, wrote the first version of the manuscript and after discussions with RK and JL, wrote the final version of the manuscript.

Publication 3: Furfural Hydrotreatment Applying Isopropanol as a Solvent – the Case of Acetone Formation.

Author prepared the catalysts, planned the experimental work together with RK, performed the planned experiments, wrote the first version of the manuscript and after discussions with RK, wrote the final version of the manuscript.

Publication 4: Hydrogen Solubility in Furfural and 2-Propanol: Experiments and Modeling.

Author planned and performed the experiments together with JT. In the modelling part, JT selected the methods for modelling, Author performed the modelling calculations and conclusions were made by author, JT and PUK. Author analyzed the reaction media with gas chromatography and wrote the first version of the manuscript. Modelling part was co-wrote with JT and PUK and all authors participated on the finalization.

Publication 5: Ni- and CuNi-modified activated carbons and ordered mesoporous CMK-3 for furfural hydrotreatment

Author planned the experimental work together with RK and MS, performed part of catalyst characterization (temperature-programmed desorption and acid titration), performed the planned experiments and wrote the manuscript together with RK and MS. MS characterized the catalysts with other methods presented in the manuscript.

1. Furfural hydrotreatment to produce valuable chemicals and fuel components

With an increasingly disquieting environmental situation, the urgent need for bio-based chemicals and fuels has been progressively highlighted. Out of the many raw materials for bio-based products, the one with most potential is abundantly available lignocellulose, which consists of cellulose, hemicellulose, and lignin.¹ The hemicellulose part of lignocellulose can be converted to sugars, which can be applied to produce a platform chemical furfural. Furfural has revealed its promise as a raw material for many valuable bio-based products as the use of furfural as such suffers from high reactivity.² The modification of furfural is possible through many reactions, such as hydrotreatment, oxidation, dehydrogenation and alkylation, of which hydrotreatment has raised much interest.^{2,3} This interest arises from a wide variety of valuable products with excellent characteristics, such as 2-methylfuran. The currently used toxic CuCr catalyst⁴⁻⁶ and a low selectivity of alternative catalysts towards many of the desired products^{3,7,8} cause challenges in the production of bio-based chemicals and fuels from furfural through hydrotreatment.

The following sections introduce the production of 2-methylfuran from furfural through hydrotreatment. In Section 1.1., the properties of platform chemical furfural are presented in detail as well as its applications. Sections 1.2. - 1.3. describe the production and types of valuable chemicals obtained from furfural through hydrotreatment. Then, in Sections 1.4. - 1.6., the production steps as well as the catalyst and support material options are compared in furfural hydrotreatment reactions. Sections 1.7. - 1.8. report on any significant production of acetone observed in the reaction conditions as well as the solubility of hydrogen in furfural and 2-propanol. Finally, Section 1.9. presents the scope of this research.

1.1 Furfural

Furfural (furan-2-carbaldehyde) is a promising bio-based platform chemical for many valuable chemicals and fuels.⁹ This chemical is produced from biomass, employing the high five-carbon content hemicellulose part. The five-carbon sugars are obtained from hemicellulose through hydrolysis. In this reaction, the oxygen-bonds between the sugar molecules are broken down with the help of strong acids or enzymes.^{2,10} Finally, furfural is produced by the dehydration of these five-carbon sugars. Usually, the five-carbon sugar applied to produce furfural is xylose. However, this sugar can isomerize to other pentose sugars such as xylulose and lyxose.¹¹ The dehydration of C₅ sugars produces one furfural molecule and three water molecules (Fig. 1).^{2,11} The yield of furfural from xylose varies between 50 – 81% depending on the catalyst and how well the process is optimized.¹² Furfural production pro-

cess may also produce undesired side products, for example formaldehyde, formic acid, lactic acid, glycolaldehyde and glyceraldehyde are commonly known.¹³ In addition, solid particles called humins, are produced while producing furfural. These humins are mostly formed from furfural oligomers with the amount increasing as a function of reaction temperature.^{13,14}

Figure 1. Production of furfural through pentose sugar dehydration. Figure reprinted with permission from Topic in Catalysis, vol 56, pages 512 – 521, Sairanen et al.¹¹: “Functionalized activated carbon catalysts in xylose dehydration”, Copyright (2013).

The production volume of furfural worldwide is in a range of 300 – 700 kilotons annually.¹⁵ Most of the furfural is produced in China, but some production also occurs in South Africa and the Dominican Republic. The process for furfural production was invented in 1921 by the food company, Quaker Oats; the raw material applied was oats and the catalyst homogeneous sulfuric acid.¹⁴ To date, most producers use homogeneous catalysts in their processes, such as sulfuric acid, acetic acid and formic acid.¹³ Homogeneous dehydration processes are usually operated between temperatures of 153 – 240 °C, applying water as a solvent. An autocatalytic reaction of xylose to furfural is also possible, but the selectivities are lower compared to processes applying catalysts.¹¹ The raw material for furfural is often bagasse or corncobs due to their affordability and the high content of the desired five-carbon sugars.¹⁵ The market price of furfural depends on the demand, in the year 2002, the price varied between 500 – 1100 \$/t, and in 2011 the price was already approximately 2000 \$/t.^{7,16} A few producers and the catalysts, reaction conditions and process type are presented in Table 1.

Table 1. Furfural producers, catalysts, reaction conditions and process type.

Producer	Catalyst	Reaction temperature (°C)	Batch/ continuous process	Furfural yield (%)	Reference
Quaker Oats	Sulphuric acid	153	Batch	< 50	15,17
Quaker Oats	Sulphuric acid	184	Continuous	55	15,17,18
Huaxia Tech./Westpro	Sulphuric acid	160 - 165	Continuous	35 - 50	17
Biofine	Sulphuric acid	150 - 200	Continuous	70	19
Supra Yield	Sulphuric acid	240	Continuous	50 - 70	17

The significance of furfural has been investigated and verified by the Department of Energy in the United States of America in 2014. In the deep analysis of "Top Value-Added Chemicals from Biomass", furfural was added to the list of the 30 most potential platform chemicals to produce value-added chemicals and fuels. The selection of the most potential building blocks was conducted by examining the market data and their technical feasibility in simultaneously producing fuels and chemicals in biorefineries.^{20,21}

1.2 Furfural hydrotreatment reactions

Furfural is a chemical full of potential; however, due to its unstable character, the use of furfural as such is not profitable. Nevertheless, the possible products produced from this chemical are considered almost limitless. As the urge to replace fossil-based products continuously increases, the bio-based character of furfural as a raw material for chemicals is highly desired in the current climate change situation.

The unstable character of furfural arises from its molecular form. The furfural molecule consists of a hetero-ring and an aldehyde group. The hetero-ring consists of two C=C double bonds and an oxygen atom in between. In addition to the C=C double bonds, the aldehyde group is easily oxidized or hydrogenated to produce other chemicals from furfural. Furfural oxidation is a somewhat studied subject; possible oxidation products of furfural include furic acid, maleic acid and succinic acid.^{3,22} Furfural oxidation products have many applications in pharmaceutical and fragrance industries. In the presence of hydrogen, furfural is hydrogenated to furfuryl alcohol (FA) and, further, for example, to tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), 2-methyltetrahydrofuran (MTHF), 2-pentanone, and 2-pentanol. Figure 2 shows a simplified process scheme of furfural hydrotreatment to illustrate the complexity of the hydrotreatment reactions. The options for the products are extremely varied with the process conditions affecting to the produced products. Currently, the most commonly produced chemical from furfural is furfuryl alcohol, approximately 65% of all available furfural is applied to furfuryl alcohol production.³ From the wide variety of furfural hydrotreatment products, 2-methylfuran is also a chemical with many uses. This chemical has excellent characteristics for use, for example, in the fuel industry as well as in the pharmaceutical and fragrance industries. However, the production of 2-methylfuran from furfural with high selectivity has turned out to be challenging due to the reactivity of furfural towards a large variety of hydrotreatment products (Fig. 2). To produce one particular product, the process conditions and catalysts need to be optimized to prevent production of undesired side products.

Figure 2. Furfural hydrotreatment reaction network. Reproduced from Publication I.

1.3 Furfural hydrotreatment products

As presented in Section 1.2., the complexity of the furfural hydrotreatment scheme is caused by the structure of the furfural molecule, as the two C=C double bonds in the furanyl ring and one carbonyl bond (C=O) can be reduced. In principle, the C=C double bond is more easily reduced compared to the C=O double bond, due to activation energies; however, the reduction preference of these parts ultimately depends mostly on the applied catalysts.^{23,24} Depending on the catalyst, the array of products and extent of hydrogenation varies; the most common hydrotreatment products include furfuryl alcohol, 2-methylfuran and tetrahydrofurfuryl alcohol.^{3,7,8} Table 2 shows several catalysts and production process conditions with the main product and yield to the main product. As Table 2 illustrates, the production of furfuryl alcohol can be very selectively performed, achieving almost 100% yields of furfuryl alcohol. However, further hydrotreatment products (MF and THFA) are produced with lower yields. In the following chapters, the properties and applications of the main furfural hydrotreatment products are discussed in more detail.

1.3.1 2-Methylfuran

Out of several value-added chemicals produced from furfural, 2-methylfuran has garnered much interest in recent years. The reasons for this interest are its excellent properties, such as a high research octane number (131), low water solubility ($7 \text{ g}\cdot\text{l}^{-1}$), and high energy density.^{25–28} These properties are desired in many applications, but the research has currently concentrated on the use of MF as an octane booster in gasoline, and as a component in medicine, fragrance and pesticide industries.^{9,29} Among these applications, the most promising use of 2-methylfuran is as an octane booster component in gasoline.^{27,30–33}

The production of 2-methylfuran can occur through two hydrodeoxygenation pathways. In the first pathway, furfural is hydrogenated to furfuryl alcohol and furfuryl alcohol reacts through hydrogenolysis to 2-methylfuran. In the second pathway, direct hydrogenolysis of furfural leads to 2-methylfuran (see Fig. 2). In both cases, additional hydrogen is needed with water being formed as a side product in the reactions. Due to easy hydrogenation of 2-methylfuran, it can be further hydrogenated to 2-methyltetrahydrofuran (MTHF). This product is also valuable as it possesses similar applications to MF. There are advantages and disadvantages in the production of MF instead of MTHF. It has been observed in the author's experiments, that every furfural hydrotreatment product step decreases the yield of the desired products due to side reactions. However, due to relatively short lifetime of intermediate products (e.g. furfuryl alcohol, MF) it might be better to aim for production of final product MTHF. The production of MF from furfural is considered less energy and less hydrogen consuming process than production of MTHF and the main property considering the use as an octane booster is advantageous in MF vs. MTHF (RON 131 vs 86, respectively).^{7,8,31} Thus, 2-methylfuran is considered to be the more desirable product in this dissertation.

Table 2. Catalysts, process conditions, furfural conversion and main products and yields in furfural hydrotreatment reaction studies.

Catalyst	Reaction temp. (C)	Pressure H ₂ (bar)	Solvent	FUR conv. (%)	Main product and yield (%)	Reaction time (min)	Ref.
5 wt-% Ru/C	160	20*	2-Propanol	95	MF (50)	960	34
CuFe	220	90	Octane	99	MF (51)	840	35
5 wt-% Pt/C	175	80	n-Butanol	99	MF (40)	30	36
5 wt-% Pt/C	175	80	n-Butanol/ water	100	MF (31)	30	36
2 wt-% Pd/Fe ₂ O ₃	180	1*	2-Propanol	100	MF (13)	450	26
5 wt-% Pt/C	175	80	n-Butanol	99	MF (40)	30	36
5 wt-% Pt/C	175	30	Water / H ₃ PO ₄	100	MF (37)	60	37
Ru/Co ₃ O ₄	170	10	THF	100	MF (93)	1440	38
5 wt-% Pd/TiO ₂	RT	3	Toluene	98	MF (43)	120	39
5 wt-% Pd/C	175	80	Water	100	THFA (36)	60	36
Ni-Pd/SiO ₂	40	80	Water	99	THFA (95)	480	40
Ni 5132P + Cu V1283	130	40	Methanol	100	THFA (97)	185	41
5 wt-% Ru/C	120	50	Methanol	99	THFA (59)	180	41
NiCrO ₄	140	7	Water	100	THFA (70)	300	42
Ru/MgO	110	150	Ethanol	100	THFA (78)	n/a	43
RuO ₂ + Cu	120	50	Methanol	100	THFA (86)	90	41
Pd/MFI	220	34	2-Propanol	84	THFA (83)	300	44
Ni-Fe-B	200	10	Ethanol	100	FA (100)	240	45
Mo-Ni-B/γ-Al ₂ O ₃	80	50	Methanol	99	FA (90)	180	46
PtSn/SiO ₂	100	100	2-Propanol	100	FA (96)	480	47
NiSn/TiO ₂	110	30	2-Propanol	99	FA (99)	75	48
Ni-P-B	80	17	Ethanol	100	FA (80)	15	49,50
RuZn-MOF	50	5	Water	95	FA (95)	240	51
Co-B amorphous alloy	110	10	Ethanol	100	FA (100)	30	4
Cu-Zn-Cr-Zn oxides	170	20	2-Propanol	100	FA (96)	210	52
5 wt-% Pd/C	160	30	Water	98	Cyclopentane (67)	60	36
5 wt-% Ru/C	175	80	Water	100	Cyclopentanol (49)	60	36

* Nitrogen pressure, the required hydrogen is retrieved from the solvent with transfer hydrogenation.

To date, liquid biofuel components applied in gasoline are limited to bioethanol.²¹ However, bioethanol has some disadvantages when blended into gasoline, for example slight corrosivity caused by water adsorption ability and low energy density.^{21,53} Thus, to increase the usability and compatibility of biofuels, better options are needed. In this case, 2-methylfuran has been observed to have excellent properties compared to bioethanol. Some important properties of 2-methylfuran, bioethanol and gasoline are compared in Table 3. The comparison reveals high research octane number (RON) of MF compared to ethanol and gasoline. The boiling point of MF is closer to gasoline, and the flash point is good for the cold properties of the final fuel blend.

Table 3. Properties of 2-methylfuran, bioethanol and gasoline. ^{27,31,54–57}

Property	2-Methylfuran	Bioethanol	Gasoline
Density 20 °C (kg·m ⁻³)	913.2	790.9	744.6
Research Octane number (RON)	131	107	96.8
Lower Heating Value LHV (MJ·kg ⁻¹)	31.2	26.8	41 - 44
Heat of vaporization (kJ·kg ⁻¹)	358.4	919.6	373
Boiling point / temperature (°C)	64.7	78.4	27 - 225
Flash point (°C)	-22	13	-43

The properties of MF as a renewable gasoline component in the direct-injection spark-ignition (DISI) engine have been investigated by a few different research groups. Thewes et al.⁵⁶ investigated the use of MF and compared the results to gasoline and ethanol. Especially its combustion performance in cold conditions was observed to be good compared to the other tested options. In 2016, Wang et al.²⁷ compared MF to the properties of fossil-based gasoline, bio-based ethanol and bio-based 2,5-dimethylfuran (DMF) in the DISI engine. In both studies, MF was observed to have many excellent properties when compared to gasoline and other biofuels, such as superior knock suppression ability compared to gasoline, higher thermal efficiency, low flash point (-22 °C), lower volumetric specific fuel consumption than ethanol and lower hydrocarbon emissions than gasoline. However, the NO_x emissions were higher than with gasoline or ethanol. This is a consequence of a low carbon/hydrogen ratio of MF (0.2) leading to more CO₂ in the exhaust gas, leading to higher adiabatic flame temperature and therefore, to higher emissions of NO_x with 2-methylfuran compared to gasoline or ethanol.⁵⁷ Due to these excellent properties, MF could stand as another option to ethanol as a bio-component in gasoline in DISI engines.²⁷ Wei et al.⁵⁷ investigated the use of MF/gasoline blend in spark-ignition (SI) engines. This study reported that a 10 vol-% of MF in gasoline enhances the engine performance compared to an ethanol/gasoline blend when comparing output torque, brake power and brake specific fuel consumptions. A similar observation was also noted in this study of decreasing HC and CO emissions as well as increasing NO_x emissions. In addition to the use of MF in gasoline engines, the use of a MF blend with diesel in diesel fuel engines has also recently been investigated with good results. Compared to diesel, the blend of MF/diesel was observed to increase the brake thermal efficiency. However, the NO_x emissions were reported to be higher with an increasing MF content, but the amount of soot emissions decreased.⁵⁵

