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DOI:

[10.1088/1757-899X/742/1/012049](https://doi.org/10.1088/1757-899X/742/1/012049)

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2020

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Soetedjo, J. N. M., Rasrendra, C. B., & Heeres, H. J. (2020). *A Systematic Study on the Utilization of Inorganic Salts as Catalyst for the Conversion of Xylose to Furfural*. Paper presented at 2019 International Conference on Chemical Engineering, ICCE 2019, Bandung, Indonesia. <https://doi.org/10.1088/1757-899X/742/1/012049>

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To cite this article: Jenny N M Soetedjo *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **742** 012049

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A Systematic Study on the Utilization of Inorganic Salts as Catalyst for the Conversion of Xylose to Furfural

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Abstract. The utilization of biomass-waste such as sugar-bagasse, water-hyacinth and palm-oil-fiber as alternative sources for transportation fuels and platform-chemicals is a very active research field. Furfural (FF) is one-of-the-13 top platform-chemicals that may be converted to derivatives such as furfuryl-alcohol, furoic-acid and furan with wide applications in the gasoline, diesel and jet-fuel blending-pool. Many studies have been conducted in the mechanism and the kinetics of FF-formation from xylose since the 1940s to maximize FF-yield and to reduce FF-decomposition to undesired-products. Previous studies showed that inorganic-salt gives positive effects on the FF-yield but systematic studies are lacking. Based on it, 60 salts were screened in the hydrolysis of 0.1M xylose-aqueous-solution ($T=180^{\circ}\text{C}$, 90 minutes, batch). The maximum FF-yield was 53 mol% using 5mM- $\text{Fe}_2(\text{SO}_4)_3$. The highest FF-selectivity was at 84 mol% using 5mM-NaCl, though at low xylose-conversion (35 mol%-FF-yield). Some transition metal-chloride i.e. FeCl_2 , CuCl_2 , SnCl_2 showed interesting FF-yields (48-50%) and selectivity (58-65%) indicating interesting roles of ion Fe^{3+} and Cl^- . Subsequent studies of two salts i.e. $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 (5mM) in combination with HCl and H_2SO_4 (0.1M) were investigated (0.1M-xylose, $T=150^{\circ}\text{C}$, 0-270 min). The result shows that salts increase no FF-yields for H_2SO_4 but increase the reaction-rate. In contrast, $\text{Fe}_2(\text{SO}_4)_3$ increase no yield nor reaction-rate for HCl-catalyzed-system. In conclusion, the inorganic-salts catalyze xylose-conversion to furfural but best results were obtained using HCl without additional salts.

1. Introduction

Indonesia is the largest palm oil producer in the world with the production up to 41.5 million MT of palm oil in 2018 [CITATION Ind19 \l 1033]. Ironically, the increase of CPO production is followed by the increase of waste generated with annual production of waste up to 129-million- m^3 POME (Palm Oil Mill Effluent) and 46-million-ton EFB (Empty Fruit Bunches). Although limited amount of EFB is used as organic fertilizer, most of it is still wasted and becomes one of the major environmental problems in palm oil industry.

EFB, containing 37.3 – 46.5% cellulose and 25.3 – 33.8% hemicelluloses, is actually an excellent source of lignocellulosic biomass which is rich of C6 and C5 sugars that can be converted further into



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high-value-chemicals such as levulinic acid (**LA**) and furfural (**FF**)[CITATION Sud13 \ 1033]. In 2016, NREL (National Renewable Energy Laboratory) of U.S. Department of energy listed **FF** in the top 12 emerging near-term deployment potential biobased platform chemicals[CITATION Bid16 \ 1033]. In fact, the high need of furfural in Indonesia is reflected by its import data of 525,3 tonnes or up to 1,7 million US dollar in 2018[CITATION Bir \ 1033].

