Production of 5-hydroxymethylfurfural (5-HMF) / 2-furfural (2-F),

platform molecules for the manufacture of bioplastics, from

renewable resources

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Submitted to:

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Abstract

The growing concern regarding environmental pollution and the depletion of fossil fuel necessitated the search for an alternative renewable carbon sources to use as a feedstock to replace fossil-fuel based products and produce value-added products. HMF and furfural are bio-derived value-added products that have wide range of applications in many areas. These products have been used to produce polymers that have similar properties as the fossil-fuel based plastics. However, the large-scale production of these products is still limited due to recalcitrance nature of lignocellulosic biomasses and hence low yields of HMF and furfural. In this study, 2-F and 5-HMF were produced from eight different lignocellulosic feedstocks, cellulose, fructose, and glucose using $AlCl_3.6H_2O$ as a catalyst in water/THF biphasic system at 160 ^{0}C in oven for 60 minutes. NaCl was applied to increase the partitioning of HMF into the organic phase. The effect of reaction time, catalyst loading, and different compositions of $AlCl_3.6H_2O$ and $FeCl_3.6H_2O$ on the yields of furfural and HMF from beechwood was also examined. The highest yield of HMF was obtained from spruce biomass. Pure $AlCl_3.6H_2O$ gives the better yield of HMF and furfural than a mixture of $FeCl_3.6H_2O$ and $AlCl_3.6H_2O$. Low yield of HMF and furfural was obtained when the catalyst loading was reduced. Reduced reaction time gave reduced yields of HMF whereas the yield of furfural remains unaffected. Further experimentation is required to verify the results as only few conditions were selected for this study.

Keywords: *Hydroxymethylfurfural (HMF), Furfural (2-F), Bioplastics, Renewable, co-catalysis*

Introduction

Today, there is a growing concern about the global warming and sustainable economy due to the diminishing fossil fuel reserve and continuous increase in demand for energy and chemicals. This obliged the search for an alternative sustainable carbon sources which can be valorized to give valuable products or serve as building blocks for many useful products, such as polymers, pharmaceuticals, biofuels, etc. Lignocellulosic biomasses are renewable carbon sources which are widely abundant and can be the potential options to replace some fossil fuel-based products. Hydroxymethylfurfural and furfural are examples of value-added products that can be produced from lignocellulosic biomasses and have wide range of uses and applications in different areas. Therefore, given the increased population, fluctuating price of oil, and political insecurities, the development of efficient processes to produce these value-added chemicals will be much more important.

Hydroxymethylfurfural (HMF) is a value-added biomass-derived compound that contains multiple functional groups, namely, aromatic aldehyde, an aromatic alcohol, and a furan ring system (Figure 1 *(a)*). HMF is produced from hexoses and can be transformed into different chemical forms, such as ethoxymethylfurfural, 2,5-furandicarboxylic acid, furfuryl alcohol, dimethylfuran, and 2,5-diformylfuran[1]. These derivatives have various applications, for example, in solvents, pharmaceuticals, fungicides, resins, biofuels, and polymers. Furfural is a solvent produced from pentoses such as xylose and arabinose and it has an aldehyde group attached to the furan ring (Figure 1 (b). Furfural is a platform compound for many chemicals, including furfuryl alcohol (FFA), tetrahydrofurfuryl alcohol (THFA), methyltetrahydrofuran (MTHF), furoic acid, furfurylamine, and methylfuran[2]. HMF has a boiling point of 114-116 ^{0}C and a density of 1290 kg/m^3 while furfural boils at 161.7°C (at 1 atm) and has a density of 1160 kg/m^3. Traditionally, furfural was used for resin production (in foundry technologies) and as a solvent for lubricant production[3].

(a)

(b)
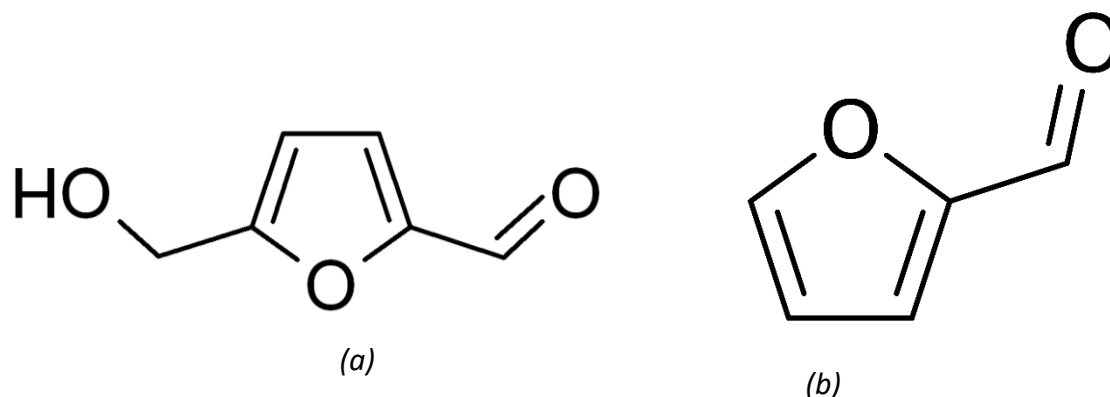
Figure 1: 5-Hydroxymethylfurfural (HMF) structure

HMF is produced by the isomerization of glucose to fructose and dehydration of glucose into HMF. HMF can also be produced from lignocellulosic biomass by hydrolyzing the glucose-based polymers (i.e., cellulose, starch, etc.) to glucose with successive isomerization into fructose and conversion into HMF. Various lignocellulosic biomasses have been studied for HMF production including, corn stover, pine sawdust, sugarcane bagasse, different weed plants, grasses, reed, popular, etc.[4]. Other lignocellulosic biomasses such as miscanthus[5] and beechwood[6] have also been studied for HMF production. The cellulose, hemicellulose, and lignin composition of the biomasses used in this study is given in Table 1.