1.3.2 Furfuryl alcohol

In furfural hydrotreatment, the main product is currently furfuryl alcohol. It has been reported that 62 – 65% of all furfural produced is used to produce furfuryl alcohol.^{7,9} Furfuryl

alcohol (FA) is produced with furfural hydrogenation in the gas or liquid phase. This chemical is colorless, miscible to water and most organic solvents, and has a boiling point between 169 – 171 °C. Furfuryl alcohol has a wide range of applications. The chemical can be used, for example, in foundry resins, the refractory industry, pharmaceutical industry, and solvent industry.^{9,59,60} Furthermore, a fraction of furfuryl alcohol is also used to produce other valuable chemicals, such as 2-methylfuran and tetrahydrofurfuryl alcohol.⁹

Only a little information is available of the furfuryl alcohol markets and prices. The price of furfural has a highly significant connection to the price of FA. The prices of these two chemicals are very closely tied, FA has a slightly higher price compared to furfural. A market intelligence provider CCM reported furfural and furfuryl alcohol prices from the years 2014 – 2016. In this report, the price of FA has been around 1150 – 1750 \$/t and the price of furfural around 950 - 1500 \$/t.⁶¹

1.3.3 Tetrahydrofurfuryl alcohol

Tetrahydrofurfuryl alcohol (THFA) is a valuable chemical produced from furfural mostly through furfuryl alcohol. THFA is a transparent chemical with a high-boiling point (178 °C) and it is miscible in water.^{7,9} THFA and MF are competing products of furfuryl alcohol and, in most cases, the production of both components occur in furfural/furfuryl alcohol processing. Further hydrotreatment of THFA can lead to the production of 2-methyltetrahydrofuran (MTHF), which is also a product of MF hydrogenation. Production of THFA is reported to occur mostly in Japan by Koatsu Chemical Industries, in which reported production volume is 30 t/a. THFA has applications as a green solvent in agriculture, printing and cleaning industry.⁷

1.4 Liquid phase vs. gas phase production

As with many reactions, furfural hydrotreatment can be performed in the vapor or liquid phase. Both options are widely applied in the research of furfural hydrotreatment, but the chemical industry tends to favor vapor phase hydrotreatment. Both production processes have their own advantages and disadvantages. In vapor phase furfural hydrotreatment, the furfural conversion and product selectivity towards furfuryl alcohol and also 2-methylfuran have been observed to be between 60 – 95%.^{5,62–64} However, the high energy consumption caused by the high reaction temperatures (130 – 300 °C) renders gas phase production expensive.^{3,7,8} In addition, catalyst deactivation has been reported at high temperatures. Multiple reasons have been proposed for the catalyst deactivation: catalyst coking^{3,6,14,65,66}, catalyst poisoning by adsorption of furfural or further hydrotreatment products^{3,6,65,66}, metal particle sintering at high temperatures^{3,6,65,66} and thermal polymerization^{14,66} as well as coking of furfuryl alcohol in the fixed catalyst beds in continuous gas phase productions.¹⁴

The liquid phase hydrotreatment of furfural offers contrastive advantages and disadvantages: the hydrotreatment in liquid phase consumes less energy due to lower reaction temperatures (40 – 220 °C), and is, thus, economically recommended with the assumption that the catalyst deactivation is assumed less severe at lower reaction temperatures.^{3,7,8,66,67} Furthermore, as the production of furfural is performed in the liquid phase, an easier merging to upstream production is possible in the liquid phase hydrotreatment of furfural.^{34,67} Solvents are often applied in the liquid phase processes. The solvents are used in industrial liquid phase processes to prevent runaway reactions of exothermic reactions, to ensure the

efficiency of mixing and stirring of the liquids or to have optimal concentrations of reactants in the mixture. The choice of solvent used in the liquid phase furfural hydrotreatment is vital, as it can significantly influence the product selectivities. Various solvents and the influence on product selectivities was investigated, for example, by Hronec et al.³⁶ and Ordonsky et al.⁶⁸. The most commonly used solvent offering good selectivity towards intermediate furfuryl alcohol is 2-propanol. Another disadvantage in liquid phase furfural hydrotreatment are the high hydrogen pressures required.^{3,67} The liquid phase hydrotreatment of furfural was chosen for this dissertation for its lower energy consuming characteristic and compatibility with furfural production as this reaction is also performed in the liquid phase.^{3,67}

1.5 Catalysts in the production of 2-Methylfuran

Catalysts represent an important and necessary part in many reactions. Over 90% of all chemical reactions require catalysts for an easier and faster production of desired products.⁶⁹ Furfural hydrotreatment to valuable chemicals is a reaction which acquires active metal catalysts for efficient production. The purpose of these metals is to activate the hydrogen molecules, which then react with the raw material to produce valuable chemicals from furfural.⁸ Traditionally, the catalyst used in furfural hydrotreatment has been copper chromite catalyst. However, due to environmental regulations, the chromite used in the catalyst should be replaced with more environmentally friendly options.^{4–6} Furfural hydrotreatment towards valuable products has been intensively studied with a variety of metal catalysts. The studies of catalytic materials have especially targeted the production of furfuryl alcohol as approximately 62 – 65% of furfural is used for the production of this chemical.^{7,9} Studies concerning the production of 2-methylfuran have been fewer, therefore, the most optimal catalyst for this reaction has yet to be discovered. The most studied metals in furfural hydrotreatment include platinum and palladium from noble metal options and copper, nickel, and cobalt from transition metal options.^{3,5,6,25,34,39,40,59,63,67,70–73} Table 1 in Section 1.3. presents some of the metal catalysts studied in furfural hydrotreatment. The properties of each metal differ and the selectivity towards products can vary significantly. For example, Pt and Pd are more prone to hydrogenate C=C double bonds. The affinity towards C=C bonds originates from the most stable adsorption mode of furfural on these metals. With Pd and Pt, the most stable mode is a flat configuration mode in which the furfural molecule is horizontally aligned.⁷⁴ With copper, the C=C bond affinity has been observed to be weak and the affinity towards the C=O bond strong.⁷³ With copper, the furfural molecule is attached to the metal surface at the oxygen atom of the aldehyde group. Nickel is usually observed as a very good hydrogenation catalyst, but in this case, it can have an overly strong hydrogenation affinity, which might cause a breaking of the adsorbed bonds. Furfural is observed to attach to nickel particles through the C=O bond, similarly to copper.⁷⁵ However, not only the metal selection, but other aspects, such as structure-sensitivity of the reactions can influence the affinities. Structure-sensitivity of reactions is considering for example metal particle size, shape of metal particles and surface sites on specific places, such as in corners, edges and kinks. In general, structure-sensitive reactions are considered to increase or decrease in activity as a function of metal particle size.^{8,76,77} Moreover, the activa-

tion energies of hydrogen dissociation differ between the metals. This causes further differences in reaction rates and product selectivities between the metal options.⁷⁸ The optimal catalyst characteristics need a more detailed investigation.

1.6 Carbon as support material in furfural hydrotreatment

Carbon materials have excellent properties for use as catalysts or catalyst support materials in many chemical reactions. The carbon materials are less utilized as support materials in industry compared to many other support material options. The reason for the lower utilization rate can be due to the less studied and understood chemistry and potential properties of carbon materials. Nonetheless, carbon materials can offer a good support performance that can be easily tailored to many industrial application purposes. Although the use of carbon materials as a catalyst is possible in some cases, the materials are most commonly used as support materials.⁷⁹

Good catalyst support materials need to fulfil many aspects for optimal use. First, the chemical and physical composition of the material should be sufficient for the intended use. The mechanical and thermal strength are important as the catalysts may need to endure high temperatures and hard handling. Secondly, the surface area of the support should be sufficient for the intended use. In many cases, high surface areas are optimal as the dispersion of active materials is better with these materials. Thirdly, the support material should be stable in the operation conditions for optimal operation. From many possible support materials for example silica, alumina and carbon fulfil these characteristics well. Out of these support materials, silica (SiO_2) and alumina (Al_2O_3) have been studied more and their activities are better known, whereas carbon materials have remained slightly undervalued.⁷⁹

There are multiple types of carbon materials that can be utilized as catalyst support materials. Carbon materials include activated carbon, carbon black, carbon fibers, carbon nanotubes, graphite and fullerenes. Out of these materials, activated carbon and carbon black are the most applied materials in the catalyst industry thus far. The advantage of the carbon materials is the flexibility of their properties. The surface areas, surface composition and porosity can be significantly altered in the preparation process, which widens the potential applications of these materials. In addition to the excellent properties and possibilities of carbon materials, the cost of carbon materials is usually lower compared to oxide materials. In some publications, regeneration of carbon supported metal catalysts have been reported. In the regeneration process of Panagiotopoulou et al.³⁴ the carbon supported Ru-catalyst is reduced at 300 °C for 3 hours and then oxidized at 130 °C in 5% O_2/He gas for 3 hours. However, these kinds of regeneration processes by burning may cause high losses of support carbon material along with the undesired coke.⁸⁰ On the other hand, recovery of metals from carbon catalysts is easy and possible through burning the carbon material away.^{79,81} In contrast, the disadvantages of the carbon materials include the materials being unusable in the presence of oxygen (above 200 °C) or at too high temperatures (>400 °C) due to disintegration.⁷⁹ Thus, the regeneration of the carbon supported catalysts by burning away coke is not possible without interrupting the material. Moreover, the high ash content of some carbon materials is a problem, because the mineral impurities in the ash may hinder the adsorption on carbon support by blocking the carbon pores.⁸²

The carbon material properties can be modified using several methods. The surface area of the support material can be very important to generate high dispersion of the supported

metal particles. In general carbon materials obtain very high surface areas, even up to 1500 m²·g⁻¹ have been reported.⁸³ The high surface areas of carbon materials are easily obtained with a microporous structure. There are also few disadvantages of too high surface areas. One disadvantage is, that too high surface areas can lead to unstable supports. Furthermore, too high dispersion of metals on the support can lead to too fast catalysis, leading to diffusion limitations by inability to transport molecules to or from the surface.⁸¹ Compared to the mostly used oxide supports, Al₂O₃ and SiO₂ in furfural hydrotreatment, the surface area is much higher. Oxide materials usually obtain surface areas between 2 – 250 m²·g⁻¹.^{84–86} The surface area of carbon materials can be influenced with the applied precursor material and the preparation treatment applied. For example, steam activation creates the porous structure of the carbon materials, and the temperature applied affects the surface area as well as pore size of the prepared material.⁸⁷ Another important property of the carbon supports is the surface functional groups. The surface functional groups on carbon materials can be, for example, basic groups, including anhydride, phenol, quinone and carbonyl; or acidic groups, such as carboxylic acid, lactone and peroxide groups.^{88,89} These groups can act as active sites themselves or as anchoring sites for the metals in the catalyst. The surface functional groups can be inserted into carbon material surfaces with acid treatments, such as with sulphuric acid (H₂SO₄) and nitric acid (HNO₃).^{11,90} In the case of sulphuric acid, surface groups, such as sulphide, sulphonate, sulphate, thiophenol, quinone and sulfoxide, can be formed.^{91–93} With nitric acid, oxygen-containing surface groups, such as carboxylic acid, phenolic, carbonyl, anhydride and quinone are formed.⁹⁴

The majority of the furfural hydrotreatment research studies have employed oxide supports, leaving the carbon materials less studied. The few carbon materials applied consist mainly of activated carbons. Activated carbon has been used in the liquid phase furfural hydrotreatment studies of Panagiotopoulou et al.³⁴ and Ordonsky et al.⁶⁸, in which Ru/C catalysts obtained 50% and 19% yield of 2-methylfuran, respectively. Hronec et al.³⁶ investigated Pt and Ru on activated carbon and achieved 36% and 3.5% MF yield, respectively. Rao et al.⁶ compared copper catalysts on three different carbon materials to produce furfuryl alcohol or 2-methylfuran as a product. The investigated carbon materials were activated carbon, diamond powder and graphitized fibers. From the studied materials, activated carbon was the most suitable material due to the best stability against catalyst deactivation. Mironenko et al.⁹⁵ studied Pd/carbon black (CB) and Pd/carbon nanotubes (CNT). The research group obtained 99% selectivity towards furfuryl alcohol with Pd/CB, with Pd/CNT, the obtained product was THFA.

In this dissertation, three activated carbons and a mesoporous carbon material CMK-3 were applied as support materials for copper, nickel and iron catalysts. Based on previous studies and literature published on the topic, the use of activated carbons has advantages in furfural hydrotreatment compared to oxide support materials. Furthermore, the physical properties of activated carbons, such as their high surface area and pore size, are beneficial for this type of reaction. The mesoporous carbon materials have not been studied for this reaction. Nevertheless, the high surface area and mesoporous structure is expected to offer good characteristics to produce 2-methylfuran from furfural.

1.7 Acetone formation in furfural hydrotreatment

Furfural hydrotreatment in the liquid phase is usually performed applying the help of solvents in the reaction. Thus, not only are the reactions of furfural important, but as it has been observed, furfural can react together with solvents and produce side products in these reaction conditions. The most common solvents used in furfural hydrotreatment reactions are alcohols. Alcohols are better solvents compared to water because water increases the amount of unwanted side reactions of furfural when aiming at producing furfuryl alcohol and 2-methylfuran. The production of cyclopentanone and cyclopentanol have been observed in those studies applying water as a solvent.^{36,37} In addition, the furfural solubility in water is limited (8.3 wt-% at 25 °C), whereas the solubility of furfural in alcohols is complete.^{7,8,34,68}

In furfural hydrotreatment reactions, the alcohol solvents are not as inert as assumed and it is possible that the solvent acts in furfural hydrotreatment as a hydrogen donor, in addition to the hydrogen gas in the reactor. As the alcohol donates a hydrogen molecule, it is converted into an aldehyde (primary alcohols) or ketone (secondary alcohols) depending on the alcohol. In addition to a direct reaction between furfural and alcohol, the alcohol solvent can also dehydrogenate in the hydrotreatment process conditions forming an aldehyde/ketone and a hydrogen molecule as a product.⁹⁶ The most common alcohol used in furfural hydrotreatment studies is 2-propanol.^{7,67,97,98} In the case of 2-propanol, dehydrogenation leads to acetone and hydrogen and the transfer hydrogenation with hydrogen donation to furfural leads initially to furfuryl alcohol and acetone.^{26,34,63,96,97}

The acetone formation can be significant in furfural hydrotreatment applying 2-propanol as a solvent. It is still unclear as to which mechanism contributes to what magnitude to produce the ketones/aldehydes when applying alcohols as solvents in furfural hydrotreatment. It is important to understand the formation mechanisms to avoid unnecessary side reactions in furfural hydrotreatment.

1.8 Hydrogen solubility in furfural

In liquid phase hydrotreatment reactions, the solubility of hydrogen in the reaction media is crucial. In these processes, an inadequate amount of dissolved hydrogen can restrict the desired reactions and results in undesired products. Furthermore, the hydrogen solubility data is decisive knowledge for the kinetic modelling of the reactions; furthermore, the knowledge of kinetics and mechanisms of the reactions are especially important in the scale up of processes. In addition, many liquid phase furfural hydrotreatment processes have issues with mass balances as many unknown products are formed. The use of precise phase equilibria models could also considerably decrease the mass balance problems.^{63,64,72}

Describing the hydrogen solubility data with appropriate models can provide important information on the applied reaction media. Alcohols are the most applied solvents in furfural hydrotreatment. Several suitable models describing solubility of gases in alcohols have been used in earlier studies, for example, predictive and cubic equation of state (EOS) models. Examples of the most commonly used cubic equation of state models are the models of Peng-Robinson (PR) and Soave-Redlich-Kwong (SRK).^{99,100} These models are suitable, for example, for modeling gas phase and refinery processes. Even though these models are suitable for modeling hydrogen solubility in substances, such as alcohols, these models might not be suitable for furfural due to differences in molecular form and polarity. Furfural is an

intermediately polar component, consisting of various chemical bonds. Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) is an equation of a state model applicable to small and large molecules with a wide temperature and pressure range.¹⁰¹ The use of PC-SAFT model has been observed as being good for oxygen-containing compounds, thus implying that the model may be more suitable for furfural and its products.^{102,103} In this dissertation, the hydrogen solubility in furfural and 2-propanol were investigated and modeled with PR, SRK and PC-SAFT models.

1.9. Scope of the research

The purposes of this doctoral dissertation are as follows:

- To develop noble metal free catalyst options for the currently applied toxic catalyst in the process and to optimize the process conditions of furfural hydrotreatment to obtain optimal process conditions to produce valuable 2-methylfuran [I, II].
- To investigate the use of environmentally benign carbon support options in the chosen reaction to offer important information about support effects on the furfural hydrotreatment, about the carbon support characteristics and about the optimization required to produce 2-methylfuran [V].
- To determine the mechanism and the side reaction of furfural with the alcohol solvents often applied in the furfural hydrotreatment processes [III].
- To obtain more information about the most important kinetic barrier, hydrogen solubility in the reaction media, thus acquiring important information for process scale up [IV].