Furfural or 2-furaldehyde (**FF**) is an important non-petroleum based chemical building block used for the productions of amongst others furfuryl alcohol, furoic acid and furans that can be extended into wide range of products such as pharmaceuticals, cosmetics, resins, cleaning agent, extracting agent, solvent, vulcanizing agents, flavoring agents, pesticides, antiseptics and disinfectants[CITATION Döb32 \ 1033 \ m Cor07 \ m Sai82 \ m Zei00 \ m Bro48 \ m HEH12 \ m Yan14]. Among its wide application, the current finding of application for furfural as a feedstock to make gasoline, diesel and jet fuel has attracted so much attention[CITATION Yan14 \ 1033].

Furfural for the first time isolated in 1821 [CITATION Döb32 \ 1033] and later produced commercially since the 1920s[CITATION HEH12 \ 1033 \ m Bro48]. It is formed by the hydrolysis of hemicellulose into pentose (C5) sugars before further dehydration in **FF**. Studies have been conducted on several acids i.e. sulfuric, hydrochloric, phosphoric, and nitric acids but sulfuric acid is still the one commercially used in the industry[CITATION Sin14 \ 1033]. In fact, a number of process concepts have been implied commercially (Quacker, Agrifurane, Rosenlew, Escher Wyss) but it still has relatively limited **FF** yields (about 50% range) so far [CITATION HEH12 \ 1033]. The main reason is the involvement of decomposition reactions including fragmentation, resinification and condensation reactions from both pentoses and **FF** that form soluble side products such as formic acid, acetic acid together with insoluble solid product known as humin [CITATION Yan14 \ 1033]. The formation of humin decreases **FF** yield and causes operational issues due to the blockage and decline of heat transfer rates as well as the irreversible deposit on the solid catalyst that leads to catalyst deactivation.

Several efforts have been applied to improve **FF** yield by the use of biphasic liquid-liquid systems^{19,22,24,25}, ionic liquids²⁶⁻³⁰ and organic solvents^{17,31-35} instead of water and the addition of salts to the reaction mixture^{18,21,23}. The addition of inorganic salts have been proven to affect the chemo-selectivity of the reaction. Rasrendra *et al.* has clearly shown that the chemo-selectivity is a clear function of the type of inorganic salt. Using 0.1 M glucose in water at 140°C and 5mM salt, it was shown that Al(III) has driven the yield selection into lactic acid while Zn(II) into 5-HMF (5-Hydroxymethylfurfural)[CITATION CBR10 \ 1057]. In another study, Rasrendra *et al.* showed that AlCl₃, Cr and Sn salts has the ability to provoke the isomerisation of d-glucose to d-fructose that increases the chemo-selectivity for the reaction of d-glucose to HMF in DMSO solution[CITATION CBR12 \ 1057].

In fact several studies on salt effect have been conducted for xylose and xylotriose. The effect of chloride salts from several kation groups on xylose and xylotriose was observed by Liu *et al.* and FeCl₃ gave an increase in the rate of reaction both on the formation and decomposition of **FF** [CITATION CLi06 \ 1057] and strong effect on hemicellulose removal[CITATION LiL09 \ 1057]. A few years later Marcotullio *et al.* studied the combination of several chloride salts in homogeneous acid catalyzed system using HCl and H₂SO₄. The addition of NaCl, KI and CrCl₃ in aqueous systems has been reported in the conversion of xylose to **FF** (see Table 1). The most successful result reported by Marcotullio *et al.* with the **FF** yield of 88 mol% was reported using a mixture of KI and KCl and H₂SO₄ as the catalyst. The addition of 5 wt% of NaCl together with HCl was also shown a promising result with **FF** yield up to 81 mol%. However the studies were still focusing on the chloride salts on HCl system with only one study using the combination of NaCl and H₂SO₄ while the commercial use in industry mostly is still using H₂SO₄. This study is conducted to explore and compare the catalytic effect of other salts on both H₂SO₄ and HCl catalyzed system on the xylose conversion and **FF** yield.

