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Production of Furfural and Carboxylic Acids from Waste Aqueous Hemicellulose Solutions from the Pulp and Paper and Cellulosic Ethanol Industries

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PAPER

Production of furfural and carboxylic acids from waste aqueous hemicellulose solutions from the pulp and paper and cellulosic ethanol industries†

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In this paper we present a new process to produce furfural and co-products of formic and acetic acids from waste aqueous hemicellulose solutions using a continuous two zone biphasic reactor. We estimate this approach uses 67% to 80% less energy than the current industrial processes to produce furfural. An economic analysis indicates that furfural can be produced with this process at 366 US$ per metric ton which is 25% of the selling price of furfural in the U.S. market today. This analysis assumes a plant capacity of 78 kiloton per year of furfural, 12 kiloton per year of formic acid and 44 kiloton per year of acetic acid (processing 160 ton per hour of hemicellulose solutions with a xylose concentration of 10.7 wt%) and is based on the data collected in this paper. Formic acid and acetic acid are probably produced from the acid hydrolysis of formylated and acetylated xylose oligomers, respectively. Furfural is produced in a two-step process consisting of the hydrolysis of xylose oligomers followed by the dehydration of xylose monomers and then extraction of the furfural into an organic solvent. Two types of hemicellulose solutions were used as the feedstock including a hot water extract and a green liquor extract derived from Northeastern hardwood trees. The hemicellulose solution contains mainly xylose oligomers as well as glucose, arabinose, lactic acid, acetic acid, formic acid, and other minor products. We found that the reaction temperature, the space velocity, the volumetric organic to aqueous phase ratio, and the acid concentration have significant effects on the furfural production. Under the optimized condition, a furfural yield of 90% can be achieved in the reactor from the hot water extract containing 10.7 wt% xylose. A conceptual design is performed for the integration of the production of furfural, formic and acetic acids, the liquid–liquid split, and subsequent three-stage distillations. We demonstrate that high purity (>99%) of furfural, formic and acetic acids can be obtained, with a final recovery of more than 97%, 56%, and 88% of the furfural, formic acid and acetic acid, respectively.

1. Introduction

Furfural, formic and acetic acids are all important renewable chemicals considered as important chemical reagents used in

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a broad range of applications. Formic acid is mainly produced as a by-product in the manufacture of acetic acid. Acetic acid is produced both synthetically and by aerobic fermentation of ethanol.[1] Furfural is universally made from agricultural raw materials rich in pentosan, *e.g.*, corncobs, oat hulls, bagasse, *etc.*[2] Traditionally the main use of furfural is as a raw material for the synthesis of a multitude of important non-petroleum derived chemicals such as furfuryl alcohol, methyltetrahydrofuran (MeTHF) and furan. Recently, furfural and its derivatives have been used to make jet and diesel fuel range alkanes,[3–5] to serve as

Broader context

Furfural, which is derived from wood in a very inefficient process, is a promising feedstock that can be used to make a variety of fuels and chemicals. This present article describes a new process to produce furfural and carboxylic acids from waste aqueous hemi-cellulose solutions in a continuous two-zone biphasic reactor. This process produces furfural in yields up to 90% with 67 to 80% less energy requirements than the current industrial process to make furfural. An economic analysis shows that in a large industrial biorefinery, furfural can be produced at 25% of the US market price of furfural with this new technology.

a gasoline blendstock,[4,6] and to develop new generation of bio-fuels and bioplastics.[7,8] With global liquid fuel production flattening out, it is likely that the demand for furfural as a major intermediate used in the production of renewable chemicals and liquid fuels will continue to increase. However, for this to happen, more efficient processes for the production of furfural need to be developed.

Currently furfural is produced in a hydrolysis process in which sulfuric acid and significant quantities of steam are used with furfural being the primary product.[2] The ground up biomass is sprayed with sulfuric acid and then fed into a semi-batch reactor with steam. In this process the hemicellulose in solid biomass is first hydrolyzed to pentose consisting mainly of xylose, then pentose is dehydrated into furfural which is removed in the gaseous phase before it can react further to form a solid carbonaceous by-product called humins. A solid stream is also produced in this process which is made up of the leftover lignin and cellulose derived products. This solid stream is burned to generate the steam for this process. Importantly, a large portion of the biomass is converted into process heat by this energy intensive process. The overall theoretical yield for this process is 0.73 kg of furfural per kg of pentosan. For the industry practice, this process operates at only around 33% of the theoretical yield.[9]

There are waste aqueous hemicellulose solutions in several biorefinery processes including pulp and paper processes,[10–12] and the cellulosic ethanol industry. Currently, these hemicellulose sugars are either burned in paper and pulp industries to create energy during the chemical recovery process[13] or used as a very low value animal feed from the dry-mill ethanol plants. It would be economically beneficial to these industries if the waste streams could be converted into high value chemicals.

Several researchers have reported on the conversion of these hemicellulose streams into liquid fuels and chemicals.[5,10,12,14,15] For example, Vially and coworkers demonstrated that hemicellulose sugar solutions, derived from the pretreatment of wheat straw, could be used to produce the valuable chemical of lactate.[14] Researchers at University of Maine reported on an integrated process of conventional Kraft pulping together with pre-extraction of hemicelluloses for producing acetic acid and ethanol.[10,12,15] Ingram et al. developed a new bacteria to ferment C-5 sugar streams into ethanol[16] or lactic acid.[17] Keasling and coworkers have developed a step towards producing fatty-acid-derived liquid fuels and chemicals directly from hemicelluloses.[18]

The dehydration of pure xylose into furfural has been studied in both monophasic[19,20] and biphasic reactors[20–22] with the use of either homogeneous mineral acids[5,20,21] or heterogeneous solid acids[23,24] as catalysts. Several kinetics studies on the furfural production from the xylose dehydration have been reported.[20,25] The chemistry of the furfural production from xylose involves the triple dehydration of xylose into furfural, followed by undesired series and parallel reactions leading to the formation of undesired humins.[20,26] Compared to the monophasic reaction system, the biphasic reaction system exhibits better dehydration performance in terms of the furfural yield and flexibility. For example, we have recently shown that with a biphasic reactor, the furfural yield of 85% could be obtained from the pure xylose whereas with the monophasic process, the maximum furfural yield was only 30%.[20] It can be explained that, in a biphasic reactor, the furfural being made in the aqueous phase is quickly

extracted to the organic phase before it decomposes or reacts with xylose to form humins. The addition of salts to the aqueous phase was found to decrease the furfural solubility inside the aqueous phase due to the "salting out" effect.[27] Most reported experiments on the biphasic dehydration of sugar have been carried out in a batch operating mode which has a single extraction stage.[21,27] McNeff and coworkers have recently reported on the continuous production of 5-hydroxymethylfurfural (HMF) from simple and complex carbohydrates using a biphasic catalytic process.[28] In their work, solid catalysts and the organic solvent of methyl isobutyl ketone (MIBK) were used with a highest yield of HMF reported as 35%. Furthermore, in the published literature, all previous researchers have only used model sugar compounds that do not contain the impurities, which are typically present in biomass feedstocks. Our research group recently reported on a four-step process to convert these waste hemicellulose streams into jet or diesel fuel range alkanes where the first step involved the production of furfural in a biphasic reactor.[5] However, in our previous study, the furfural was produced in a batch process and it would be highly desirable to develop a continuous process for the furfural production. Furthermore, the previous process was primarily designed for the production of diesel and jet fuel range alkanes, whereas it should be more economical to produce furfural, formic and acetic acids from hemicellulose feedstocks.

The objective of this work is to optimize the reaction conditions for the furfural production (formic and acetic acids are the co-products) in a continuous flow biphasic reactor with the aqueous hemicellulose solution as the feed, which is representative of a by-product that could be produced in the pulp and paper industries. These feedstocks contain mainly xylose oligomers and are produced by extracting hardwood chips with either hot water or green liquor in a custom-built rotating digester at the University of Maine Process Development Center. Fig. 1 depicts the overall reaction chemistry for the production of furfural and carboxylic acids (mainly formic and acetic acids) from xylose oligomers inside the continuous biphasic reactor. The furfural production consists of two steps. The first step involves the acid-catalyzed hydrolysis, where xylose oligomers are hydrolyzed under a mild condition to xylose monomers in an aqueous media. In the second step, xylose is converted into furfural via the biphasic dehydration, in which most of the furfural produced is extracted into the organic phase. During the reactions, some decomposition by-products of humins are formed from either the
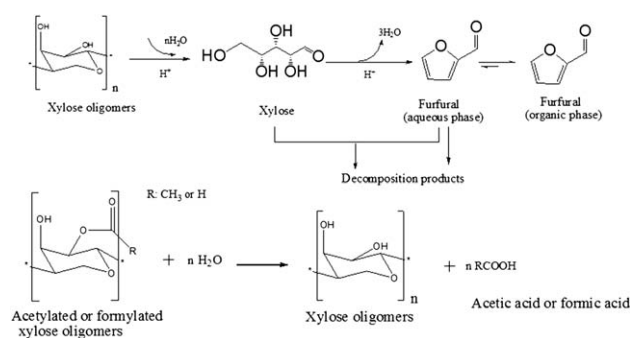

Fig. 1 Overall reaction chemistry for the production of furfural, formic and acetic acids from xylose oligomers.

self-polymerization of furfural or the cross-polymerization between furfural and xylose.[2,29] The origins of formic acid and acetic acid probably come from the elimination of formyl and acetyl groups originally linked to xylose oligomers (*i.e.*, formylated and acetylated xylose oligomers), respectively, *via* the acid-catalyzed hydrolysis.[2] The ratio of acetyl to formyl groups is usually in the order of 10 : 1 for most woods.[2] It should be noted that formic acid can also be formed as a result of hydrolytic fission of the aldehyde group in furfural.[26,30] In this paper, we will also perform a conceptual design and a preliminary economic analysis for this process and compare it to the currently existing furfural production processes.

