Green Chemistry

Accepted Manuscript

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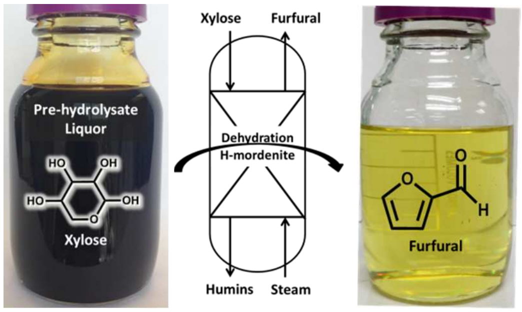

A novel continuous reactive distillation process with solid acid catalysts is demonstrated for the production of furfural from synthetic and pre-hydrolysate liquor feeds containing xylose.

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This paper presents a continuous reactive distillation process using solid acid catalysts to produce furfural from synthetic and real (pre-hydrolysate liquor (PHL) from wood chip digestion) feeds containing xylose. The reactive distillation process provides a unique advantage of immediate furfural separation from the reaction zone as it is formed, thus minimizing the formation of undesired by-products (e.g., oligomers of furfural/humins) from subsequent furfural condensation reactions. A comprehensive experimental study was carried out using synthetic xylose feeds containing a mixture of pure xylose, water, and sulfolane as a solvent. Among various solid acid catalysts screened for their ability to produce furfural from dehydration of xylose, the zeolite H-mordenite (Si/Al=10) gave the highest furfural yield (>75%). During this process, the aqueous feed was introduced at the top of the column, and xylose was dehydrated to furfural which was co-distilled with water out of the top of the column. The high-boiling sulfolane, with dissolved undesired byproducts, was collected at the bottom of the column. Steam-stripping was found to be helpful in effective separation of furfural from the reaction zone, thus further enhancing furfural yield.

This study was extended to using authentic aqueous PHL feed. Salts present in this feed resulted in significant catalyst deactivation. Pre-treatment of the PHL feed with ion-exchange resin was found to be effective in achieving furfural yields of ~75%. An *in situ* catalyst regeneration method was demonstrated successfully and resulted in achieving extended catalyst lifetime and furfural yield, similar to that obtained with synthetic xylose feeds.

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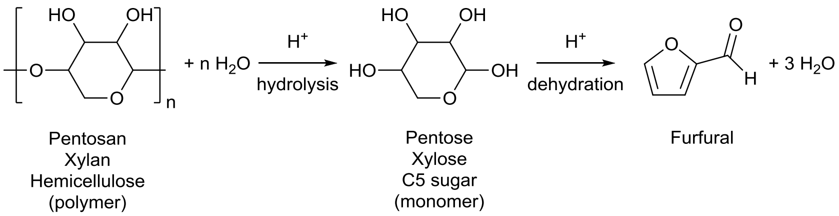
Introduction

There is an increasing interest in using renewably-sourced feedstocks for the production of chemicals and fuels as an alternative to using petrochemicals because of rising petroleum prices, limited availability of petroleum resources, and increasing consumer consciousness about sustainable processes.[1-5] Furthermore, use of fossil fuels for the manufacture of chemicals and fuels typically has a greater environmental footprint relative to that for renewable feedstocks. The overall concept of converting biomass into chemicals provides several benefits including an inherently safer, sustainable, and environmentally-friendly process.[6, 7]

Furfural (furan-2-carbaldehyde) is currently used in the production of various resins, pharmaceuticals, herbicides, and stabilizers, and it is produced globally at about 300 kt/y from biomass feedstocks such as corn cob and sugarcane bagasse.[8, 9] Furfural is considered to be a potential platform chemical and one of the key renewably-sourced feedstocks for products that can compete with petroleum-based chemicals.[6, 10-13] **Scheme 1** shows a simplified mechanism for furfural synthesis from the hemicellulose portion of lignocellulosic biomass. Monomeric C_5 sugar moieties such as xylose and arabinose are obtained by mineral acid-catalyzed hydrolysis of this pentosan polymer. The C_5 sugars are then dehydrated under these same acidic conditions to form furfural.



