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#### 1 FURFURAL HYDROTREATMENT APPLYING ISOPROPANOL AS A SOLVENT - THE CASE

#### **OF ACETONE FORMATION** 2

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#### 10 ABSTRACT

11 In this study, acetone formation was investigated as a side reaction in furfural hydrotreatment applying isopropanol 12 as a solvent. Acetone formation was observed to depend strongly on the metal and metal loading of catalysts as copper, 13 nickel, and iron catalysts supported on activated carbon were studied. Furfural has an important role in acetone 14 formation: the initial formation rate for acetone was high as long as furfural reacted further. After furfural was 15 consumed the acetone formation decelerated except with the catalysts including iron. Two formation mechanisms 16 were derived: first mechanism includes direct and transfer hydrogenation of furfural and isopropanol dehydrogenation, 17 as mechanism two consists only of isopropanol dehydrogenation. Another novel discovery of the study was the 18 confirmation of the formation mechanism for 2-methylfuran through transfer hydrogenation of furfuryl alcohol in the 19 experiments. In conclusion, the acetone formation as a side product was observed significant and could not be totally 20 prevented. 21 22 23 24

25 Keywords: Acetone, catalyst, furfural, hydrotreatment, isopropanol

# 1. Introduction

27 Replacing fossil based chemicals and fuels with bio-based ones is increasingly important as environmental concerns and need for energy, chemicals, and fuels are continuously increasing.<sup>1</sup> Platform chemicals 28 29 produced from renewable feedstocks are promising chemicals for the production of desired chemicals and 30 fuels. One excellent platform chemical produced from lignocellulosic biomass is furfural, which is produced from hemicellulosic pentose sugars with dehydration.<sup>2-4</sup> Furfural itself is a quite unstable chemical 31 32 and further refining is needed to obtain stable components. An excellent method for furfural refining is hydrotreatment. With furfural hydrotreatment many valuable chemicals such as furfuryl alcohol (FA), 33 34 tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), and 2-methyltetrahydrofuran (MTHF) can be 35 produced.<sup>5</sup> These chemicals have many applications varying from solvents to pharmaceutical components. 36 2-Methylfuran with its excellent properties has recently attracted attention with potential use as a biofuel 37 component. This chemical has a high research octane number (131), low water solubility (7 g dm<sup>-3</sup>), and high energy density (31.2 MJ kg<sup>-1</sup>) that could compete with the current octane boosting components in 38 39 gasoline.<sup>6</sup> The furfural hydrotreatment scheme with the most common products is presented in Figure 1.

40 Figure 1.

Production of MF with furfural hydrotreatment has proved to be challenging as many by-products can be produced at the same conditions. The most common product in furfural hydrotreatment is furfuryl alcohol, which is produced at mild temperatures and low hydrogen pressures.<sup>7</sup> Production of MF is carried out at higher temperatures compared to furfuryl alcohol production.

Solvents used in furfural hydrotreatment studies include alcohols, alcohol-water mixtures, and water.<sup>8-11</sup> Applying pure water generates a problem as furfural has a limited water solubility. Thus, alcohols are mostly used in these studies as the solubility of furfural in alcohols is good. The most used solvent in furfural hydrotreatment studies is isopropanol.<sup>9</sup> However, this solvent can be dehydrogenated in the reaction conditions to acetone and hydrogen.<sup>12</sup> The isopropanol dehydrogenation scheme is presented in Figure 2. 50 The other alcohols have a similar kind of behavior. As secondary alcohols are used as solvents they are 51 dehydrogenated to ketones and hydrogen, whereas primary alcohols produce aldehydes and hydrogen. 52 Thus, the use of n-propanol, ethanol, or i-butanol as a solvent will result in propanal, acetaldehyde, or 53 butanone, respectively.<sup>6</sup>

54 In addition to dehydrogenation, the solvent can react also with furfural. The solvent can act as a hydrogen 55 donor with furfural and produce furfuryl alcohol and acetone as products. The transfer hydrogenation 56 reaction of furfural and isopropanol is presented in Figure 3.

