

1 **Enhancing the conversion of D-xylose into furfural at low temperatures using chloride**  
2 **salts as co-catalysts: Catalytic combination of AlCl<sub>3</sub> and formic acid**

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10 **Abstract**

11 Furfural is a potential platform chemical derived from biomass, which has gained increased  
12 attention as a potential substitute for the displacement of petrochemicals and the production  
13 of biofuels. The catalytic effect of different metal tri-chlorides (FeCl<sub>3</sub>, AlCl<sub>3</sub> and CrCl<sub>3</sub>)  
14 with formic acid (FA) was investigated for the selective conversion of D-xylose to furfural  
15 in aqueous solutions. Reactions were carried out at various temperatures (100-170 °C), FA  
16 concentrations (0-65 wt.%), and metal chloride concentrations (0.2-0.8 M). Lyxose was  
17 identified as primary intermediate of the conversion of xylose at low temperatures and FA  
18 concentrations. A mixture containing 0.4 M AlCl<sub>3</sub> and 55 wt.% FA was the most selective  
19 and active system for the production of furfural at low temperatures (130 °C, selectivity  
20 ≈70-90%). A simplified kinetic model was developed to describe the overall xylose

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1 conversion and furfural formation under the selected conditions, offering a valuable tool for  
2 process optimisation and design.

3 **Keywords:** Xylose, Furfural, aluminium chloride, Formic acid, platform chemicals.

4

## 5 **1 Introduction**

6 Xylose is one of the most abundant pentose present in the hemicellulose fraction of various  
7 lignocellulosic materials, such as hardwoods, herbaceous plants and agricultural residues.  
8 Utilisation of this biomass component is essential in developing efficient and sustainable  
9 lignocellulosic biorefineries. Xylose can be dehydrated to furfural using an acid catalyst in  
10 aqueous phase. Furfural is a heterocyclic aldehyde that can be used as a precursor for a  
11 variety of fuel molecules and materials. It is mainly used for the production of furfuryl  
12 alcohol which is employed in the polymer industry, in foundry binders and directly as a  
13 solvent in the purification of lubricant oils [1]. Furfural has been identified as one of the  
14 potential top 30 high-value bio-based molecules [2]. The reaction kinetic mechanisms for  
15 furfural formation have been widely investigated and it is commonly described as a  
16 dehydration reaction *via* an unidentified intermediate compound [3, 4]. Studies have shown  
17 that simultaneous molecular breakdown and condensation reactions lead to the formation of  
18 a black residue referred to as humins [1]. However, the general consensus on the specific  
19 molecular mechanism for the formation of these by-products has yet to be achieved.

20

21 Several catalysts have been investigated for the conversion of xylose to furfural, including  
22 sulphuric and hydrochloric acids [4, 5], as well as solid catalysts, such as zeolites and  
23 modified metal oxides [6-9]. However, these catalysts do not overcome the kinetic

1 limitations related to the fundamental molecular dehydration reactions in aqueous phase.  
2 Temperature remains the most important operational parameter defining xylose conversion  
3 and to a significant extent furfural selectivity. Low temperatures not only lead to long  
4 reaction times but also to low furfural selectivity, since large amounts of undesired by-  
5 products are formed. Consequently, alternative catalysts have been explored to improve the  
6 selectivity of the conversion of pentose carbohydrates. Recently, advances have been made  
7 through the use of chloride salts as co-catalysts in aqueous phase. Marcotullio and De Jong  
8 [10] investigated the use of different chloride salts (potassium, sodium, calcium and iron  
9 (III) chloride) for the conversion of xylose, highlighting the high furfural yield (62%)  
10 shown by iron (III) chloride ( $\text{FeCl}_3$ ) in a 50 mM HCl aqueous solution at 200 °C. Chloride  
11 salts behave as Lewis acids in aqueous phase, i.e. as an electron pair acceptor. This is  
12 considered to lead to the enolisation of xylose to form xylulose, and thus to the increase of  
13 furfural selectivity [11]. Other reports have pointed out that additional chloride salts, such  
14 as  $\text{AlCl}_3$  and  $\text{CrCl}_3$ , also promote the isomerisation of carbohydrates, i.e. glucose and  
15 xylose, to their respective ketose form, fructose and xylulose [12]. Ketoses are readily and  
16 selectively converted to the furanic products, 5-hydroxymethylfurfural and furfural,  
17 respectively, in the presence of a Brønsted acid, thus improving the selectivity of the  
18 process [13]. Other studies have shown that xylose can undergo epimerisation in the  
19 presence of Lewis acid catalysts to form lyxose. Lyxose was the major intermediate formed  
20 from xylose dehydration to furfural using ZSM-5 zeolites at 140-160 °C [7]. This study  
21 also found that the selectivity to furfural *via* lyxose remained relatively high for a long  
22 period of time, while high xylose conversion was achieved when the reaction was carried at  
23 200 °C [7].

1  
2 On the other hand, formic acid, a weak organic acid, is a biomass-based acid catalyst,  
3 which has been successfully used in hemicellulose fractionation and hydrolysis biorefining  
4 applications [14, 15]. Commonly, high formic acid concentrations are used in pretreatment  
5 technologies for the fractionation of lignocellulosic biomass, e.g. papermaking industry and  
6 other biorefining processes [14, 16-19]. By contrast, low formic acid concentrations (<30  
7 wt.%) have been most studied for catalytic conversion of carbohydrates [15, 20]. Similar to  
8 inorganic acids, formic acid leads to furfural yields lower than 65 mol% at temperatures  
9 above 170 °C [3, 15]. Previous studies by the authors have shown that Lewis acid salts  
10 ( $\text{FeCl}_3$ ,  $\text{AlCl}_3$  and  $\text{CrCl}_3$ ) enhanced the catalytic performance of formic acid during the  
11 conversion of xylose to furfural at mild temperatures [21]. Zhang, Hewetson and Mosier  
12 [22] also showed that the use of  $\text{AlCl}_3$  with maleic acid significantly reduced the formation  
13 of humins when converting glucose to 5-hydroxymethylfurfural and levulinic acid.

14  
15 In this study, an extended investigation was carried out of the use of aluminium (III) and  
16 iron (III) chlorides ( $\text{AlCl}_3$  and  $\text{FeCl}_3$ ) with formic acid (FA) as catalysts for the conversion  
17 of xylose to furfural in aqueous phase. The catalytic concentrations were varied between  
18 0.2-0.8 M of metal chlorides and 0-65 wt.% of FA. An investigation of a wider range of  
19 formic acid concentration was considered relevant since it would propose advances in  
20 downstream processing of biorefining products that employ this organic acid for  
21 fractionation of lignocellulosic biomass. Thus, this study aims to provide both experimental  
22 data and a kinetic analysis of the conversion of xylose under mild temperatures (100-170  
23 °C). Furfural selectivity using formic acid as a stand-alone catalyst was used as the

1 benchmark in order to assess the synergetic effects arising from the presence of the metal  
2 chlorides with said organic acid. Additionally, reactions using lyxose and furfural were  
3 performed to investigate simplified mechanistic pathways for the chemical process.

4

## 5 **2 Experimental section**

### 6 2.1 Materials

7 D-(+)-Xylose (99%, Sigma-Aldrich), D-(+)-lyxose (99%, Sigma-Aldrich), D-xylulose  
8 (Carbosynth), iron (III) chloride (anhydrous reagent grade, 97%, Sigma-Aldrich),  
9 aluminium chloride hexahydrate (reagent grade, 99%, Sigma-Aldrich), chromium (III)  
10 chloride hexahydrate ( $\geq 98.0\%$ , Sigma-Aldrich), formic acid (98-100%, Merck), furfural  
11 (99.0%, Sigma-Aldrich) were all commercially available and used without further  
12 purification. All reacting solutions and dilutions for HPLC analysis were prepared with  
13 deionised water (18.2 M $\Omega$ ·cm).