2. Materials and Methods

In this chapter, the materials and methods applied in this doctoral thesis are presented. Section 2.1. presents the chemicals and materials used in this thesis, Section 2.2. introduces the applied catalyst preparation methods and Section 2.3. the catalyst characterization methods of this dissertation. Sections 2.4. and 2.5. describe the procedures and the setup for the furfural hydrotreatment and hydrogen solubility experiments. Then, Section 2.6. presents the product analysis and calculation methods and finally, Section 2.7. introduces the applied uncertainty calculations.

2.1 Chemicals and materials

The chemicals and materials used in this dissertation are presented in Table 4. All chemicals were applied as received with exception of furfural. Furfural was purified with distillation procedure, where purity of 99.8% was analyzed by gas chromatography. The furfural purification was performed to remove impurities formed in storage conditions under air. Oxygen in air is known to cause colorification of furfural due to formation of long conjugated double bond molecules in the sample.¹⁷ The amount of these side products has been estimated small ($< 1\%$),¹⁷ however, the effect of these side products was removed by distillation procedure.

Table 4. Chemicals and materials used in this thesis.

Chemical / material	Chemical formula	Supplier	Purity (%)	Publication
2-Propanol	C ₃ H ₈ O	Sigma-Aldrich	≥99.5	I, II, III, IV, V
2-Butanol	C ₄ H ₁₀ O	Sigma-Aldrich	99	I, II, III, IV, V
Hydrogen	H ₂	AGA	99.999	I, II, III, IV, V
Furfural	C ₅ H ₄ O ₂	Sigma-Aldrich	99.8*	I, II, III, IV, V
Furfuryl alcohol	C ₅ H ₆ O ₂	Sigma-Aldrich	98	I, II, III, IV, V
2-Methylfuran	C ₅ H ₆ O	Sigma-Aldrich	99	I, II, III, IV, V
Tetrahydrofurfuryl alcohol	C ₅ H ₁₀ O ₂	Sigma-Aldrich	99	I, II, III, IV, V
Furan	C ₄ H ₄ O	Sigma-Aldrich	>99	I, II, III, IV, V
2-Methyltetrahydrofuran	C ₅ H ₁₀ O	Sigma-Aldrich	≥99	I, II, III, IV, V
Copper nitrate	Cu(NO ₃) ₂ ·H ₂ O	Sigma-Aldrich	99.9	II, III, V
Nickel nitrate	Ni(NO ₃) ₂ ·6H ₂ O	Sigma-Aldrich	≥98.5	I, II, III, V
Iron nitrate	Fe(NO ₃) ₂ ·9H ₂ O	Sigma-Aldrich	≥98	II, III
Tetraethyl orthosilicate	Si(OC ₂ H ₅) ₄	Sigma-Aldrich	≥99.0	V
Triblock copolymer Pluronic	P-123	Sigma-Aldrich		V
Sucrose	C ₁₂ H ₂₂ O ₁₁	Sigma-Aldrich	99.5	V
Hydrofluoric acid	HF	Sigma-Aldrich	≥40	V
Activated carbon Norit RB4C	C	Norit		I, II, III, V
Activated carbon Norit RX3	C	Norit		V
Activated carbon Norit Darco	C	Norit		V

* Purified with distillation procedure from < 99% purity.

2.2 Catalyst preparation

The studied carbon supports in this dissertation were steam-activated carbon Norit RB4C, steam-activated and acid-washed carbon Norit RX3 and Norit Darco and mesoporous carbon material CMK-3. The activated carbons used in this dissertation were commercial carbon materials. The activated carbon materials were crushed and sieved to particle size of 200 - 300 µm [V] or 1.68 – 2.00 mm [I – IV]. The mesoporous carbon material CMK-3 applied in Publication V was prepared in-house. The preparation of this material was performed by replication method, using a well known SBA-15 material as a template and sucrose as a carbon source, following the procedure of Xia et al.¹⁰⁴. The CMK-3 was applied in Publication V in a catalyst particle size range of 200 - 300 µm. All the carbon materials were dried at 110 °C in an oven before metal deposition to remove moisture attached to the carbon materials. Two metal deposition methods were used; incipient wetness impregnation (IWI) and wet impregnation (WI) methods. In incipient wetness impregnation, the liquid/solid ratio was measured empirically and, thus, kept at 1 cm³·g⁻¹. In the empirical measurement, liquid was added to 2 g of carbon support until excess of liquid was observed. In IWI, the deposition of two metals for bimetallic catalysts was performed simultaneously in an aqueous solution applying precalculated amounts of nitrate precursors to obtain desired metal content for the catalyst. The impregnated catalysts were dried at room temperature for 24 hours and at 110 °C oven for 18 hours. Catalysts (2 g) were calcined in presence of oxygen, or heat treated in presence of nitrogen at 300 °C (heating rate 5 °C·min⁻¹) for 4 hours. In wet impregnation method, 5 grams of carbon support material was stirred together with 50 cm³ of distilled water and a calculated amount of metal precursor. The mixture was stirred for 24 hours at room temperature, water was evaporated under vacuum,

and finally the sample was dried at 110 °C overnight. The wet impregnated catalysts were heat treated at 450 °C for 2.5 hours applying an inert nitrogen flow. All tested catalysts were reduced in situ at 250 °C for 1.5 hours, with 40 bar hydrogen pressure. Table 5 presents all prepared and tested catalysts and some characterization data.

Table 5. Prepared and tested catalysts.

Active metal	Support material	Publication	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Average metal particle size with TEM (nm), (±stddev, nm)	Catalyst particle size
n.a.	Norit RB4C	I,II,III,V	1012	0.40	0.36	n.a.	n.a.
n.a.	Norit RX3	I,II,III,V	1594	0.74	0.57	n.a.	n.a.
n.a.	Norit Darco	I,II,III,V	750	0.73	0.27	n.a.	n.a.
n.a.	CMK-3	I,II,III,V	1038	0.94	0.38	n.a.	n.a.
2 wt-% Ni	Norit RB4C	I,II,III	n.a.	n.a.	n.a.	3.5 (±0.81)	1.68 – 2.00 mm
5 wt-% Ni	Norit RB4C	I,II,III	n.a.	n.a.	n.a.	3.2 (±0.97)	1.68 – 2.00 mm
10 wt-% Ni	Norit RB4C	I,II,III	710	0.28	0.09	3.6 (±2.1), 50 – 100 (agglomerates)	1.68 – 2.00 mm
10 wt-% Ni	Norit RB4C	V	891	0.38	0.32	2.7 (0.6)	200 – 300 µm
10 wt-% Ni	Norit RX3	V	1594	0.62	0.50	2.0 · 5.2 (0.4 – 1.0)	200 – 300 µm
10 wt-% Ni	Norit Darco	V	750	0.67	0.25	4.3 (0.8)	200 – 300 µm
10 wt-% Ni	CMK-3	V	1038	0.90	0.35	14.5 (5.6)	200 – 300 µm
1 wt-% Cu	Norit RB4C	II	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm
2 wt-% Cu	Norit RB4C	II,III	516	0.31	0.06	5 – 30 (±4.1)	1.68 – 2.00 mm
5 wt-% Cu	Norit RB4C	II,III	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm
2/2 wt-% CuNi	Norit RB4C	II,III	887	0.22	0.12	7 – 9	1.68 – 2.00 mm
5/2 wt-% CuNi	Norit RB4C	II,III	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm
2/5 wt-% CuNi	Norit RB4C	II,III	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm
5/5 wt-% CuNi	Norit RB4C	V	890	0.37	0.32	n.a.	200 – 300 µm
5/5 wt-% CuNi	Norit RX3	V	1508	0.71	0.54	n.a.	200 – 300 µm
5/5 wt-% CuNi	Norit Darco	V	660	0.60	0.23	n.a.	200 – 300 µm
5/5 wt-% CuNi	CMK-3	V	877	0.90	0.30	n.a.	200 – 300 µm
2/2 wt-% CuFe	Norit RB4C	II,III	765	0.15	0.08	20 – 100	1.68 – 2.00 mm
5/2 wt-% CuFe	Norit RB4C	II,III	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm
2/2 wt-% NiFe	Norit RB4C	II,III	975	0.22	0.14	>100	1.68 – 2.00 mm
5/2 wt-% NiFe	Norit RB4C	II,III	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm
5/5 wt-% NiFe	Norit RB4C	II,III	n.a.	n.a.	n.a.	n.a.	1.68 – 2.00 mm

2.3 Catalyst characterization

The characterization methods applied in this dissertation are atomic absorption spectroscopy (AAS), nitrogen physisorption, temperature-programmed desorption (TPD), temperature-programmed reduction (TPR), high-resolution transmission electron microscopy

(HR-TEM) and X-ray diffraction (XRD). Following subsections present the used characterization methods in detail.

2.3.1 Atomic absorption spectroscopy

Atomic absorption spectroscopy (AAS) was applied for detecting the metal loading of the prepared catalysts. The catalysts samples (0.2 g) were dissolved in a mixture of nitric acid (2.5 cm³) and hydrochloric acid (7.5 cm³). The mixture of acids and catalyst sample was heated to 120 °C for overnight in a closed Teflon vessel. The next day, the sample was cooled down to room temperature and diluted with distilled water. An air-acetylene flame was applied in Varian AA-240 equipment for analysis.

2.3.2 Nitrogen physisorption

Nitrogen physisorption was applied for catalyst specific surface area, pore volume and pore size distribution analysis. The physisorption analysis was performed with Autosorb-1C (Quantachrome) for calcined catalysts (0.1 g) applying desorption isotherms at -196 °C for calculation. Prior to the measurement, all moisture was removed by vacuum treatment. Specific surface area was calculated with Brunauer-Emmett-Teller (BET) theory, and pore volume and pore diameter distribution with Barrett-Joyner-Halenda (BJH) theory.

2.3.3 Temperature-programmed desorption

Temperature-programmed desorption (TPD) analysis was performed to identify the surface groups of the catalysts with Altamira AMI-200 equipped with a mass spectrometer (Hiden QIC-20). In the analysis, the catalysts (0.05 g) were pretreated with calcination in presence of oxygen at 300 °C for four hours (heating rate 5 °C·min⁻¹) and flushing in helium at 30 °C for one hour. After, the catalysts were analyzed under 20 cm³·min⁻¹ helium flow during heating ramp of 25 – 800 °C with heating rate 12 °C·min⁻¹. The mass spectrometer was applied to analyze desorbing carbon monoxide, carbon dioxide and water during heating.

2.3.4 Temperature-programmed reduction

Temperature-programmed reduction (TPR) was performed with Altamira AMI-200 equipped with a mass spectrometer (HIDEN QIC-20). Prior to the reduction, the catalyst (0.05 g) was calcined in situ with 5% O₂/He flow (50 cm³·min⁻¹) with heating ramp of 5 °C·min⁻¹ from 25 to 300 °C and a hold of 240 min. After calcination, the catalyst was cooled down to 50 °C and held for 60 minutes under helium flow to remove any excess oxygen. Next, the catalyst was held under 5% H₂/He flow at 50 °C for 90 minutes. Finally, the TPR was performed with a temperature ramp of 5 °C·min⁻¹ from 50 to 300 °C under 5% H₂/He flow (50 cm³·min⁻¹) and a hold of 15 minutes.

2.3.5 High-resolution transmission electron microscopy

High-resolution transmission electron microscopy (HR-TEM) analysis was performed for analyzing the metal particle shape and rough size distribution on the carbon supports. The analysis was performed with an aberration-corrected JEOL-2200FS microscope (JEOL

Ltd.) equipped with an energy dispersive spectroscope (EDS), able to analyze sample elemental composition. The sample was grinded to powder in a mortar and placed to a sample holder applying acetone solvent. The particle size of particles was measured manually due, minimum of 60 particles were measured for further calculations in Publication I – III. In Publication V, minimum of 14 particles were measured for particle size estimation. The mean average metal particle size d (nm) was calculated with Equation (1). In Equation (1), n_i is the number of particles and d_i is the diameter of the particles in certain diameter range (nm).

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

2.3.6 X-ray diffraction

X-ray diffraction (XRD) was applied to analyze the metal phases on the monometallic and bimetallic catalysts. The XRD analysis was performed to the catalysts between calcination (or heat treatment) and reduction procedures. The equipment applied was PANalytical X'Pert PRO MPD Alpha-1 with Cu K α 1 radiation (45 kV and 40 mA). The XRD data was recorded at 2θ 10 - 85 ° with 0.013° step size. Crystal size of metallic particles were calculated with Scherrer equation (2). The Scherrer equation was applied to calculate the metal particle size from half height of the most intensive diffraction peak. In equation 2, T is mean size of the ordered domains (nm), K is the dimensionless shape factor (0.9 for assumed spherical particles), λ is the X-ray wavelength (nm), β is the line broadening at half the maximum intensity (°) and θ is the Bragg angle (°).

$$\tau = \frac{K \lambda}{\beta \cos \theta} \quad (2)$$

2.3.7 Furfural hydrotreatment experiments

Furfural hydrotreatment experiments were performed in a 50 cm³ batch reactor (Autoclave Engineers) equipped with a Robinson-Mahoney type catalyst basket.¹⁰⁵ The basket was applied in all experiments, even in experiments performed in slurry phase to ensure similar mixing behavior in all experiments. Reaction temperatures applied were between 180 – 230 °C, hydrogen pressures between 0 – 50 bars and stirring speed 300 – 1000 rpm. The catalyst (0.2 g) reduction was performed in situ before reaction at 250 °C in 40 bar hydrogen pressure, for 1.5 hours. The reaction mixture contained furfural or furfuryl alcohol (1 cm³) and 15 cm³ of the solvent 2-propanol. Liquid samples were collected during the reaction at 0, 15, 30, 60, 120 and 300 min. A gas sample was collected after the reaction, at room temperature. Reactor, catalyst basket and liquid phase dimensions during the experiments are presented in Figure 3. Catalyst particles are placed on the bottom of the catalyst basket in Publications I – III, and they are fully wetted to ensure sufficient use of the catalyst particles. In Publication V, the catalyst was applied as slurry, and placed at the bottom of the reactor. This should as well ensure fully wetted particles. Liquid phase (furfural + solvent) was calculated to account for 32% of total reactor volume. Mixing of liquid feed was performed with a fixed propeller in the middle of the catalyst basket, at the bottom of the reactor.

Figure 3. Hydrotreatment reactor with inside catalyst basket and catalyst particles.

2.4 Hydrogen solubility experiments

The hydrogen solubility in furfural and 2-propanol was investigated with a continuous flow apparatus at 50, 125 and 200 °C, in a pressure range of 3 – 127 bars. Hydrogen flow was injected in liquid stream of furfural or 2-propanol to obtain predetermined molar flow of hydrogen. The hydrogen solubility was determined monitoring the formation of two phases in the view cell with visual observation, detailed description of the equipment is presented in the article of Saajanlehto et al.¹⁰⁶. Hydrogen gas flow was increased steadily, and hydrogen solubility limit was discovered when gas bubbles were observed in the liquid flow. To avoid thermal reactions of furfural, the residence time of hydrogen and liquid was kept short in the column, between 2.2 – 11.8 min. The purity of furfural and 2-propanol was investigated before and after measurement with gas chromatography.

2.5 Product analysis and calculations

The liquid samples taken during the furfural hydrotreatment experiments were analyzed quantitatively with gas chromatography (Agilent 6890 series) equipped with a flame ionization detector (GC-FID). The analysis was performed with Zebron ZB-wax Plus column (60 m x 25 mm x 0.25 µm), with temperature ramp from 40 to 100 °C with heating rate of 5 °C·min⁻¹, and from 100 to 230 °C with heating rate of 20 °C·min⁻¹. Injector temperature was 230 °C, injector volume 1 µl, and internal standard added to the product sample after experiments was 2-butanol. The samples were analyzed three times to decrease the experimental error, caused by the GC-analysis. A qualitative analysis of the unknown products was performed with GC (Agilent 7890-5975) equipped with a mass spectrometer (GC-MS). The electron ionization impact was recorded at 70 eV.