2. Experimental and materials

2.1. Materials

All hemicellulose solutions were obtained from the University of Maine.[13,31] Two sources of wood chips, *i.e.*, Mixed Northern Hardwood (MNH) chips and aspen strands, were used to make hemicellulose extracts. The majority of experiments was carried out by using MNH chips. The MNH chips were obtained from Red Shield Pulp & Chemicals (Old Town, ME, USA) and aspen strands were produced at the University of Maine Advanced Engineering Wood Composite Center. The MNH chips consist primarily of maple ($\sim$50%) with lesser amounts of beech, birch and poplar, with a composition of 42.1% glucan, 18.3% xylan and 24.2% lignin.[32] The MNH chips were screened to include only chips which passed through 22 mm round hole screens and collected on a screen with 16 mm round holes.[13] The aspen strands have a dimension of 10.2 cm in length with a thickness of 0.8 mm. After screening, all wood chips were dried, then extracted with either hot water or green liquor (a solution mixture of sodium carbonate, sodium sulfide and sodium hydroxide[13]) in a custom-built pilot-scale rotating digester. Typically in each batch, 7 kg of wood (on an oven-dry basis) was added to the digester at a liquor to wood ratio of 4 : 1. The extraction was performed at a maximum temperature of 160 °C for a target H-factor of 360 h, under which the extract we obtained is composed of mostly xylose oligomers with 17 xylose units estimated by the gel permeation chromatography at the University of Maine. Dionex ion chromatogram shows that the hemicellulose extract also contains small amounts of xylose oligomers with the polymerization degree ranging from 1 to 14 (see Fig. S1 in the ESI†). The hemicellulose solutions containing the xylose content of equal or lower than 10.7 wt% were used as received. It should be noted that the 10.7 wt% hemicellulose extracts were concentrated by the evaporation of unconcentrated extracts (about 2 wt%) at the University of Maine. The hemicellulose solutions with the xylose content higher than 10.7 wt% were obtained by using a rotary evaporator (Model R-210, BUCHI Corp.) in our lab to further concentrate the hemicellulose extract at 40 °C. In order to quantify the content of xylose monomers in the feed, a small amount of the hemicellulose extract was taken to do acid hydrolysis, which was conducted at pH 1.0 with sulfuric acid at 130 °C for 30 min in an autoclave.[13] Tetrahydrofuran (THF, 99+%), 2-butanol (certified), NaCl (granular), and HCl (37 wt%) were all purchased from Fisher Scientific and used as received.

2.2. Experimental and analysis

A schematic of the continuous flow system used in this work is shown in Fig. 2. A high pressure stainless steel tubing served as the two-zone biphasic reactor. For the reactor with a half inch outer diameter, the glass beads (4 mm, McMaster) were packed into the first zone with 10 inches in length, and the quartz tubings (1 mm i.d. × 2 mm o.d. × 2 mm length, Quartz Scientific) were packed into the second-zone with 9 inches in length. For the reactor with one inch outer diameter, the glass beads (6 mm diameter, Fisher Scientific) were packed into the first zone with 9 inches in length, and the quartz tubings (4 mm i.d. × 6 mm o.d. × 6 mm length, Quartz Scientific) were packed into the second-zone with 20.7 inches in length. The first zone was designed for the acid hydrolysis of aqueous hemicellulose solutions, *i.e.*, the depolymerization of xylose oligomers into xylose monomers and the hydrolysis of formylated and acetylated xylose oligomers into formic acid and acetic acid, respectively. The second zone was designed to dehydrate xylose monomers into furfural. The two zones were outfitted with thermocouples. Each zone was heated by using a heating tape, and the temperature of each zone was controlled separately by two temperature controllers obtained from Cooper B-Line. Two high pressure HPLC pumps obtained from Varian (Model Prostar 210) and Eldex (Model 2LM) were used to draw from an aqueous phase and an organic phase reservoir, respectively. The aqueous phase was prepared by first adding sufficient amounts of NaCl into the hemicellulose solution, then the resulting mixture was centrifuged at 8000 rpm for 30 min to remove solid precipitates, and finally the required amount of HCl or H_2SO_4 was added into the centrifuged sugar solutions before feeding to the reactor. We observed that the amounts of NaCl required to saturate the hemicellulose solution varied with the xylose concentration in the hemicellulose extracts. Typically, 20 g NaCl was needed to saturate 100 g unconcentrated hemicellulose solutions (about 2 wt% xylose). Compared to high amounts of salts (30 wt%) used in biphasic systems where the aqueous phase contains the model sugar
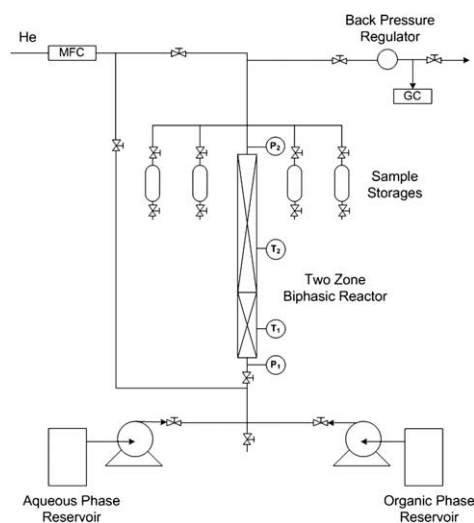

Fig. 2 Schematic of the continuous flow system used for the production of furfural, formic and acetic acids from waste aqueous hemicelluloses solutions.

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Energy Environ. Sci., 2011, **4**, 2193–2205 | 2195

compounds and pure water,[5,33,34] low amounts of NaCl were able to saturate the waste hemicellulose solutions, possibly due to the presence of many impurities including inorganic salts, sugar degradation products, acids, solid lignins, and other minor compounds in the wood-derived sugar streams. For the concentrated hemicellulose extracts ($\geq$ 10.7 wt% xylose), even less amounts of NaCl were needed to saturate the aqueous phase, *e.g.*, 5 g NaCl was needed to saturate 100 g hemicellulose solutions of 10.7 wt% xylose. As a result, the aqueous phase consisted of the centrifuged hemicellulose solution, NaCl, and the acid catalyst of HCl or H_2SO_4. The NaCl-pretreated THF was primarily used as the organic phase due to its great affinity for furfural, low-boiling point, and ease of separation from water. For comparison, 2-butanol was used as the organic phase for selected conditions. Before starting the reaction, the reactor was first purged with helium to remove air, then charged to 300 psig helium pressure. The back pressure regulator (Swagelok, CT) was used to maintain a closed reaction system. For all runs, the back pressure was set constant at 800 psig. The temperature of each zone was elevated to the respective setting value and was stabilized for at least 30 min before the biphasic feeds were pumped into the reactor. Both the aqueous phase and organic phase were pumped through each feed line at the same time. Two feed lines were connected together *via* a cross union and co-fed into the first zone of the reactor. For each run, three data points were collected at least every 3 h after it reached the steady state.

The biphasic products were analyzed by using a Shimadzu high performance liquid chromatography (HPLC) equipped with both UV and RI detectors. The contents of xylose, glucose, and arabinose were detected with an RI detector (RID-10A, cell temperature 30 °C). The concentrations of furfural, formic acid, acetic acid, lactic acid, and HMF were detected with a UV-vis detector (SPD-20A) at a wavelength of 254 nm. The column was a Biorad©Aminex HPX-87H sugar column, and the column oven temperature was held constant at 30 °C. Isocratic elution mode was used with the mobile phase of 0.005 M H_2SO_4 at a flow rate of 0.6 ml min^{-1}. Authentic samples of D-xylose, D-glucose, arabinose, furfural, acetic acid, formic acid, HMF and lactic acid in water or THF or 2-butanol were used as standards and calibrated curves were used for quantification. The total organic carbon (TOC) amounts of liquid samples were analyzed with a Shimadzu Total Organic Carbon analyzer (Model VCPH).