Table 1. The examples of xylose conversion to **FF** by the additional salt in aqueous solution

Entry	C _{Xylose}	T (°C), t	Acid	C _{acid}	Salt	Y _{FF, max} (mol%)	Ref
1.	35 mM	200, 485 s	H ₂ SO ₄	0.05 M	KI-KCl 250-500mM	88	[CITATI

							ON Mar11 \ 1057]
2.	35 mM	200, 250 s	HCl	0.05 M	NaCl 5 wt%	81	[CITATI ON Mar09 \ 1057]
3.	56 mM	145, 300 min	HCl	0.10 M	CrCl ₃ 6 mM	39	[CITATI ON Cho12 \ 1057]
			HCl	0.10 M	-	29	

2. Experimental Procedures

All chemicals were used as received without further purification. Milli-Q water was used for all reactions and analysis procedures. Xylose (99.5%) was from Sigma-Aldrich, FF (99%) was from Fluka-Aldrich. H₂SO₄ (95-97 wt-%), HCl (37 wt-%), formic acid (98% wt-%) and all salts were purchased from Merck GmbH (Darmstadt, Germany).

The reactions were carried out in glass ampoules with an internal diameter of 3 mm, a wall thickness of 1.5 mm, and a length of 15 cm. The ampoules were filled at room temperature with a solution (0.5 cm³) of 0.1M xylose-aqueous-solution with acid catalyst and salt before subsequently sealed with a torch. A series of ampoules was placed in a rack and subsequently positioned in a constant temperature oven ($\pm 0.1^\circ\text{C}$) which was pre-set at the desired reaction temperature. At different reaction times, an ampoule was taken from the oven and directly cooled in an ice-water bath to quench the reaction. The liquid content was then filtered using a PTFE syringe filter (0.45 mm, VWR, the Netherlands). The particle free aliquot was diluted 7-8 times with water prior to analysis.

The composition of the liquid phase after reaction was determined by HPLC using an Agilent 1200 HPLC equipped with a HP 1200 pump, a Bio-Rad organic acid column (Aminex HPX-87H), and an RID or an UV detector. The mobile phase consists of aqueous sulfuric acid (5 mM) at a flow rate of 0.55 cm³/min. The column was operated at 60°C. The analysis for a sample was complete in 60 minutes.

The xylose conversion (X_{XYL}), FF yield (Y_{FF}) and FF selectivity (S_{FF}) are mol% based and calculated using equations 1-3:

$$X_{XYL} = \frac{(C_{XYL,i} - C_{XYL,t})}{C_{XYL,i}} \quad (1)$$

$$Y_{FF} = \frac{C_{FF,t}}{C_{XYL,i}} \quad (2)$$

Here, $C_{XYL,i}$ is the initial xylose concentration (mol/l), $C_{FF,i}$ the initial FF concentration and $C_{XYL,t}$ and $C_{FF,t}$ the xylose and FF concentration at a certain batchtime. For experiments using FF as the feed, the FF conversion (X_{FF}) is defined as:

$$X_{FF} = \frac{C_{FF,i} - C_{FF,t}}{C_{FF,i}} \quad (3)$$

3. Results and discussion

The studies conducted to observe the effect of anion and cation. The study on the effect of cations on the hydrolysis of xylose is presented in Figure 1 while the study on the effect of anions can be observed in Figure 2.