Biomass	% Cellulose	% Hemicellulose	% Lignin	References
Oak bark	23.00-24.00	12.00-16.10	19.50-32.70	[7]
Beechwood	43.00-49.00	20.00-25.00	25.00-30.00	[8]
Spruce	39.01-42.51	34.98-35.30	23.69-26.06	[9]
Poplar	44.75 ± 2.01	20.51 ± 1.93	24.35 ± 2.74	[10]
Miscanthus	44.00 ± 4.80	25.40 ± 2.20	20.4 0± 4.80	[11]
Dialium lopense	52.00 ± 2.50	14.40 ± 1.60	23.10 ± 1.90	[12]
Dialium angolense	57.70 ± 2.50	15.10 ± 1.30	23.80 ± 1.90	[12]
Klainedoxa gabonensis	53.40 ± 2.60	12.8 0± 1.70	24.80 ± 2.30	[12]

Table 1: Composition of the Biomasses

Many furan-based polymers have been explored by researchers. 2,5-bis(hydroxymethyl)furan (BHMF)[14], 5-ethoxymethylfurfural (EMF)[15], ethyl levulinate (EL) and γ-valerolactone (gVL)[16], 2,5-bis(hydrxymethyl)tetrahydrofuran (BHMTF) and potential biofuel candidates (2,5 dimethylfuran (DMF)[17,18] are few examples which have been produced from HMF platform molecule. 2,5-furandicarboxylic acid (FDCA) is also furan-based polymer which have been recognized as one of the top 12 value-added bio-derived chemicals by the US department of energy. FDCA is used as a platform chemical for many polymers including polyamides, polyurethanes, polyesters, and epoxy resins[19]. Thus, there are remarkable applications of HMF and furfural in polymer industry. Indeed, some furan-based plastics have shown attractive performances than the traditional polymers. For example, furan-based polymers such as poly(propylene furanoate) (PPF)[20], poly(butylene furanoate) (PBF)[19], Poly(ethylene furanoate) (PEF)[21] exceed the performance of PET in terms of gas permeability. This reduces the permeability of the packages which intern increases the shelf life of the food or beverage. The reaction pathway of HMF and furfural, and some HMF and furfural-based products are given in Figure 2.

Although the market coverage of HMF is at its infancy, there is a huge market potential of its derivatives, such as FDCA for the replacement of terephthalic acid in the PET industry with around 40 MT/year market and adipic acid (~3.2 MT per year market for the nylon industry)[22]. Other polymers are also produced in huge mega tons. Therefore, the transformation into the bio-based polymers would hugely contribute to sustainable development with less impact on environment.
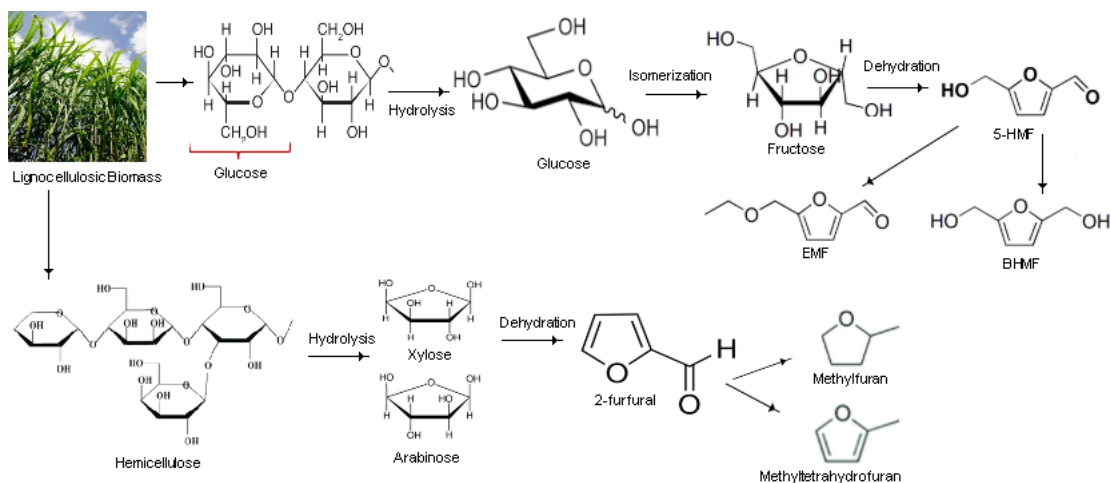

Figure 2: The reaction pathway of HMF and Furfural and their constituent products

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Nowadays, furfural and it's derivatives are produced by many countries such as China, South Africa, and the Dominican Republic from corncobs and bagasse[3]. Ideally, all pentose found in lignocellulosic biomasses can be used as a raw material and converted to furfural. The first plant for the industrial scale production of furfural was built in USA by Quaker Oats. In this process, sulfuric acid or phosphoric acid were used to hydrolyze the biomass at 153 ^{0}C. The yield of furfural was below 50 %. Owing to the low yield and other factors, the large-scale production of furfural is limited. Factors that affect the yield of HMF and furfural, include catalyst, solvent, heating method, reaction temperature, and reaction time.

Catalysts

The hydrolysis of lignocellulosic biomass, isomerization of glucose to fructose, and dehydration of fructose into HMF are catalyzed by a catalyst or a mixture of catalysts. Bronsted acids promote hydrolysis of lignocellulosic biomass and dehydration of fructose while Lewis acids (e.g., $AlCl_3$) stimulate isomerization of glucose into fructose[23]. Bronsted acids catalyze the hydrolysis of lignocellulosic biomasses by attacking the oxygen atom found in the glycosidic bond (the C-O-C linkage) of polysaccharides by the protons of the acid[24]. Whereas in the catalysis of fructose dehydration, the proton attaches to the C2 hydroxyl group of fructose thereby initiating the elimination of the first water molecule[25] (the detailed mechanism is given below). Generally, the catalyst properties, such as active species, active sites, pore size, and surface area determine the efficiency of catalysts[26].