Experimental data obtained from this research, literature information, and the ASPEN Engineering Suite[35,36] software were used as a basis for the conceptual design, simulation and economic analysis of this process. A rigorous simulation was built for the distillation systems. For the simulation of distillation systems, the properties of pure components were taken from the Aspen Plus databank.[35] The UNIQUAC model was used to describe non-idealities in the liquid phase. The UNIQUAC parameters for binary mixtures were also taken from the Aspen Plus databank,[35] except those for the binary mixtures of THF–formic acid and THF–furfural estimated with group contribution methods by Aspen Plus,[35] and those for the binary mixture of furfural–acetic acid taken from the literature.[37] Vapor phase dimerizations of formic and acetic acids were taken into account by Hayden-O'Connell model.

Economic analysis was performed using the Aspen Icarus Process Evaluator,[36] an industry standard costing tool, to estimate the costs of installed equipments and associated utilities for this process.

2.3. Calculations

The xylose conversion and furfural selectivity were calculated as shown below. Assuming that the xylose solubility in THF is negligible, the xylose concentration (micromoles ml^{-1}), [Xylose], represents the aqueous phase concentration.

$$\text{Conversion} = \frac{[\text{Xylose}]_{\text{feed}} \times V_{\text{feed}} - [\text{Xylose}]_{\text{aq.}} \times V_{\text{aq.}}}{[\text{Xylose}]_{\text{feed}} \times V_{\text{feed}}} \times 100\%$$

$$\text{Selectivity} = \frac{[\text{Furfural}]_{\text{aq.}} \times V_{\text{aq.}} + [\text{Furfural}]_{\text{org.}} \times V_{\text{org.}}}{[\text{Xylose}]_{\text{feed}} \times V_{\text{feed}} - [\text{Xylose}]_{\text{aq.}} \times V_{\text{aq.}}} \times 100\%$$

V represents the phase volume (ml), and the reaction yield is defined as the product of conversion times selectivity.

3. Results and discussion

3.1. Furfural production in a continuous two zone biphasic reactor

3.1.1. Feed and product analysis. As described in Section 2.2 we have designed and built a continuous two-zone biphasic reactor for the production of furfural, formic and acetic acids from aqueous hemicellulose solutions. Table 1 summarizes the data for furfural production by using the reactor. Table 2 shows the chemical compositions of hydrolyzed and un-hydrolyzed hot water extracts derived from the MNH chips. The un-hydrolyzed extract contains mainly xylose oligomers as well as a small concentration of monomeric sugars, acetic and formic acids liberated from hemicellulose polymers, trace amounts of lactic acid, solid lignin, sugar degradation products like furfural and HMF, and other minor products. After the acid-hydrolysis, the hydrolyzed extract contains mainly xylose monomers and acetic acid. It should be noted that the hemicellulose solutions we used in this work were un-hydrolyzed extracts. The acetic acid content increases from 70.4 mmol l^{-1} to 308.4 mmol l^{-1}, probably due to the acid-hydrolysis of acetylated xylose oligomers as indicated in Fig. 2. The furfural content increases from 9.8 mmol l^{-1} to 35.6 mmol l^{-1} most likely due to the degradation of xylose. The glucose degradation product of HMF is not generated in measurable quantities for both un-hydrolyzed and hydrolyzed extracts. For the hydrolyzed extract, about 60 wt% of the total organic carbon amount can be identified. The remaining carbon is probably present as lignin or unidentified carbohydrate polymers. An analysis of the compositions for both the organic and aqueous products after a typical reaction (*i.e.*, Run 7) in the one inch reactor is also shown in Table 2. As can be seen, the organic phase contains mainly furfural, acetic acid, formic acid as well as trace amounts of HMF. No sugars were detected in the organic phase. The aqueous phase contains mainly formic acid, acetic acid as well as residual amounts of xylose, glucose and their degradation products of furfural and HMF.

3.1.2. Effect of the reaction temperature. The combined acid hydrolysis of xylose oligomers and the dehydration of xylose

Table 1 Furfural production by the dehydration of aqueous hemicellulose solutions in a continuous two-zone biphasic reactor. Feed for reactions were hemicellulose solutions containing 1.9–20 wt% xylose. THF was used as the organic solvent except for Runs 35 and 36 where 2-butanol was used. The Mixed Northern Hardwood chips were used as the wood source of hemicellulose solution for all runs except for Run 37. Sufficient amounts of NaCl were added to saturate the hemicellulose solution except for Run 35 where there was no NaCl added. For Runs 1 through 6, the reactions were conducted in the half inch reactor, and those after Run 6 in the one inch reactor. The back pressure was set at 800 psig for all runs

Run #	$T_1{}^a$/°C	$T_2{}^a$/°C	Xylose/wt%	$[H^+]$/M	$V_{org}/V_{aq.}{}^b$	LHSV^c/h^{-1}	$[Fur]_{aq}$/g l^{-1}	$[Fur]_{org}$/g l^{-1}	R^d	Xylose conv.	Fur. select.	Fur. yield
1	110	164	1.9	0.44	1.0	0.56	0.35	10.32	25.8	98.8	76.4	75.5
2	110	164	1.9	0.44	1.0	1.12	0.45	7.98	17.7	95.4	81.8	78.1
3	110	164	2.2	0.44	1.0	1.68	0.35	6.32	18.1	45.3	87.1	39.5
4	110	164	1.9	0.44	1.0	2.80	0.19	5.85	30.8	42.1	85.1	35.8
5	110	164	1.9	0.44	1.0	5.61	0.2	5.81	29.0	24.6	69.6	17.3
6	110	200	2.7	0.44	2.2	1.40	0.44	12.02	30.1	99.4	88.4	87.9
7	110	200	10.7	0.44	2.0	1.44	1.8	30.7	17.1	97.8	92.0	89.8
8	110	200	10.7	0.22	2.0	1.44	1.9	32.5	17.1	94.5	79.4	75.0
9	110	200	10.7	0.33	2.0	1.44	2.0	30.6	15.3	97.1	86.4	83.9
10	110	200	10.7	0.57	2.0	1.44	2.2	30.5	13.9	100	84.0	84.0
11	110	200	10.7	0.44	1.8	1.62	1.4	28.2	20.1	89.9	87.4	78.6
12	110	200	10.7	0.44	1.3	1.62	2.2	36.2	16.5	81.7	90.0	73.5
13	110	200	10.7	0.44	0.9	1.62	3.2	44.7	14.0	74.2	91.5	67.9
14	110	200	10.7	0.44	0.5	1.62	5.9	67.4	11.4	57.2	93.9	53.7
15	110	160	10.7	0.44	2.0	1.44	1.1	22.4	20.4	57.8	94.1	54.4
16	110	180	10.7	0.44	2.0	1.44	1.0	31.7	31.7	85.0	93.2	79.2
17	110	220	10.7	0.44	2.0	1.44	1.6	30.1	18.8	99.4	90.5	90.0
18	70	200	10.7	0.44	2.0	1.44	2.4	33.5	14.0	97.3	87.5	85.1
19	140	200	10.7	0.44	2.0	1.44	2.4	32.5	13.5	100	86.8	86.8
20	110	210	3.2	0.44	2.3	1.36	0.6	12.8	21.8	100	92.2	92.2
21	110	210	10.7	0.44	2.3	1.36	1.9	31.9	16.8	100	89.9	89.9
22	110	210	16.0	0.44	2.3	1.36	2.9	36.3	12.7	100	82.4	82.4
23	110	210	20.0	0.44	2.3	1.36	3.0	44.0	14.9	100	80.0	80.0
24	110	210	16.0	0.44	2.7	1.54	2.3	33.9	14.8	100	85.4	85.4
25	110	180	10.7	0.44	1.5	1.2	1.5	39.6	26.4	94.7	85.6	81.0
26	110	220	10.7	0.44	2.2	1.5	1.6	29.4	18.4	98.3	92.1	90.6
27	110	170	10.7	0.44	2.4	1.08	0.8	16.9	21.1	80.3	81.7	65.6
28	110	180	10.7	0.44	2.7	1.32	1.1	23.4	21.3	98.0	74.0	72.5
29	110	180	10.7	0.44	1.1	1.02	1.9	36.1	19.0	95.1	79.0	75.1
30	110	180	10.7	0.22	1.1	1.02	2.4	38.3	16.0	98.2	63.0	61.9
31	110	180	10.7	0.44	0.7	0.78	3.4	55.0	16.2	98.2	62.9	61.7
32	110	180	10.7	0.44	1.8	1.02	1.3	29.4	22.6	99.9	72.2	72.1
33^e	110	200	10.7	0.48	2.0	1.44	1.9	31.9	16.8	100	89.1	89.1
34^e	110	200	10.7	0.48	2.4	1.62	1.6	29.3	18.3	98.8	91.8	90.7
35^f	110	200	10.7	0.44	2.1	1.39	7.4	27.5	3.70	95.0	72.3	68.6
36^g	110	200	10.7	0.44	2.1	1.39	10.6	43.7	4.1	99.5	78.4	78.0
37^h	110	200	3.4	0.44	2.0	1.44	0.65	15.5	23.8	98.7	91.4	90.2
38^i	110	200	4.0	0.44	2.3	1.36	0.28	4.5	16.1	96.5	48.1	46.4
39^i	110	200	4.0	0.66	2.3	1.36	0.4	4.8	12.0	97.1	60.9	59.1