57 Figure 2 and 3.

The formation of acetone during the furfural hydrotreatment experiments can be significant. However, as the formation is not straightforward and there are two possible reaction routes for the formation, the mechanism of acetone formation during furfural hydrotreatment is still unclear. To minimize the loss of reactants in side reactions and to decrease the need of the downstream purification of the product in furfural hydrotreatment reactions it is important to know the mechanism for acetone formation.

In our study, the formation of acetone in furfural hydrotreatment reactions in the presence of isopropanol
was studied. Also, the formation mechanism of acetone from isopropanol through transfer hydrogenation
with furfural and dehydrogenation was studied in detail.

# 66 2. Experimental

### 67 2.1. Materials

All chemicals were purchased from Sigma-Aldrich and applied without further purification. The following
chemicals were used in this study: furfural (99 %), furfuryl alcohol (98 %), tetrahydrofurfuryl alcohol (99
%), furan (≥99 %), 2-methylfuran (99 %), 2-methyltetrahydrofuran (anhydrous, inhibitor free, ≥99 %),
isopropanol (ACS reagent, ≥99.5 %), 2-butanol (99 %), 2-pentanol (98 %), 2-pentanone (CHROMASOLV
for HPLC, 99.5 %), cyclopentanol (99 %), and cyclopentanone (SAFC, ≥99 %).

The chemicals used for catalyst preparation were: Cu(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (Aldrich, trace metal basis, 99.9 %),
Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Sigma-Aldrich, puriss. p.a., ≥98.5 %), Fe(NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O (ACS reagent, ≥98 %). Material
used as a catalyst support was steam activated carbon from Norit (Norit RB4C).

76

#### 2.2. Catalyst preparation

77 Several catalytic materials supported on steam activated carbon (Norit RB4C) were prepared with wet 78 incipient impregnation method. The applied metals on the catalysts were copper, nickel, and iron in monoand bimetallic forms. The support was dried from moisture at 110 °C and the deposition of the metal 79 80 precursors (Cu(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) was performed keeping the liquid/solid ratio 81 at 1 cm<sup>3</sup>·g<sup>-1</sup>. Drying of catalysts was performed at room temperature (24 h) and subsequently in a oven at 82 110 °C (18 h). Calcination of catalysts was done at 300 °C for 4 hours applying linear heating ramp of 5  $^{\circ}$ C·min<sup>-1</sup>. The calcination was performed under air flow of 4 dm<sup>3</sup>·h<sup>-1</sup>. In situ reduction of catalysts was 83 84 performed at 250 °C with 4 MPa pure hydrogen pressure for 90 minutes.

## 85 2.3. Furfural hydrotreatment and acetone formation studies

Experiments were performed in an Autoclave Engineers 50 cm<sup>3</sup> batch reactor, where the catalyst (0.2 g) was placed in a Robinson-Mahoney type of catalyst basket. 1 cm<sup>3</sup> of furfural or furfuryl alcohol and 15 cm<sup>3</sup> of solvent isopropanol with 4 MPa pure hydrogen were placed to the reactor as the reaction temperature was achieved. The same procedure was applied in isopropanol experiments except no furfural was added to the reactor. External diffusion limitations during the reaction were avoided with high stirring speed (1000 rpm), which was confirmed in pre-experiments.

During the experiments the reactions were monitored by taking liquid samples at 0, 15, 30, 60, 120, and 300 minutes. The samples were analyzed quantitatively with a GC-FID (Agilent 6890) and a Zebron ZBwax Plus column (60 m x 0.25 mm x 0.25  $\mu$ m). The temperature ramp used with GC was from 40 °C to 100 °C with heating rate of 5 °C·min<sup>-1</sup> and from 100 °C to 230 °C with heating rate of 20 °C·min<sup>-1</sup>. Injection volume was 1  $\mu$ l, injection temperature 230 °C and internal standard used was 2-butanol. Qualitative analysis of unknown components was performed with a GC-MS (Agilent 7890-5975) applying similar
column and method. The mass spectra was recorded in electron impact ionization at 70 eV.