In the mechanism of cellulose hydrolysis to glucose, a Lewis acid forms hydrated complexes in aqueous solution which helps the breakdown of the glycosidic linkages of cellulose. The water molecules coordinated with the Lewis acid act as a nucleophile to form glucose. In the isomerization step, mutarotation of the α-anomer of glucose caused by the hydrogen bonds of the anion of the Lewis acid with hydroxyl groups results in β-anomer. Subsequently, the hemiacetal portion of β-glucopyranose forms the metal enolate anion resulting in isomerization and consequent dehydration to HMF[34]. Figure 3 shows the detailed mechanism of the catalyst during hydrolysis and isomerization reactions.
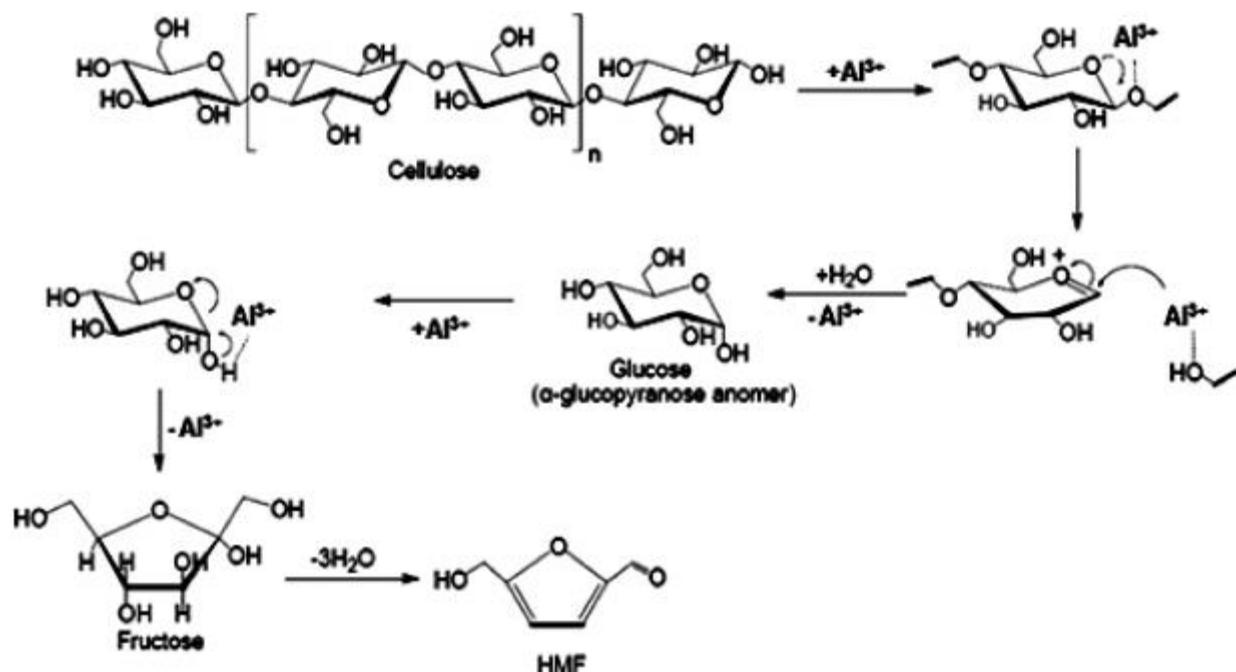
Figure 3: Proposed mechanism of AlCl₃ salt conversion of amorphous cellulose into fructose and HMF

Figure 4 shows AlCl₃ catalyzed hydrolysis of xylan and consecutive dehydration to give furfural. In this mechanism Al catalyzes xylose isomerization through a 1,2-hydride shift with successive conversion of xylulose into an oxocarbenium ion. Then, oxocarbenium ion gets deprotonated to give enol which finally loses two molecules of water to form furfural[35].
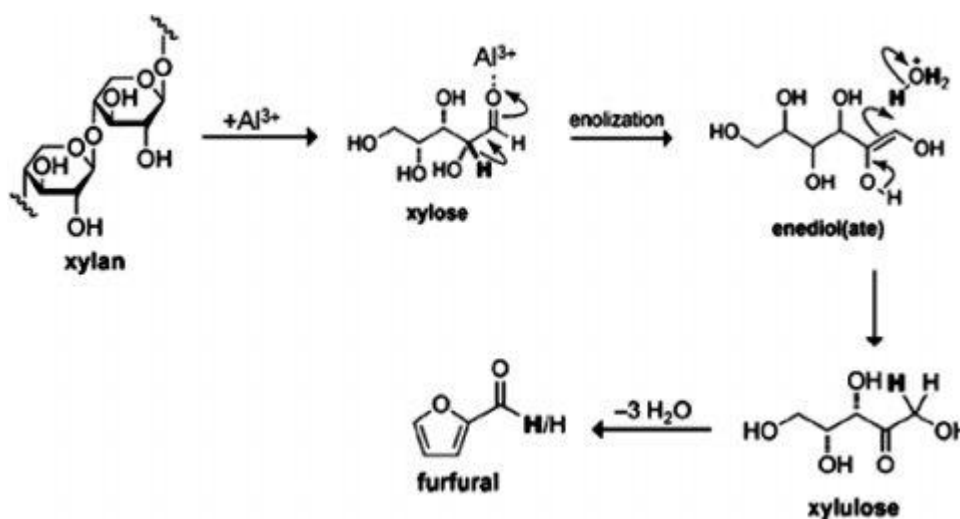
Figure 4: Mechanism of AlCl₃ catalyzed conversion of xylose into furfural through a hydride shift mechanism

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It has been reported that metal chlorides are able to catalyze both the isomerization and dehydration steps. $CrCl_2$, $CrCl_3$, and $AlCl_3$ produce good yields (i.e., 52-54%) of HMF from glucose using DMSO solvent[27]. $CrCl_2$ catalyst achieved 67% yield f HMF using ionic liquid solvent [28]. Paired catalytic system also give better HMF yield. Su et al. has proven that CuCl/PdCl were more effective in hydrolyzing the glycosidic bonds of cellulose than using strong mineral acids, such as H_2SO_4 and HCl at the same molar loading alone[29]. In addition, catalysts having both Bronsted and Lewis catalytic sites (bifunctional catalysts) allow the one-pot conversion of the lignocellulosic substrate into HMF. Yu and Tsang obtained ~21% HMF yield from bread waste and glucose by heating at 140 & 160 ^0C for 20 minutes using $SnCl_4$ that has a strong Bronsted acidity and moderate Lewis acidity[30]. H- ZSM-5 zeolite, another Lewis-Bronsted acid catalyst yielded 42% of HMF from glucose in a biphasic system[31]. Therefore, metal chlorides have a promising potential to be used for large-scale production of furfural and HMF.

Furthermore, the use of two catalysts, one having Bronsted acidity, and the other Lewis acidity can also substitute the bifunctional catalysts. Amberlyst 38 and $CrCl_3$ have been used as combined catalysts and 40% HMF yield from cellulose was observed[32]. These suggest that careful manipulation of the Lewis to Bronsted acid ratio could eliminate or reduce the undesirable reactions thereby getting high yield of HMF and furfural[33]. However, there might be chemical interactions between the catalysts which may affect the yield of HMF and furfural. In addition, the strength of the selected acids could also affect the yield of HMF and furfural. Therefore, more research is required to determine efficient Lewis-Bronsted acid compositions and optimize the ratio to get reasonable yields of HMF and furfural from lignocellulosic biomass.

Solvents

The use of solvents, such as polar aprotic solvents (e.g., dimethyl sulfoxide (DMSO), methyl isobutyl ketone and tetrahydrofuran), water, and ionic liquids enhance the dissolution of the reactants and extraction of products, and these solvents have been used to produce HMF and furfural in many studies. Solvent properties, such as partition coefficient, boiling point, and thermal stability are the major parameters affecting the performance and recyclability of solvents[36].

Among the different solvents studied for HMF and furfural production, polar aprotic solvents have a promising efficiency for HMF production. Jia et al. have obtained a 67% yield of HMF from fructose using DMSO solvent at 130 ^{0}C in the absence of catalyst[37]. More HMF yield (>90%) was also obtained with the use of Amberlyst-70 and sulfonated carbon catalysts[38].