^{a} T_1—the first-zone temperature, T_2—the second-zone temperature. ^{b} $V_{org}/V_{aq.}$—the volumetric of organic to aqueous phase ratio. ^{c} LHSV is defined as the volumetric flow rate of feed solution divided by the volume of packing materials in the second zone reactor. ^{d} $R = [Furfural]_{org}/[Furfural]_{aq.}$ (g l^{-1} : g l^{-1}). ^{e} H_2SO_4 as the acid catalyst. ^{f} 2-Butanol without adding NaCl. ^{g} 2-Butanol with adding NaCl. ^{h} Mixed 62aspen/38MNH strand was used as the wood source. ^{i} Green liquor as the feed.

Table 2 Chemical compositions of the hot water extract derived from MNH chips and biphasic products obtained from Run 7 in the one inch reactor. The reaction conditions: $T_1 = 110$ °C, $T_2 = 200$ °C, LHSV = 1.44 h^{-1}, $V_{org}/V_{aq.} = 2.0$, and [HCl] = 0.44 M

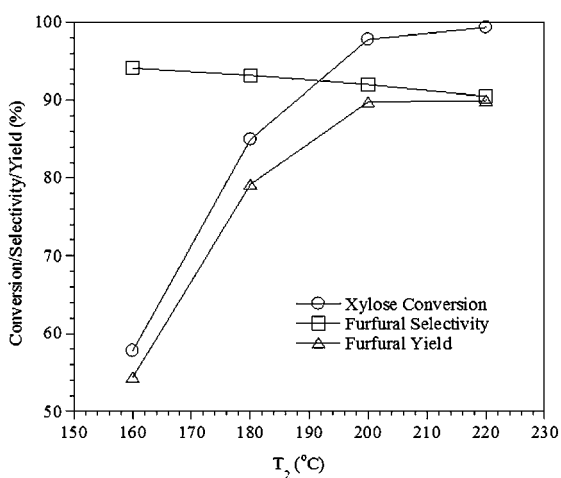| Composition	Feed concentration/mmol l^{-1}		Aqueous product/mmol l^{-1}	Organic product/mmol l^{-1}
	Before hydrolysis	After hydrolysis		
Xylose	171.1	713.0	20.3	—
Glucose	20.7	62.6	10.0	—
Arabinose	38.5	38.5	—	—
Acetic acid	70.4	308.4	63.9	296.4
Lactic acid	2.11	7.10	—	—
Formic acid	22.6	25.2	106.7	132.3
Furfural	9.8	35.6	18.4	319.8
HMF	—	—	2.62	20.4
TOC (ppm)	99 992		41 891.6	
Identified C	16 727.16	59 692.8	6044.6	32 986.5

Fig. 3 Effect of the reaction temperature T_2 on furfural production. Reaction conditions: $T_1 = 110\,°C$, equal feed xylose concentration of 10.7 wt%, LHSV = 1.44 h^{-1}, [HCl] = 0.44 M, and in the one inch reactor.

monomers were conducted in the two-zone biphasic reactor. The flow rates for the organic to aqueous phase were 3.2 cm^3 min^{-1} and 1.6 cm^3 min^{-1}, respectively. The effect of the reaction temperature of each zone on the furfural production was studied using water–THF as a solvent with HCl as the catalyst. A series of runs were first carried out by varying the first-zone temperature (T_1) from 70 °C to 140 °C with a fixed second-zone temperature (T_2) of 200 °C (Runs 7, 18 and 19). The furfural yield went through a slight maximum of 89.8% at 110 °C, and 85.1% and 86.8% at 70 °C and 140 °C, respectively.

Next, a series of runs, i.e., Runs 7, 15, 16, and 17, were conducted by varying the temperature of T_2 from 160 °C to 220 °C with the fixed temperature of T_1 of 110 °C. Fig. 3 shows the influence of T_2 with respect to the xylose conversion, furfural selectivity and yield. The xylose conversion and furfural yield increased with increasing temperature showing maximums of
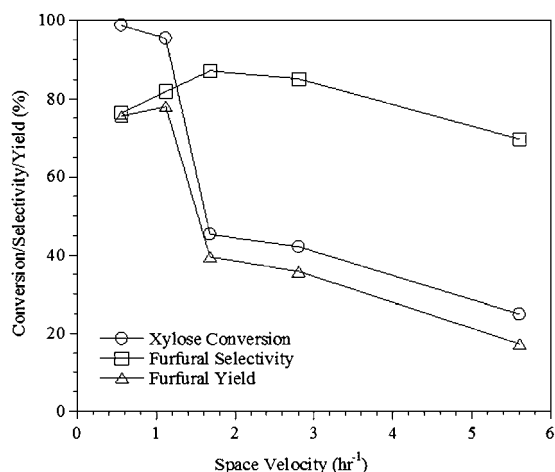
99.4% conversion and 90% furfural yield. However, the furfural selectivity decreased from 94.1% to 90.5% with increasing temperature. This indicates that the high reaction temperature greatly reduces furfural losses possibly caused by both resin-ification and condensation.[2] These results are consistent with the work of Weingarten et al., which shows that the dehydration of xylose into furfural is a higher activation energy process compared to the furfural degradation process.[20]

3.1.3. Effect of the liquid hourly space velocity (LHSV). A series of runs, i.e., Runs 1 through 5, were conducted to identify how the space velocity affected the furfural production. The experiments were carried out in the half inch reactor by varying the LHSV from 0.56 h^{-1} to 5.61 h^{-1}, and the results are shown in Fig. 4. The xylose conversion increased with decreasing space velocity. At an LHSV of 0.56 h^{-1}, the xylose conversion was 98.8%. The furfural yield increased with the decrease of the space velocity stabilizing at a value of 77.8% when the LHSV was 1.1 h^{-1}. The furfural selectivity showed an initial increase from 76.4% to 87.1% as the LHSV increased from 0.6 h^{-1} to 1.7 h^{-1}, followed by the decrease to 69.6% when the LHSV was 5.61 h^{-1}. The optimal furfural selectivity was identified to be 87.1% at the LHSV of 1.68 h^{-1}, but the optimal furfural yield was found to be 78.1% when the LHSV was 1.12 h^{-1}. This indicates that at these lower space velocities, furfural is converted into undesired humins.

3.1.4. Effect of the volumetric organic to aqueous phase ratio. The effect of the volumetric organic to aqueous phase ratio (i.e., $V_{org.}/V_{aq.}$) on the furfural production was studied at a constant LHSV of 1.62 h^{-1} (Runs 11–14) as shown in Fig. 5. The $V_{org.}/V_{aq.}$ ratio was varied from 0.5 to 1.8. We observed that the $V_{org.}/V_{aq.}$ ratio significantly affected the xylose conversion, the furfural selectivity and its yield. At the low $V_{org.}/V_{aq.}$ ratio of 0.5, the xylose conversion was only 57.2% with a furfural selectivity of 93.9%. Increasing the $V_{org.}/V_{aq.}$ ratio to 0.92, the xylose conversion and furfural yield increased up to 74.2% and 64.9%,

Fig. 4 Effect of space velocity on furfural production from hemi-cellulose extracts. Reaction conditions: $T_1 = 110\,°C$, $T_2 = 164\,°C$, equal volume feed of sugar solution and THF, feed concentrations 1.9 wt% (except that the sample tested at 1.68 h^{-1} was 2.2 wt%), and in the half inch reactor.
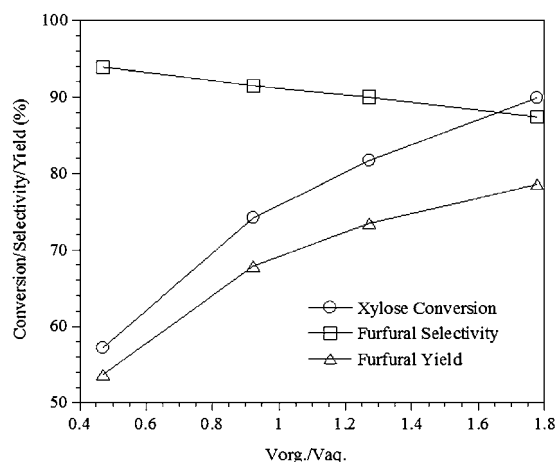