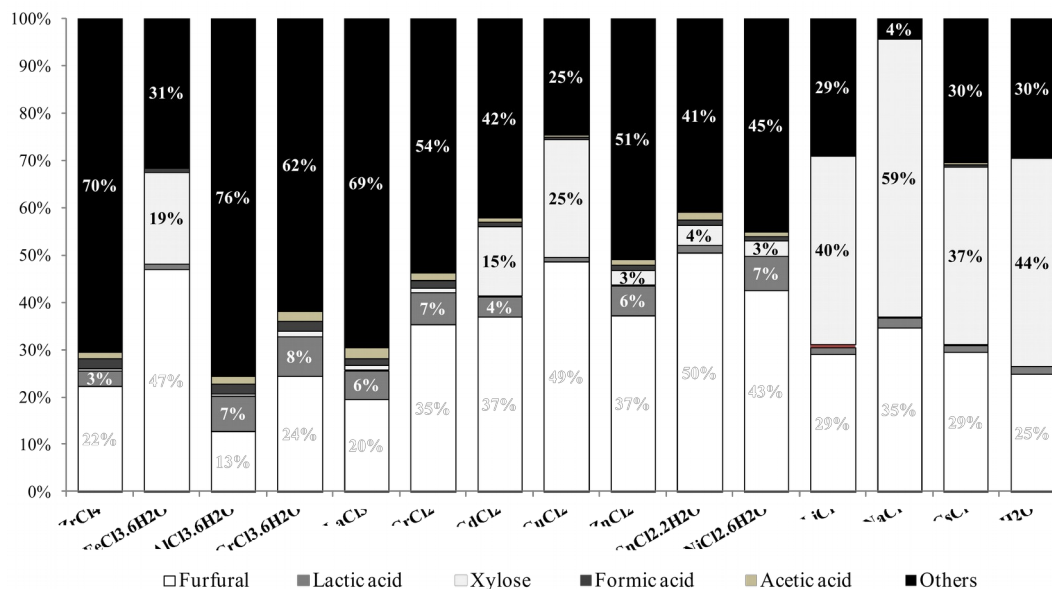


Figure 1. The effect of cations on the hydrolysis of xylose

From Figure 1, it can be seen directly that the cations give different effect on the hydrolysis of xylose. Interesting results were shown on SnCl₂, FeCl₃ and CuCl₂ and which successfully convert xylose almost 50% of FF. The last two salts together with NaCl were of the highest interest due to their low selectivity to other decomposition products indicating the important role of Fe³⁺, Cu²⁺, Na⁺ and Sn²⁺ in the hydrolysis reactions involved. In fact, NaCl is of the highest interest due to its limited transformation to other products which is only about 5%.