14

### 15 2.2 Experimental setup and analytical techniques

16 A solution (5 mL) containing 0.3 M D-xylose and the corresponding amounts of formic  
17 acid (0-65 wt.%) and of chlorides salts (0.2-0.8 M) was placed in a sealed glass tube  
18 reactor. The reactor was immersed in a stirred (360 rpm) oil bath set at constant  
19 temperature for specified times. Once the reaction time was reached, the reactor tube was  
20 quenched in an ice batch to instantly cool the solution. The products were diluted, filtered  
21 using a 0.2  $\mu\text{m}$  membrane, and then analysed by an ICS-3000 chromatographic system  
22 (Dionex Corp., Sunnyvale, CA). The system was equipped with integrated electrochemical  
23 and UV (278 nm) detectors, and with both H<sup>+</sup> ion exchange guard (Hi-Plex H 50  $\times$  7.7 mm)

1 and analytical (300 × 7.7 mm) columns connected in series. The column was eluted  
2 isocratically at 65 °C with deionised water at a flow rate of 0.65 mL min<sup>-1</sup>. When an  
3 intermediate sugar was detected, a Gaussian deconvolution method was used for data  
4 treatment after acquisition.

5  
6 The catalytic performance of the chloride salt-formic acid mixtures was evaluated through  
7 the conversion of D-xylose, and the yields and selectivities of furfural that were attained  
8 under each reaction condition. These were calculated as follows:

9 Conversion<sub>XYL</sub> ( $X_{C5}$ , %) =  $(C_{XYL,o} - C_{XYL,t}) / C_{XYL,o} \times 100$  (1)

10 Yield<sub>P</sub> ( $Y_P$ , %) =  $(C_{P,t} - C_{P,o}) / C_{XYL,o} \times 100$  (2)

11 Selectivity<sub>P</sub> ( $S_P$ , %) =  $(C_{P,t} - C_{P,o}) / (C_{XYL,o} - C_{XYL,t}) \times 100$  (3)

12 Where  $C_{XYL}$  and  $C_P$  correspond to the molar concentrations of xylose and products (lyxose  
13 and furfural), respectively, and the subscripts  $o$  and  $t$  correspond to the beginning of the  
14 reaction and the reaction time  $t$ , respectively.

15

### 16 **3 Results and discussion**

#### 17 3.1 Tri-chloride salts in formic acid: effect of metal salts, catalyst concentration and 18 temperature

19 A previous study carried out by the authors demonstrated that tri-chloride salts, i.e. iron,  
20 aluminium, and chromium chlorides, improved the performance of formic acid as a catalyst  
21 for the conversion of carbohydrates [21]. Metal chloride salts are catalytically active in the  
22 conversion of xylose in aqueous and organic solvents [23]. However, in the absence of a

1 Brønsted acid, low furfural yields (35 to 45 mol%) with poor selectivities were obtained  
2 using FeCl<sub>3</sub>, AlCl<sub>3</sub> and CrCl<sub>3</sub> for xylose conversion at 130 °C [21]. **Fig. 1** presents the  
3 furfural selectivity observed with mixtures of formic acid (55 wt.%) and metal chlorides  
4 at 130°C. In contrast to the mono-catalytic systems, mixtures of formic acid (FA) and  
5 chlorides salts, FeCl<sub>3</sub>-FA, AlCl<sub>3</sub>-FA and CrCl<sub>3</sub>-FA, gave maximum furfural yields of 55, 68  
6 and 65 mol%, respectively, corresponding to selectivities above 68%. Additionally, the  
7 xylose conversion rate was increased by a factor of 6 in the chloride-FA systems compared  
8 to the system in which FA was used as a stand-alone catalyst. The FeCl<sub>3</sub>-FA system  
9 showed lower selectivity at the early stages of the reaction, while achieving a maximum  
10 selectivity of 65% at  $X_{C5} \approx 80\%$ . In the latter case, the FeCl<sub>3</sub> appeared to hinder the  
11 selectivity at low xylose conversion ( $X_{C5} < 30\%$ ) compared to the selectivity observed when  
12 formic acid was the only catalyst. The CrCl<sub>3</sub>-FA catalytic system showed a high selectivity  
13 to furfural (60-70%) at  $X_{C5} > 20\%$ , compared to the FA system. This was in agreement with  
14 the work carried out by Choudhary, Sandler and Vlachos [13]. In their work, the furfural  
15 yield was increased from 29 mol% when the reaction was carried out at 145 °C in the  
16 presence of HCl to 39 mol% with HCl/CrCl<sub>3</sub>. The AlCl<sub>3</sub>-FA system showed the highest  
17 selectivity (above 70%) of the catalytic mixtures considered, even after achieving xylose  
18 conversions greater than 80%. This was in agreement with earlier investigations, where  
19 AlCl<sub>3</sub> gave a better performance than CrCl<sub>3</sub> for the conversion of xylose to furfural in  
20 aqueous phase with HCl [13, 24].  
21  
22 For the purpose of identifying the optimum catalyst combination and conversion  
23 conditions, the FA concentration and reaction temperature were varied using 0.4 M FeCl<sub>3</sub>

1 or AlCl<sub>3</sub> as co-catalyst. Attention was centred on the use of these two tri-chloride salts as  
2 they represented low and high catalytic activity/selectivity, respectively (see **Fig. 1**). **Fig. 2**  
3 presents the furfural selectivity observed in these catalytic systems as a function of xylose  
4 conversion using different formic acid concentrations and temperatures. The highest  
5 furfural selectivity obtained using the FeCl<sub>3</sub>-FA system was 65-69%, independent of the  
6 formic acid loading. With FeCl<sub>3</sub>, the furfural selectivity at X<sub>C5</sub> ≈ 30% was higher when  
7 using 15 wt.% FA (S<sub>FUR</sub> ≈ 55%), than when using 30 or 55 wt.% FA (S<sub>FUR</sub> ≈ 10-20%). As a  
8 consequence, the FeCl<sub>3</sub>-FA 15 wt.% system achieved the maximum furfural selectivity at  
9 an early stage (X<sub>C5</sub> ≈ 40%) followed by a continuous decrease of the chemo-selectivity to  
10 furfural. Previous research has shown that in aqueous FA solutions, furfural degradation is  
11 weakly affected by the FA concentration [3]. This suggested that the increase in FA  
12 concentration increased the rate of xylose conversion and furfural formation in the FeCl<sub>3</sub>-  
13 FA systems even when approaching complete conversion. The reacting aqueous solution  
14 with FeCl<sub>3</sub> as a stand-alone catalyst was strongly acidic at room temperature (pH 1.16).  
15 However, the acidity of the reaction medium increased after 1 h at 130 °C (pH 0.62). This  
16 was due to the *in situ* formation of complexes in the aqueous system, such as  
17 [FeOO(H<sub>2</sub>O)<sub>4</sub>]<sup>3+</sup>, which contributed to the acidity [25]. This was not observed in the  
18 systems containing 15 and 30 wt.% FA, since modest increases in their pH were observed,  
19 varying from 0.46 to 0.52 and from 0.16 to 0.18, in the respective catalytic FeCl<sub>3</sub>-FA  
20 systems after 1 h at 130 °C. In acetic acid solution, FeCl<sub>3</sub> leads to a greater formation of  
21 metal complexes that may reduce the pH of the solution compared to other chlorides, such  
22 as ZnCl<sub>2</sub> or CuCl<sub>2</sub> [26]. Similarly to acetic acid, FA is a weak Brønsted acid with low  
23 tendency to dissociate. The fact that furfural selectivity was not significantly affected by the