Gas phase in the reactor was analyzed as the reactor had cooled down to the room temperature. The gas samples were collected to a container under vacuum and analyzed with GC-FID/TCD containing gas pneumatics (Agilent 6890). CO, CO<sub>2</sub>, H<sub>2</sub>, and N<sub>2</sub> were analyzed quantitatively with TCD applying HP-PLOT/Q ( $30 \text{ m x } 0.53 \text{ mm x } 40 \text{ } \mu\text{m}$ ) and HP Molesieve ( $30 \text{ m x } 0.53 \text{ mm x } 25 \text{ } \mu\text{m}$ ) columns. Hydrocarbons were analyzed with FID applying HP-AL/KCL column ( $50 \text{ m x } 0.32 \text{ mm x } 8 \text{ } \mu\text{m}$ ).

# 104 3. Results and discussion

#### 105 3.1.

## . Furfural hydrotreatment studies

Furfural hydrotreatment studies were performed with a variety of monometallic and bimetallic catalysts, testing also the effect of reaction temperature and metal loading of the catalyst. The acetone formation was monitored closely during reactions and differences between catalysts and operating conditions were observed, as there are two possible reaction routes for acetone formation.

### 110 3.1.1. Effect of metal on acetone formation

111 Monometallic 5 wt-% Cu/C and Ni/C, and bimetallic 2/2 wt-% CuNi/C, CuFe/C, and NiFe/C were tested 112 in furfural hydrotreatment experiments. Figure 4 presents the acetone formation as a function of contact 113 time in each of these experiments. The acetone concentration was monitored as a function of contact time 114 to avoid differences caused by different metal loading between the catalysts. Contact time indicates the 115 reaction time multiplied with the metal loading of the catalyst. The highest concentration of acetone was 116 observed with bimetallic CuFe/C catalyst. With this catalyst the acetone concentration after 300 minutes 117 was as high as initial furfural concentration in the beginning of the experiment. In each experiment the 118 acetone formation in the beginning had a very high reaction rate and it was noticed to cease after conversion of furfural had achieved over 90 % (typically in 60-120 minutes). This indicates that either equilibrium 119 state is achieved or the reactants for the reaction are running out or that the formed acetone is reacting 120

121 further. However, the iron containing catalysts had a constantly increasing trend in acetone formation 122 throughout the whole experiment (300 min), whereas the formation of acetone was observed to stabilize 123 with the catalysts without iron. This indicates that formation of acetone has at least two mechanisms.

With nickel catalyst even a decreasing trend of acetone formation can be observed after 60 minutes of experiment clearly indicating further reactions of acetone. Known reactions of acetone include for example condensation reaction of acetone with furfural or furfuryl alcohol to furanmethanol acetate (FMA) and aldol condensation of acetone to methyl isobutyl ketone (MIBK). MIBK formation was observed in quantitative GC-FID analysis and the results indicated that with the iron containing catalysts MIBK was formed. With the 5 wt-% Ni/C the further reaction of acetone was mainly caused by FMA formation.

130 **Figure 4**.

#### 131 3.1.2. Effect of metal loading on acetone formation

Effect of metal loading on acetone formation was studied with all the catalyst options and it was observed that each catalyst had a characteristic trend in acetone formation as a function of metal loading. The highest amount of acetone formed during the experiments with each catalyst is presented in Figure 5.

135 With monometallic nickel catalyst metal loadings of 2, 5, and 10 wt-% were tested. The difference in 136 acetone formation between 2 and 5 wt-% catalysts was low but with higher metal loading (10 wt-%) 137 remarkably more acetone was formed. With all the tested nickel catalysts acetone concentration started to stabilize after 60 minutes of reaction time, when most of the furfural was consumed as described above. 138 139 With monometallic copper increasing the metal loading from 2 wt-% to 5 wt-% decreased the amount of 140 formed acetone. Furthermore, due to the low overall activity of copper catalysts neither the stabilization of 141 acetone concentration nor the complete conversion of furfural were reached during the experiments, which 142 supports that furfural is involved in the acetone formation mechanism. The lower activity of copper in the 143 acetone formation and furfural hydrotreatment reactions can be explained with a weaker adsorption of 144 furfural on copper as well as with poor dissociation of hydrogen on copper surface compared to nickel and

145 iron.<sup>13,14</sup> E.g. Pozzo and Alfe <sup>14</sup> studied  $H_2$  dissociation and calculated that the activation energies for  $H_2$ 146 dissociation on copper, nickel, and iron were 0.56, 0.06, and 0.03 eV, respectively.