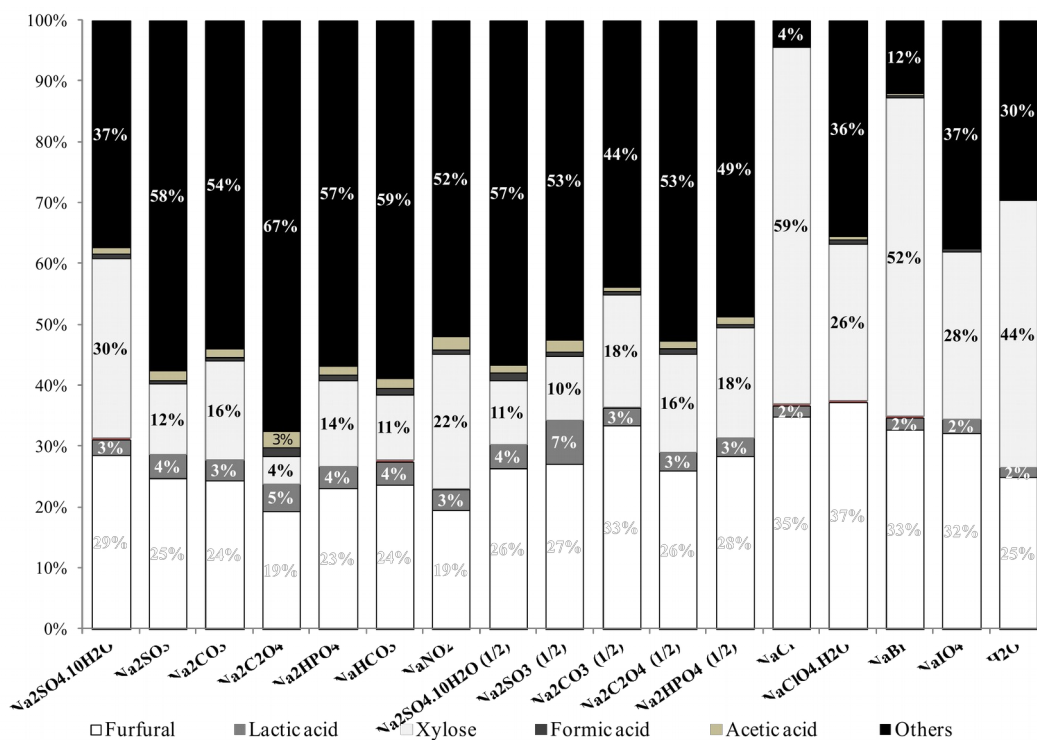
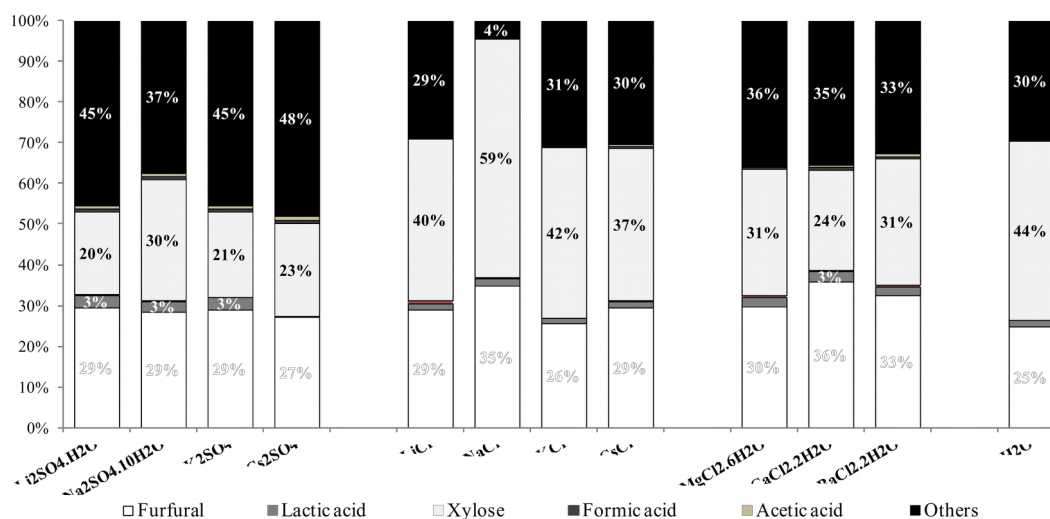


Figure 2. The effect of anions on the hydrolysis of xylose

The effect of anions can be observed in Figure 2. The results show that Cl^- and Br^- can drive the preference of reactions more to **FF** than to decomposition products. Categorizing the results into the same group of cations (see Figure 3), it shows that almost the same yield of **FF** achieved (26-36 mol-%). It confirms the previous results from Marcotullio which indicates that Cl^- in solution seems to be the main feature for the kinetics of xylose reaction and the different cations seem to play only a minor role [CITATION Mar11 \ 1057]. The most interesting result is shown again on NaCl which showed the highest selectivity on **FF**.

**Figure 3.** The effect of anions on the hydrolysis of xylose

The highest FF-selectivity was at 84 mol% using 5mM-NaCl, though at low xylose-conversion (35 mol%-FF-yield). The results showed the interesting roles of ion Fe^{3+} and Cl^- . Subsequent studies of two salts $\text{Fe}_2(\text{SO}_4)_3$ and FeCl_3 (5mM) in combination with HCl and H_2SO_4 (0.1M) were investigated on 0.1M-xylose, $T=150^\circ\text{C}$, 0-270 min. The result shows that salts increase the reaction-rate but not the FF-yields for H_2SO_4 . In contrast, $\text{Fe}_2(\text{SO}_4)_3$ increases no yield nor reaction-rate for HCl.

According to the results gained in this works, there should be different roles in the reactions between the Cl^- and H^+ or Fe^{3+} . In fact these results also confirm the acid catalyzed hydrolysis mechanism suggested by Marcotulio as shown in Figure 4.