1 FA concentration and that the pH of the mixtures increased during the experiments  
2 indicated that the speciation products of the FeCl<sub>3</sub>-FA system had a more pronounced effect  
3 on the acidity and the catalytic performance of the system than the neat FeCl<sub>3</sub> or formic  
4 acid.  
5  
6 The maximum furfural selectivity attained with AlCl<sub>3</sub> increased with the increase in FA  
7 concentration from 0 ( $X_{C5} \approx 92\%$ ,  $S_{FUR} \approx 42\%$ ) to 55 wt.% ( $X_{C5} \approx 92\%$ ,  $S_{FUR} \approx 68\%$ ). Even  
8 though raising the FA concentration from 55 to 65 wt.% increased the rate of xylose  
9 conversion, similar furfural selectivities were observed in both systems. After complete  
10 xylose conversion, furfural yields were between 45 and 60 mol% with any amount of FA.  
11 The system that used AlCl<sub>3</sub> as a stand-alone catalyst had an initial pH of 2.45, which was  
12 further reduced to 1.14 after 1 h at 130 °C. Akin to the aqueous FeCl<sub>3</sub> solution, this  
13 decrease in pH after thermal treatment was in agreement with previous studies in which  
14 trivalent metal chlorides (i.e. CrCl<sub>3</sub>) showed an irreversible pH decrease due to  
15 precipitation of stable hydroxides [27, 28]. However, the pH of the mixture of AlCl<sub>3</sub> and 10  
16 wt.% FA (pH = 0.68) also decreased irreversibly (pH = 0.58) after 1 h at 130 °C. This  
17 phenomenon was no longer seen with higher FA/AlCl<sub>3</sub> ratios. Despite the fact that the  
18 initial pH of the AlCl<sub>3</sub>-FA mixtures (10 and 30 wt.%) were lower than the pH of the system  
19 using AlCl<sub>3</sub> as a stand-alone catalyst, the latter mixture showed a higher xylose conversion  
20 rate and poorer selectivity towards the formation of furfural (see **Fig. 2b** and **Fig. A.1-b** in  
21 the **Supporting Information**). As demonstrated in previous investigations, AlCl<sub>3</sub> and  
22 FeCl<sub>3</sub> speciation in aqueous phase plays the most important role in the functioning of these  
23 metal salts as catalysts [27, 28]. Using X-ray spectroscopy and molecular dynamics

1 simulations, Choudhary, Caratzoulas and Vlachos [27] postulated that the  $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$   
2 cation was the active catalytic agent promoting the isomerisation of glucose to fructose in  
3 aqueous phase when catalysed by  $\text{CrCl}_3/\text{HCl}$  at  $140\text{ }^\circ\text{C}$ . Active complexes, such as  
4  $[\text{FeOO}(\text{H}_2\text{O})_4]^{3+}$  in the  $\text{FeCl}_3$ -water system or  $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  in the  $\text{AlCl}_3$ -water mixture,  
5 presumably promote the isomerisation of xylose to intermediate sugar species. The  
6 inclusion of FA in the aqueous mixture affects the speciation equilibrium, thus tentatively  
7 reducing the number of active complexes and consequently diminishing the xylose  
8 conversion rates. This is in agreement with the findings by Choudhary, Caratzoulas and  
9 Vlachos [27]. In their study, it was also found that with the addition of  $\text{HCl}$ , which reduced  
10 the pH, the formation of the active cation was inhibited ( $>0.1\text{ M HCl}$ ) leading to lower  
11 glucose conversion rates. Drábek, Kiplagat, Komarek, Tejnecký and Borůvka [29]  
12 investigated the interactions of organic acids (i.e. citric, malic, oxalic and fulvic acid) with  
13  $\text{AlCl}_3$  using liquid chromatography and kinetic modelling. At a pH between 1.35 and 1.40,  
14  $\text{Al}^{3+}$  was the dominant species with oxalic acid-to-Al (OA:Al) molar ratios lower than 0.2.  
15 Other oxalate-coordinated species were predominantly formed when the OA:Al ratio in the  
16 solution was increased, e.g. 72%  $\text{Al}(\text{oxalate})^+$  at OA:Al = 2.7, and 62%  $\text{Al}(\text{oxalate})_3^{3-}$  at  
17 OA:Al = 270. Similarly, at a given OA:Al ratio, the decrease in the pH of the catalytic  
18 reaction mixture led to the preferred formation of  $\text{Al}^{3+}$  species. By comparison, FA:Al  
19 molar ratios in the present study were higher than 30 with FA concentrations above 15  
20 wt.% and high acidities ( $\text{pH}<0.7$ ). Despite the high FA:Al ratios observed, high selectivities  
21 were observed at high FA concentrations suggesting that favourable complexes such as  
22  $[\text{Al}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  or  $\text{Al}(\text{formate})^{\text{n}\pm}$  were possibly formed, promoting the isomerisation of  
23 xylose. In general, the activity of the  $\text{AlCl}_3$  and of the  $\text{AlCl}_3$ -FA systems was higher than

1 that of the FeCl<sub>3</sub>-related systems. This is in agreement with previous reports for aqueous  
2 systems. In their experimental and computational study of the glucose-fructose conversion  
3 in aqueous phase, Loerbroks, van Rijn, Ruby, Tong, Schüth and Thiel [25] concluded that  
4 the reduced reactivity of FeCl<sub>3</sub> compared to AlCl<sub>3</sub> and CrCl<sub>3</sub> was due to the high acidity of  
5 the former system which prevented the preferential formation of active ligands.  
6  
7 Low temperatures (100-170 °C) were selected in order to evaluate the thermal activity of  
8 the metal chloride salts-FA systems. The use of mild temperatures reduces energy  
9 consumption in comparison to conventional systems that operate at temperatures above 180  
10 °C. This is an essential factor for the design, scaling-up and techno-economic performance  
11 of the process. The reaction temperature had different effects on the catalytic performance  
12 of FeCl<sub>3</sub> and AlCl<sub>3</sub>. In the FeCl<sub>3</sub>-FA system, an increase in temperature from 130 to 150 °C  
13 did not alter the furfural selectivity to any appreciable extent ( $X_{C5}=80\%$ ,  $S_{FUR}\approx 68\%$ ). The  
14 reaction times required to reach the maximum furfural yield at 130 and 150 °C  
15 corresponded to 10 and 60 min, respectively (see **Supporting Information**). A lower  
16 selectivity ( $X_{C5}=80\%$ ,  $S_{FUR}=53\%$ ) was observed when the reaction was carried out at 170  
17 °C (**Fig. 2c**). This was attributed to simultaneous promotion of the degradation of furfural at  
18 high temperatures [4]. On the other hand, minor variations in the furfural selectivity were  
19 observed using AlCl<sub>3</sub>-FA (55 wt.%) at temperatures between 130 and 170 °C. The highest  
20 furfural selectivities varied between 85-90%, mainly observed between 20 and 50% xylose  
21 conversion (**Fig. 2d**). At the final stages of xylose conversion, a decline in the furfural  
22 selectivity was observed due to the acid-catalysed degradation of furfural. High selectivities  
23 (~90%) were obtained at 100 °C when low amounts of xylose were converted ( $X_{C5}<20\%$ ).