Moreover, high HMF yield (52%) was achieved from glucose using tetrahydrofuran (THF) solvent and $AlCl_3$ catalyst[39]. However, lower yield was obtained by the same authors using water instead of THF, at the same conditions and this might be due to slow rate of HMF formation and rapid rehydration to furan ring opening products, levilininc acid (LA) and formic acid[40]. This suggests that the use of water alone as a solvent is less efficient and less viable option than polar aprotic solvents.

Methyl isobutyl ketone (MIBK), another polar aprotic solvent, have also been studied for HMF production. Due to its low solubility, MIBK forms a biphasic system with water. HMF yield of 55% have been obtained from fructose using MIBK/water biphasic solvent and HCl catalyst[41]. Ma et al. reported high yield of HMF (74%) from fructose by replacing the water partly with DMSO[42]. Although MIBK shows an attractive yield of HMF, according to Karimi and Mirzaeithere, MIBK can react with HMF to form undesirable side products[43] which arises the discourage to use MIBK for large scale production.

N,N-Dimethylacetamide (DMA), a water soluble polar aprotic solvent, was found to give 60% HMF yield from fructose and glucose using carbon based catalyst[38]. Methyltetrahydrofuran (MTHF), a new bio-derived solvent, which resembles THF yielded 555–1570 mg L^{-1} of HMF from cellulose and glucose in a biphasic system with water and levulinic acid catalyst[44]. A two-step conversion of corn stover can give 60% yield of HMF using γ-Valerolactone (GVL) as catalyst[45].

Another class of solvents which have been studied for HMF production are ionic liquids. These are salts that melt at temperatures below 100 ^{0}C. Siankevich et al. have reported an excellent yield of HMF (90%) from glucose using ionic liquid solvent and metal chloride as catalyst[46]. The same authors have reported that the yield of HMF from cellulose can be increased by adding co-solvents such as MIBK to the ionic liquids. However, there are some major drawbacks of using ionic liquids, including the high cost of ionic liquids and energy intensive process to separate HMF

and furfural from ionic liquids. Moreover, ionic liquids can be deactivated by the water produced in the dehydration step.

Yu Yang et al. have demonstrated the efficiency of THF based biphasic system which gives high yield (61%) of HMF from glucose[47]. As THF is miscible with water, addition of salts will decrease the miscibility by generating high partition coefficient and transform the solution into biphasic system. This intern improves the selectivity and yield of HMF by extracting the HMF produced in the aqueous phase into organic phase. In addition to increasing the partitioning of HMF, Román-Leshkov et al. have reported that increasing NaCl concentrations from 0 to 30 wt.% in water-2-butanol biphasic system increases the selectivity of HMF product from 65 to 90%[48]. That being the case, more investigations need to be carried out to find an optimum amount of the salt that need to be added in the reaction mixture to get a maximum selectivity and yield of HMF.

Moreover, Shi et al. found a good yield of HMF (43-53%) from cellulose by adding $NaHSO_4/ZnSO_4$ salts[49]. However, THF thermally degrades at temperatures above 180 ^{0}C which arises major challenges for processes involving intensive thermal conditions. Therefore, relatively lower temperatures could be investigated while changing the other factors to get reasonable yield of HMF and furfural. Generally, biphasic systems give better HMF yields than monophasic systems. Thus, careful selection of the two solvents is an important factor to get the highest HMF yield.

Heating Methods

Among the conventional methods of heating (such as aluminum heating block, autoclave, oil bath, and salt bath), oil bath is the most widely used method. Carraher et al. reported that using 1-L oil bath allows to reach the desired temperature in 2 minutes and only small changes in temperature (a difference in 5 ^{0}C)[51]. However, conventional heating methods take long reaction time due to low efficiency of heat transfer.

Microwave heating is one of the most attractive methods of heating that have been studied by different researchers for HMF production. Fructose was used as substrate to produce 91% of HMF within 1 minute using microwave heating[32]. Similar observations were made by different researchers using different catalysts. Rasrendra et al. used microwave based heating and

reported HMF yield of 52 %, 54 %, and 54 % using AlCl$_3$, CrCl$_2$, and CrCl$_3$ catalysts, respectively[27]. Saha et al. also found satisfactory yields of HMF using different solvents[52].

Compared to the traditional methods of heating, microwave saves up to 85-fold more energy[53]. In addition, microwave assisted heating gives increased product yields, shortens the reaction time, and diminishes the side reactions[52]. The major limitation of microwave assisted heating system is that the reacting substance must absorb microwave radiation. Therefore, microwave absorptivity of the mixture of solvents is required and possible methods of enhancing absorptivity need to be applied. Oven heating method can prevent this challenge.

Reaction temperature and time

Depending on the methods applied and/or the components of reaction, a wide range of temperatures have been examined to study the effect on the yield of HMF and furfural. According to Swift et al. temperature doesn't increase the yield of HMF but reduces the time required to reach the maximum HMF yield[54]. However, the optimum time for the reaction should be considered because the prolonged reaction can result in the loss of HMF due to the occurrence of side reactions that lower HMF yield[55]. The choice of the mixture of solvents used for HMF production also determines the degree of the HMF loss.

Challenges

There are many challenges associated with the production of HMF and furfural industrially. Small impurities can cause rapid aging of HMF due to dimer and oligomer formation[56]. Therefore, high HMF purity is required even for storage. Off-path reactions such as rehydration of HMF and polymerization between the sugars and HMF are the major challenges that reduce the product selectivity[57]. The yield is another limiting factor for the scaling up of the process. Although some conditions can give a higher yield of HMF and furfural, many factors including, the recalcitrance of the lignocellulosic biomass, efficiency of catalyst, low partitioning efficiency of the biphasic systems, etc. can affect the yield.

Moreover, the separation and purification are the major bottlenecks that halt the development of industrial scale production of HMF and furfural due to high separation cost. Besides these, there is a limited study made on the recyclability of the solvent and the catalyst in a biphasic

system which arose another limitation for the scaling up of the process. Further studies are required to look for answers to these challenges to get more economic revenue out of furfural and HMF. This study aimed to look for an optimized conditions of catalyst compositions, reaction time, and catalyst mount that give good yield of HMF and furfural from different feedstocks.

Materials and Methods

Solvents and reagents

Tetrahydrofuran (THF), $AlCl_3.6H_2O$, $FeCl_3.6H_2O$, NaCl, and Millipore water were all analytical grade chemicals provided by Gembloux Agro-Bio Tech-University of Liege.

Plant Materials and other substrates

Eight plant materials (Oak, Beechwood, Spruce wood, Poplar wood, Miscanthus straw, Dialium lopense sapwood, Dialium angolense sapwood, and Klainedoxa gabonensis sapwood), C-200 Cellulose, Glucose, and Fructose were used as substrates for 5-HMF and 2-Furfural production. The dry weight of the lignocellulosic biomasses and C-200 cellulose was analyzed using oven-dry method (drying at 105 ^{0}C for 24 hours).