The gas phase was analyzed with a GC (Agilent 6890) containing gas pneumatics system. The GC was equipped with two detectors: FID and a thermal conductivity detector (TCD). Non-condensable gases (CO, CO₂, H₂ and N₂) were analyzed with TCD applying two columns (HP-PLOT/Q 30 m x 0.53 mm x 40 µm, HP-Molesieve 30 m x 0.53 mm x 25 µm), and argon as a carrier gas. Hydrocarbon analysis was performed with FID applying HP-AL/KCL column (50 m x 0.32 mm x 8 µm), and helium as carrier gas.

The furfural / furfuryl alcohol conversion (X_i) was calculated with Equation (3). In this Equation, X_A is the conversion of component A, N_{A0} is the concentration of component A at time 0 and N_A is the concentration of the component A at time t (mmol·g⁻¹_{sample}).

$$X_i = \frac{N_{A0} - N_A}{N_{A0}} \quad (3)$$

Product selectivity (S_i) and yield (Y_i) were calculated with Equations (4) and (5). In Equations (4) and (5), $N_{i,t}$ is the concentration of component i at time t ($\text{mmol}\cdot\text{g}^{-1}\text{sample}$).

$$S_i = \frac{N_{i,t}}{N_{A0} - N_A} \quad (4)$$

$$Y_i = \frac{N_{i,t}}{N_{A0}} \quad (5)$$

2.6 Uncertainty calculations

The furfural conversion and product selectivities/yields were calculated based on gas chromatography results. The error sources were divided to systematic error sources and analysis error sources. The systematic error was not considered in this dissertation. There are two known analysis error sources in this study; the scale error and the GC area measurement error. Scale error is ± 0.1 mg based on the manufacturer specification, thus the maximum error in this thesis was 1%. This value was applied for uncertainty calculations. GC error for area measurement was calculated for each component separately. Error for each component was estimated from standard deviation of three repetitive measurements multiplied with 1.96. This procedure gives the measurement error with 95% confidence level.¹⁰⁷ Finally, the error for each component was estimated as an average from minimum 50 standard error measurements. Following errors presented in Table 6 were estimated for the components. Most of the components analysed have a measurement error between 1.4 – 2%. However, the internal standard 2-butanol has a measurement error of 3.2%. This difference is assumed to result from difference in molecular structure; furfural and its products contain a heteroring, as 2-butanol has an open structure.

Table 6. Estimated maximum GC area measurement error for furfural and furfural hydrotreatment main products.

Component	GC area measurement error (%)
Furfural	1.4
2-Butanol (standard)	3.2
2-Methylfuran	1.7
Furfuryl alcohol	1.8
Tetrahydrofurfuryl alcohol	2.0
Furan	1.4
2-Methyltetrahydrofuran	2.0
Acetone	1.8

The molar concentration of each component i (C_i , $\text{mmol}\cdot\text{g}^{-1}\text{sample}$) in each sample was calculated with Equation 6 from gas chromatography results. In Equation 6 F_i is the response factor of component i , A_i is the area of component i , m_{std} is the weighed amount of standard 2-butanol (g), A_{std} is the area of standard, $M_{W,i}$ is the molar mass of component i ($\text{g}\cdot\text{mol}^{-1}$) and m_{sample} is the weighed sample amount (g).

$$C_i = \frac{F_i A_i m_{std}}{A_{std} M_{W,i} m_{sample}} \quad (6)$$

The response factor in molar concentration calculations was calculated with Equation 7. In equation 7, P_i is the mass fraction of component i and P_{std} is the mass fraction of the standard.

$$F_i = \frac{P_i A_{std}}{P_{std} A_i} \quad (7)$$

The uncertainty for the molar concentration $u(F_i)$, presented in Equation 8, was estimated with partial derivative of Equation 7. In Equation 8, ΔP_i and ΔP_{std} are the uncertainty of the scale, and ΔA_i and ΔA_{std} are the uncertainty of the GC area measurements of the component i and the standard.

$$u(F_i) = \left| \frac{A_{std}}{P_{std} A_i} \right| \Delta P_i + \left| \frac{-P_i A_{std}}{A_i P_{std}^2} \right| \Delta P_{std} + \left| \frac{-P_i A_{std}}{P_{std} A_i^2} \right| \Delta A_i + \left| \frac{P_i}{P_{std} A_i} \right| \Delta A_{std} \quad (8)$$

The calculated uncertainty for furfural response factor is 1.03 ± 0.26 and for 2-methylfuran 0.75 ± 0.18 .

Finally, the uncertainty of the molar concentration $u(C_i)$, presented in Equation 9, was calculated with partial derivative of Equation 6. In equation 9, Δm_{sample} and Δm_{std} are the uncertainty of the scale, ΔA_i and ΔA_{std} are uncertainty of GC area measurements of component i and standard, and ΔF_i is the uncertainty of response factor.

$$u(C_i) = \left| \frac{-F_i m_{std}}{A_{std} M_{W,i} m_{sample}^2} \right| \Delta m_{sample} + \left| \frac{F_i A_i}{A_{std} M_{W,i} m_{sample}} \right| \Delta m_{std} + \left| \frac{F_i m_{std}}{A_{std} M_{W,i} m_{sample}} \right| \Delta A_i + \left| \frac{-F_i A_i m_{std}}{M_{W,i} m_{sample} A_{std}^2} \right| \Delta A_{std} + \left| \frac{A_i m_{std}}{A_{std} M_{W,i} m_{sample}} \right| \Delta F_i \quad (9)$$

Uncertainty in furfural conversion was calculated with Equation 10 and uncertainty in component i yield calculations with Equation 11. In Equation 10, $C_{FUR,t}$ is the furfural concentration at time t , $C_{FUR,0}$ is the furfural concentration at time 0. In Equation 11, $C_{i,t}$ is the component i concentration at time t .

$$u(FUR \text{ conversion}) = \left| \frac{C_{FUR,t}}{C_{FUR,0}^2} \right| \Delta C_{FUR,0} + \left| \frac{-1}{C_{FUR,0}} \right| \Delta C_{FUR,t} \quad (10)$$

$$u(Yield) = \left| \frac{-C_{i,t}}{C_{FUR,0}^2} \right| \Delta C_{FUR,0} + \left| \frac{1}{C_{FUR,0}} \right| \Delta C_{i,t} \quad (11)$$

In conclusion, the uncertainty calculations revealed the two identified analysis errors (scale error and GC error for area measurement) were minor compared to analysis results. The error sources were minimized with repetitive GC measurements of each analysis data point. The error bars were added to the furfural conversion and product yield figures, however, the error bars remained too small to be visible under the data markers.

3. Results and discussion

This chapter presents and discusses the results obtained in this doctoral dissertation. Section 3.1. considers the results of furfural hydrotreatment process optimization in a batch reactor, and Section 3.2., the use of copper, nickel and iron catalysts on carbon support in furfural hydrotreatment. Section 3.3. examines carbons as a catalyst support material in furfural hydrotreatment reactions, and Section 3.4. concentrates on the acetone formation mechanism study in furfural hydrotreatment. Finally, Section 3.5. forms conclusions on hydrogen solubility in furfural and solvent 2-propanol.

3.1 Optimization of laboratory scale batch reactor conditions for furfural hydrotreatment

The process conditions are important factors affecting reaction rates and product selectivity, especially in the complex furfural hydrotreatment reaction scheme (see Fig. 2). The most important process conditions and experimental procedures affecting the furfural hydrotreatment into valuable products were studied in Publication I. The purpose of the study was to optimize the process conditions for the selective production of 2-methylfuran from furfural in a laboratory scale batch reactor. The process conditions studied were reaction temperature and hydrogen partial pressure. In addition, other relevant parameters were investigated in the batch reactor furfural hydrotreatment, such as the metal-loading of the catalyst, effect of the hydrogen addition method, gas atmosphere in the heating phase, catalyst precursor heat treatment atmosphere, and the stirring speed during the experiment.

3.1.1 Hydrogen addition method

The availability of hydrogen is necessary for hydrotreatment reactions to occur. Without a sufficient amount of hydrogen being used in the reactions, the conversion and selectivity will be compromised. In Publication I, the initial hydrogen pressure inserted in the reactor with the reaction mixture was 40 bars (reactor gas volume 34 cm³). In atmospheric pressure, this amount counts for 1360 cm³ of hydrogen. During the experiment, the amount of hydrogen decreases according to the reaction and sampling procedure. Thus, the decreased amount may need replacing to maintain sufficient hydrogen partial pressure inside the reactor. The hydrogen addition method was investigated with three experiments at 230 °C.

In the first experiment, the hydrogen was manually added after obtaining each sample to achieve similar pressure levels as before obtaining the sample. The average drop in reactor pressure in the sample-collection procedure was 1 – 1.5 bars. In the second experiment, the hydrogen bottle remained open during the whole experiment, maintaining the reactor pres-

sure at the same level with the gas bottle pressure regulator. The third experiment was performed without adding any hydrogen after collecting samples. The pressure decreased approximately 11 bars during this experiment.

The experimental results revealed no significant differences in furfural conversion levels and full conversion of furfural was achieved in 60 minutes in all cases. The effect of the hydrogen addition method on product selectivity was minor. A slightly higher yield of 2-methylfuran was achieved by adding hydrogen after each sample collection (Fig. 4). This could be caused by a faster spreading of additional hydrogen to the reaction mixture by the spray of gas in the liquid, thus creating more turbulence which leads to more efficient adsorption. At the end of experiments, the differences in product selectivity disappeared.

In conclusion, the hydrogen partial pressures were observed to be sufficient in all cases, and the effect on product selectivity was minor. The hydrogen addition method is not a procedure which significantly influenced the results. The hydrogen addition after obtaining samples was applied for further experiments in this dissertation. The errors caused by analysis errors were calculated and discovered to be too small to be visible in Figure 4.

Figure 4. Effect of hydrogen addition method to yield of MF as a function of reaction time. Reaction temperature 230 °C, hydrogen partial pressure 40 bar, stirring speed 1000 rpm, catalyst 10 wt-% Ni/Norit RB4C. The error bars for the measurement data are too small to be visible in the figure. Previously unpublished data.

3.1.2 Atmosphere in heating

To prevent undesired reactions and to optimize product selectivity towards 2-methylfuran, the reactor was heated to reaction temperature before the reaction mixture or hydrogen were inserted into the reactor containing the pre-packed and reduced catalyst. The heating procedure can be performed using hydrogen or inert nitrogen atmosphere inside the reactor during the heating phase. The atmosphere in the heating phase might influence the catalyst inside the reactor.

Figure 5 presents the product concentrations as a function of reaction time using hydrogen and nitrogen atmosphere in heating. The experiments did not reveal differences in fur-

fural conversion, but product selectivity was significantly affected by the heating atmosphere. In both cases, a maximum yield of 2-methylfuran was achieved in 60 minutes; however, the amount of 2-methylfuran was higher in the case of hydrogen atmosphere heating. In this case, the hydrogen was adsorbed on the catalyst surface during the heating phase and the reaction rate was faster after furfural insertion. The adsorbed hydrogen in heating phase resulted in more hydrogenated products at the beginning of the experiment. In addition, the further hydrotreated products of 2-methylfuran were affected by the heating atmosphere. In the case of hydrogen, 2-methylfuran was hydrogenated further to 2-methyl-tetrahydrofuran (MTHF) and, in the case of nitrogen, further hydrogenation to MTHF and 2-pentanone was observed. A nitrogen atmosphere resulted in a decreased amount of tetrahydrofurfuryl alcohol (THFA) towards the end of the experiment, simultaneously increasing the amount of MTHF. This implies that heating in the nitrogen atmosphere increases the ring-opening of MF to 2-pentanone, and the MTHF was mostly formed from hydrogenation of THFA. Ring-opening reactions were suppressed in further experiments with a hydrogen atmosphere inside the reactor during heating (see Fig. 5).

Figure 5. Effect of gas atmosphere during the heating procedure in furfural hydrotreatment. Heating performed in a) N₂ atmosphere, b) H₂ atmosphere. Reaction temperature 230 °C, hydrogen partial pressure 40 bar, stirring speed 1000 rpm, catalyst 10 wt-% Ni/Norit RB4C. The error bars for the measurement data are too small to be visible in the figure. Reproduced from Publication I.

3.1.3 Catalyst pretreatment atmosphere

The catalysts for Publication I were prepared using the incipient wetness impregnation (IWI) method. After the metal precursor impregnation procedure presented in Section 2.2., the metal precursors should be heat-treated. In the heat treatment procedure, the catalyst is treated at a high temperature in the presence of air or nitrogen flow. In the presence of oxygen, the heat treatment is called calcination. In the heat treatment, the metal nitrates

used as precursors are converted to oxides by oxidation or decomposition reactions, depending on the gas phase. Possible by-products in addition to the metal oxide are HNO_3 , NO , NO_2 , N_2O , O_2 and H_2O , depending on the calcination / heat treatment temperature.¹⁰⁸ After forming metal oxides, the reduction procedure inside the reactor will activate the catalyst by reducing the metal oxides to active metallic form.

The atmosphere options for the heat treatment procedure are oxygen, air and nitrogen. In this study, the support material for the catalysts was carbon. With carbon, the presence of air or oxygen may burn away some of the material or affect the material characteristics in other ways. In this case, inert nitrogen is a better option for heat treatment gas. On the other hand, air and oxygen are oxidative gases and may lead to a better performance of the catalysts.

In Publication I, the effect of nitrogen and air was investigated as heat treatment gas options. The results indicated air calcination caused more disintegration of the carbon-supported catalysts compared to nitrogen heat treatment. However, the remaining carbon catalysts were observed to have smaller metal particles than with the nitrogen heat treatment, thus causing a better dispersion of the metal particles on the catalyst surfaces. In furfural hydrotreatment experiments, a mildly higher reaction rate of furfural and higher selectivity at 2-methylfuran was observed with the air-calcined catalysts. Further hydrogenation products of 2-methylfuran were observed more with air-calcined catalyst, which is an indication of better selectivity towards MF over these catalysts (Fig. 6). The products presented in Figure 6 are the main products of furfural hydrotreatment, in addition with one known condensation product of furfural / furfuryl alcohol and acetone (furanmethanol acetate). The remaining products were not identified and are responsible for the remaining yield in the experiments. The furfural conversion was high in all samples, conversion level with air calcined catalyst were 98.4% (60 min), 99.8% (120 min) and 99.9% (300 min). Furfural conversions with heat treated catalyst (N_2 treatment) were 91.0% (60 min), 98.4% (120 min) and 99.5% (300 min).

Figure 6. Effect of calcination gas in product yields. Reaction temperature 230 °C, hydrogen partial pressure 40 bar, stirring speed 1000 rpm, catalyst 10 wt-% Ni/Norit RB4C. Reproduced from Publication I. FMA = furanmethanol acetate.

3.1.4 Stirring speed

The external mass transfer limitations (gas-liquid, liquid-solid interfaces) in the reactor system were examined by various stirring speeds. The external mass transfer limitations were tested at three different stirring speeds: 300, 800 and 1000 rpm. Reasonably similar reaction rates of furfural consumption were observed with all stirring speeds, but the product yields were affected. The formation rate of the desired 2-methylfuran was observed to be slower at 300 rpm compared to higher stirring speeds, as a notable amount of furfuryl alcohol (yield 40%) was still present after 60 minutes. Furthermore, the amount of further hydrogenation products 2-methyltetrahydrofuran (MTHF) and 2-pentanone (2-PN) increased with higher stirring speeds. At 300 rpm, no further hydrogenation products were observed; at 1000 rpm, the total yield of MTHF and 2-PN was 40% at the end of the experiment. The stirring speed of 1000 rpm led to the highest yield of 2-methylfuran due to lower external mass transfer limitations, therefore leading to it being selected for further studies.

3.1.5 Metal loading

The metals and metal loading chosen for the catalyst can influence the reaction rate and product selectivity. In Publication I, nickel was chosen for the metal to observe differences in metal loading in furfural hydrotreatment to 2-methylfuran, as nickel is known for a good hydrogenation ability.¹⁰⁹ Three different metal loadings were tested: 2, 5 and 10 wt-% of nickel on activated carbon support (Norit RB4C). The preparation, calcination with air, and reduction methods were similar for all the prepared catalysts ensuring that the results are comparable. The results indicated a lower reaction rate of furfural with 2 wt-% Ni/C catalyst (Fig. 7A). With 5 wt-% Ni/C, the furfural consumption rate even exceeded the rate of 10 wt-% catalyst (Fig. 7A); however, the difference of these two catalysts is obviously a consequence of metal particle size. High-resolution transmission electron microscopy (HR-TEM) images revealed a smaller particle size with a 5 wt-% Ni/C catalyst compared to a 10 wt-% catalyst. With a 5 wt-% Ni/C, the metal particle size was between 2 – 4 nm, as with 10 wt-%, the particle size was between 1.5 – 4 nm, but agglomerates of 50 – 100 nm were also observed (see Publication I, Figure 2.). With a smaller particle size, the availability of active metal surface area in the catalyst surface is higher and the availability to reactions is better. Thus, a smaller particle size can be responsible for the higher reaction rates.