1 However, a lower selectivity (58%) was achieved at higher xylose conversion (>80 mol%).  
2 At 170 °C, xylose was rapidly converted using the AlCl<sub>3</sub>-FA system (X<sub>C5</sub>>60% after 2  
3 min) with high furfural selectivity (85%), followed by an immediate decrease of the  
4 furfural yield due to subsequent product degradation. Intermediate temperatures (130 and  
5 150 °C) were deemed more appropriate to obtain high furfural yields (~70%) with high  
6 selectivity (S<sub>FUR</sub>≈65-75%) after complete xylose conversion (X<sub>C5</sub>≈90-95%) for reaction  
7 times of 10 and 30 min, respectively (see **Supporting Information**). These temperatures  
8 are associated with lower energy consumption than that of typical industrial production of  
9 furfural (>200 °C).

10

11 The conditions identified for the AlCl<sub>3</sub>-55 wt.% FA system at 130 °C were used for further  
12 investigation due to its highly selective catalytic activity. **Fig. 3** shows the effects of AlCl<sub>3</sub>  
13 concentration on the performance of the selected system with and without FA. The highest  
14 furfural yields using AlCl<sub>3</sub> as a single catalyst were ~45 mol% (S<sub>FUR</sub>>30%), achieved after  
15 reaction times longer than 60 min. When using AlCl<sub>3</sub> solely as a catalyst, the furfural yield  
16 did not increase with increasing AlCl<sub>3</sub> concentrations above 0.4 M. In the presence of FA,  
17 the maximum furfural yield increased from 57 mol% using 0.2 M AlCl<sub>3</sub> to 68 and 70 mol%  
18 using 0.4 and 0.8 M AlCl<sub>3</sub>, respectively. The reaction time required to reach the maximum  
19 furfural yield was significantly shortened when increasing the AlCl<sub>3</sub> concentration from 0.4  
20 M ( $t_{\max, \text{FUR}}=30$  min) to 0.8 M ( $t_{\max, \text{FUR}}=10$  min). This resulted in a steady increase of the  
21 reaction selectivity towards furfural with the increase in AlCl<sub>3</sub> concentration, from 60%  
22 using 0.2 M AlCl<sub>3</sub> to 74 and 78% with 0.4 and 0.8 M AlCl<sub>3</sub>. The FA-to-Al molar ratios  
23 corresponded to 60, 30 and 15, respectively. According to Drábek, Kiplagat, Komarek,

1 Tejnecký and Borůvka [29], the formation of active complexes such as  $\text{Al}(\text{formate})^{n+}$  is  
2 favoured when reducing the FA-to-Al molar ratios. This was corroborated by the more  
3 rapid xylose conversion and high selectivity observed with high  $\text{AlCl}_3$  concentration as  
4 promoted by  $\text{Al}(\text{formate})^{n+}$  species.  
5  
6 These results also suggested that the relative abundance of active catalytic species, as  
7 represented by the high molar ratios of  $\text{AlCl}_3$  to xylose, may have also contributed to the  
8 performance of the system. However, other studies imply an opposite effect when organic  
9 solvents other than FA are used. Zhang, Yu, Wang, Dong and Peng [5] observed that  
10 furfural formation decreased from 81 mol% to 75 mol% when increasing the molar ratio of  
11  $\text{AlCl}_3$  to xylose from 0.5 to 2:1, using an ionic liquid ( $[\text{BMIM}]\text{Cl}$ ) as reaction solution.  
12 Likewise, they observed that systems using an excess of  $\text{AlCl}_3$  reached the maximum  
13 furfural formation in shorter reaction times. These finding was in agreement with the results  
14 presented herein. Zhang, Yu, Yu, Chen and Yang [30] observed that when increasing the  
15  $\text{AlCl}_3$  concentration from 12.5 to 25 mM, the maximum furfural yields obtained from xylan  
16 decreased from 44.8 mol% to 39.1 mol% in a catalytic mixture containing choline chloride  
17 and oxalic acid. On the other hand, the  $\text{CrCl}_3/\text{HCl}$  catalytic system investigated by  
18 Choudhary, Sandler and Vlachos [13] showed similar behaviour to the catalytic mixtures  
19 considered in the present study. The maximum furfural yield was the same (~38%) when  
20 using 0.1 M HCl and either 6 or 13 mM  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ; however, the maximum furfural yield  
21 was obtained after a shorter reaction time and with higher selectivity when using the  
22 highest  $\text{CrCl}_3$  concentrations. In their study, Choudhary, Sandler and Vlachos [13]  
23 concluded that xylose isomerisation was rate controlling, meaning that  $\text{CrCl}_3$  and HCl had

1 independent roles as Lewis and Brønsted acids, respectively. Overall, it was determined  
2 that an increase in the AlCl<sub>3</sub> concentration above 0.8 M improved the catalytic activity of  
3 the mixture by providing more rapid xylose conversion; however, AlCl<sub>3</sub> concentrations  
4 greater than 0.4 M did not improve the selectivity of the process, due to the coexistence of  
5 furfural degradation reactions. Unlike HCl, it is clear that FA gave rise to a more complex  
6 behaviour in terms of the dissociation and speciation equilibrium involved.

7

### 8 3.2 Xylose dehydration and furfural degradation in metal chloride-FA systems:

#### 9 Mechanistic observations

10 Earlier investigations have suggested that the acyclic form of xylose can  
11 isomerise/epimerise in the presence of a Lewis acid catalyst to form different tautomers,  
12 such as xylulose and lyxose, prior to the formation of furfural [6, 7, 27, 31]. As part of the  
13 current study, the formation of lyxose and xylulose as stable products or intermediates was  
14 evaluated. The presence and concentration of these pentoses was determined using liquid  
15 chromatography by comparing the elution time and electrochemical response with  
16 standardised solutions of these compounds (see **Section 2.2**). A detailed chromatogram of  
17 the peaks corresponding to these intermediates is presented in the **Supporting**  
18 **Information**. The intermediate sugar peak was only seen in experiments when chlorides  
19 were used either as a stand-alone or co-catalyst. Furthermore, this peak was predominantly  
20 detected at earlier stages of the reaction and at low temperatures/FA concentrations. Due to  
21 the similar retention times ( $t = 11.8-11.9$  min) of lyxose and xylulose, a deconvolution  
22 method was developed using calibration equations generated from standard samples that  
23 allowed the independent estimation of the concentration each of these species. The width of