147 With bimetallic catalysts significant differences in acetone formation were detected as the metal loading was altered (Figure 5). From these results it can be concluded, that with bimetallic catalysts containing 148 149 copper (CuNi/C and CuFe/C) the increase of copper loading actually decreased the amount of acetone 150 formed. This trend is in line with the monometallic copper catalyst. With bimetallic nickel catalysts 151 (CuNi/C and NiFe/C) the acetone formation was similar as with monometallic nickel catalyst, the increase 152 of nickel loading increased also the amount of acetone formed. The highest amount of acetone formed 153 during the experiment was observed with the 5/5 wt-% NiFe/C catalyst. As iron was observed to increase 154 acetone formation, acetone concentration can be assumed to increase also in case of CuFe/C with increasing 155 iron loading.

#### 156 **Figure 5**.

157 3.1.3. Effect of reaction temperature on acetone formation

158 To observe how acetone formation is affected as a function of temperature the reaction was studied at 159 reaction temperatures of 200 and 230 °C. With most of the catalysts an increasing temperature led to an 160 increased amount and rate of acetone formation, as can be assumed with the law of Arrhenius (Figure 6). 161 The only exception was CuNi/C, as with this catalyst a decrease in acetone concentration as a function of 162 reaction temperature was observed. This is mostly due to the above mentioned further reactions of acetone. 163 In this case no MIBK formation was observed in either reaction temperature but the FMA formation was 164 significant. In conclusion, higher temperatures promoted the furfural hydrotreatment reactions to furfuryl 165 alcohol (and other products) as well as acetone formation. Thus, higher temperatures are needed to achieve 166 the best result for the furfural hydrotreatment although the side reaction to acetone intensifies as well.

167 **Figure 6**.

### 168 3.2. Isopropanol dehydrogenation

169 Acetone formation can also be a result from the solvent dehydrogenation to acetone and hydrogen. All the 170 chosen metals in this study have also been studied earlier in isopropanol dehydrogenation with good results.<sup>12,15-18</sup> Most of the reported catalysts for dehydrogenation have had oxide supports or they have been 171 172 in oxide form themselves. This has been reported to be beneficial for isopropanol dehydrogenation. 173 Especially iron has been reported as a good dehydrogenation catalyst, which would support our results of the massive acetone production with our iron catalyst.<sup>12,16-20</sup> To study the acetone formation mechanism 174 175 more deeply, the formation of acetone from isopropanol was studied with experiments applying only the 176 solvent isopropanol and with experiments applying an intermediate product of furfural hydrogenation 177 (furfuryl alcohol) as a reactant to disregard the furfural transfer hydrogenation and furfural hydrogenation 178 routes.

179 An experiment with pure isopropanol was performed with 10 wt-% Ni/C catalyst at 230 °C and 4 MPa 180 hydrogen pressure, i.e. in the same reaction conditions as the furfural hydrogenation experiments. In this 181 dehydrogenation experiment the acetone concentration was observed to increase constantly as a function 182 of reaction time. However, signs of acetone concentration stabilization were seen as the experiment 183 proceeded further (Figure 7). As the experiment was compared to the furfural hydrogenation experiments 184 performed with the same catalyst at the same reaction conditions it was discovered, that in the presence of 185 furfural the initial acetone formation reaction rate was higher and the acetone concentration stabilized much 186 earlier than with pure isopropanol as a feed. In addition, the amount of acetone remains lower as furfural is 187 present in the experiment. It is assumed that in the case of pure isopropanol the amount of catalytically 188 active sites for dehydrogenation is higher than in the case of furfural/isopropanol mixture experiments as 189 furfural is not competing on the available sites on the catalyst and dehydrogenation can occur more 190 efficiently until the equilibrium state is reached.