Metal loadings influenced the product yields; however, a similar trend in formation and consumption of 2-methylfuran was observed with all the metal content options (Fig. 7B). The amount of MF increased in the beginning of the experiment, reached a maximum, and decreased as further hydrogenation reactions occurred. The highest maximum concentration of MF was observed with the 10 wt-% Ni/C catalyst (yield 48.9%), and the lowest with 2 wt-% Ni/C (yield 31.7%). This indicates the 2-methylfuran net production is dependent on nickel metal loading. This is confirmed because the 2 and 5 wt-% Ni/C catalysts have nearly similar average particle sizes (3.5 and 3.2 nm), but maximum concentration of MF is significantly higher with the 5 wt-% Ni/C catalyst. The larger average particle size (3.6 nm and 50 – 90 nm agglomerates) of 10 wt-% Ni/C has not influenced the formation of 2-methylfuran. Evidently, furfural hydrotreatment reactions are dependent on the number of active sites.

Figure 7. Effect of metal loading on A) conversion of furfural and B) yield of 2-methylfuran as a function of reaction time. Reaction temperature 230 °C, pressure 40 bar, stirring speed 1000 rpm. The error bars for the measurement data are too small to be visible in the figure. Reproduced from Publication I.

3.1.6 Reaction temperature

The influence of reaction temperature in furfural hydrotreatment was investigated at three different reaction temperatures in Publication I. The reaction temperatures tested were 180, 200 and 230 °C. These reaction temperatures were chosen for the study as previous literature reveals furfuryl alcohol is often produced in the liquid phase at lower temperatures (< 200 °C) and products requiring further hydrotreatment at higher temperatures (> 200 °C).^{3,8} Significant differences in furfural conversion were detected between the chosen reaction temperatures (Fig. 8A). A total conversion of furfural was obtained at 230 °C in 60 minutes, while at 180 °C, total conversion of furfural was achieved after 300 minutes. A distinct difference is present in furfural conversion at 180 °C and 200 °C, however, the difference between 200 °C and 230 °C is much smaller. Furfural conversion is very fast in the beginning of the experiments at high temperatures which may cause this smaller difference in reaction rate. Nevertheless, mass transfer issues can not be ruled out in this case. High stirring speed

should overcome external mass transfer issues, but internal mass transfer issues may be present.

The reaction temperature influences the product selectivities. At a lower reaction temperature (180 °C), furfuryl alcohol was the main product, whereas with higher reaction temperatures (200 and 230 °C), selectivity towards 2-methylfuran increased from 23% (180 °C) to 35% (200 °C) and 48% (230 °C). As the selectivity towards 2-methylfuran was investigated as a function of time, a maximum in the yield of 2-methylfuran was observed to be faster at higher temperatures. At reaction temperatures of 200 and 230 °C, a maximum of 2-methylfuran was observed in 120 minutes (Fig. 8B). At 180 °C, no maximum of MF was observed, as the yield of MF increased monotonically throughout the total reaction time of 420 minutes. These results indicate that 2-methylfuran maximum is obtained relatively quickly after a total conversion of furfural. An increase in reaction temperature influences the reaction rate of further MF hydrogenation; the formation of MTHF, and other products were non-existent at 180 °C for the experimental time of 420 minutes.

Even though higher reaction temperatures are more selective in producing MF, the highest temperature applied in this dissertation was 230 °C. Higher temperatures were not tried as the literature shows that temperatures of 250 °C and above can cause very exothermic reactions (polymerisation / resinification) of furfuryl alcohol in closed systems, such as a batch reactor.¹¹⁰ The large amount of intermediate furfuryl alcohol during the experiments prohibits the use of higher temperatures.

Figure 8. Effect of reaction temperature on A) furfural conversion and B) yield of 2-methylfuran as a function of reaction time. Hydrogen partial pressure 40 bar, stirring speed 1000 rpm, catalyst 10 wt-% Ni/Norit RB4C. The error bars for the measurement data are too small to be visible in the figure. Reproduced from Publication I.

The study of reaction temperatures revealed that high temperatures ($> 200\text{ }^{\circ}\text{C}$) are more favorable for the selective production of 2-methylfuran. The higher temperatures increase furfural conversion and selectivity towards 2-methylfuran. Besides the reaction temperature, optimization of the reaction time is needed to obtain the highest possible yield of 2-methylfuran when operating in a batch reactor. This is due to the further reactions of 2-methylfuran. The most optimal temperature to produce 2-methylfuran was $230\text{ }^{\circ}\text{C}$ and it was chosen for further experiments.

3.1.7 Hydrogen pressure

The available hydrogen in the hydrotreatment reactions can have a significant effect on the reaction products. The effect of hydrogen amount was studied applying four different initial hydrogen pressures in the reactor in Publication I. The studied initial hydrogen pressures

were 1, 20, 30 and 40 bars of hydrogen. The pressures presented are hydrogen cold pressures, which stand for hydrogen pressure inserted in the reactor before the vapor pressures of hydrogen and liquid reaction mixture have increased the total pressure measurement due to the high reaction temperature. After the vapor pressure increase of the reaction mixture, the pressure inside the reactor increased approximately to 27, 31, 53 and 65 bars, respectively. The experiments with various hydrogen pressures revealed faster furfural consumption rate with increasing hydrogen pressure. In the experiment with 1 bar hydrogen partial pressure, the total conversion of furfural was achieved in 300 minutes, whereas with higher pressures, total conversion was achieved in 120 minutes (Fig. 9).

Figure 9. Effect of H_2 pressure on furfural hydrotreatment as a function of reaction time. Reaction temperature 230 °C, stirring speed 1000 rpm, catalyst 10 wt-% Ni/Norit RB4C. The error bars for the measurement data are too small to be visible in the figure. Reproduced from Publication I.

The hydrogen pressures also influenced the product selectivities. With the lowest hydrogen partial pressure (1 bar), the amount of furfuryl alcohol was the highest, and with the highest hydrogen partial pressure (40 bar), the yield of 2-methylfuran was the highest. The high hydrogen pressures promoted further hydrogenation of the desired 2-methylfuran to 2-methyltetrahydrofuran and 2-pentanone. Calculations prior to the experiments revealed 40 bar hydrogen partial pressure should be enough for all hydrogenation reactions. With differences in product selectivity, the amount of hydrogen was proven to influence the process. In addition to the amount of hydrogen available, the amount of hydrogen soluble in the reaction mixture is also important. According to Henry's law, the solubility of gas in liquid depends on the partial pressures of gas in the equilibrium conditions (Equation 12). Thus, a higher solubility of gas is also obtained with higher pressure. With higher solubility, the amount of available hydrogen for reactions on the catalyst particles surrounded by the liquid phase (for totally wetted particles) reactions is higher, promoting hydrotreatment reactions. This is valid if no mass transfer limitations are present. The hydrogen solubility in furfural and 2-propanol was further studied in Publication IV. In Equation 12, C is the solubility of gas in the solvent in equilibrium conditions ($\text{mol}\cdot\text{dm}^{-3}$), H is the Henry's constant ($\text{mol}\cdot\text{dm}^{-3}\cdot\text{atm}^{-1}$) and P_{gas} is the partial pressure of the gas (atm).

$$C = H * P_{gas} \quad (12)$$

3.2 Furfural hydrotreatment with earth abundant copper, nickel and iron catalysts

In furfural hydrotreatment to 2-methylfuran, a combination is required of hydrogenation and hydrogenolysis reactions. In the reaction, the carboxyl group of furfural is hydrogenated to an alcohol group (formation of furfuryl alcohol), which then passes through a hydrogenolysis reaction releasing a water molecule and forming 2-methylfuran. As presented in Section 1.5., nickel, copper, cobalt and silver are good alternatives for carbon-oxygen double bond hydrogenation. When comparing these metals, nickel and copper offer good characteristics combined with a cheaper price, compared to many noble metal options. In addition, transition metals offer a more sustainable option compared to rare noble metals. Iron has been investigated earlier to promote the reactions by decreasing the possible decarbonylation, thus highlighting it as a promoter metal of great interest.²⁵ In the study by Sithisa et al.²⁵, iron was concluded as a structural promotor, stabilizing the planar configuration mode of furfural on NiFe-alloy catalyst. The ability of nickel, copper and iron as such, or as bimetallic combinations in furfural hydrotreatment were studied in Publication II.

3.2.1 The effect of metal in 2-methylfuran production

The effect of metals and metal combinations in the production of 2-methylfuran were investigated at 230 °C and 40 bar hydrogen partial pressure as a function of contact time [II]. Comparing the results as a function of contact time normalizes the differences in the catalyst metal loadings with the real differences between catalysts being observable. The contact time is calculated by multiplying metal content with reaction time in each sampling situation. The tested metal combinations were 5 wt-% copper (Cu), 5 wt-% nickel (Ni), 2/2 wt-% copper-nickel (CuNi), 2/2 wt-% copper-iron (CuFe) and 2/2 wt-% nickel-iron (NiFe). All the catalysts were supported on the same activated carbon (Norit RB4C) to prevent differences caused by the support material, as the support itself was observed to influence the performance with the production of furfuryl alcohol through transfer hydrogenation [I]. The calculated initial reaction rates revealed significant differences between the catalysts. Initial reaction rates were calculated from 30 min liquid sample results. The lowest reaction rate was observed with copper ($2.3 \text{ mol} \cdot \text{g}^{-1}_{\text{cat}} \cdot \text{wt}^{-1} \cdot \text{min}^{-1}$), as the highest was observed with copper-iron combination ($6.0 \text{ mol} \cdot \text{g}^{-1}_{\text{cat}} \cdot \text{wt}^{-1} \cdot \text{min}^{-1}$). Only small differences were observed between catalysts with bimetallic combinations. The furfural conversion as a function of contact time with various catalyst options is presented in Figure 10A.

Although the highest initial reaction rate for furfural consumption was observed with CuFe on activated carbon, the highest yield of 2-methylfuran was achieved with CuNi/C, indicating better selectivity of this metal combination (Fig. 10B). The formation of MF was increased throughout the experiment with CuFe/C, reaching a 41% yield of MF in 300 minutes with no observation of further hydrogenation products of MF. With CuNi/C, a 44% yield of MF was observed in 60 minutes and further hydrogenation products reached 5% total yield at the end of experiment (300 min).

Figure 10. Furfural conversions (A) and 2-methylfuran yields (B) as a function of contact time with chosen metal combinations. Reaction temperature 230 °C, hydrogen partial pressure 40 bar, stirring speed 1000 pm. The error bars for the measurement data are too small to be visible in the figure. Previously unpublished data.

There are several surface reaction steps that need to occur in the production of hydrotreated products from furfural: hydrogen and furfural adsorption on the active site, surface reaction and desorption of the product from the catalyst surface. However, the mechanisms for the product formation are still unknown. One option for hydrogen adsorption mechanism is dissociation,¹¹¹ which was proposed by Srivastava et al.¹¹² for copper and nickel particles. Former studies have revealed there are differences in hydrogen dissociation on copper, nickel and iron. The activation energies of hydrogen dissociation were studied by computational chemistry by Pozzo and Alfè,⁷⁸ and the results indicated activation energies of 54.0, 5.8 and 2.9 kJ/mol for hydrogen dissociation on copper, nickel and iron, respectively. These differences in the hydrogen dissociation activation energies between the metals could explain the poorer activity of copper in 2-methylfuran production. In addition, the furfural adsorption on copper has been detected to be weak in previous studies (higher

activation energy for furfural adsorption), compared to nickel and iron. This is another reason that could explain the poor activity of monometallic copper in furfural hydrotreatment.²⁵

The study on different active metals in Publication II revealed that copper on activated carbon is a poorer furfural hydrotreater compared to monometallic nickel or bimetallic combinations of copper, nickel and iron at 230 °C. The combination of copper and nickel had a beneficial effect on product selectivities, despite no significant effect being observed on furfural conversion. The yield of 2-methylfuran was observed as being higher with the bimetallic 2/2 wt-% CuNi/C combination (MF yield 44.2%), compared to monometallic 5 wt-% Cu (MF yield 20.4%) and 5 wt-% Ni (MF yield 32.6%) catalysts. Another advantage of the bimetallic CuNi combination was the reduced C=C double bond hydrogenation activity, leading to less formation of THFA and MTHF. This speculation is also supported by the previous literature, where copper has been observed excellent for C=O hydrogenation, leaving C=C double bonds unaffected.^{65,113}

Combining copper and iron increased the furfural conversion rate compared to Cu/C. It is speculated that this is most probably due to better dissociation of hydrogen on the iron surface, as previous literature shows much higher activation energy for copper compared to iron.⁷⁸ Combining nickel and iron did not significantly affect the furfural conversion rate compared to the nickel catalyst. However, the decarbonylation common with nickel catalysts was observed to mildly decrease with the addition of iron with the furan yield decreasing from a maximum of 1.5% (Ni/C) and 2.2% (CuNi/C) to 1% with NiFe/C (II, Table 3). This is desirable because decarbonylation is a competing reaction of furfural hydrogenation towards furfuryl alcohol and, therefore, to the production of 2-methylfuran. The decrease of decarbonylation with Fe promoted catalysts has already been observed earlier by Sitthisa et al.²⁵.

3.2.2 The effect of metal loading in 2-methylfuran production

In addition to the choice of metal, finding an optimal loading of metal on the support material is important. Generally, the addition of more metal provides a more active surface area for the reactions, which was also confirmed in Subsection 3.1.5 with nickel catalysts. However, an excess of metal on the catalyst support may lead to larger metal particles on the catalyst surface, resulting in a smaller active metal surface area for the reactions. As the price of metals is often high, finding the optimal amount of metal is also important for economic reasons. Various loadings of metals in copper, nickel, copper-nickel, copper-iron and nickel-iron catalysts were investigated in Publication II. Table 7 presents the furfural conversion and yields of the most important products of furfural hydrotreatment at maximum MF yield with the tested catalysts.

Table 7. Furfural conversion, reaction time and product yields at the highest MF yield with various catalysts. T=230 °C, p=40 bar, stirring speed 1000 rpm, MF=2-methylfuran, FA=furfuryl alcohol, THFA=tetrahydrofurfuryl alcohol, 2-MTHF=2-methyltetrahydrofuran, PN=2-pentanone, FMA=furanmethanol acetate. Reproduced from Publication II.

Catalyst	Metal cont. [wt-%]	Furfural conv. at max. MF yield [%]	Time of max. yield of MF [min]	Product yields at maximum MF yield [%]						
				MF	FA	THFA	Furan	MTHF	PN	FMA
Ni/C	2	95.2	120	31.7	10.3	3.5	1.5	0.0	1.2	3.2
	5	96.4	60	32.6	10.9	7.3	1.5	1.9	0.0	1.9
	10	99.8	120	48.9	5.2	15.9	1.4	8.8	10.0	1.2
Cu/C	1	54.0	300	2.3	28.4	0.3	0.0	0.0	0.0	0.8
	2	75.6	300	2.8	68.0	0.2	0.1	0.0	0.0	0.5
	5	98.5	300	20.4	20.5	0.2	0.0	0.0	0.0	0.5
CuNi/C	2/2	91.1	60	44.2	27.3	5.7	2.1	0.0	1.0	4.6
	5/2	97.7	120	29.5	10.6	4.6	0.8	0.0	0.3	0.4
	2/5	94.9	120	32.4	13.4	10.2	1.7	2.7	0.0	1.2
CuFe/C	2/2	99.8	300	41.0	2.0	0.5	0.1	0.0	0.7	0.1
	5/2	99.5	300	36.7	2.8	0.7	0.0	0.0	0.0	0.2
NiFe/C	2/2	98.7	60	31.2	27.8	4.7	1.0	0.0	1.2	1.4
	5/2	100.0	300	35.7	0.4	0.3	0.0	0.0	0.0	3.6
	5/5	99.7	120	25.9	5.0	4.8	0.4	1.2	1.8	0.6

Few common findings could be concluded from all the metal option experiments. The highest yield of 2-methylfuran was usually achieved after the full conversion of furfural. This indicates that furfural is first converted to furfuryl alcohol, and after that, further hydrotreatment reactions occur of furfuryl alcohol towards 2-methylfuran and other products. It is also possible that a competitive adsorption occurs, because earlier studies have published furfural has lower adsorption energy on all metal catalyst options compared to furfuryl alcohol.^{25,114} However, no knowledge on the adsorption energy of other hydrotreatment products is available and the mixture complexity may affect the reactions occurring. A more detailed research of component affinities would be needed to conduct a more defined analysis of competitive adsorption in the prepared catalysts.