1 the peak generated by each compound was fixed using a curve fitting method based on the  
2 standard samples. Lyxose was identified as the primary intermediate compound formed  
3 during dehydration of xylose when metal chlorides were catalytic presented. **Fig. 4a** shows  
4 the maximum yields of lyxose formed from xylose in different catalytic mixtures at 130 and  
5 170 °C. A maximum lyxose formation of 20 mol% was obtained after 10 min when the  
6 reaction was catalysed by AlCl<sub>3</sub> at 130 °C. The maximum lyxose yield achieved with FeCl<sub>3</sub>  
7 was 4 mol% after 5 min at 130 °C. An increase in the reaction temperature to 170 °C  
8 consistently resulted in lower lyxose formation, which was observed at shorter reaction  
9 times (5 and 2 min) in the respective catalytic systems with AlCl<sub>3</sub> and FeCl<sub>3</sub>. The effect of  
10 temperature on the lyxose yield was particularly evident when using AlCl<sub>3</sub> as the sole  
11 catalyst, since the maximum Y<sub>LYX</sub> decreased from 20 mol% at 130 °C to 12 mol% at 170  
12 °C. Lyxose yields also decreased when adding FA to the reacting mixtures at 130 °C. In the  
13 presence of 10 and 30 wt.% FA, the maximum lyxose yield decreased from 20% to 7% and  
14 2%, respectively. No intermediate sugar was detected once the FA concentration was over  
15 30% or when the reaction temperature was above 130 °C with low FA concentrations. This  
16 was attributed to the promotion of the Brønsted acid-catalysed pathways leading to the  
17 dehydration of the tautomers of xylose to form furfural. As shown in **Fig. 2**, the selectivity  
18 observed using AlCl<sub>3</sub>-30% FA was higher than when using AlCl<sub>3</sub>-10% FA at any xylose  
19 conversion. This confirms that when the Brønsted-acid concentration was increased, there  
20 was a corresponding increase in the rate of conversion of xylose tautomers to form furfural  
21 [31]. Through deconvolution and standardised calibration, it was determined that xylulose  
22 was detected as secondary intermediate compound achieving yields of up to 10%, observed  
23 only in the systems with AlCl<sub>3</sub> as the sole catalyst. The reactivity of lyxose and xylulose in

1 aqueous media catalysed by HCl have been reported previously [13]. Using this inorganic  
2 acid at mild temperatures (100-145 °C), lyxose had a similar reactivity as xylose  
3 ( $S_{\max, \text{FUR}} \approx 35\%$ ). However, xylulose was converted more rapidly and selectively  
4 ( $S_{\max, \text{FUR}} \approx 70\%$ ) to furfural than the aforementioned aldoses. **Figs. 4b and 4c** show the  
5 conversion of lyxose and its selectivity towards furfural in catalytic systems with FA,  $\text{AlCl}_3$   
6 and  $\text{AlCl}_3$ -FA at 130 °C. FA had a poor catalytic performance for the conversion of lyxose  
7 ( $X_{\text{LYX}} < 25 \text{ mol}\%$ ) to furfural ( $S_{\text{FUR}} \approx 48\%$ ), even after long reaction times (100 min).  
8 Compared to xylose, lyxose was converted with a lower reaction rate and similar selectivity  
9 to furfural ( $X_{\text{XYL}} \sim 33 \text{ mol}\%$ ,  $S_{\text{FUR}} \sim 48\%$ ). Using  $\text{AlCl}_3$  as a stand-alone catalyst, lyxose  
10 selectivity to furfural after 100 min was lower than from xylose ( $X_{\text{XYL}} \sim 31\%$ ). The catalytic  
11 activity of the Al species resulted in the degradation of the sugar, forming other molecules,  
12 such as acetic and lactic acid (detected but not quantified). The  $\text{AlCl}_3$ -FA mixture was more  
13 catalytically-active thus converting lyxose after 30 min. However, the chemo-selectivity to  
14 furfural was improved only marginally ( $S_{\text{FUR}, \max} \approx 40\%$ ) in comparison to the FA or  $\text{AlCl}_3$  as  
15 stand-alone catalyst. Furthermore, lyxose conversion occurred more rapidly than xylose  
16 conversion using the  $\text{AlCl}_3$ -FA mixture. Unequivocally, the furfural selectivity from lyxose  
17 was 38% lower than from xylose. These results suggest that the catalytically active species  
18 present in the  $\text{AlCl}_3$  and  $\text{AlCl}_3$ -FA systems promoted mainly parasitic reactions that  
19 decreased the formation of furfural from lyxose. This also suggests that the epimerization  
20 of xylose to lyxose had, in fact, a minor contribution in the selective formation of furfural.  
21 Therefore, the improvement in the catalytic performance of FA with the addition of  $\text{AlCl}_3$   
22 was presumably caused by the formation of xylulose as an intermediate. This indicated that  
23 xylulose conversion was strongly catalysed by  $\text{AlCl}_3$  rendering the intermediate



1 undetectable. Future work is required to extend the knowledge of the catalytic performance  
2 of the  $\text{AlCl}_3$ -FA mixtures for the dehydration of xylulose.

3  
4 Previous work by Dussan, Girisuta, Lopes, Leahy and Hayes [3] proposed that the presence  
5 of furfural hinders the selectivity of the conversion of D-xylose to furfural in the presence  
6 of formic acid. **Fig. 5a** shows the effects of furfural on the xylose conversion and furfural  
7 yields achieved using the different catalytic systems at 130 °C. It was observed that the  
8 conversion of xylose was not affected to a significant extent by the presence of furfural  
9 under the conditions evaluated herein. The selectivity of the reaction using FA as a stand-  
10 alone catalyst was not altered by the presence of furfural at 130 °C. However, furfural  
11 yields were notably lower when furfural was present in the reaction systems involving the  
12 metal tri-chlorides with  $\text{FeCl}_3$  having the most significant impact with a negative furfural  
13 yield observed after 30 min. Negative yields resulted from degradation rates being faster  
14 than those of furfural formation, leading to the rapid consumption of the furfural present in  
15 the mixture from the start of the reaction. Furthermore, the furfural yield was 23% lower in  
16 the  $\text{FeCl}_3$ -FA system when furfural was available from the beginning of the reaction while  
17 in the  $\text{AlCl}_3$  and  $\text{AlCl}_3$ -FA systems, furfural yields were 18% and 15% lower respectively  
18 when furfural was present in the mixture. The negative effect of furfural in the  $\text{FeCl}_3$  and  
19  $\text{AlCl}_3$  systems suggested that the active species formed by these salts promoted irreversible  
20 side reactions involving intermediate/transitory sugar species and furfural towards  
21 condensation products. It is important to highlight that the  $\text{AlCl}_3$ -FA system reported the  
22 lowest reduction in furfural formation among the catalytic systems evaluated.

23

1 In addition to the previous analysis, the furfural degradation promoted by the  $\text{FeCl}_3$  and  
2  $\text{AlCl}_3$  catalytic systems was evaluated. **Fig. 5b** presents the furfural conversion to  
3 degradation products at 130 °C. Furfural was not significantly degraded using concentrated  
4 formic acid at such low temperature, in agreement with previous reports [3].  $\text{FeCl}_3$  as a  
5 stand-alone catalyst promoted the degradation of furfural to a significant extent since over  
6 65% was converted after 60 min.  $\text{AlCl}_3$  reported a lower activity for this reaction,  
7 promoting only the degradation of 19% of the initial furfural after 60 min. The presence of  
8 formic acid in the  $\text{FeCl}_3$ -FA system reduced the degradation of furfural by over 20%.  
9 Unlike the iron chloride, the  $\text{AlCl}_3$ -FA system reported similar furfural degradation as  
10 when using  $\text{AlCl}_3$  as a single catalyst. This indicated that the poor selectivity observed with  
11 the  $\text{FeCl}_3$  and  $\text{FeCl}_3$ -FA systems may be attributed mostly to the significant promotion of  
12 furfural degradation by active species. On the other hand, the catalytic activity shown by  
13 the  $\text{AlCl}_3$  and  $\text{AlCl}_3$ -FA systems suggested that complexes derived from the salt speciation  
14 that were catalytically active in the degradation of furfural were present in similar  
15 concentrations in both aqueous and formic acid-rich solutions.