Fig. 5 Effect of volumetric ratio of organic phase to aqueous phase on the furfural production from aqueous hemicellulose extracts. Reaction conditions: $T_1 = 110\,°C$, $T_2 = 200\,°C$, equal feed xylose concentration of 10.7 wt%, LHSV = 1.62 h^{-1}, the HCl concentration of 0.44 M, and in the one inch reactor.
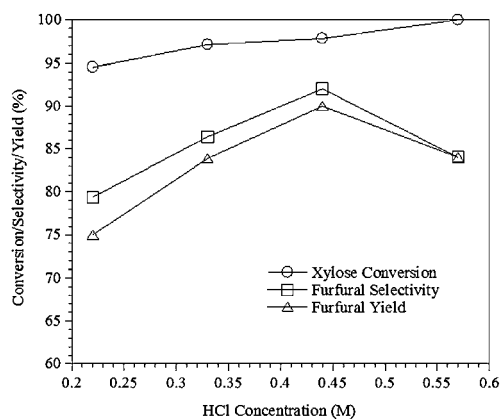
Fig. 6 Effect of acidity on the furfural production from aqueous hemicellulose extracts. Reaction conditions: $T_1 = 110$ °C, $T_2 = 200$ °C, equal feed xylose concentration of 10.7 wt%, LHSV = 1.44 h^{-1}, $V_{org.}/V_{aq.}$ = 2, and in the one inch reactor.

Fig. 7 Effect of feed xylose concentration on the furfural production from hemicellulose extracts. Reaction conditions: $T_1 = 110$ °C, $T_2 = 210$ °C, LHSV = 1.36 h^{-1}, $V_{org.}/V_{aq.}$ = 2, [HCl] = 0.44 M, and in the one inch reactor.

respectively. Conversion of xylose and furfural yield reached to 82.4% and 74.4%, respectively, when the ratio was 1.27. Further increasing the ratio to 1.78, the xylose conversion increased to 89.9% and the furfural yield was 78.6%. It was found that the furfural selectivity gradually decreased from 93.9% to 87.4% as the $V_{org.}/V_{aq.}$ ratio increased from 0.47 to 1.78.

This indicates that a high $V_{org.}/V_{aq.}$ ratio favors a high xylose conversion but a low furfural selectivity.

3.1.5. Effect of the acid concentration and the type of acid catalyst. Two homogeneous mineral acids were selected as the acid catalyst, HCl and H$_2$SO$_4$, due to their strong acidity and low cost. The effect of acid concentration on the furfural production was studied by using HCl, and the results are shown by Runs 7–10 in Fig. 6. The xylose conversion increased almost linearly from 94.5% to 100% as the HCl concentration increased from 0.22 M to 0.57 M. The furfural selectivity increased from 79.4% to 92.0% as the HCl concentration increased from 0.22 M to 0.44 M. This indicates that high acid concentration is necessary to obtain high furfural selectivity. However, further increasing the HCl concentration to 0.57 M, the furfural selectivity decreased to 84% probably due to the formation of byproducts resulting from the use of excessive HCl. As such, the optimal HCl concentration was identified to be 0.44 M, which was much higher than the reported optimal HCl concentration used to make furfural from the pure xylose solutions *via* the biphasic dehydration.[21] A higher acid concentration is needed for the hemicellulose extract than the pure xylose solutions probably because hydrolysis reactions are necessary for the hemicellulose extract whereas the pure xylose solutions do not require any hydrolysis reactions. Under selected conditions, H$_2$SO$_4$ was used as the acid catalyst as shown in Runs 33 and 34 in Table 1. A furfural yield of 90% could be achieved when the [H$^+$] was 0.48 M, which was slightly higher than that when HCl was used. These data suggest that any strong acid can be used for these aqueous phase dehydration reactions.

3.1.6. Effect of the feed xylose concentration. The effect of feed xylose concentration on the furfural production was also investigated as shown by Runs 20–23 in Fig. 7. The furfural
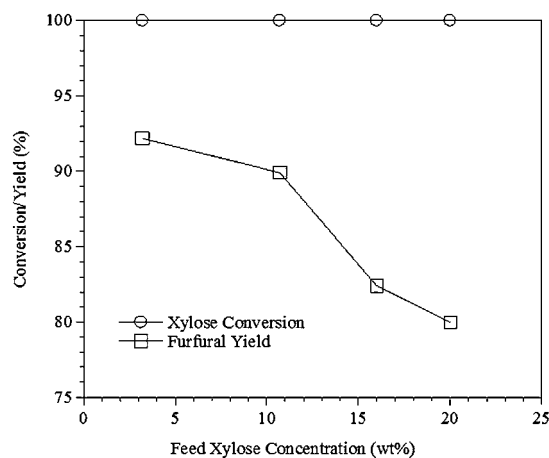
selectivity was found to be dependent on the feed xylose concentration. The furfural selectivity decreased as the feed xylose concentration increased, probably due to an increased xylose degradation at the high xylose concentration. This suggests that decomposition byproducts are formed from the reaction of xylose with furfural as illustrated in Fig. 1, which is in agreement with the work of Weingarten *et al.*[20] Our results showed that the furfural yield of 80% could be obtained when the feed xylose concentration of 20% was used.

3.1.7. Other factors affecting the furfural production. In addition to the above-mentioned factors affecting the furfural production, the furfural yield was found to be strongly dependent on the added NaCl amount in the aqueous phase. Based on the experimental results obtained in a biphasic batch reactor, the furfural yield increased with an increase in the NaCl concentration (not shown for brevity). The yield reached a maximum when the aqueous solution was saturated with NaCl. Separate experiments showed that at room temperature, the water solubility of furfural decreased from 8.4 g/100 ml, to 3.9 g/100 ml, to 1.9 g/100 ml, as the NaCl content increased from 0 to 16.8 wt% to 26 wt% in pure water. Thus, this yield increase is most likely because the NaCl decreases the solubility of furfural in the aqueous phase thereby improving the extraction of the furfural into the organic phase and increasing the overall furfural yield.

Previous research has shown that the type of organic solvent greatly affected the yields of furfural or HMF produced from the biphasic dehydration of sugars.[27] In this paper, the solvent of 2-butanol was used by replacing THF for selected conditions. As compared to THF which is miscible in pure water, 2-butanol has a water solubility of 12.5 g/100 ml at 20 °C.[38] For comparison, the experiments were carried out by replacing THF with 2-butanol as shown by Runs 35 and 36 in Table 1. Run 35 was carried out without adding NaCl to the aqueous phase and using the 2-butanol as the organic phase resulted in a biphasic product.

Run 35 had a furfural yield of 68.6%, which was higher than the yield of 45% when THF was the organic phase under the same reaction conditions. When the NaCl-saturated aqueous

Table 3 Chemical compositions of the hot water extract derived from a mixture of MNH chips and aspen strands (62Aspen/38MNH) and biphasic products obtained from Run 37. The reaction conditions: $T_1 = 110\,°C$, $T_2 = 200\,°C$, LHSV = 1.44 h^{-1}, $V_{org.}/V_{aq.}$ = 2.0, [HCl] = 0.44 M, and in the one inch reactor

Composition	Feed concentration/mmol l^{-1}		Aqueous product/mmol l^{-1}	Organic product/mmol l^{-1}
	Before hydrolysis	After hydrolysis		
Xylose	15.1	228.8	0.47	—
Glucose	6.28	41.5	2.11	—
Arabinose	8.6	29.5	—	—
Acetic acid	22.3	108.6	32.8	191.5
Lactic acid	1.0	3.55	—	—
Formic acid	23.5	6.95	95.6	91.2
Furfural	—	—	6.77	161.5
HMF	—	—	1.04	15.1
TOC (ppm)	39 336		16 895.2	
Identified C	2733.36	21 303.6	2595.6	18 502.9

phase was used with 2-butanol as a solvent, the furfural yield increased to 78% (Run 36). This was lower than the furfural yield of 89.8% obtained with THF as the organic solvent under similar reaction conditions (Run 7). The difference between Runs 7 and 36 can be explained by looking at the extraction ratio R, which compares the ratio of furfural in the organic phase with furfural in the aqueous phase. The extraction ratios of furfural in Runs 7 and 36 were 17.1 and 4.1 respectively. Thus the THF was able to extract the furfural more effectively than the 2-butanol, which is in agreement with the report by McNeff et al.[28] THF may be able to better extract the furfural than 2-butanol because it has a lower solubility in the NaCl saturated water solution.