Experimentation

The method used for production of 5-HMF, and 2-F was based on Yang Y. et al.[47] with some modifications. A weight of 0.2 g of each substrate (i.e., biomass or other substrates) was weighed in a Schott. A salt (1.4 g of NaCl), 4 mL of Millipore water, 12 mL (or 3 folds volume of water) of THF, and 0.4 mmol of $AlCl_3.6H_2O$ catalyst were added to the substrate. The mixture was allowed to stir mix at 900 rpm and 160 ^{0}C temperature in an oven. A reaction time of 90 minutes was applied for the lignocellulosic biomasses, 40 minutes for C-200 Cellulose, Glucose, and Fructose. A 20 minutes of reaction time was also applied for C-200 Cellulose and Fructose.

After the reaction was complete, the reaction mixture was allowed to cooldown for 20 minutes. Then the reaction mixture was poured into falcon tube and centrifuged at 1500 G for 5 minutes. The organic phase was taken from the falcon tube and poured into round-bottom flask for vacuum evaporation to remove THF. After vacuum evaporation was complete, 2 mL of Millipore water was added to the remaining residue and shaken slowly. The mixture was filtered with 0.45

μm pore size syringe into an Eppendorf. Finally, 1 mL of the sample was taken and added to HPLC vials for HPLC analysis.

In addition to the above experiment, to study the effect of different catalyst compositions on the yield of HMF and furfural from beechwood biomass, the conditions presented in (Table 2) were chosen for the study. All the weights and volumes used were the same as the previous experiment except the weight and nature of catalytic system applied. $AlCl_3.6H_2O$ and $FeCl_3.6H_2O$ were used at different molar ratio.

Experiment	$AlCl_3.6H_2O$ (mmol)	$FeCl_3.6H_2O$ (mmol)
1	0.40	0.00
2	0.30	0.1
3	0.20	0.2
4	0.10	0.3
5	0.00	0.4

Table 2: Experiment at different composition of catalysts

Moreover, another study was carried out by lowering the $AlCl_3.6H_2O$ catalyst loading from 0.4 mmol to 0.1 mmol to determine the effect of catalyst loading on the yield of both HMF and furfural. Finally, to understand the effect of reaction time on HMF and furfural yield, lower reaction temperature was applied (60 minutes).

Determination of the calibration curve

The area of the peaks from HPLC result reflect the concentration of the substances in the reaction product. To calculate the concentration of both HMF and furfural in our reaction product, a calibration curve data was given by the lab assistants in Gembloux Agro-bio Tech laboratory. The calibration curves are given in Figure 5 below. The R^2 is close to 1 which suggests the close linear relationship of the concentration with area under the peak. Therefore, the higher the are the higher the concentration of furfural or HMF. the retention time of HMF and furfural are 47.559 and 72.323 minutes respectively.
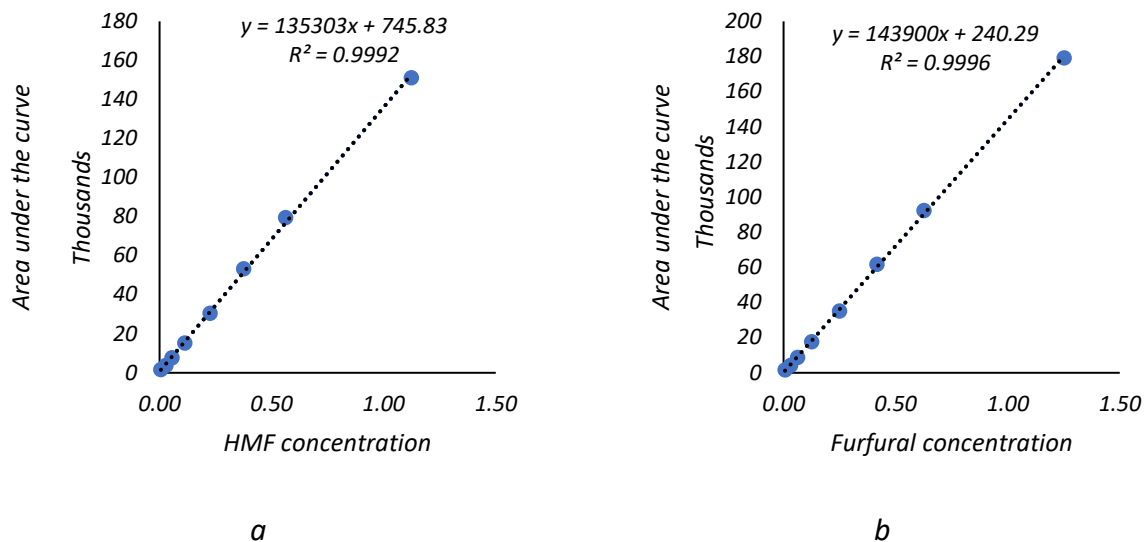
Figure 5: HMF (a) and Furfural (b) calibration curves

Result and discussion

The aim of this study was to produce 5-HMF and 2-F and to compare the yields obtained from different substrates. In addition, the study was aimed to compare the yield of 5-HMF with the yield of furfural in each substrate. All the yields 5-HMF and 2-F are in molar percentages and on the basis of the dry weight of the biomass except for glucose and fructose.

Dry weight determination

The dry weight analysis of all the biomass is given in Table 3. All the analysis for the dry weight were done in triplicate. All biomasses have a dry weight above 90%. C-200 Cellulose have the least moisture content. All the standard deviations for the determination of dry weight are low suggesting the high reproducibility and reliability of the experiments.

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Substrate	dry weight	SD
Oak bark	93.52	0.13
Beechwood	94.80	0.30
Spruce	91.44	0.23
Poplar	93.96	0.35
Miscanthus	92.50	0.21
Dialium lopense	92.96	0.38
Dialium angolense	91.11	0.27
Klainedoxa gabonensis	94.18	0.07
C-200 Cellulose	96.14	0.14

Table 3: Dry weight of all biomasses

Determination of 5-HMF, and furfural concentration

In the experiment to determine the yield of 5-HMF and 2-F, all experiments were done in triplicate except few which were done more than triplicate. But not all results were available for all the experiments due to loss of samples or unavailability of HPLC results for some samples. The raw data for the yield of 5-HMF and concentration of 2-Furfural are given in Table 44. A column graph is also given (**Error! Reference source not found.**) to show the differences in the yields for all the substrates and the difference in the yield of both 5-HMF and 2-F.