**Figure 7.** 

192 In addition to the experiment with pure isopropanol, experiments with the furfural hydrotreatment 193 intermediate furfuryl alcohol were performed. These experiments were performed to avoid reactions of 194 furfural, but to offer more comparable reaction conditions for isopropanol dehydrogenation that are present 195 in furfural hydrotreatment experiments. The acetone formation experiments with furfuryl alcohol were 196 performed at two different temperatures (210 and 230 °C) and from these experiments it was discovered 197 that the acetone concentration increased with the increasing temperature (Figure 8). At the higher 198 temperature (230 °C) some sign of stabilization for the acetone concentration was noticed. However, the 199 amounts of formed acetone are much lower than in the furfural/isopropanol or isopropanol experiments. 200 This indicates that in the furfuryl alcohol experiments a similar situation occurs as in furfural experiments, 201 the catalytically active sites of catalysts are more actively occupied by FA than isopropanol, and less 202 acetone is formed by isopropanol dehydrogenation. The low amount of acetone in the FA experiment 203 compared to the furfural experiment can be explained with higher affinity of FA on the catalyst compared to furfural and isopropanol, as reported in previous studies.<sup>13,21,22</sup> The decrease in acetone concentration at 204 205 230 °C can be explained with further reactions of acetone, as MIBK formation was observed to increase as 206 a function of temperature in the FA experiments.

207 **Figure 8**.

## 208 3.3. Comparison of acetone formation routes

### 209 3.3.1. Thermodynamic calculations

With three main reaction routes present in the reaction media during the experiments and two of them producing acetone as a product, it is important to know the thermodynamic limitations of the reactions. For comparison of the routes thermodynamic calculations were performed with HSC Chemistry 6 simulation software.<sup>23</sup> The equilibrium constants were calculated with the software at reaction temperature (230 °C) in the gas phase and the results are presented in Table 1. In our system the reaction takes place in liquid phase, but thermodynamic calculations in gas phase give a good indication of the equilibrium although the 216 values are not directly applicable for the liquid phase. From the results it can be concluded that the only 217 reaction that was limited by equilibrium at 230 °C was isopropanol dehydrogenation.

218 **Table 1.** 

219 3.3.2. Experimental results

220 As the thermodynamics of all three known reactions were calculated the results were compared to the 221 experiments performed. Also, more comparisons were made to discover which of the reaction routes prevail 222 in the experiments. In furfural transfer hydrogenation, one mole of furfuryl alcohol is formed as one mole 223 of acetone is formed according to the stoichiometry. Thus, the maximum of formed furfuryl alcohol and 224 acetone moles during the catalyst experiments were compared (Figure 9). The maximum of FA and acetone 225 were not usually achieved at the same reaction time, the maximum of FA formation was usually reached in 226 15 to 60 minutes as the maximum of acetone appeared somewhat later between 30 and 300 minutes. 227 Furthermore, the experiments indicated that with most of the catalysts a lower amount of acetone was 228 formed compared to the furfuryl alcohol amount, although one exception of this were the iron containing 229 catalysts discussed earlier. For more thorough investigation, the acetone concentration with all the metal 230 catalysts was compared as a function of FA concentration and as a function of furfural conversion. Both 231 these comparisons confirmed the same information, with Cu/C, Ni/C, and CuNi/C catalysts the acetone 232 formation ceased as the formation of furfuryl alcohol achieved its maximum and most of the furfural was 233 consumed. However, as iron was included in the catalyst acetone formation was observed to increase 234 significantly after the raw material furfural and most of the intermediate product FA had reacted further. 235 This implies that isopropanol dehydrogenation occurs significantly at least in the presence of iron.

In conclusion, furfural hydrogenation reaction with hydrogen is present during the experiments and produces at least part of the furfuryl alcohol along this route. As acetone is nevertheless produced in large quantities, also transfer hydrogenation of furfural or/and isopropanol dehydrogenation reactions occur during experiments. All these observations indicate of two mechanisms. The first mechanism takes place in the beginning of the experiments with high reaction rate and it includes all three reactions presented above. After total furfural conversion mechanism two with slower reaction rate takes place. This mechanism is confirmed to consist only of isopropanol dehydrogenation and it occurs only with the iron containing catalysts. As the results were compared to the thermodynamic calculations, the amounts of acetone and FA were observed to be in the same order of magnitude as expected.