The hemicellulose solutions derived from two different sources of wood chips were used and compared for the furfural production including from MNH chips and a mixture of MNH chips and aspen strands with a weight ratio of 38 : 62. After the hot water extraction, the chemical composition of the MNH-derived hemicellulose solution is shown in Column 2 in Table 2, and that of the mixture-derived hemicellulose solution is shown in Column 2 in Table 3. After the biphasic reaction, we could achieve a similar furfural yield of around 90% under similar reaction conditions by using these two types of hemicellulose solutions as the feedstock as compared in Runs 7 and 37. The Columns 4 and 5 in Table 3 show the chemical compositions of biphasic products from Run 37. The formic and acetic acids were

the major organic components in the aqueous product for both of the feedstocks with acetic acid being the major component.

The hot water extract was primarily used in this work. However, the green liquor extract is a more abundant feedstock than the hot water extract in the pulp and paper industries.[13] For comparison, the green liquor extract was also used as a feed in Runs 38 and 39 in Table 1. As can be seen, the furfural yield was significantly lower (89.8% vs. 46.4%) when the green liquor extract was used as the feedstock compared to the hot water extracted feedstock. We observed that the green liquor extract acted like a buffer solution reacting with the HCl as evidenced by pH changes in the solution when HCl was added. Increasing the amount of HCl by 50% in the green liquor feedstock, as shown in Run 39, caused the furfural yield to increase from 46.4% up to 59.1%. This suggests that a higher HCl concentration is needed to achieve a high furfural yield for the green liquor extract compared to the hot water extract. Table 4 shows the chemical compositions of the feed and biphasic products obtained from Run 39. The products from the green liquor extract contain much higher concentration of acetic acid, formic acid and the total organic carbon than the products from the hot water extract. In addition, the products from the green liquor extract contain a lower concentration of furfural than the products from the hot water extract. After the biphasic dehydration, the acetic acid content of 519.6 mmol l^{-1} obtained in the organic product

Table 4 Chemical compositions of the green liquor extract derived from MNH chips and biphasic products obtained from Run 39. The reaction conditions: $T_1 = 110\,°C$, $T_2 = 200\,°C$, LHSV = 1.36 h^{-1}, $V_{org.}/V_{aq.}$ = 2.3, [HCl] = 0.66 M, and in the one inch reactor

Composition	Feed concentration/mmol l^{-1}		Aqueous product/mmol l^{-1}	Organic product/mmol l^{-1}
	Before hydrolysis	After hydrolysis		
Xylose	11.9	265.4	4.9	—
Glucose	5.8	11.7	—	—
Arabinose	6.8	17.9	—	—
Acetic acid	490.1	643.1	172.5	519.6
Lactic acid	22.4	3.9	—	—
Formic acid	159.9	136.9	139.0	35.0
Furfural	1.9	6.0	4.2	56.4
HMF	—	—	2.2	3.3
TOC (ppm)	121 009.9		56 462.0	
Identified C	16 140.7	35 423.9	6355.0	18 281.6

represents the most, and the next most was the furfural content of 56.4 mmol l^{-1}.

Our experimental results have demonstrated the technological feasibility of obtaining furfural at high yields and carboxylic acids (mainly formic and acetic acids) as the co-products from hot water extracts in the continuous flow two-zone biphasic reactor.

3.2. Conceptual design and economic analysis

3.2.1. Mass and energy flows in the process. Fig. 8 shows an integrated process flow diagram for the production of furfural, formic and acetic acids from aqueous hemicellulose solutions. The material balance for the process is given in Table 5, with assumptions of (1) the feed hemicellulose solution contains 10.7 wt% xylose oligomers and monomers, (2) the xylose conversion is 100%, and the yields for furfural and the decomposition product

of humins are 90% and 10%, respectively, (3) all humins stay in the aqueous phase, (4) formic acid/acetic acid is produced from hydrolysis of formyl/acetylated xylose oligomers, and (5) those chemical species not shown in Table 5 are negligible due to their residual amounts. The material balance data from Stream 1 to Stream 5 was determined from our experimental data. Sequences of Columns in the distillation system are determined by two heuristics:[39] (1) removing off the most plentiful component (THF) at first and (2) leaving the most difficult separation (i.e., split between formic acid and acetic acid) at last. Extensive simulations were made for the distillation system with a consideration of a variety of process alternatives and decision variables including the recycle composition, the column stage numbers, the reflux and reboil ratios, etc. As a result, the material balance data from Streams 6 to 12 were obtained from our simulation results. The design basis for this work is to process 160 ton per hour of hemicellulose solutions supplied from the Red Shield Pulp &
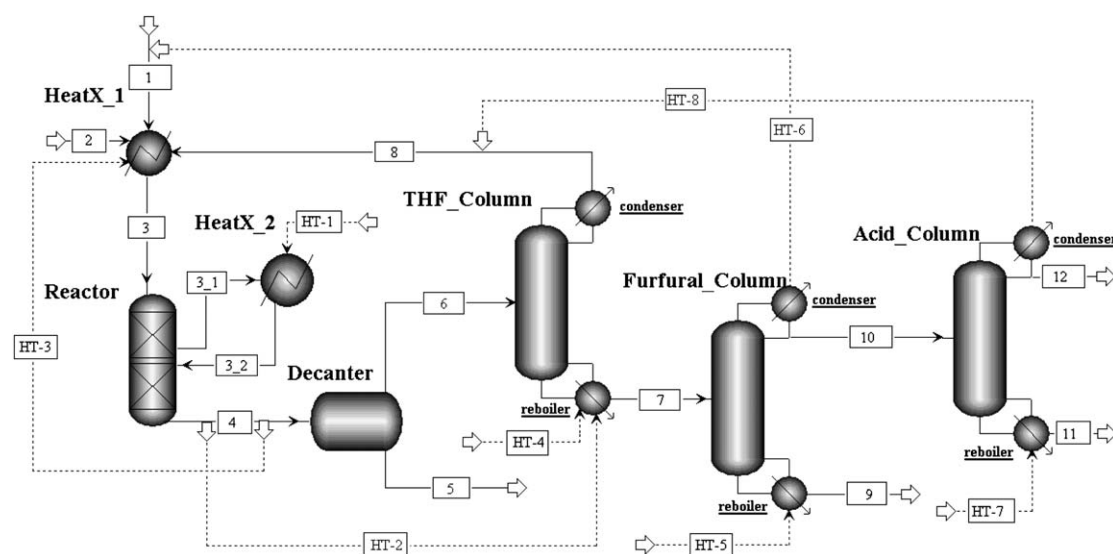

Fig. 8 Process flow diagram for the production of furfural, formic acid and acetic acid from aqueous hemicellulose solutions. Process stream key: (1) 10.7 wt% hemicellulose solution with added NaCl and HCl (0.44 M), (2) makeup THF, (3) heated hemicellulose solution, (4) furfural + THF + acetic acid + formic acid + aqueous phase, (5) aqueous phase, (6) furfural + THF + acetic acid + formic acid, (7) furfural + acetic acid + formic acid, (8) recycled THF, (9) furfural, (10) acetic acid + formic acid, (11) acetic acid, and (12) formic acid.

Table 5 Representative mass flow rates (unit: ton h^{-1}) for production of furfural, formic acid and acetic acid from waste aqueous hemicellulose solutions. Assuming that (1) the xylose conversion and the furfural yield are 100% and 90%, respectively, (2) all humins produced stay in the aqueous phase, (3) the presence of very slight amount of formic acid in recycled THF does not affect the yield of furfural. The mass flow rates for Streams 1 to 5 were obtained based on experimental results, and those after Stream 5 were calculated based on ASPEN simulation

Stream #	Xylose monomer	Xylose oligomer	Water	NaCl	HCl (37%)	THF	Furfural	Acetic acid	Formic acid	Humins	Sum
1	0.60	21.50	136.70	8.00	7.10	—	0.08	0.80	0.30	—	175.08
2	—	—	—	—	—	0.40	—	—	—	—	0.40
3	0.60	21.50	136.80	8.00	7.10	255.50	0.08	0.80	0.70	—	431.08
4	—	—	140.40	8.00	7.10	255.50	9.78	6.0	2.60	1.70	431.08
5	—	—	140.30	8.00	7.10	0.40	0.28	0.60	0.70	1.70	159.08
6	—	—	0.10	—	—	255.10	9.50	5.40	1.90	—	272.00
7	—	—	—	—	—	—	9.50	5.40	1.50	—	16.40
8	—	—	0.10	—	—	255.10	—	—	0.40	—	255.60
9	—	—	—	—	—	—	9.50 (99.3%)	0.07	—	—	9.57
10	—	—	—	—	—	—	—	5.33	1.50	—	6.83
11	—	—	—	—	—	—	—	5.32 (99.3%)	0.04	—	5.36
12	—	—	—	—	—	—	—	0.01	1.46 (99.3%)	—	1.47

Table 6 Summary of heat flow rates (MM Btu h^{-1}) for the process. Assumptions are the same as in Table 1. The heat flow rates were calculated by ASPEN simulation

Heat stream #	Heat flow rate	Note
HT-1	118.39	Supplied by 250 PSIG steam 144.4 (1000 lb h^{-1})
HT-2	97.95	Supplied to the THF_column reboiler by heat released from Stream 4
HT-3	15.19	Supplied to the HeatX_1 by heat released from Stream 4
HT-4	23.72	Supplied by 150 PSIG steam 27.7 (1000 lb h^{-1})
HT-5	9.51	Supplied by 150 PSIG steam 11.1 (1000 lb h^{-1})
HT-6	9.18	Supplied to preheat Stream 1 at the furfural_column condenser
HT-7	24.06	Supplied by 150 PSIG steam 28.1 (1000 lb h^{-1})
HT-8	15.86	Supplied to preheat Stream 8 at the acid_column condenser

Chemicals, an integrated forest bio-refinery plant located at Old Town, ME, where the hemicellulose is removed in a separated process for making ethanol and other valuable bioproducts before the wood chips are turned into pulp.[15] The production capacities for furfural, formic acid and acetic acid are estimated to be 78 kiloton per year, 12 kiloton per year and 44 kiloton per year, respectively.