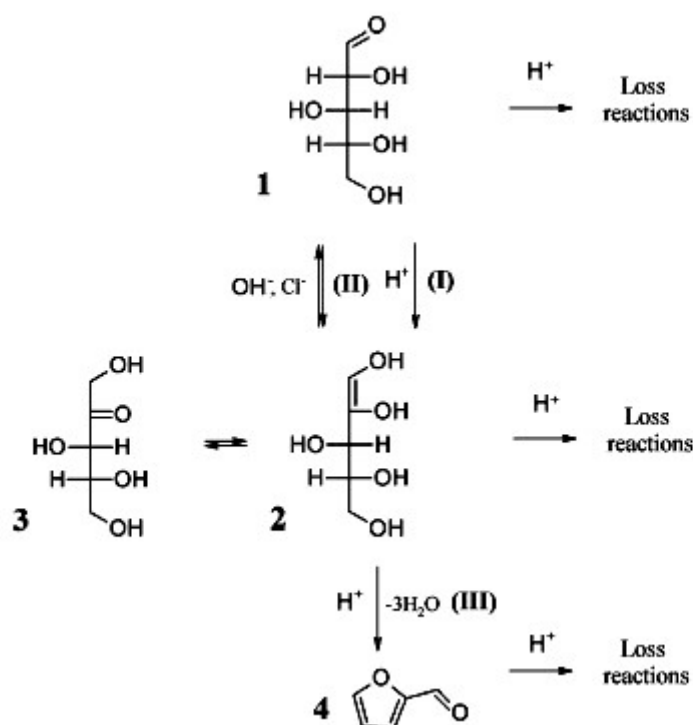


Figure 4. proposed mechanism of furfural formation from xylose with **1** Aldo form of sugar, **2** 1,2-enediol, **3** keto form of sugar and **4** FF [CITATION Mar11 \ 1057]

H_2SO_4 as the Bronsted acid donates the H^+ in reaction (I) to form 1,2-enediol or **2** and in reaction (III) to form FF. In such mechanism the presence of Cl^- as the Lewis acid of donor of electron favors the formation of the **2**, which can equilibrate with both the aldo **1** and keto **3** form of the sugar, and reacts to form furfural or **4** in presence of an acid. It seems that the speed of reaction in which the Cl^- involved is higher than the one to the loss reactions and resulted in better performance in term of FF yield. It may also explain the reason that chloride salt performed better than hydrochloric acid since HCl releases the H^+ which accelerate not only the formation of **2** but also the loss reactions. However in high concentration of chloride salt, there will be high concentration of **2** that may give a driving force to the increase of loss reactions and may give an adversed effect on the yield of FF. In fact, the presence of strong acid is needed to favor the selectivity of FF [CITATION Mar11 \ 1057]. As for the effect of Fe^{2+} there is no data available to explain its role in the proposed mechanism. However considering the acidic character of Fe^{2+} , it can be assumed to follow the function of H^+ . Further involvement of Cl^- and kation such as Fe^{2+} and Na^{2+} in the stabilization of intermediate products was proposed but still need verification and further investigastion [CITATION Mar11 \ 1057].

4. Conclusions

The addition of salts has been proven to affect the mechanism in the hydrolysis of xylose to FF. The involvement of Cl^- increase the yield of FF most probably by its catalysis role in the formation of 1,2-enediol while the involvement of Fe^{2+} may be assumed to follow the function of H^+ . Another interesting salt is NaCl that can increase the selectivity to FF up to 84mol%. Further investigation and verification is still need to be conducted to understand the role of kation and anion in salts in the mechanism of hydrolysis xylose to FF and FF decomposition.

Acknowledgement

This research was funded by RISTEKDIKTI and Parahyangan Catholic University and supported by University of Groningen. Authors wishes to acknowledge assistance or encouragement from

colleagues, special work by technical staff from University of Groningen and Parahyangan Catholic University.

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