The yield of HMF and furfural from the lignocellulosic biomasses were calculated as follows:

$$HMF\ yield\ (mol\ \%) = \frac{(HMF\ concentration \times Liquid\ volume/126)}{(grams\ of\ cellulose/162)} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 1$$

$$Furfural\ yield\ (mol\%) = \frac{(Furfural\ concentration \times Liquid\ volume/96)}{(grams\ of\ hemicellulose/132)} \times 100 \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 2$$

Where 126, 96, 180, and 150 are the molecular weights of HMF, furfural (FF), glucose or fructose, and xylose, respectively[58]. A 162 g/mol of glucose and 132 g/mol of xylose were used in the calculation because the yield is based on the molecular mass after dehydration (i.e., after removal of water molecule) from glucose and xylose. Hence, the molecular mass of water (i.e., 18 g/mol) is subtracted from the molecular mass of glucose and xylose.

The HMF yield from glucose and fructose is calculated as:

$$HMF \; yield \; (mol \; \%) = \frac{HMF \; concentration \; \times Liquid \; volume/126}{grams \; of \; glucose \; OR \; fructose/180} \times 100 \; ....3[59].$$

Substrate	5-HMF yield (molar %)	SD	2-F Conc. (mg/ml)	SD	No of Experiments
Oak bark	1.38	0.58	0.45	0.34	3
Beechwood	1.15	0.46	0.36	0.13	3
Spruce	4.02	0.71	0.21	0.09	3
Poplar	0.71	0.03	0.65	0.08	3
Miscanthus	1.08	0.49	1.09	1.03	4
Dialium lopense	0.38	0.21	0.45	0.37	5
Dialium angolense	0.34	0.22	0.21	0.03	2
Klainedoxa gabonensis	1.32	0.60	1.25	0.67	3
C-200 Cellulose[a]	0.00	0.00	0.16	0.16	3
C-200 Cellulose[b]	0.58	0.00	N/A	N/A	1
Glucose	3.47	0.26	0.00	0.00	2
Fructose[b]	2.12	0.30	0.04	0.02	3
Fructose[a]	N/A	N/A	N/A	N/A	N/A

Table 4: 5-HMF yield (molar %) and conc. of 2-F of different substrates (a=20 min heating, b=40 min heating)

As can be seen from Table 44 or **Error! Reference source not found.**6 below, the highest yield of 5-HMF was obtained from spruce wood. Glucose and Fructose give the next highest yields consecutively. Yu Yang et al. have used the same catalyst and biphasic system but they obtained higher yields of HMF (61% from glucose and 26% from poplar)[47]. Compared to these results, very low yield of HMF was obtained in this study. This could be due to the difference in the method of heating applied. In this study, oven heating method was applied instead of microwave heating. In addition to the difference in the method of heating, the reaction temperature used in this study for the lignocellulosic biomass was reduced by 20 ^{0}C (i.e., 160 ^{0}C). Nevertheless, the higher

yield of HMF from spruce than from glucose remains strange and this could also be due to some possible manipulation errors during the experimentation or mistakes when taking the readings from the HPLC result. Generally, all the yield are very low as compared to the yields obtained by many researchers. Although different solvent and catalyst are used for the production of HMF, higher yield of HMF were obtained from fructose[13], beechwood[60], and miscanthus[61] than yields found in this study.
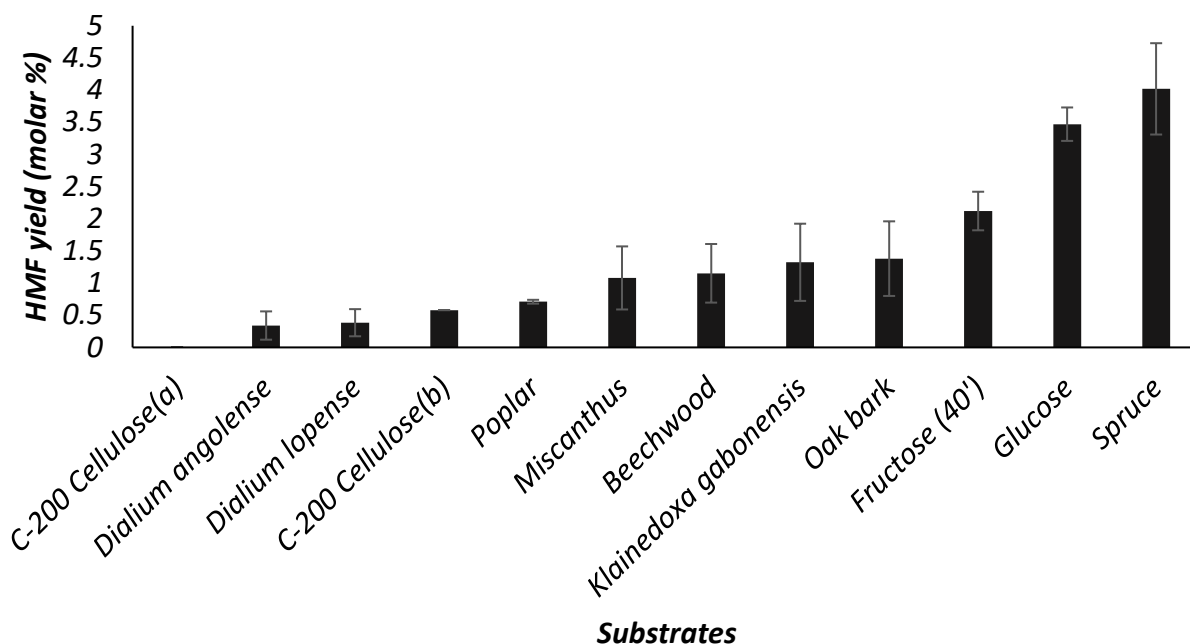

Figure 6: Yield of HMF in molar %

In Figure 77, we observe that there is no furfural produced from glucose. This is because glucose is a 6-carbon sugar while furfural is a compound containing 5 carbon atoms. Although furfural can be produced from glucose it requires an energy intensive process of decarboxylation and dehydration of glucose. Therefore, zero yield of furfural from glucose was expected. Indeed, Dutta Saikat et al. have reported that the yield of furfural from glucose is generally lower than the yield of HMF[62]. But in the case of fructose, we can see that there was some amount of furfural produced. There is quite low yield of HMF from C-200 Cellulose. However, there is even more furfural concentration in C-200 Cellulose which might have been arisen from possible mistakes in taking the readings from the HPLC result. However, we cannot rely on the concentrations to