In our process, the hemicellulose extract consisting of 10.7 wt % xylose (mainly xylose oligomers) is pretreated by adding the required amounts of NaCl and HCl (37 wt%) before feeding to the reactor. In this analysis, the NaCl content relative to the sugar solution is 5 wt% as shown in Table 5. The pretreated hemicellulose solutions (Stream 1), the recycled THF (Stream 8), and the makeup THF (Stream 2) are mixed together and heated by the HeatX_1 to 110 °C (Stream 3), then fed to the first zone of a continuous flow biphasic reactor. The volume ratio of THF to the hemicellulose solution is kept at 2. The effluent from the first zone of the reactor (Stream 3_1) is heated to 200 °C *via* the HeatX_2 and sent to the second zone of the reactor. The effluent from the second zone of the reactor containing biphasic products (Stream 4) is sent to the decanter (operating at 25 °C), where the aqueous phase (Stream 5) is separated from the organic phase (Stream 6). After the liquid–liquid split, the aqueous phase can be further processed to recover NaCl, HCl, formic acid, and acetic acid.[12] The organic phase (Stream 6) containing mainly THF, furfural and carboxylic acids is sent to the THF_column, in which THF is recovered with a high purity of 99.8% *via* the distillation and recycled back to the reactor (Stream 8). The bottom stream (Stream 7) of the THF_column containing mainly furfural, formic and acetic acids is sent to the furfural_column, where furfural with a high purity of 99.3 wt% (Stream 9) is obtained from the column bottom. The distillate (Stream 10) of the furfural_column is sent to the acid_column to get a high purity of acetic acid (99.3 wt%) and formic acid (99.3 wt%) from the bottom product (Stream 11) and the distillate (Stream 12), respectively. In this process, the projected operating pressure in all distillation systems is 1 atm.

In order to decrease the external energy inputs and minimize the total heating energy, we studied energy integration alternatives by Aspen Plus[35] simulation. It should be noted that the heat integration in this work is based on the naturally available energy in the process, *i.e.*, we do not manipulate the operating pressure of distillation systems to control the operating temperature for heat integration (*e.g.*, "column stacking"[39]). As a result of the energy integration, the condenser of the acid_column provides

heating energy for Stream 8, and Stream 1 passes through the condenser of the furfural_column to take up the energy released there. The heating energies needed for the reboiler of THF_column and the HeaX_1 are supplied by the heat released from Stream 4 leaving the biphasic reactor. Table 6 summarizes the calculated heat flow rates for the process. As we can see the HT-1, HT-4, HT-5 and HT-7 represent the external energy inputs for this process, among which HT-1 accounts for nearly 70% of the total amount of external energy inputs.

3.2.2. Preliminary economic analysis

3.2.2.1. Raw materials cost. The raw materials cost is summarized in Table 7. The raw materials consist of dry xylose (representing the hemicellulose solution), NaCl, HCl and the makeup THF, and their costs are calculated based on the mass balances as shown in Table 5. Preliminary analysis by researchers at the University of Maine shows that the estimated cost of xylose derived from pre-processing extracts at an integrated forest products refinery co-located at a hardwood Kraft mill or biomass boiler is $130 per ton xylose on a dry basis. This cost accounts for sugar heating value lost by the host mill, the costs of extracting and concentrating the extract, and the cost and revenue associated with recovering acetic acid as a co-product. The current plant capacity in the Red Shield Pulp & Chemicals allows for the production of 160 ton per hour hemicellulose solutions containing 10.7 wt% xylose, *i.e.*, 17.1 ton per hour of dry xylose. As a result, the calculated cost of dry xylose is K$18 117 per year. The price of HCl (37 wt%) at the time of this analysis is available for $215 per ton, so the HCl cost is K$12 441 per year for the amount of 57.9 kt per year needed as the catalyst. If the sulfuric acid ($144 per ton[40]) is used instead of HCl, the

Table 7 Summary of raw materials cost.[43–45] Plant capacity: 78 kiloton furfural per year, 12 kiloton formic acid per year and 44 kiloton acetic acid per year (8150 h y^{-1})

Costs	Dry xylose	NaCl (bulk solar salt)	HCl (37 wt%)	Makeup THF
Unit price/$ per ton	130	35	215	3500
Hourly amount/ton per hour	17.1	8	7.1	0.4
Annual cost/K$ per year	18 117	2282	12 441	11 410
Total annual raw materials cost/K$ per year				44 250

Table 8 Summary of equipment specifications and installed equipments cost calculation. Plant capacity: 78 kiloton furfural per year, 12 kiloton formic acid per year and 44 kiloton acetic acid per year (8150 h y^{-1})

Equipment	Characteristic size	Material	Installed equipment costs in US K$ (2nd Quarter 2009)
Reactor	$D = 2$ m, $H = 12.0$ m	Titanium clad	732
Decanter	$D = 2.5$ m, $H = 7.5$ m	Titanium clad	436
Heat exchanger 1	Area $= 389.4$ m^2	TI50A tube, TI50A shell	1083
Heat exchanger 2	Area $= 1427.3$ m^2	TI50A tube, SS304 shell	3398
THF distillation column			
Column and trays	$D = 6.9$ m, $H = 37.3$ m, number of sieve trays $= 56$, tray efficiency $E_0 = 0.5$	SS317	4593
Reboiler	Portion 1 area $= 1260.7$ m^2, Portion 2 area $= 157.1$ m^2	Portion 1: HASTB tube; SS317 shell, Portion 2: SS317 tube, SS304 shell	6655
Condenser	Area $= 1512.2$ m^2	CS tube, CS shell	420
Reflux pump	Flow rate $= 112.4$ l s^{-1}	CS	85
Cond. accum.	$D = 2.6$ m, $L = 8.1$ m	CS	174
Subtotal			11 927
Furfural distillation column			
Column and trays	$D = 2.3$ m, $H = 25.1$ m, number of sieve trays $= 36$, tray efficiency $E_0 = 0.5$	SS317	881
Reboiler	Area $= 1165.0$ m^2	SS304 tube, SS304 shell	698
Condenser	Area $= 141.1$ m^2	HASTB tube, SS317 shell	1181
Reflux pump	Flow rate $= 7.2$ l s^{-1}	SS316L	52
Cond. accum.	$D = 1.1$ m, $L = 3.2$ m	SS317	181
Subtotal			2993
Acid distillation column			
Column and trays	$D = 3.1$ m, $H = 49.5$ m, number of sieve trays $= 76$, tray efficiency $E_0 = 0.5$	SS317	2252
Reboiler	Area $= 327.3$ m^2	SS317 tube, SS304 shell	580
Condenser	Portion 1 area $= 500.5$ m^2, Portion 2 area $= 110.7$ m^2	SS317 tube, SS304 shell	887
Reflux pump	Flow rate $= 15.0$ l s^{-1}	SS316L	59
Cond. accum.	$D = 1.4$ m, $L = 4.1$ m	SS317	203
Subtotal			3981
Total installed equipment costs (US K$)			24 550

cost of acid would be K$9037 per year. The costs of NaCl and the makeup THF are K$2282 per year and K$11 410 per year, respectively. It should be noted that the cost of NaCl is insignificant, accounting for only 5.2% of total raw materials cost, while the costs of HCl and the makeup THF account for 53.9% of the raw materials cost. This suggests that the raw materials cost can be greatly reduced if we find a solid catalyst to replace HCl and a cheaper organic solvent to replace THF without losing their performances.