Scheme 1: Simplified reaction mechanism for the production of furfural

Zeitsch[14] and Xing, *et al.*[15] provide excellent summaries of historical furfural production and recent research on this chemical transformation. Surprisingly, the industrial furfural production process has not changed substantially over the last ninety years. Furfural was first produced commercially in the 1920s by the Quaker Oats Company in Iowa using oat hulls as the feedstock and sulfuric acid as the catalyst.[16] The process relies on steam injection to a digester to heat and hydrolyze the starting biomass with simultaneous steam stripping of the furfural dehydration product (batch catalytic distillation concept with homogeneous catalyst). The process is limited by poor mass transfer and low reactivity, which results in an approximately 40-50% molar yield of furfural.[14] However, due to the low capital intensity and relatively inexpensive feedstocks, this original process is still used commercially to manufacture furfural from corn cobs by batch dehydration of this pentosan-rich biomass using sulfuric acid as a catalyst, and about 80% of the current global furfural supply is produced using this process.[9] There are several other processes (e.g., SupraYield®, Biofine, biphasic, etc.) that have been investigated in the literature for the production of furfural.[14, 17-24]

Current commercial production and many of the new furfural processes under evaluation use a soluble inorganic acid catalyst, such as sulfuric, phosphoric, or hydrochloric acid, for the sequential hydrolysis and dehydration reactions. These homogeneous acid catalysts are difficult to separate from the reaction medium or the product stream, and a major difficulty with use of these mineral acids is the formation of undesirable byproducts including polymeric materials commonly referred to as humins,[25, 26] which not only leads to yield loss but also causes fouling of exposed reactor surfaces and negatively impacts heat transfer characteristics. Furthermore, use of mineral acids can require increased capital costs because of associated corrosion and environmental emission issues.

There has been a renewed interest in biomass-derived furfural as a renewable source of chemicals and possibly transportation fuel in recent years,[11, 27-29] and research is being conducted to develop newer processes, some of which use solid acid catalysts in an attempt to find more efficacious, sustainable, and commercially-viable production options.[30] Gürbüz *et al*. reported 80% yield of furfural from xylose when dilute sugar solutions were used in the presence of a solid acid catalyst and γ-valerolactone as a solvent.[31] Suzuki *et al*. found that sulfated tin oxide could be an effective catalyst for the dehydration of xylose to furfural in a biphasic mixture at low temperature (100 ^{o}C).[32] The effect of shape-selective zeolites, including a plethora of H-forms of pentasils, faujasites, and mordenites, has also been studied for the conversion of xylose to furfural in various solvents such as water, methyl isobutylketone, and toluene.[33-41] However, these processes, and even the conventional batch furfural synthesis processes, in the presence of solid acid catalysts suffer from high yield losses and rapid catalyst deactivation due to the formation of resinous humins on the catalyst surface.

Reactive distillation, on the other hand, provides a simpler, innovative approach to overcoming most of the difficulties, limitations and disadvantages encountered in some of the chemical processes described above. This process has the advantage of providing a means of separating product(s) from reactant(s) (and undesired byproducts) which can lead to higher yields in those chemical processes which typically suffer from lower yields due to equilibrium limitations, poor selectivity of desired products, and catalyst deactivation due to the formation of fouling species. Therefore, in recent years, there has been a renewed interest in reactive distillation as a unique, cost-effective technology to increase capital productivity, reaction selectivity and process yield while decreasing catalyst deactivation, and avoiding/eliminating expensive and extensive separation steps related to product separation.[42]

Mandalika and Runge delineated an acid-catalyzed batch reactive distillation (BRD) process to produce furfural.[43] Furfural was produced in a batch reactor by continuously removing a dilute aqueous product stream in the vapor phase by azeotropic distillation in a separate unit. In this process, either aqueous solutions of pure xylose, chopped and untreated biomass samples, or biomass hydrolysates were used as reactants in the presence of a homogeneous acid catalyst. High yields of furfural (~70%) could be achieved in this process by removing furfural and water from the reaction mixture. However, it is envisioned that in the BRD process, recycle and reuse of the catalyst will be extremely difficult, as it will require expensive separation steps to recover the catalyst from the pot residue. Agirrezabal-Telleria *et al*. achieved significantly high yield of furfural just with N_2 stripping using Amberlyst® 70 catalyst in a semi-continuous process carried out in a stirred tank reactor.[21, 22] Even though this process provides high furfural yield, a continuous process is still needed for commercial-scale production of furfural as the formation and build-up of humins over time would be challenging to handle in this process, and this would eventually result in catalyst deactivation and reactor plugging. Also, in the event of catalyst deactivation, the catalyst would need to be removed from the reactor and regenerated separately which would lead to significant downtime in a commercial scale unit. Therefore, a “one-pot” continuous reactive distillation process in the presence of a solid acid catalyst would be more beneficial and cost-effective, and this approach would alleviate the problems faced by the BRD and semi-continuous process.