In the case of monometallic copper on activated carbon, the reaction rate for furfural consumption was exceedingly slow resulting in full conversion of furfural not being achieved in 300 minutes. Thus, the main product with Cu/C catalyst was furfuryl alcohol and the yield of 2-methylfuran remained at 20% even with the highest metal loading (5 wt-% Cu/C). The highest yield of 2-methylfuran was observed with 10 wt-% Ni/C (48.9%). The maximum of 2-methylfuran was observed in 120 minutes, followed by further hydrogenation reactions towards 2-methyltetrahydrofuran and 2-pentanone. A high nickel content leading to large nickel particles seems to contribute to further reactions of 2-methylfuran (Table 5). The

other side products reveal that the competitive product THFA is produced in large quantities with nickel-containing catalysts. The production of THFA rises with an increasing nickel loading. Particle size dependency was concluded as being nonexistent, because with 2 wt-% and 5 wt-% Ni/C catalysts, the average particle size was almost similar. All these observations indicate that nickel is active in C=C double bond hydrogenation, and eventually also in ring-opening reactions. Previous literature is also supporting this observation.⁶ The addition of iron to nickel catalyst decreased the C=C bond hydrogenation which was observed in the decreased production of THFA. This finding has been previously also observed in the study by Sitthisa et al.²⁵ with NiFe catalyst. Furthermore, the addition of copper to a nickel catalyst decreased the amount of THFA and ring-opening reactions. The amount of other hydrogenation products was low as copper and iron combinations were tested, backing up the previous knowledge of C=O hydrogenation activity of copper and iron.^{25,65,113} No maximum of MF was achieved in 300 minutes with CuFe/C, the yield of MF was observed to have an increasing trend as a function of reaction time. Figure 11 shows the 2-methylfuran yields as a function of reaction time with the versions of each metal/ metal combination providing the highest MF yield.

Figure 11. The most active option of each metal/ metal combination in production of 2-methylfuran as a function of reaction time. Reaction temperature 230 °C, hydrogen partial pressure 40 bar, stirring speed 1000 rpm. The error bars for the measurement data are too small to be visible in the figure. Reprinted from Publication II.

3.2.3 The effect of reaction temperature in 2-methylfuran production

In principle, the optimal reaction temperature for each metal combination can vary significantly. The effect of temperature on the production of MF was investigated for the best metal combinations from Subsection 3.2.2. The tested metal combinations were monometallic nickel, as well as bimetallic CuNi and CuFe. All the catalysts were tested at 200 and 230 °C. Figure 12 presents the 2-methylfuran yields as a function of reaction time at reaction temperatures of 200 and 230 °C. All the chosen catalysts performed better at 230 °C. With Ni/C, a maximum yield of 2-methylfuran was achieved in both temperatures during the 300 min experiment; as with CuNi/C, the maximum of MF was achieved only with the higher testing temperature. With CuFe/C, the maximum of MF was not achieved during the 300

minutes at either of the temperatures. The results reveal nickel is prone to hydrogenate C=O and C=C bonds with the highest reaction rate, because an addition of copper shifts the reaction more towards C=O hydrogenation. With the CuFe combination the reaction rate is much slower and only C=O bond hydrogenation is observed in the 300 min reaction time.

Figure 12. The effect of temperature as a function of reaction time with Ni/C, CuNi/C and CuFe/C catalysts. Hydrogen partial pressure 40 bar, stirring speed 1000 rpm. The error bars for the measurement data are too small to be visible in the figure. Reprinted from Publication II.

3.3 Carbon as a support material in furfural hydrotreatment reactions

Several catalyst support materials have been studied in furfural hydrotreatment reactions. One of the less studied support materials has been carbon. Several carbons as support materials in furfural hydrotreatment were investigated in Publication V. The studied carbon materials were three different activated carbons and one mesoporous carbon material (CMK-3). The activated carbons differ from each other by the activation procedures used in the production of these materials. Two of the activated carbons were steam-activated carbons (RB4C and Darco) and one activated carbon was steam-activated and acid-washed (RX3).

The comparison of the chosen carbon materials was performed applying two metal options for all the support materials, 10 wt-% Ni/C and 5/5 wt-% CuNi/C. The metals for the study were chosen due to their excellent ability to produce 2-methylfuran from furfural in the selected reaction conditions [I, II]. The prepared carbon catalysts were characterized with multiple characterization methods to investigate the differences in the physical state of the support as well as the effect of the support material on the chosen reaction.

3.3.1 Physical characteristics of carbon materials

Nitrogen adsorption is an analysis technique to obtain information of the carbon and catalyst surface area, pore volume and pore size distribution. Table 8 presents the surface area, total pore volume, micropore volume data as well as the average pore volume of the carbon

materials and the studied catalysts. All the compared carbon materials had a high specific surface area, above 750 m²·g⁻¹. The high surface area of carbon enables better dispersion of the active metals. Total pore volumes and micropore volumes of the materials indicated that the activated carbon materials, RX3 and RB4C, consisted mostly of micropores, as CMK3 and Darco contained both micro- and mesopores in their structure. The small size of micropores (< 2 nm) may restrain some reactions due to the active metal particle size often being larger than 2 nm, and large molecules may not fit the pores. Thus, mesopores (2 - 50 nm) may enable a broader range of reactions compared to the purely microporous materials. Figure 13 presents the adsorption – desorption isotherms of the carbon supports applied in Publication V. In Figure 13, the mesoporous structure of Darco and CMK-3 is well presented as a hysteresis loop is present in the isotherms. The hysteresis loop is formed due to capillary condensation in mesopores, causing differences in condensation and evaporation of the adsorbate. Hysteresis loop is visible in adsorption-desorption isotherms after relative pressures above 0.4 P/P₀.¹¹⁵ The pore size distribution of catalysts applied in Publication V are presented in Figure 14. The Figures 13 and 14 show that although the average pore size of all catalysts is approximately the same, the volume of the mesopores is larger with Darco and CMK-3 supported catalysts.

Table 8. Surface area, total pore volume, micropore volume and average pore size of carbon materials and catalysts. Reproduced from Publication V.

Support	Metal	Specific surface area (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore volume (cm ³ g ⁻¹)	Average pore size (nm)
RB4C	-	1012	0.40	0.36	4.1
	Ni	891	0.38	0.32	4.1
	CuNi	890	0.37	0.32	4.1
RX3	-	1594	0.74	0.57	4.1
	Ni	1425	0.62	0.50	4.1
	CuNi	1508	0.71	0.54	4.1
Darco	-	750	0.73	0.27	4.1
	Ni	715	0.67	0.25	4.1
	CuNi	660	0.60	0.23	4.1
CMK-3	-	1038	0.94	0.38	3.8
	Ni	928	0.90	0.35	3.4
	CuNi	877	0.90	0.30	3.4

Figure 13. Adsorption – desorption isotherms of the carbon supports applied in Publication V. Previously unpublished data.

Figure 14. Pore size distribution of the carbon supports, and catalysts applied in Publication V. Reproduced from Publication V.

3.3.2 Active surface groups of carbon materials

The carbon materials contain active oxygen-containing surface groups due to the steam activation and acid washing treatments. The oxygen-containing surface groups can be acidic or basic in nature, which affects the affinity of the metal deposition. The acidic surface

groups are known to decrease the hydrophobicity of the carbon materials, thus aiding aqueous phase metal precursors in the preparation phase to enter the surface.^{79,116} The oxygen-containing surface groups were analyzed using temperature-programmed desorption (TPD). In this analysis, the acidic oxygen-containing surface groups are decomposed from the surface as carbon dioxide and basic groups, as carbon monoxide, while the decomposition temperature reveals the surface group in question. Multiple studies have been performed concerning the decomposing surface groups and their decomposition temperatures.^{88,117–121} A summary of the studies is presented in Table 9. Anhydrides are present in both decomposition groups, a carbon monoxide and a carbon dioxide group is produced while breaking an anhydride.

Table 9. Decomposition temperatures of oxygen-containing surface groups. Reprinted from Publication V.

Decomposition as CO		Decomposition as CO ₂	
Surface group	Decomposition temperature / °C	Surface group	Decomposition temperature / °C
Anhydride	400 – 450 ¹²²	Carboxyl anhydride	580 ¹¹⁷
	500 ¹²³		500 – 570 ¹²¹
	375 – 625 ¹²⁴		375 – 625 ¹²⁴
	460 – 540 ¹²¹	Weak carboxylic acid	200 – 290 ¹²¹
Carbonyl ether	> 890 ¹²¹		350 – 400 ¹²²
	800 – 900 ¹²²	Strong carboxylic acid	200 – 250 ¹²²
Quinone	750 ¹²³		300 ¹²³
	830 ¹¹⁷		350 – 460 ¹²¹
	> 890 ¹²¹		150 – 450 ¹²⁴
Phenol	600 – 700 ¹²²	Lactone	350 – 400 ¹²²
	750 ¹²³		600 ¹²³
	680 ¹²⁴		680 ¹¹⁷
	500 – 725 ¹²⁴		600 – 800 ¹²⁴
Carbonyl	600 – 670 ¹²¹	Peroxide	580 – 660 ¹²¹
	750 ¹²³		550 – 600 ¹²²
	675 – 975 ¹²⁴		

The TPD analysis of the studied carbon materials revealed differences. All the support materials contained basic and acidic surface groups on the surface before and after metal modification (Publication V, Fig. 4). The surface groups in each analyzed material are gathered in Table 10. The results indicate the metal modification has no or minimal effect on the basic surface groups; however, the amount of acidic surface groups has significantly decreased after metal modification. Thus, the nickel deposition has occurred on the acidic surface groups. A more detailed analysis reveals carboxyl anhydride surface groups as the most desired deposition sites due to a significant decrease of these sites. It is also possible that carboxylic anhydrides have reacted with water during the metal modification to form carboxylic acids ($\text{RCOOCOR} + \text{H}_2\text{O} \rightarrow \text{RCOOH} + \text{RCOOH}$), which then have also been involved in the metal modification. Calibration of the TPD could not be conducted to observe the amount of various oxygen-containing surface groups, resulting in all observations being based on changes in ion currents.

Table 10. Oxygen-containing surface groups on plain carbon support materials and metal-modified catalysts.

Catalyst	RB4C	10 wt-% Ni/RB4C	Darco	10 wt-% Ni/Darco	RX3	10 wt-% Ni/RX3	CMK-3	10 wt-% Ni/CMK-3
CO decomposition (basic groups)	An-hydride	An-hydride	An-hydride	-	An-hydride	-	-	-
	Phenol	Phenol	Phenol	Phenol	Phenol	Phenol	Phenol	Phenol
	Carbonyl	Carbonyl	Carbonyl	Carbonyl	Carbonyl	Carbonyl	Carbonyl	Carbonyl
	-	Quinone	-	Quinone	-	Quinone	Quinone	Quinone
CO ₂ decomposition (acidic groups)	Carboxyl anhydride	-	Carboxyl anhydride	Carboxyl anhydride	Carboxyl anhydride	-	-	-
	Lactone	Lactone	Lactone	Lactone	-	-	-	-
	Carb. acid	Carb. acid	Carb. acid	Carb. acid	Carb. acid	Carb. acid	Carb. acid	Carb. acid

3.3.3 Crystallographic structure of carbon supported catalysts

The crystallographic structure of carbon-supported catalysts reveals information on the phase of active metals and support materials. The crystallographic structure of carbon catalysts was investigated with X-ray diffraction (XRD) in Publication V. The patterns of carbon materials revealed an amorphous support material character, which is common with activated carbon materials.

The nickel-containing catalyst analysis revealed diffraction peaks of a crystalline face-centered cubic NiO. Three out of a total of five NiO diffraction peaks were clearly visible with all the catalysts, indicating nickel is present in oxide form after the heat treatment procedure under nitrogen flow. The oxide phase is desired for further reduction into the active metallic nickel phase. More narrow diffraction peaks were observed with RB4C, Darco, and CMK-3, compared to RX3. The wider diffraction peaks of nickel on RX3 propose a smaller size of nickel particles and, hence, better dispersion of the deposited metal. The smaller particle size of active metals on the support material is a known phenomenon of acidic surface materials, such as RX3. With acidic carbon supports, the point of zero charge is on the acidic range during the metal deposition, leading to better adsorption of positively charged metal ions on the support material and, consequently, to a better dispersion of metals.^{77,125,126} With CMK-3, some of the surface nickel was observed to be present in the reduced Ni phase before the actual reduction process. This is assumed to originate from the reaction of carbon and nickel oxides under an inert atmosphere. The partial reduction of NiO is assumed to be beneficial as some studies have reported a combination of metallic and oxide phase of metals is good in furfural hydrotreatment reactions.³⁴ The reduction of NiO in heat treatment can occur through the following reactions:

With copper-nickel catalysts, NiO and Cu₂O phases were observed after nitrogen heat treatment on the activated carbon surfaces. Again, with RX3 the NiO peaks were the most

widely spread, indicating of smaller metal particle size and better dispersion of metals. With CMK-3, both metals were again also detected in a metallic phase.

3.3.4 Metal particle size on carbon supported catalysts

The X-ray diffraction results can be used to calculate the crystal size of metallic particles on the support material. The Scherrer equation (Equation 2) together with the width of the most intensive peak of Ni or Cu₂O at half height of the peak (FWHM) was used to calculate the metal particle sizes. The results of the nickel and copper particles are presented in Table 11. The nickel particles on monometallic nickel catalysts indicate a small particle size (4 - 6 nm) on activated carbon supports. The size of the nickel particles on mesoporous CMK-3 are larger, approximately 9.5 nm. The size of nickel particles is the same or slightly larger in the bimetallic catalyst options. The metal particles were observed separately, thus enabling the estimation of the particle size for NiO and Cu₂O. The size of copper crystals is significantly larger compared to nickel particles, with the size varying between 20 - 30 nm. Overlapping peaks of Ni and Cu on CMK-3 prevented the crystal size analysis of CuNi/CMK-3.

Table 11. Crystal size of nickel and copper particle on the carbon support surfaces. Reprinted from Publication V.

Catalyst	d_{NiO} (nm)	Catalyst	d_{NiO} (nm)	d_{Cu_2O} (nm)
Ni/RB4C	5.0	CuNi/RB4C	6.1	30.5
Ni/RX3	4.5	CuNi/RX3	4.5	21.1
Ni/Darco	4.7	CuNi/Darco	5.0	19.5
Ni/CMK-3	9.5*	CuNi/CMK-3	n.a.	n.a.

* Metallic Ni crystal size determined using peak at 2θ 51.7°.

High-resolution transmission electron microscopy (HR-TEM) is another way of investigating the particle size of active metals. This technique enables a nanometer scale visualization of the particles; however, it must be emphasized that the area of visualization is very small and multiple images are needed to confirm the homogeneity of the sample and consequently a reliable analysis. A HR-TEM analysis of the carbon materials revealed clearly visible nickel particles on all the carbon supports, except on RX3 [V]. With RX3, the nickel particles were less visible on the surface as the acidic surface led to a stronger interaction between the support material and metal particle and, in turn, to more penetrated metal particles.

Table 12 presents the minimum, maximum and average metal particle size and shape of metal particles. The shape of most particles with RB4C, Darco and CMK-3 are spherical, whereas with RX3, the shape of particles is rod like. In addition, an agglomeration of nickel particles was detected with RB4C. The comparison of metal particle sizes from the XRD analysis to the HR-TEM results reveals no great differences, a small deviation is assumed to originate from the Scherrer equation assumptions of spherical particles. HR-TEM images of the analyzed catalysts are presented in Figure 15.

Table 12. Nickel particle sizes on different carbon supports with HR-TEM analysis. Reproduced from Publication V.

Catalyst	Ni/ Darco	Ni/ RB4C		Ni/ RX3	Ni/ CMK-3
Min diameter (nm)	2.9	1.7	6.0	1.3 x 3.9	8.6
Max diameter (nm)	5.4	2.9	-	2.8 x 7.5	30.9
Average (nm)	4.3	2.7	8.5	2.0 x 5.2	14.5
Particle shape	Spherical	Spherical	Agglomerates	Rods	Spherical

Figure 15. TEM images of nickel containing catalysts a) Ni/Darco (dark field), b) Ni/RB4C (dark field), c) Ni/RX3 (dark field), d) plain CMK-3 (bright field), e-f) Ni/CMK-3 (bright field). Reproduced from Publication V.