16

### 17 3.3 Empirical reaction kinetics of D-xylose conversion in the $\text{AlCl}_3$ -FA system

18 An empirical kinetic model was developed and the qualitative behaviours of the model was  
19 evaluated for the estimation of kinetic parameters for xylose dehydration catalysed by  
20  $\text{AlCl}_3$ -FA. For this study the following assumptions were established, based on the  
21 observations presented in **Section 3.2**:

- 22 ○ The formation of intermediate carbohydrates, i.e. lyxose and xylulose, was not  
23 considered in the kinetic model since these compounds were detected in low

1 concentrations only at early stages of conversion in the binary catalytic system under  
2 mild reaction conditions, i.e. low reaction temperature and low formic acid  
3 concentrations. Besides, these intermediate compounds were negligible or not  
4 detected in reactions conducted at more severe conditions, such as high temperatures  
5 (> 130°C) and acid concentrations (> 30 wt.%).

- 6 ○ The formation of active metal complexation was correlated to the concentrations of  
7 active catalytic species from formic acid (dissociated H<sup>+</sup> cation) and aluminium  
8 chloride (AlCl<sub>3</sub> concentration) in the binary catalytic systems.

9  
10 Thus, a modified Arrhenius equation was proposed using a pseudo-first order reaction with  
11 respect to each active species from catalysts involved. The following equation describes the  
12 reaction rate constants applied in the model:

$$13 \quad k_i = (A_{[FA],i} \times [FA] + A_{[Cl],i} \times [AlCl_3]) \times \exp\left(\frac{-E_{a,i}}{RT}\right) \quad (5)$$

14 Where  $k_i$  corresponds to the reaction rate constant,  $A_{[FA],i}$  and  $A_{[Cl],i}$  correspond to the pre-  
15 factors to formic acid and chloride sites, respectively. The activation energy ( $E_{a,i}$ ) was  
16 correlated to both active species from formic acid ([FA]) and aluminium chloride ([AlCl<sub>3</sub>]).

17 The term [FA] corresponded to the hydrogen ion concentration (H<sup>+</sup>) from dissociation  
18 calculated using a non-linear equation as described elsewhere [15]. The variable  $T$   
19 corresponded to reaction temperature and  $R$  the universal gas constant. The term  $i$  referred  
20 to the chemical reaction step identified in the simplified mechanism displayed in **Fig.6**.

21 In this model a total of 112 data values were used, describing the concentrations of xylose  
22 and furfural from 16 different sets of experimental conditions, using different formic acid

1 (0-65 wt.%) and AlCl<sub>3</sub> concentrations (0.2, 0.4 and 0.8 M), and reaction temperatures  
2 between 100 and 170 °C. The reaction kinetic parameters were optimised using a non-linear  
3 regression function in Matlab R2015b. The measured concentrations of xylose and furfural  
4 were used as inputs in the estimation routine using the *fminsearch* optimisation tool in  
5 Matlab. The values of the estimated kinetic parameters, pre-exponential factors, activation  
6 energies, reaction orders and the goodness-of-fit of the model are shown in **Table 1**. The  
7 behaviour of furfural formation and xylose conversion was adequately predicted for the  
8 various conversion conditions tested experimentally following this simplified first-order  
9 kinetic model, as seen in **Fig. A5** in the Supplementary Information.

10

11 **Fig. 6** shows the combined effects of temperature and the concentrations of formic acid and  
12 AlCl<sub>3</sub> on the maximum furfural yields obtained from the dehydration of 0.3 M D-xylose. In  
13 the first scenario (**Fig.6a**, [AlCl<sub>3</sub>] = 0.38 M), the maximum furfural yields attained were  
14 between 50 and 70 mol%. The increase of either temperature or FA concentration had a  
15 promoted the formation of furfural, since higher furfural yields (>60 mol%) were achieved  
16 using FA concentrations above 30 wt.% and temperatures above 170 °C. In the second  
17 scenario (**Fig.6b**, [FA] = 60 wt.%), however, the increase of the aluminium chloride  
18 concentration led to a mild decrease of the maximum furfural concentration, especially at  
19 lower reaction temperatures, in agreement with the experimental results presented in  
20 Section 3.1. Using 0.1 M AlCl<sub>3</sub>, the formation of furfural was higher than 62% at  
21 temperature above 140 °C and was promoted with the increase of temperature.

22

1 The activation energy of the xylose conversion using the  $\text{AlCl}_3$ -FA system ( $E_{a,1}=67.20 \text{ kJ}$   
2  $\text{mol}^{-1}$ ) was lower than the activation energy reported for the system using formic acid as  
3 stand-alone catalyst (140.3 and 152  $\text{kJ mol}^{-1}$ ) [3][15]. This was expected due to the  
4 formation of distinct complexation species that reduced the energy barrier involved in the  
5 dehydration of xylose. Likewise, the value of  $E_{a,1}$  was lower than observed in catalytic  
6 systems using other organic and mineral acids, such as acetic acid (108.6  $\text{kJ mol}^{-1}$ ) [32] and  
7 0.05 M HCl combined with 0.5 M NaCl (133.3  $\text{kJ mol}^{-1}$ ) [33]. On the other hand, the  
8 activation energy of the xylose conversion to furfural was comparable to the value reported  
9 for the isomerisation of xylose to xylulose using 6 mM  $\text{CrCl}_3$  (64.85  $\text{kJ mol}^{-1}$ ) [13].  
10 Regarding the pre-exponential factors of the reaction 1 ( $A_{[\text{FA}],1}$  and  $A_{[\text{AlCl}_3],1}$ ), the higher  
11 value of  $A_{[\text{AlCl}_3],1}$  indicated a major catalytic contribution of the presence of aluminium  
12 chloride in the promotion of the dehydration of xylose.

13  
14 The activation energy of the xylose condensation ( $E_{a,2}=99.52 \text{ kJ mol}^{-1}$ ) was within the  
15 range of values reported in the literature using sole formic acid (82.9 and 161  $\text{kJ mol}^{-1}$ ) [3,  
16 15] and using other acids, such as acetic acid (104.99 – 125.8  $\text{kJ mol}^{-1}$ ) [32, 33].

17 Additionally, the activation energy of the furfural degradation ( $E_{a,3}=90.81 \text{ kJ mol}^{-1}$ ) was  
18 also similar to that reported in other studies using sole formic acid or sole  $\text{AlCl}_3$  (75 -131  $\text{kJ}$   
19  $\text{mol}^{-1}$ ) [3, 15, 34]. However,  $E_{a,3}$  in this system was higher than the corresponding  
20 activation energy reported for most mineral acids, such as HCl and  $\text{H}_2\text{SO}_4$  ( $\approx 48$ -67  $\text{kJ mol}$ )  
21 [4, 35], which showed the advantage of this catalytic system in hindering the loss of  
22 furfural through parasitic reactions of this product.

23

## 1    **4    Conclusion**

2    The present study investigated the use of metal tri-chlorides and FA as catalytic mixtures  
3    for D-xylose dehydration to furfural at mild temperatures. The most selective and active  
4    catalytic system contained 0.4 M AlCl<sub>3</sub> and 55% FA. Some mechanistic findings included:  
5    a) complex salt speciation and synergetic catalytic effects required a parametric  
6    optimisation of the catalytic performance; b) intermediate compounds formed *via* xylose  
7    isomerisation/epimerization were not detectable at >130 °C and >30 wt.% FA; c) metal tri-  
8    chlorides promoted parasitic reactions involving furfural even at low temperatures. A  
9    simplified kinetic model was proposed offering a valuable tool for process design and  
10    optimisation that includes the overall effects of temperature, and concentrations of formic  
11    acid and aluminium chloride on the formation of furfural.