3.2.2.2. Installed equipments cost and associated utilities cost. Table 8 shows a summary of equipment specifications and installed equipments cost calculation. Except for the installed costs of the reactor and the decanter, which were calculated based on the cost correlations described by Douglas,[41] all other installed costs were obtained from the Aspen Icarus Process Evaluator[36] calculation. Titanium materials (Titanium clad and TI50A) were selected to address the corrosion concerns arising from using HCl and NaCl. The stainless steel materials including SS316L and SS317 were selected to address the corrosion concerns arising from the presence of formic and acetic acids, and the Hasteloy B (HASTB) was selected to address the corrosion-resistance challenge of facing HCl, NaCl, formic and acetic acids simultaneously. The total installed equipments cost was calculated as K$24 550 for the plant capacity of 78 kiloton furfural per year, 12 kiloton formic acid per year and 44 kiloton acetic acid per year. If the plant is considered to be a plant expansion of an existing facility, the fixed capital investment

(FCI) is K$49 468 as shown in Table 9. The THF_column, which accounts for 24.1% of the FCI, is the major contributor to the FCI. We also estimate the utilities cost for this process as K$9678 per year by assuming the cost of 150 PSIG steam as US$4.8/1000 lb, the cost of 250 PSIG steam as US$6.0/1000 lb.

3.2.2.3. Production cost. Based on the raw materials cost, the utilities cost and the FCI, we calculated the total annual product cost. The total annual product cost is a sum of variable costs and fixed costs, and detailed calculations are shown in Table 10. The major costs are raw materials and utilities, accounting for a combined 46% of the total production cost. The unit production cost for a plant that produces 78 kiloton per year of furfural, 12 kiloton per year of formic acid and 44 kiloton per year of acetic acid

Table 9 Summary of Fixed Capital Investment. Plant capacity: 78 kiloton furfural per year, 12 kiloton formic acid per year and 44 kiloton acetic acid per year (8150 h y^{-1})

Investment item	Cost factor	Cost/US K$
Installed of equipments	From Table 8	24 550
Building improvements	30% of cost of installed equip.	7365
Subtotal direct costs		31 915
Engineering and supervision	20% of direct cost	6383
Construction and fee	20% of direct cost	6383
Contingency	15% of direct cost	4787
Subtotal indirect costs		17 553
Fix Capital Investment (FCI)		49 468

Table 10 Summary of annual production calculation. Plant capacity: 78 kiloton furfural per year, 12 kiloton formic acid per year and 44 kiloton acetic acid per year (8150 h y^{-1})

Cost items	Calculation	US K$ per year	%
1. Raw materials cost	From material balances	3465[a]	12.1
2. Utilities cost	From energy balances	9678[b]	33.9
Variable costs	1 + 2	13 143	46.0
3. Maintenance	4% of FCI	1979	6.9
4. Supply	0.6% of FCI	297	1.0
5. Operating labor	10^5 $ per year per operator × 12	1200	4.2
6. Supervision	20% of labor cost	240	0.8
7. Lab costs	15% of labor cost	180	0.6
8. Royalty	3% of annual production cost	857	3.0
9. Tax and insurance	3% of FCI	1484	5.2
10. S.A.R.E[c]	2.5% of revenue	3165	11.1
11. Overheads	72% of labor + 2.4% FCI	2051	7.2
12. Interest	8% of FCI	3957	14.0
Fixed costs	3 + 4 + 5… + 12	15 410	54.0
Annual production costs	1 + 2 + …12	28 553	100
Unit production cost		366 US$ per ton furfural	

[a] Deducting the formic acid (US$1200 per metric ton) and acetic acid (US$600 per metric ton) revenues. [b] Cost of 150 PSIG steam as US$4.8/1000 lb, cost of 250 PSIG steam as US$6.0/1000 lb. [c] Costs of sale, administration, research and engineering.

acetic acid is estimated to be $366 per ton furfural after deducting formic acid and acetic acid revenues. This is much lower than the current market price of furfural in the US market which is reported to be $1450 per ton in 2007.[42] The furfural cost can be further decreased if a heterogeneous solid acid catalyst is used instead of a homogeneous acid and the solvent of THF can be more efficiently recovered.

3.3. Comparisons with other existing processes

In this work a novel process for the production of high purity of furfural, formic and acetic acids from aqueous hemicellulose solutions is reported and its economics has been assessed for a plant capacity of 78 kiloton furfural per year, 12 kiloton formic acid per year and 44 kiloton acetic acid per year. Our results suggest that the process is technically feasible and economically attractive. As compared to currently existing furfural plants, our process features the advantages over the existing processes in the following aspects:

(1) Cheap and abundant raw materials: current existing processes usually employ agricultural pentosan-rich materials, which limit the resource of furfural production. Furthermore, other useful wood fractions are used as process heat during the furfural production. In our process, waste hemicellulose sugar streams from the pulp and paper industries are used as raw materials. The sugar streams can be derived from abundant and cheap non-food lignocellulosic biomass, thus holding promise to be some of the cheapest streams available.

(2) Low energy intensity: current furfural production process, using either batch or continuous reactors, has a low furfural yield of less than 50% of the theoretical yield and is an energy-intensive

process, in which a huge amount of steam (typically 30 to 50 tons of steam per ton of furfural produced)[2,21] is required. Given the same furfural production rate of 78 kiloton per year, the steam requirement will be 2340 kiloton per year to 3900 kiloton per year, not including the part required to recover any co-products, in currently existing furfural processes, while our process only requires 781 kiloton per year steam which includes the portion required to recover co-products of formic and acetic acids. There are at least two reasons for our process to be less energy intensive: (1) our continuous two-zone biphasic reactor can produce a high furfural yield of 90% under optimized conditions, which is almost double the current furfural yield of around 50%, and (2) due to the liquid–liquid split and the lower boiling point (66 °C vs. 100 °C), lower specific heat capacity (1.72 J g^{-1} K^{-1} vs. 4.18 J g^{-1} K^{-1}),[46] and significantly lower heat of vaporization (413.4 J g^{-1} vs. 2258.7 J g^{-1})[47] for THF as compared to those for water, the ratio of steam consumption to furfural production is calculated to be 10, which is only 20% to 33% of the energy intensity of the current furfural production processes, as reported in Table 6.

(3) Good compatibility with existing pulp and paper and bioethanol processes: our process can be easily integrated with the current existing pulp and paper and bioethanol processes to convert waste hemicellulose streams into furfural, acetic and formic acids without reducing the quantity or quality of original products that are ultimately produced, thus improving the overall economics in these industries.

In addition, similar to existing commercial furfural processes which lead not only to furfural but also to carboxylic acids, among which the formic and acetic acids are the principal components, our process can produce high purity of formic acid as well as high purity of acetic acid as the co-products. Moreover, the carboxylic acids obtained in commercial furfural processes are recovered from the waste water of the furfural process by either solvent extraction or freezing (recovery of only acetic acid), or extractive condensation, or multi-effect azeotropic distillation (recovery of only acetic acid), etc.[2] Due to the low concentration (on the order of 2 wt%) of carboxylic acids in the waste water stream, all these processes require a complicated system, multi-step separation, and intensive energy consumption. In our process, most of carboxylic acids (formic acid > 70% and acetic acid ∼ 90%) are extracted with furfural into the organic phase. After distillation of THF and furfural, the feed containing predominantly formic and acetic acids enters the acid_column, in which both formic and acetic acids can be recovered by one-step distillation. Overall, more than 56% and 88% of the total formic acid and acetic acid, respectively, effusing from the biphasic reactor can be recovered in our process.

4. Conclusions

High purity of furfural, formic and acetic acids can be produced from aqueous hemicellulose solutions in a biorefinery process composed of a biphasic dehydration, a liquid–liquid split, and subsequent three-stage distillations. The biphasic dehydration of hemicellulose solutions is conducted in a continuous two-zone biphasic reactor, in which the xylose oligomers in the hemicellulose solution first break down into xylose monomers, which are then converted into furfural, formic and acetic acids. The co-products of formic and acetic acids are mainly produced via the

hydrolysis of formylated and acetylated xylose oligomers, respectively. Some key parameters that impact the furfural yield, including the reaction temperature, the volumetric of the organic to aqueous phase ratio, the type of acid catalyst and acid concentration, the feed xylose concentration, and the LHSV, have been investigated in detail. Other parameters such as the wood source of hemicellulose solutions, the extraction methods, and the type of solvent are also studied and compared under selected conditions. The optimal temperatures for the furfural production are identified to be 110 °C and 200 °C for the first reaction zone and the second reaction zone, respectively. The furfural yield increases as the volumetric ratio of the organic to aqueous phase increases. The optimized LHSV is identified to be 1.12 h^{-1} when the temperatures are 110 °C and 164 °C for the first zone and the second zone, respectively. The optimal acid concentration identified is 0.44 M with HCl as the acid catalyst. Increasing the feed xylose concentration decreases the furfural yield. The type of organic solvent used in the system affects the yield of furfural production. The furfural yield of 90% can be achieved under the optimized condition by using the hot water extract containing 10.7 wt% xylose (mainly xylose oligomers). The furfural production process proposed in this paper is 3 to 5 times more energy efficient and has a yield almost double the current industrial processes to make furfural. In addition, we estimate our cost of furfural production to be 25% of the current market value of furfural.

Acknowledgements

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