3.3.5 Comparison of carbon support materials in the production of 2-methylfuran

The analysis of the prepared carbon support materials revealed some differences in the structure of the carbon, as well as in the morphology of the active metals. The catalysts were investigated in furfural hydrotreatment to obtain data on the beneficial characteristics of the carbon catalyst in the production of 2-methylfuran [V].

The tested catalysts in Publication V included 10 wt-% nickel and 5/5 wt-% CuNi on RB4C, Darco, RX3 and CMK-3. All the catalysts were studied in 120 min batch reactor experiments to have an appropriate comparison between the catalysts. Figure 16 shows furfural conversion after 120 min with all the catalysts. High furfural conversions were achieved with all the tested catalysts, except CMK-3. With nickel-containing catalysts, the highest conversion of furfural was achieved with Ni/RB4C in 120 minutes (Fig. 16). The reaction rate for furfural consumption with CMK-3 was significantly lower; furfural conversion of only 57% was achieved in the 120-minute experiment. Thus, twice longer, 240-minute experiments were performed for the CMK-3 catalysts, resulting in 99% furfural conversion. With bimetallic CuNi-catalysts, the highest furfural conversion was achieved with CuNi/RX3 and CuNi/CMK-3 (96.6%). However, the furfural conversion levels of other carbon support options were reasonably similar; all catalysts except CMK-3 achieved over 90% furfural conversion in 120 minutes. In the case of CMK-3, >90% conversion was achieved in 240

minutes. In conclusion, all the tested carbon supported catalysts were highly active in furfural hydrotreatment.

Figure 16. Furfural conversion of carbon supported nickel- and copper-nickel catalysts. Reproduced from Publication V.

3.3.5.1. Product yield with nickel-modified carbon supported catalysts

The selectivity and yield of the desired products are even more important than the furfural conversion. The product distribution was investigated with nickel-containing carbon-supported catalysts in Publication V. The yields of the most common hydrotreatment products are presented in Figure 17. The results indicated a surprisingly high yield of 2-methylfuran with most of the tested catalysts. The highest yield achieved with 10 wt-% Ni/Darco (59.7%) is, to the authors knowledge, one of the highest reported in the liquid phase batch reactor studies of furfural hydrotreatment towards 2-methylfuran. The bench-mark studies for the production of furfural are the study by Yan & Chen ³⁵, in which a 51% yield of MF was achieved and study the by Panagiotopoulou et al.³⁴ in which a 50% yield of MF was achieved. In some studies, higher yields of 2-methylfuran have been achieved, for example, with CuNi/ γ -Al₂O₃, CuCo/ γ -Al₂O₃ and Ru/NiFe₂O₄. However, in these studies the reaction times have been significantly longer compared to our study.^{97,112,127} The higher selectivity towards MF compared to the results obtained in Publications I and II could at least be partly explained by the operation in the slurry phase, which decreases the external mass transfer limitations. In addition, the size of the catalyst particles in slurry experiments was smaller compared to the catalyst basket tests (see Table 5), which decreases the internal mass transfer limitations.

The analysis of other known hydrotreatment products revealed differences between the catalysts. Tetrahydrofurfuryl alcohol (THFA), a competing product of 2-methylfuran, was observed with all catalysts, but in larger quantities with RB4C and CMK-3 (240 min experiment). This is assumed to result from nickel particle size, as the average particle size is

larger with these catalysts compared to RX3 and Darco. Another observation concerns the formation of furanmethanol acetate, a condensation product of furfural or its hydrotreated products. The amount of FMA is significantly higher with CMK-3 at 120 minutes. This indicates that the more mesoporous CMK-3 has enabled the formation of a larger condensation product FMA. The decrease of FMA with CMK-3 at 240 minutes can be explained with further reactions of FMA. However, the decomposition or condensation products are not known and could not be followed from the GC-MS analysis. The decarbonylation of furfural producing furan and carbon monoxide was observed with all the nickel catalysts; the furan yield varied from 2 - 4% between the catalysts. All in all, the side reactions of furfural hydrotreatment appear to be metal particle size and pore size-sensitive.

Figure 17. Product distribution with monometallic nickel catalysts. Reprinted from Publication V.

3.3.5.2 Product yield with copper-nickel-modified carbon-supported catalysts

The metals and metal combinations might also have a significant effect on product distribution. The effect of different metals was investigated with a bimetallic combination of copper and nickel on the previously mentioned carbon supports in Publication V. CuNi metal loading 5/5 wt-% was used to have the same total metal content as in the monometallic nickel catalysts. The product distribution with the CuNi/C catalysts is presented in Figure 18. Due to observations with Ni/CMK-3, only a 240 min experiment was performed for the CuNi/CMK-3. The results indicated the main product with all the catalysts was 2-methylfuran. The highest yield of MF was achieved with CuNi/RB4C (60.2%), although the results with CuNi/Darco and CuNi/CMK-3 did not fall much behind with 59.3% and 58.3% MF yields, respectively. The only less effective catalysts in terms of MF production was CuNi/RX3. If the results are compared to the only nickel-containing catalysts, the bimetallic combination of copper and nickel was observed to increase the yield of MF with RB4C and CMK-3. No effect on product yield was observed with CuNi/Darco, and a decreased yield of MF was observed with CuNi/RX3. The lower amount of MF with RX3 is easily explained as a high amount of further hydrogenation product 2-MTHF was detected with this catalyst.

Thus, CuNi/RX3 was more active in furfural hydrotreatment producing further hydrogenated products in this 120 min experiment with a shorter reaction time being needed to obtain the maximum amount of desired MF. Characteristics explaining the high activity of CuNi/RX3 are the small particle size of active metals well distributed on the catalyst surface (confirmed with HR-TEM) and the high surface area of the support material. With CuNi/RX3, the yield of quantified and known side products was 20%, in comparison with all other catalysts, the amount was smaller; under 8%. Some production of FMA was observed with Darco and CMK-3, which can be explained by the mesoporosity of these materials.

Figure 18. Product distribution of bimetallic copper-nickel catalysts. Reprinted from Publication V.

In addition to the known furfural hydrotreatment products, there was a significant quantity of unknown products with all the catalysts. The yield of unknown components depends on the catalyst but varies between 20 - 40%. The products are most probably condensation and polymerization products of the unstable furfural and its hydrotreated products. This has also been acknowledged in previous studies, where the acidic supports were observed to catalyze other reactions, such as dehydration and polymerization.^{3,128,129} In Publication V, the acidity of the catalysts was observed to have a connection to the amount of side products. The acidity of the supports and catalysts was tested with Boehm titration. The acidity of the catalysts supports from the least acidic to the most acidic was RB4C < Darco < RX3 < CMK-3 (Publ. V, Table 2). The acidity of CMK-3 support can be explained by the acid remaining from the preparation phase. With increasing acidity, the amount of side products increased.

In conclusion, the carbon materials tested were active in the furfural hydrotreatment, and compared to earlier studies, a high selectivity towards desired 2-methylfuran was achieved with many metal and support material combinations. The yields of the desired 2-methylfuran were, to the authors knowledge, among the highest reported in the liquid phase batch

reactor experiments with a short reaction time. Side reactions towards THFA and FMA were observed to be structure-sensitive in terms of metal particle and support pore size. The acidity of the carbon materials was observed to increase the amount of unknown side products and increase the reaction rate to the desired product, 2-methylfuran. Overall, the carbon materials tested in furfural hydrotreatment towards 2-methylfuran had many advantageous properties and good results were obtained with the prepared catalysts. Thus, the use of these carbon-supported materials is possible in the production of 2-methylfuran from furfural through hydrotreatment.

3.4 Acetone formation in furfural hydrotreatment with carbon supported copper, nickel and iron catalysts

Significant amounts of formed acetone were observed in Publications I, II and V, due to 2-propanol being used as a solvent in furfural hydrotreatment reactions. The formation mechanism of acetone in furfural hydrotreatment process conditions has remained unstudied in the available literature; therefore, this was investigated in Publication III. In this study, the formation of acetone was investigated using carbon-supported nickel, copper and iron catalysts, and furfural or furfuryl alcohol in 2-propanol as a reaction mixture.

Figure 19 presents the acetone concentration as a function of contact time with various catalysts, and furfural conversion as a contact time in Figure 20. The results revealed that acetone is formed in significant amounts with all the tested metal-containing catalysts. The initial formation rate of acetone is very high with all the catalysts, and after most of the furfural is consumed, the formation rate decelerates. The highest acetone formation rate was observed with CuFe/C, and the lowest with Ni/C and CuNi/C. With a nickel catalyst, a decreasing trend in acetone concentration was observed at the end of the experiment, which could be caused by further reactions of acetone. For example, acetone can react through condensation and polymerization reactions to yield products, such as furanmethanol acetate (FMA) and methyl isobutyl ketone (MIBK). Neither of these components were observed with the 5 wt-% Ni/C; hence, a reversible reaction of acetone formation cannot be excluded from possible options. An increasing acetone concentration trend with both iron-containing catalysts was observed during the experiment. As acetone formation ceased after a high conversion of furfural (>90%) with other catalysts, with iron-containing catalysts, there must be at least two formation mechanisms for the production of acetone (Figures 19 and 20). With a copper catalyst, the acetone formation already ceased at a furfural conversion of 70%, also indicating a time dependency of acetone formation in the furfural hydrotreatment process conditions.

Figure 19. Acetone concentration as a function of contact time in furfural hydrotreatment experiments with varying catalysts. T = 230 °C, p = 40 bar, t = 300 min. Reprinted from Publication III.

Figure 20. Furfural conversion as a function of contact time in acetone formation experiments. Previously unpublished data.

To gain more information on the acetone formation mechanisms, the maximum amount of produced furfuryl alcohol and acetone were compared with all the catalysts. This comparison was performed, because equivalent amounts of furfuryl alcohol and acetone are formed in furfural transfer hydrogenation. The results indicated that with most of the catalysts, the furfuryl alcohol amount was higher compared to the acetone amount. However, with iron-containing catalysts, the acetone concentration exceeded the furfuryl alcohol concentration. Furthermore, iron-containing catalysts performed better in acetone production when the formation was observed as a function of furfural conversion and furfuryl alcohol

concentration, which implies 2-propanol dehydrogenation with iron catalysts. Iron catalysts have been studied as good dehydrogenation catalysts in earlier studies,^{130,131} thus supporting this finding.

3.4.1 Effect of metal loading on acetone formation

To obtain more data of the acetone formation, the same metal combination catalysts tested in the previous Section 3.4. were tested with different metal loadings in Publication III. Figure 21 presents the results of maximum acetone concentration during the 300 min experiments. These results revealed an increasing acetone concentration as a function of increasing nickel content of the catalysts. With copper-containing catalysts, an increasing copper content does not significantly affect acetone formation. Overall, the catalysts containing iron produce more acetone in the experiments. In terms of preventing acetone formation, replacing part of the metal with copper is recommended for nickel and iron catalysts.

Figure 21. Maximum acetone concentration in furfural hydrotreatment experiments with varying metal loadings. T = 230 °C, p = 40 bar, t = 300 min. Reproduced from Publication III.

3.4.2 Effect of temperature on acetone formation

The effect of temperature on acetone formation was studied at 200 and 230 °C with Cu/C, Ni/C, CuNi/C and CuFe/C catalysts in Publication III. The results indicated that higher reaction temperatures promote the production of acetone. This is presumable as the furfural conversion is also accelerated at higher reaction temperatures.

3.4.3 Acetone formation mechanism in furfural hydrotreatment conditions

The formation mechanism for acetone was further investigated applying furfural + 2-propanol, furfuryl alcohol + 2-propanol and 2-propanol as reactants [III]. Using furfuryl alcohol as a reactant excludes the reactions caused by furfural and applying only 2-propanol provides information on the pure solvent reactions. Possible acetone formation mechanisms through furfural hydrogenation and through reaction of 2-propanol are presented in Figures 22 and 23. The experiment with plain solvent, 2-propanol, revealed a higher acetone

formation compared to the reaction with furfural in 2-propanol. With furfural + 2-propanol mixture, an acetone concentration of $0.7 \text{ mmol}\cdot\text{g}^{-1}$ was observed, as with pure 2-propanol, the acetone concentration was $1 \text{ mmol}\cdot\text{g}^{-1}$ after 300 minutes (see Publication III, Fig. 7). A constantly increasing trend in acetone formation was observed with pure 2-propanol, whereas with furfural, the acetone formation occurred relatively rapidly in the beginning of the experiment. Both acetone formation reactions use active metal sites for reaction, and as hydrogenation of furfural is clearly dominant in the beginning of the experiment, this indicates that furfural has a lower adsorption energy and, thus, a higher affinity on the catalyst active sites compared to 2-propanol. In the case of the 2-propanol experiment, no competition of the active sites is present, and the acetone concentration increases until a thermodynamic equilibrium is achieved. Acetone dehydration was confirmed to be thermodynamically equilibrium limited with HSC thermodynamic calculations. Publication III, Figure 7 illustrates that 2-propanol is reaching an equilibrium.

Figure 22. Transfer hydrogenation of furfural to furfuryl alcohol with isopropanol as hydrogen donor.

Figure 23. Isopropanol dehydrogenation to acetone and hydrogen.

An increasing acetone formation trend was observed with the furfuryl alcohol + 2-propanol mixture. However, the amount of produced acetone was much lower compared to the furfural + 2-propanol and 2-propanol experiments. This indicates that the reaction rate of furfuryl alcohol transfer hydrogenation is lower compared to furfural transfer hydrogenation. Furfuryl alcohol has been reported to adsorb more strongly on the active metals compared to furfural and 2-propanol. The adsorption energy of furfuryl alcohol, furfural and 2-propanol on various metals has been reported in references ^{25,114,132}. The adsorption energy of furfural on nickel and nickel-iron surfaces have been reported -15.6 and $-20.9 \text{ kcal}\cdot\text{mol}^{-1}$, as with furfuryl alcohol, the adsorption energy on the same surfaces has been -27.6 and $-27.1 \text{ kcal}\cdot\text{mol}^{-1}$, respectively.²⁵ 2-propanol adsorption energy on the nickel surface is reported between -4 and $-8 \text{ kcal}\cdot\text{mol}^{-1}$.¹³² Furfural adsorption energy on copper surface is reported as being much lower compared to nickel or iron, the adsorption energy of furfural on copper is reported to be $-4.8 \text{ kcal}\cdot\text{mol}^{-1}$.¹¹⁴

Additional tests were performed with furfural + 2-propanol mixture, with and without additional hydrogen in the process. The section marked with “Mechanism 1” in Figure 24

presents the part in which furfural hydrogenation occurs; and the part marked with “Mechanism 2”, the part in which total furfural conversion is achieved and 2-propanol dehydrogenation is the only source of acetone formation. With Ni/C catalyst furfural hydrogenation is the only source of acetone (Fig. 24). The results indicated an efficient production of furfuryl alcohol without additional hydrogen, but the amount of further hydrogenation products decelerated. This indicates furfuryl alcohol is produced efficiently though transfer hydrogenation, but efficient hydrogenation of this intermediate requires additional hydrogen.

Nevertheless, as the transfer hydrogenation of furfuryl alcohol is possible yielding further hydrogenation products, an experiment was performed with furfuryl alcohol + 2-propanol without any additional hydrogen. The experiment revealed production of 2-methylfuran with transfer hydrogenation, while other hydrogenation products remained low (total yield of THFA and MTHF < 2%). The formed acetone in the FA experiment with additional hydrogen remained lower than in the experiment without hydrogen. This is an adverse finding to the furfural + 2-propanol experiment. The reaction network seems to affect the reaction routes with more kinetic experiments being required to determine the formation mechanism of acetone outside the furfural experiments.

Figure 24. Acetone and furfuryl alcohol (FA) concentrations as a function of reaction time in furfural hydrogenation experiments with 10 wt-% Ni/C, with and without additional hydrogen. $T = 230\text{ }^{\circ}\text{C}$, $p = 40\text{ bar}$, $t = 300\text{ min}$. In Mechanism 1 both hydrogenation/ dehydrogenation reactions are possible, Mechanism 2 for only iso-propanol dehydrogenation. Reproduced from Publication III.

3.5 Hydrogen solubility in furfural hydrotreatment

A knowledge of hydrogen solubility in the reaction media is important to discover the kinetics and finally to up-scale the reaction processes towards a full-scale industrial production of the chemicals and fuels. In this doctoral dissertation, the conversion of furfural into valuable products through hydrotreatment was investigated, thus hydrogen solubility in furfural was investigated as well as in the most usual solvent in the process, 2-propanol.