12

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15

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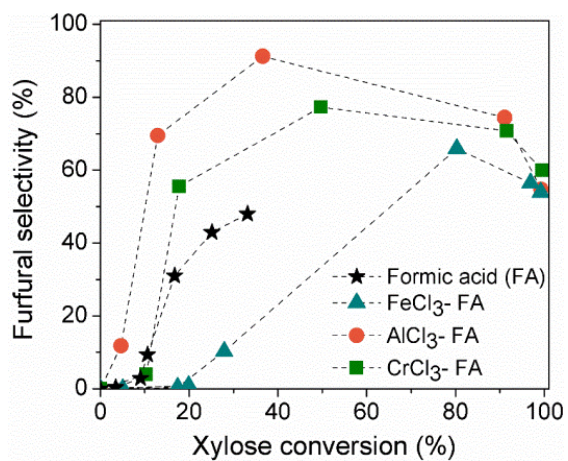


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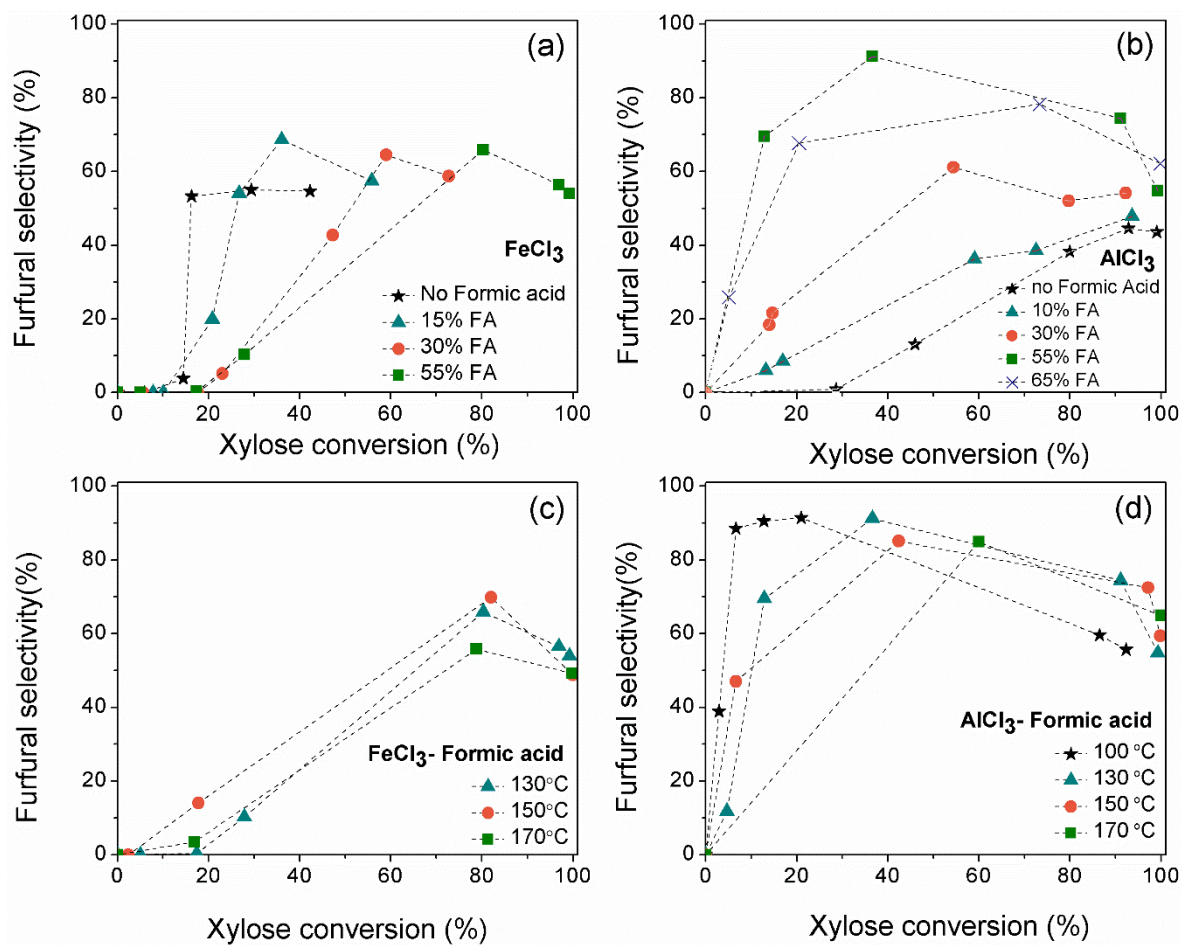
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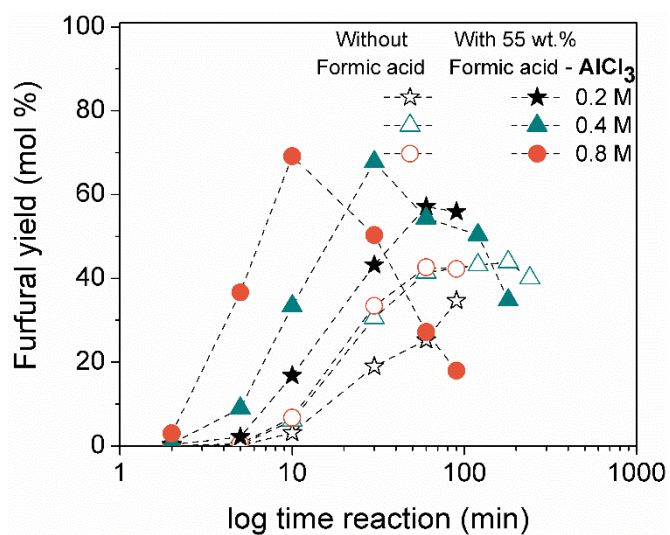
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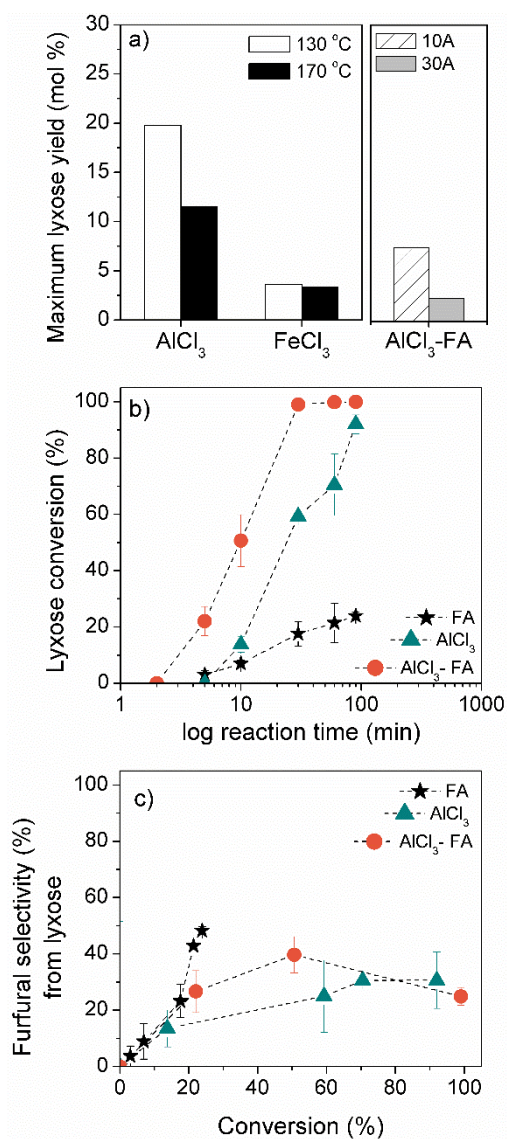
**Fig. 1.** Furfural selectivity as a function of xylose conversion using formic acid (55 wt.%) and different metal tri-chlorides (0.4 M) at 130 °C.