245 **Figure 9.** 

246 Additional experiments were performed to get more information about the reactions. Furfural experiments 247 without any additional hydrogen and without any catalyst were performed at 230 °C and compared to the 248 experiment with 10 wt-% Ni/C catalyst. Based on the results from the experiment without any catalyst it 249 can be concluded that thermal reactions are not significant in these conditions and a catalyst is needed for 250 the reactions to proceed. In the experiment without any additional hydrogen, the reactor was pressurized 251 with 4 MPa of nitrogen. The amount of acetone formed remained lower and stabilized later than in the 252 experiment with H<sub>2</sub> (Figure 10). Furfuryl alcohol was produced as efficiently in both experiments, but the 253 formation of further hydrogenation products was decelerated and obviously needs additional hydrogen to 254 occur efficiently. Thus it can be concluded, that furfuryl alcohol can be produced efficiently without any 255 additional hydrogen, which would make this process safer. In these Ni/C experiments with and without any 256 added hydrogen, only the first mechanism proposed above was visible. In the case of iron containing 257 catalysts the mechanism two with isopropanol dehydrogenation would be significant and acetone 258 concentration would increase also after total conversion of furfural.

259 Figure 10.

As transfer hydrogenation is also possible with the intermediate products of furfural hydrogenation, experiments with furfuryl alcohol were performed. The catalyst used in the experiments was 10 wt-% Ni/C and the reactor was pressurized either with 4 MPa of  $H_2$  or  $N_2$ . Interesting results were obtained, as without any additional hydrogen the main product was MF, and only traces of THFA and other hydrotreatment products of MF were detected. As these results were compared to the FA experiments with additional hydrogen, the difference was significant as much THFA and MTHF were formed. The results indicate that 266 MF is actually formed from FA through transfer hydrogenation, but for the other products direct 267 hydrogenation route is dominant. The amount of acetone was observed significantly lower in the FA 268 experiments with additional  $H_2$  compared to the FA experiments without  $H_2$ . The reason for this may be 269 that the additional hydrogen occupies the active sites and suppresses the isopropanol dehydrogenation 270 reaction or the equilibrium limited isopropanol dehydrogenation reaches the equilibrium state due to excess 271 amount of hydrogen. The acetone formation in the furfural and furfuryl alcohol experiments with and 272 without additional hydrogen is presented in Figure 11. It was observed that the amount of acetone produced 273 in the furfural experiments was higher than in the FA experiments. This can be explained as in the case of 274 furfural there are two transfer hydrogenation reactions from the reactant to MF, whereas with FA as a 275 reactant there is only one transfer hydrogenation step present.

276 Figure 11.

# 277 4. Conclusions

Furfural hydrotreatment to many valuable products is an important reaction route to replace many fossil based chemicals and fuels with renewable options. Acetone formation was observed to be prominent during the liquid phase furfural hydrotreatment experiments. The acetone formation in furfural hydrotreatment has not been studied deeply and is the purpose of this study.

282 Acetone formation was observed to occur in furfural hydrotreatment reactions as long as a metal catalyst 283 was applied in the experiments. Differences in acetone formation were noticed between metals as copper, 284 nickel, and iron in mono- or bimetallic combinations were tested. The lowest activity was observed with 285 nickel, copper was slightly more active, and iron was observed to be significantly more active. Metal 286 loading of these tested catalysts was also observed to have a significant effect on the acetone formation. 287 With nickel and iron the increase of metal loading increased the amount of acetone, but with copper the 288 amount of acetone decreased with the increasing metal loading. This can be explained with poor 289 dissociation of hydrogen on copper surface as well as with weaker adsorption of furfural on copper.