compare the yields of furfural. Even if we consider the volumes after the vacuum evaporation were equal, the yield depends on the percentage of hemicellulose and dry weight of each biomass. Therefore, no conclusion was done on the difference in the yield of furfural for the biomasses.
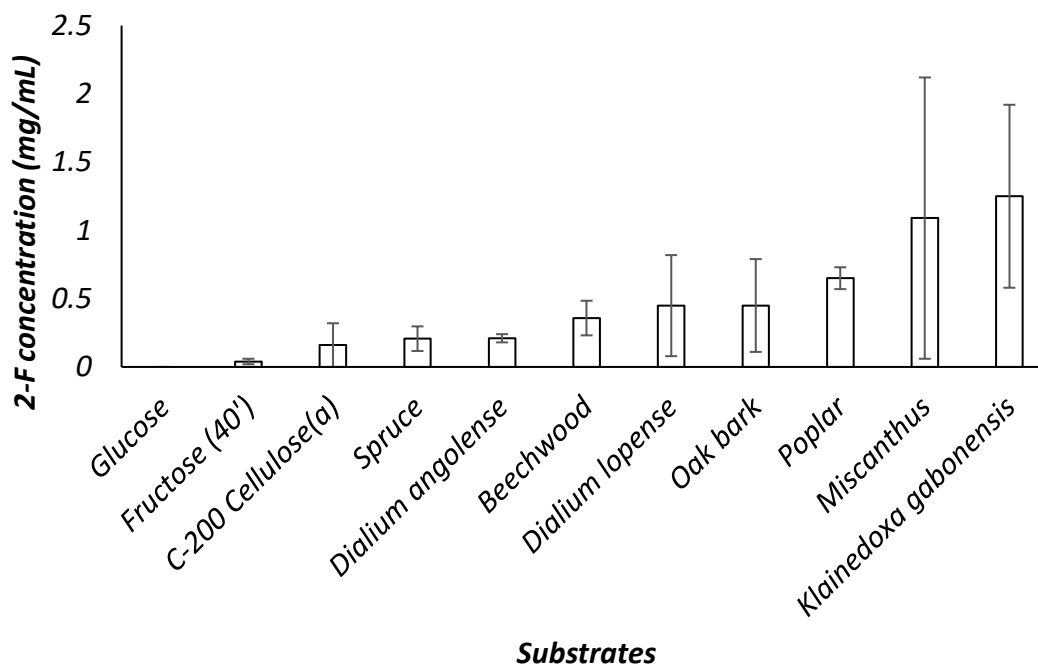

Figure 7: Concentration of 2-F for different substrates

Effect of co-catalysis on HMF and furfural yield

In another experiment to determine the effect of co-catalysis at different molar compositions of $AlCl_3 \cdot 6H_2O$ and $FeCl_3.6H_2O$ were tested. $FeCl_3.6H_2O$ has higher Bronsted acidity[63] than $AlCl_3 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ has higher Lewis acidity than $FeCl_3.6H_2O$[64]. Chao Wang et al. have obtained a higher yield of HMF when they used a combination Lewis acid and Bronsted acid than when the two catalysts were used separately[65]. It is on the basis of this principle of co-catalysis that this study was proposed, expecting more HMF yield than using $AlCl_3 \cdot 6H_2O$ alone. Four different conditions (Table 52) were selected. In addition, one more experiment was undertaken to examine the effect of $AlCl_3 \cdot 6H_2O$ loading on the yield. The yields of HMF and the corresponding furfural concentrations are given in Table 5. All these the experiments were done in triplicate.

AlCl$_3$·6H$_2$O (mmol)	FeCl3.6H2O (mmol)	5-HMF Yield (molar %)	SD	2-F yield (mol %)	SD
0.40	0.00	1.15	0.46	2.44	0.86
0.30	0.10	0.08	0.12	1.07	0.92
0.20	0.20	0.31	0.03	1.55	0.98
0.10	0.30	0.07	0.03	2.27	0.46
0.00	0.40	0.02	0.03	1.20	0.38

Table 5: 5-HMF and furfural yield at different catalyst compositions

The highest yield of both was obtained at catalyst load of 0.4 mmol of *AlCl$_3$·6H$_2$O (*Figure 8*8).* There is a significant decrease in HMF and furfural yield when co-catalysis of *AlCl$_3$·6H$_2$O* with *FeCl3.6H2O* is applied. Even when the moles of *AlCl$_3$·6H$_2$O* are reduced only by 0.1 mmol, the HMF yield gets close to zero (i.e., 0.08%) and the furfural yield also reduced significantly. This could be due to increased acidity when the two acidic catalysts are added to the reaction mixture. Fe (III) has higher pKa value than Al (III) which means Fe (III) is stronger acid than Al (III)[66]. Paul Körner et al. have reported that moderate acidity favor increased HMF yield but with increased acidity the HMF degrades into levulinic acid[67]. Shalini Aurora et al. have also investigated the effect of pH on the yield of furfural. According to these researchers, furfural yield decreased from 85 to 51% when the acidity increased from 1.0 to 3.0[68]. However, with further reduction of *AlCl$_3$·6H$_2$O* and addition of *FeCl3.6H2O* the yield slightly increased but only by small amount.

Moreover, at low catalyst loading (i.e., 0.1 mmol *AlCl$_3$·6H$_2$O*), the yield of HMF and furfural decreases (Table 6, Appendix) as compared to higher catalyst loading (i.e., 0.4 mmol *AlCl$_3$·6H$_2$O*). The increased yield at higher catalyst loading is attributed to the increase in the active sites of the catalyst and vice versa[69]. However, optimum amount of catalyst need to be determined as the catalysts may also catalyze the degradation of HMF if the catalyst are used at larger loading[70]. Generally, the low amount of *AlCl$_3$·6H$_2$O* loading and the use of the mixture of catalysts give very

low yields of HMF than pure $AlCl_3 \cdot 6H_2O$ at relatively higher catalyst loading (i.e., 0.4 mmol). Furthermore, $FeCl3.6H2O$ gives lower yield than $AlCl_3 \cdot 6H_2O$ and pure $FeCl3.6H2O$ favors the production of furfural than HMF as compared to pure $AlCl_3 \cdot 6H_2O$..
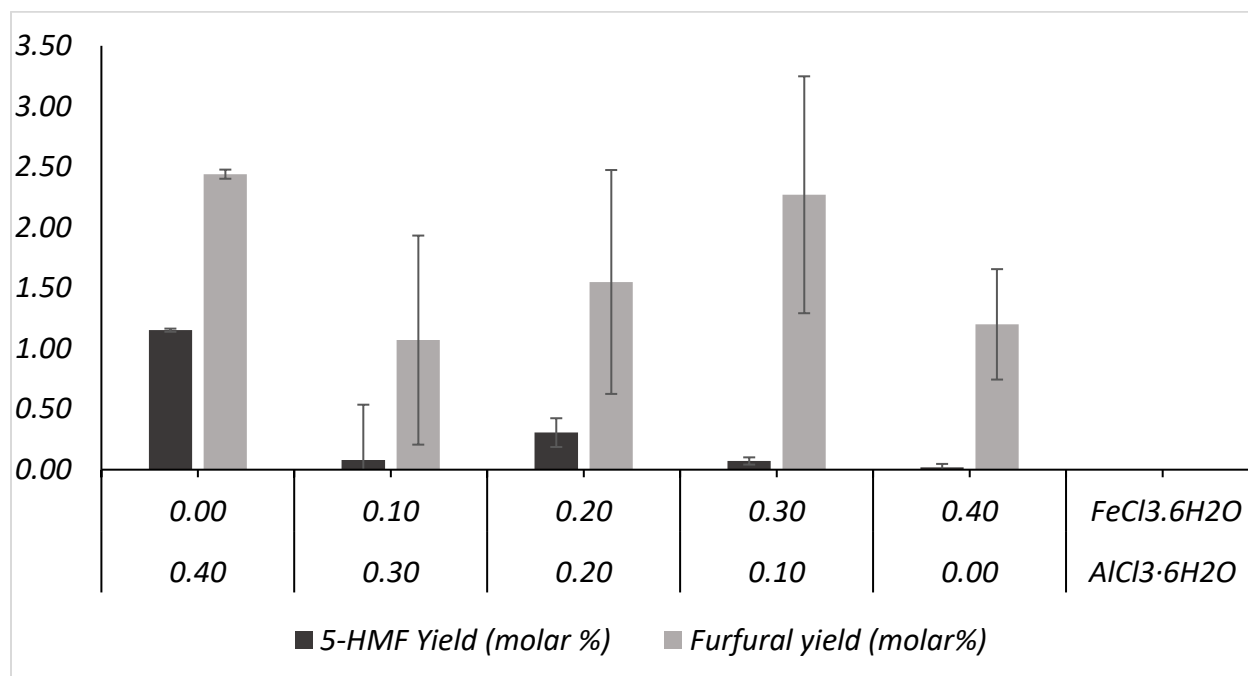