3.5.1 Hydrogen solubility in furfural and 2-propanol

The hydrogen solubility in 2-propanol has been earlier studied by Lühning et al.¹³³ and Krüger et al.¹³⁴. These hydrogen solubility measurements were performed at low temperatures, 20 and 25 °C, respectively. In the study by Lühning et al.¹³³, the solubility was investigated by evaluating the value for Henry's constant from a measured pressure drop. The measured Henry's constant for 2-propanol was 30910 Pa·m³·mol⁻¹. In the study by Krüger et al.¹³⁴, Nuclear Magnetic Resonance (NMR) was applied to measure hydrogen concentrations in liquids at a pressure of 1 bar. The hydrogen solubility in 2-propanol was measured 3.07±0.14 mmol·dm⁻³. The solubility measurement temperatures and pressures in these previous studies are considered to be very low, as many industrial hydrotreatment processes applying higher temperatures and pressures and the solubility of gas being known to increase as a function of pressure. With hydrogen, the increase of temperature increases solubility but with other gases the trend is opposite.^{135–138}

Hydrogen solubility in furfural has remained unstudied in the past. This is most probably caused by the instability of furfural at higher temperatures and due to the fast reactions with hydrogen. Hydrogen solubility in furfural requires new measurement methods for obtaining reliable solubility data. In furfural hydrotreatment studies, the reaction temperatures vary mostly between 160 and 250 °C. In this dissertation, the hydrogen solubility in furfural and 2-propanol was measured with a continuous flow apparatus at 50, 125 and 200 °C and in the pressure range of 3 - 125 bar. Higher temperatures were not used to avoid reactions of furfural. As another way to avoid the reactions of hydrogen and liquid media, the hydrogen solubility in furfural and 2-propanol was measured with a continuous flow apparatus. The continuous flow apparatus has been built by Aalto University Chemical Engineering research group to obtain hydrogen solubility data with a short residence time, preventing the reactions of the unstable and reactive chemicals, such as furfural.¹³⁹ In this equipment, an increasing amount of hydrogen gas flow was mixed with furfural or 2-propanol stream in each selected data measurement point. The hydrogen solubility was visually observed through a glass window. The hydrogen solubility limit was achieved, when bubbles indicating of two phases (gas + liquid) were observed in the system. An example of a gas-liquid phase region and liquid region is presented in Figure 25.

Figure 25. a) Gas-liquid region with hydrogen bubble, b) liquid phase in hydrogen solubility experiment. Reprinted from Publication IV.

3.5.2 Hydrogen solubility calculations

The hydrogen solubility at bubble point was calculated as an average of the calculated hydrogen solubility in the last observed liquid phase region point and the first gas-liquid phase region point. The calculation method for hydrogen solubility (molar fraction of hydrogen) in furfural or 2-propanol is presented in Equation (13). In Equation 13, x_{H_2} is the mole fraction of hydrogen in the total flow, $H_{2,FLOW}$ is the hydrogen flow measured with a mass flow controller ($\text{cm}^3 \cdot \text{min}^{-1}$), V_m is the ideal gas molar volume ($22\,414 \text{ cm}^3 \cdot \text{mol}^{-1}$), L_{FLOW} is the volumetric liquid flow ($\text{cm}^3 \cdot \text{min}^{-1}$), and ρ_L is the liquid density ($\text{mol} \cdot \text{cm}^{-3}$). Another important factor in hydrogen solubility is the uncertainty of the measurements. The uncertainty of the measurements was calculated with Equation (14). In Equation 14, $u(x_{H_2})$ is the uncertainty of the hydrogen mole fraction, $\Delta H_{2,FLOW}$ is the uncertainty of the hydrogen flow rate, ΔL_{FLOW} is the uncertainty of the liquid flow rate, and $\Delta \rho_L$ is the uncertainty of the liquid density.

$$x_{H_2} = \frac{\frac{H_{2,FLOW}}{V_m}}{L_{FLOW}\rho_L + \frac{H_{2,FLOW}}{V_m}} \quad (13)$$

$$u(x_{H_2}) = \left| \frac{\frac{L_{FLOW}\rho_L}{V_m}}{\left(\frac{H_{2,FLOW}}{V_m} + L_{FLOW}\rho_L\right)^2} \right| \Delta H_{2,FLOW} + \left| \frac{-\frac{H_{2,FLOW}\rho_L}{V_m}}{\left(\frac{H_{2,FLOW}}{V_m} + L_{FLOW}\rho_L\right)^2} \right| \Delta L_{FLOW} \\ + \left| \frac{\frac{H_{2,FLOW}L_{FLOW}}{V_m}}{\left(\frac{H_{2,FLOW}}{V_m} + L_{FLOW}\rho_L\right)^2} \right| \Delta \rho_L + \left| \frac{x_{H_2,L} + x_{H_2,GL}}{2} \right| \quad (14)$$

The results of the hydrogen solubility in furfural and 2-propanol are presented in Table 13. The results obtained were logical and the uncertainty of the measurements was small. Hydrogen solubility in 2-propanol was observed to be higher compared to the hydrogen solubility in furfural. At 50 °C the difference was observed to be the largest, and hydrogen solubility to 2-propanol was 2.5 times higher compared to the hydrogen solubility to furfural. Higher temperatures and pressures lead to higher hydrogen solubility with both liquids as assumed.

Table 13. Hydrogen solubility data for 2-propanol and furfural (x_{H_2}) at selected temperature (T) and pressure (P) data points with calculated uncertainty of mole fraction of hydrogen in liquid ($u(x_{H_2})$). Reproduced from Publication IV.

2-Propanol				Furfural			
$T / ^\circ\text{C}$	P / bar	x_{H_2}	$u(x_{H_2})$	$T / ^\circ\text{C}$	P / bar	x_{H_2}	$u(x_{H_2})$
50.3	124.7	0.0347	0.0014	49.9	124.5	0.0138	0.0009
50.3 *	124.5	0.0350	0.0013	126.1	124.4	0.0290	0.0012
50.3	99.6	0.0288	0.0012	126.1	99.5	0.0229	0.0011
50.3	69.7	0.0199	0.0010	126.1	69.7	0.0154	0.0010
50.3	53.0	0.0139	0.0009	203.0	124.5	0.0381	0.0014
50.4 *	53.0	0.0139	0.0010	203.0	99.5	0.0305	0.0013
126.0	124.7	0.0501	0.0022	203.2	69.6	0.0229	0.0011
126.0	99.6	0.0395	0.0022				
126.0	69.7	0.0305	0.0014				
202.8	124.4	0.0637	0.0021				
202.9	99.5	0.0379	0.0020				
202.9	69.7	0.0365	0.0020				

*Repeated measurements with changed fluid and gas flow rates.

To the author`s knowledge, the measured hydrogen solubilities in furfural in this dissertation were the first ever measured, but a comparison is possible of hydrogen solubilities to 2-propanol with previously published data. Krüger et al.¹³⁴ measured hydrogen solubility to 2-propanol at 20 °C and Lühning et al.¹³³ at 25 °C, both in atmospheric pressures. However, the measurement conditions of these studies are very different to the study performed in Publication IV, and a direct comparison of these studies cannot be performed. Nevertheless, applying the Henry`s constant from study of Lühning et al.<sup>133</sup> and assuming that hydrogen solubility follows Henry`s law in study of Krüger et al.¹³⁴, the results could be converted and calculated at two isobaric conditions (124.7 and 69.7 bar). The comparison of these references and the hydrogen solubility to 2-propanol in Publication IV are presented in Figure 26. The results of the references are well in line with the results obtained in Publication IV. Thus, the measurement results can be considered to be reliable.

Figure 26. Comparison of hydrogen solubility in 2-propanol at isobaric conditions. Comparison at 124.7 bar: ref ¹³³ (●), ref ¹³⁴ (◆), this work (▲). Comparison at 69.7 bar: ref ¹³³ (○), ref ¹³⁴ (◇), this work (△). Reproduced from Publication IV.

3.5.3 Modeling the hydrogen solubility in furfural and 2-propanol

To obtain more important information of the hydrogen solubility in furfural and 2-propanol, the solubility data was described with three different equations of state models. The models tested were Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT). These models are developed and intended for different purposes. The SRK and PR models are widely used to describe the behavior of nonpolar or mildly polar mixtures. These models have been successfully used to describe hydrogen solubility in polar 2-propanol.^{99,100,136,140,141} The same models suitable for alcohols may not be optimal for intermediately polar and oxygen-containing furfural; therefore PC-SAFT was chosen for the study. This model has been effectively used in earlier studies of oxygenated and polar systems.¹⁴²

Aspen Plus software was applied to model the obtained hydrogen solubility data. All data was modeled with all the chosen models with an interaction parameter (k_{ij}) of zero and a regressed interaction parameter value. With the interaction parameter of zero, the model does not include a fitting of the interaction parameter with the interaction being based on pure compound properties. The results with the interaction parameter zero indicate that the most suitable model was SRK to describe the hydrogen solubility in furfural and 2-propanol. However, the calculated average absolute deviation (AAD) and relative average deviation (RAD) were observed to be relatively high even for the highest accuracy SRK; the RAD was 11.5% for the H₂ + furfural mixture and 12.3% for the H₂ + 2-propanol mixture. The calculation method for AAD and RAD are presented in Equations (15) and (16), where N presents the number of observations and P the pressure in bar.

$$AAD = \frac{1}{N} \sum_{i=1}^N |P_{measured} - P_{calculated}| \quad (15)$$

$$RAD = \frac{100}{N} \sum_{i=1}^N \left| \frac{P_{measured} - P_{calculated}}{P_{measured}} \right| \quad (16)$$

With a regressed binary interaction parameter k_{ij} , the most accurate model describing the hydrogen solubility data was PC-SAFT. The binary interaction parameters were observed to be temperature-dependent in both cases (furfural and 2-propanol) with the regression method. The data description with PC-SAFT was obtained with RAD 6.3% for the H_2 + furfural mixture and RAD 5.3% for the H_2 + 2-propanol mixture. The hydrogen solubility data and the prediction of PC-SAFT is presented in Figure 27 for 2-propanol and Figure 28 for furfural. The PC-SAFT model was observed to predict hydrogen solubility data well.

Figure 27. Hydrogen solubility in 2-propanol: at 50.3 °C (◆), 126.0 °C (◇), and 202.9 °C (■). The vapor pressures presented at $x_{H_2} = 0$ (pure liquids) are obtained from DIPPR correlation.¹⁴³ Prediction with PC-SAFT, at 50.3 °C (—), at 126.0 °C (...), and at 202.9 °C (- · -). Reproduced from Publication IV.

Figure 28. Hydrogen solubility in furfural: at 50.0 °C (♦), 126.1 °C (◇), and 203.0 °C (■). The vapor pressures presented at $x_{H_2} = 0$ (pure liquids) are obtained from DIPPR correlation.¹⁴³ Prediction with PC-SAFT, at 50.0 °C (—), at 126.1 °C (...), and at 203.0 °C (- · -). Reproduced from Publication IV.

Due to the instability of furfural, the reactions of furfural with hydrogen are possible during the hydrogen solubility experiments in furfural. This was prevented as much as possible by employing a short residence time (< 12 min) of the mixtures before visual observation. Confirmation of negligible furfural conversion in the measurement cell was followed from a product sample analysis with gas chromatography. The GC results revealed no reactions of furfural at temperatures 50 and 125 °C; however, at 200 °C, traces of hydrotreatment products were found (4.7% furfural conversion). This amount was assumed to have only a minor effect on the hydrogen solubility in furfural.

4. Summary and Conclusion

This dissertation investigates furfural hydrotreatment to 2-methylfuran applying earth abundant metals on carbon-supported catalysts. The dissertation consists of five publications, which all concentrate on various important aspects in furfural hydrotreatment. The aim of this dissertation was to investigate the production of valuable 2-methylfuran from furfural through hydrotreatment. First, noble metal free catalyst options were developed for the currently used toxic CuCr catalyst and the process conditions were optimized for the desired reaction [I, II, V]. Secondly, environmentally benign carbon materials were investigated as a support material to produce 2-methylfuran from furfural through hydrotreatment [V]. Thirdly, the mechanism and magnitude of the side reaction caused by the solvent was investigated [III]. Finally, the most important kinetic barrier of hydrotreatment reactions in liquid phase, hydrogen solubility in the reaction media, was investigated [IV].

The purpose was to find noble metal free, non-toxic and cheap catalysts for production of 2-methylfuran from furfural. The metal options for the hydrotreatment reaction were selected through literature study and were copper, nickel and iron. The optimization of process conditions revealed high temperature and high hydrogen pressure (> 40 bar) favour the production of 2-methylfuran. The catalysts were investigated as monometallic and bimetallic options to find the optimal combination for 2-methylfuran production. The best combination was found to be 5/5 wt-% CuNi on activated carbon support in a slurry mode (60% yield of 2-methylfuran). The high yield results were obtained in short reaction time (60 – 120 minutes) compared to the catalyst options in the literature. A good example of a catalyst option achieving high yield of 2-methylfuran, but having a long reaction time is Ru/Co₃O₄ catalyst of Wang et al.³⁸ This catalyst achieved 93% MF yield, but the time needed for the reaction was 24 hours. Other studies considered as benchmark studies for this dissertation, such as Panagiotopoulou et al.³⁴ (50% MF yield) and Yan et al.³⁵ (51% MF yield), had also longer reaction times, 16 and 14 hours, respectively. Overall, the results obtained with the prepared catalysts were considered desirable especially considering the reaction time.

The carbon materials investigated in this thesis were activated carbon materials and mesoporous carbon material CMK-3. Carbon materials offer many good properties for support material, such as high surface area (even up to $1500 \text{ m}^2\cdot\text{g}^{-1}$) and cheaper price compared to oxides.⁸³ All the carbon supports tested were observed to have high surface area and porous structure. The pore size distribution and surface groups were observed to alternate due to activation and preparation method. The production of 2-methylfuran was observed to benefit from high surface area enabling good metal dispersion, and surface acidity. All the tested carbon materials were observed potential for furfural hydrotreatment support materials to replace mostly used oxide materials.

Part of the dissertation was to obtain more information of the unstudied side reaction, acetone formation in furfural hydrotreatment, when 2-propanol is applied as a solvent. The acetone formation and the mechanism has not been studied in detail before. There are two possibilities for acetone formation in furfural hydrotreatment reactions, transfer hydrogenation of furfural with 2-propanol or 2-propanol dehydrogenation. Acetone formation was observed metal dependent, both mechanisms were detected with iron, with copper and nickel transfer hydrogenation was the origin of acetone. With all catalysts, acetone formation rate was high before total conversion of furfural; however, with copper the formation rate was observed lower. To decrease acetone formation, copper was observed beneficial. Bimetallic combinations of copper and nickel have high reaction rate for 2-methylfuran, but decreased reaction rate towards acetone. In the industry, the produced acetone can be separated and sold.

Hydrogen solubility in furfural and solvent 2-propanol was investigated with a continuous flow apparatus at 50 – 200 °C and pressures up to 127 bars. In this apparatus, the reactions of unstable furfural were avoided with short residence time. The information of the solubility is important for further process optimization and for the scale up of the process. The solubility data was predicted with PC-SAFT with good accuracy with regressed interaction values. The hydrogen solubility in furfural has not been studied before and this dissertation gives new information for the research field of furfural hydrotreatment.

Overall, the goals of this dissertation were achieved and new knowledge of the catalysts and supports, side reactions and features of the reaction media were offered. However, more studies are required to transfer the new knowledge to industrial scale process. Future recommendations for following researchers include further investigation of the catalyst deactivation rate of the carbon supported catalysts in liquid phase hydrogenation of furfural. This is an important aspect in choosing the catalyst for a process, but this dissertation focused on finding optimal metal combination for the process. The prepared carbon supported catalysts would require more deep catalyst characterization to make more certain conclusions about structure-sensitivity of the catalysts. In this dissertation, chemisorption analysis was missing and thus, metal dispersions were not obtained for the basis of the conclusions. Kinetic studies would be necessary to understand all aspects of the reaction mixture, and to scale up the process towards an industrial scale. In this dissertation, the kinetic studies remained in hydrogen solubility measurements. This is a very wide topic and a separate dissertation would be required for this. Solvents are often used in lab scale experiments to understand the basic phenomena and in process scale the use of solvents is much less or non-existent. In case of solvent use in industrial scale, process design requires a method for solvent recovery. The use of carbon catalysts in industrial scale process needs further investigation as regeneration of carbon catalysts through oxidation is not as easy as with oxide support materials. Instead of regeneration, recovery of the valuable metals from catalysts is important for example by burning the carbon material away. In addition, the profitability of the process should be investigated.

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