290 Acetone formation can occur through two reaction routes and discovering the actual reaction route for the 291 formation has appeared very challenging. From the performed experiments the first conclusion is that 292 acetone formation appears to apply two mechanisms, and furfural has an important role in the acetone 293 formation. With all the catalysts the reaction rate for acetone formation is very high in the beginning of the 294 experiment as furfural hydrogenates further. After furfural is almost completely consumed the reaction rate 295 for acetone formation decelerates or even ceases with copper and nickel catalysts. With catalysts including 296 iron the acetone formation was noticed to continue and even intensify after all furfural had reacted. Thus, 297 in the case of iron, isopropanol dehydrogenation is apparent. This has been found to be in line with 298 literature, as iron oxides are presented as good dehydrogenation catalysts. From experiments performed 299 with furfuryl alcohol it was be discovered that the MF production from FA occurs through transfer 300 hydrogenation as the other reactions (to THFA or MTHF) need additional hydrogen for hydrogenation. 301 This has not been earlier tested or discovered.

In conclusion, the acetone formation as a side product when applying isopropanol as a solvent in furfural hydrotreatment experiments is significant and cannot be prevented as copper, nickel, and iron catalysts are applied. The furfuryl alcohol production can be performed efficiently without any additional hydrogen utilizing the solvent as hydrogen donor. This would make the process safer and simultaneously the amount of acetone could be slightly decreased. Same applies also for the direct MF production from furfuryl alcohol. However, for the production of other hydrogenation products like THFA or MTHF, applying additional hydrogen is necessary for efficient production.

# 309 5. Acknowledgements

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#### **Figure titles:**

- 350 Figure 1. Furfural hydrotreatment.
- 351 Figure 2. Isopropanol dehydrogenation to acetone and hydrogen.
- 352 Figure 3. Transfer hydrogenation of furfural to furfuryl alcohol with isopropanol as hydrogen donor.
- 353 Figure 4. Acetone concentration as a function of contact time in furfural hydrotreatment experiments with
- 354 varying catalysts. T = 230 °C,  $p = 4 \text{ MPa H}_2$ , t = 300 min, m(cat) = 0.2 g.
- 355 Figure 5. Maximum acetone concentration in furfural hydrotreatment experiments with varying metal
- 356 loadings. T = 230 °C,  $p = 4 \text{ MPa H}_2$ , t = 300 min, m(cat) = 0.2 g.
- Figure 6. Maximum acetone concentration in furfural hydrotreatment experiments at temperatures of 200
- 358 and 230 °C. P = 4 MPa H<sub>2</sub>, t= 300 min, m(cat) = 0.2 g.
- Figure 7. Acetone concentration as a function of reaction time in furfural and isopropanol experiments with 10 wt-% Ni/C. T = 230 °C, p = 4 MPa H<sub>2</sub>, t = 300 min, m(cat) = 0.2 g.
- Figure 8. Acetone concentration as a function of reaction time in furfuryl alcohol experiments with 10 wt-% Ni/C at 200 and 230 °C. P = 4 MPa H<sub>2</sub>, t = 300 min, m(cat) = 0.2 g.
- Figure 9. A ratio of maximum acetone concentration and maximum furfuryl alcohol concentration with various metal catalysts. T = 230 °C, p = 4 MPa H<sub>2</sub>, t = 300 min, m(cat) = 0.2 g.
- Figure 10. 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 °C, t = 300min, m(cat) = 0.2 g.
- 368 Figure 11. Acetone concentration as a function of reaction time in furfural and furfuryl alcohol (FA)
- 369 experiments, with and without additional hydrogen. T = 230 °C, t = 300 min, m(cat) = 0.2 g.

# **Table titles:**

Table 1. Reaction enthalpies and equilibrium constants of reaction routes at reaction temperature of 230 °C.

372 Figure 1.

































390 Figure 10.



392 Figure 11.



## 394 Table 1.

Reaction	Reaction enthalpy $\Delta H / kJ \cdot mol^{-1}$	Equilibrium constant
Isopropanol dehydrogenation	-0.406	1.36.10-1
Transfer hydrogenation of furfural	-68.919	1.66·10 <sup>3</sup>
Furfural hydrogenation to furfuryl alcohol	-68.513	$1.22 \cdot 10^4$