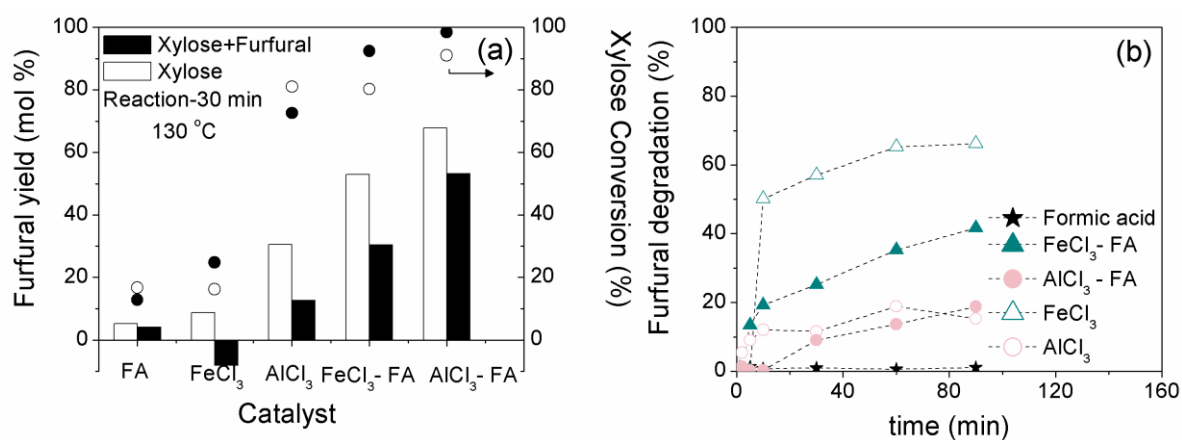
**Fig. 2.** Furfural selectivity as a function of xylose conversion using formic acid and metal tri-chlorides (0.4 M): a) FeCl<sub>3</sub> and different formic acid concentrations at 130 °C; b) AlCl<sub>3</sub> and different formic acid concentrations at 130 °C; c) FeCl<sub>3</sub>-formic acid (55 wt.%) at different temperatures; d) AlCl<sub>3</sub>-formic acid (55 wt.%) at different temperatures.



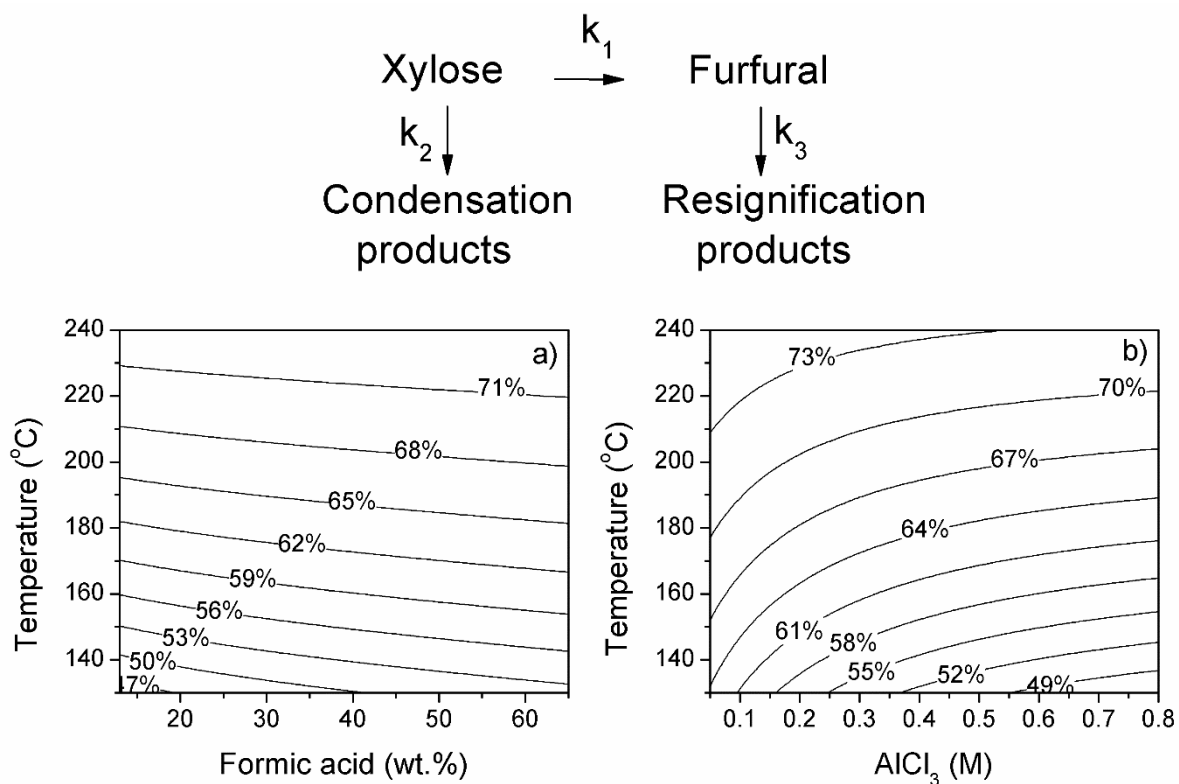
**Fig. 3.** Furfural yield as a function of reaction time using different AlCl<sub>3</sub> concentrations (0.2, 0.4 and 0.8 M) with and without formic acid (55 wt.%) at 130 °C.



**Fig. 4.** Lyxose reactivity within the conversion of xylose to furfural: a) Maximum lyxose yield from the xylose dehydration using different metal chlorides as single catalysts at 130 and 170 °C; b) Lyxose conversion in different catalytic systems at 130 °C (Initial lyxose concentration 0.4 M); c) Furfural selectivity as a function of lyxose conversion with different catalytic systems at 130 °C. Experimental conditions: 0.4 M metal chloride, 55 wt.% formic acid.



**Fig. 5.** Effect of catalysts in reactions containing furfural: a) Comparison of catalytic xylose dehydration in absence and with furfural feed, after 30 min at 130 °C; b) Time evolution of furfural degradation by different catalytic system at 130 °C. Experimental conditions: initial furfural concentration 0.15 M.



**Fig. 6:** Maximum furfural yields predicted by the simplified kinetic model of the catalytic D-xylose dehydration using an AlCl<sub>3</sub>-formic acid system as various temperatures: a) 0.38 M AlCl<sub>3</sub>; b) 60 wt.% formic acid.



**Table 1.** Kinetic parameters for the xylose dehydration in AlCl<sub>3</sub>-formic acid catalytic systems.

	<b>GF (%)</b>	<b>Parameters</b>	<b>k<sub>1</sub></b>	<b>k<sub>2</sub></b>	<b>k<sub>3</sub></b>
[XYL]=	84.5	log A <sub>[FA]</sub> (M <sup>-1</sup> s <sup>-1</sup> )	5.85	12.63	10.79
[FUR]=	74.5	log A <sub>[Cl]</sub> (M <sup>-1</sup> s <sup>-1</sup> )	7.36	11.44	9.42
		<i>E<sub>a</sub></i> (kJ mol <sup>-1</sup> )	67.20	99.52	90.81