Figure 8: 5-HMF and furfural yield at different catalyst compositions

The effect of reaction time on the yield of HMF was also studied. Due to the limit in time, only one experiment (in triplicate) was done. The reaction time was lowered to 60 minutes instead of 90 and an HMF and furfural yield of 0.48 % and 2.45 % was obtained (Table 7, Appendix), respectively. As reaction time increases, the yield of HMF from fructose was observed to decrease at temperatures above 150 ^{0}C[69]. According to this, higher yield of HMF was expected than in 90 minutes of reaction time because the temperature is above 150 ^{0}C. This low yield of HMF might be due to the difference in the feedstocks used. Usually, lignocellulosic feedstocks require more reaction time than glucose and fructose due to their recalcitrant nature. However, the yield of furfural is not affected by lowering the reaction time. Therefore, no conclusion can be made on this because we cannot count on limited number of experiments to wrap up the effect of time on the yield. The yield of furfural was also determined to be almost zero for all conditions.
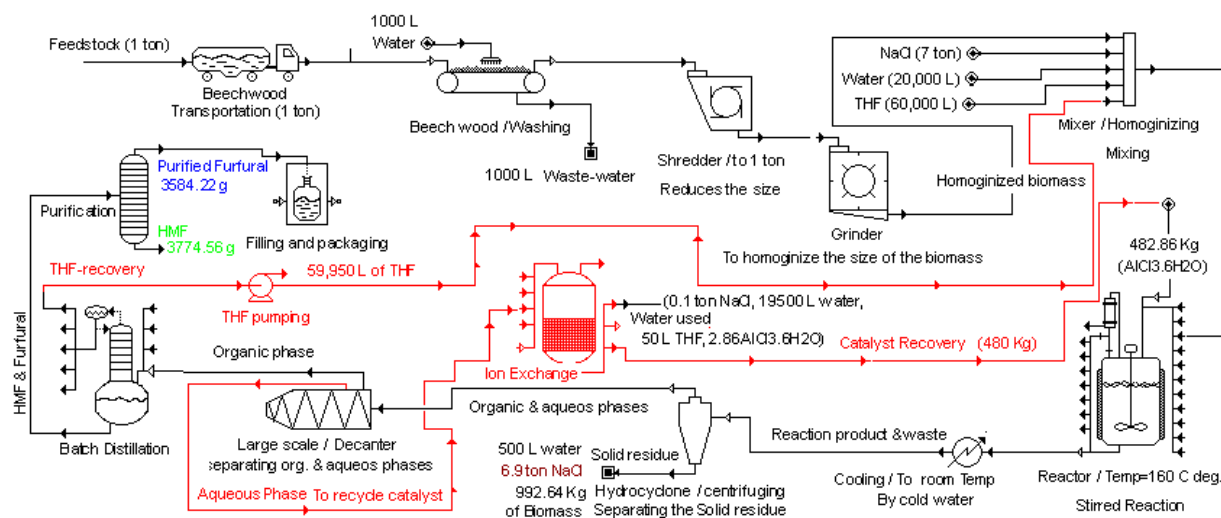
Figure 9: Flowsheet of HMF and furfural production (batch process and recycling included)

Conclusion and perspectives

In this study, HMF and furfural were produced from a variety of substrates and different yields were obtained. The effect of different catalytic compositions and reaction time were also investigated with the aim of optimizing the yield of HMF and furfural. *AlCl₃·6H₂O* showed excellent catalytic activity whereas FeCl₃.6H₂O gives reduced yields. The reaction time also showed more significant impact on the yields of HMF than on furfural. However, all the yield are quite low as compared to different literatures.

 The deployment of lignocellulosic biomasses to replace fossil-fuel based polymers is vital for a sustainable development and environmental benefit. HMF and furfural are bioderived chemicals that have a wide range of uses and applications in polymer industry. These value-added products have the potential of replacing some fossil fuel-based polymers. Various parameters affect the yields of both furfural and HMF from lignocellulosic biomass, including the nature and/or composition of the substrate, efficiency of catalyst, type of solvent, heating method, reaction temperature, reaction time, etc. Optimum reaction conditions that give high yields are required to encourage the large-scale production of HMF and furfural.

The yields of HMF and furfural have been found to increase significantly when biphasic system is used. This surmounts the inefficiencies that are observed in mono-phasic systems. Metal chlorides are also a promising catalyst whose efficiency have been reported in many studies.

Moreover, sodium chloride is an excellent partitioning agent that help improve the yield. Therefore, given the huge abundance of lignocellulosic biomasses and large market potential of HMF and furfural, further studies need be made at different reaction times using different heating methods to optimize the conditions to improve the yields of HMF and furfural. Solving these issues could inspire the expansion of large-scale production of these value-added products for various applications in bioplastic industry.

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Appendix

5-HMF Yield (molar %)	SD	2-F yield (mol %)	SD
0.00	0.01	0.04	0.04

Table 6: HMF and furfural yield at 0.1 mmol AlCl$_3$.H$_2$O loading

5-HMF Yield (molar %)	SD	2-F yield (mol %)	SD
0.48	0.0244546	2.45	0.304351

Table 7: Yield of HMF and Furfural (reaction time=60 min and AlCl3.6H2O catalyst loading= 0.4 mmol)