Based on the drawbacks observed in the traditional batch commercial processes including poor yield of furfural, use of homogeneous acid catalysts (and hence the issues related to corrosion/material of construction), excessive formation of humins, difficulty in recovery and recycle of catalyst, and rapid catalyst deactivation observed in the predominantly batch processes using solid acid catalysts, we undertook a research endeavor to develop a novel, continuous reactive distillation process for the production of furfural from xylose in the presence of a solid acid catalyst. Furthermore, one of the objectives of this study was also to examine the feasibility of this process with “real” dissolving wood pulp feeds containing xylose (C_5-sugar), where one could achieve significantly higher furfural yields compared to those reported in the literature using solid acid catalysts with little or no catalyst deactivation over a sufficiently long time-on-stream. Even though several studies in the literature focus on furfural production from xylose, very few studies have reported furfural production from aqueous biomass feeds. In the current paper, a systematic study of a reactive distillation process using solid acid catalysts to produce furfural from synthetic and industrial pre-hydrolysate liquor (PHL) feeds is presented. Additionally, an *in situ* catalyst regeneration procedure performed during the continuous reactive distillation process is reported.

Experimental

Reactive distillation set up

Figure 1 shows a schematic diagram of the reactive distillation set up used in this study. The reactive distillation unit consisted of a jacketed glass tube reactor. The glass reactor, enclosed in an outer jacket, was 21.6 cm long and 3.5 cm in diameter. The reactor was filled with 10 g of catalyst (in extrudate/granule form). The catalyst bed was positioned in the middle of the glass reactor, and the rest of the reactor tube was packed with 2.0 mm glass beads (Chemglass Inc. Catalog No. CG-1101-01) on the top and bottom of the catalyst bed. Stainless steel wire mesh was placed below the glass beads (in the bottom section of the reactor) to support the catalyst bed and glass beads. A thermocouple (TC) was used to monitor the catalyst bed temperature and was placed inside a thermowell located in middle of the glass reactor. Through the outer jacket (outer diameter (O.D.): 5.7 cm), heated oil (Lauda® Brinkmann LZB 222, THERM240) was circulated continuously to maintain the reactor temperature at a desired value.

A high temperature oil bath (Lauda® LCN 4708 Proline P5) was used to control the oil temperature and the flow rate of the oil through the outer jacket of the reactor. The oil bath temperature was maintained in the range 195-210 °C so that about 170-180 °C temperature was maintained in the catalyst bed. A distillation head including a condenser was attached at the top of the reactor, where a temperature of 15 °C was maintained with continuous circulation of a coolant comprised of a mixture of 50 wt% ethylene glycol (VWR, BDH 2033) and 50 wt% water. A circulation bath (Lauda® Ecoline Staredition RE112) was used for this purpose.

The reactor was connected to a continuous HPLC pump (Lab Alliance Series I) capable of precisely delivering a constant flowrate of liquid feed to the reactor. This paper summarizes the results obtained with different catalysts using both synthetic and "real" feeds. Here, synthetic feed refers to a solution of 5 wt% commercial xylose (Sigma Aldrich, X1500) and 15 wt% water in 80 wt% sulfolane (Sigma Aldrich, T22209). "Real" feed refers to a mixture of hardwood PHL from a pulp mill mixed with sulfolane (more details about the PHL feed are provided below). These feeds contained 20 wt% PHL dissolved in 80 wt% sulfolane. [Note: All the experiments carried out with PHL feed are referred to as real/PHL feed runs. The PHL solution was a dark brown liquid and contained some undissolved solids. The minimum pretreatment of filtration (with 0.20 µm filter media) was used in all the experiments performed with this PHL feed]. The feed mixture was added to a glass beaker in which the inlet line of the HPLC pump was submerged. The glass beaker was kept on a balance to continuously monitor the amount of feed introduced into the reactor. The feed rate to the reactor was maintained at 0.75 mL/min, and the feed was introduced above the catalyst bed. The stripping section (containing glass beads) also aided in uniform distribution of the liquid feed to the catalyst bed. Dehydration of carbohydrates occurred when the feed solution contacted the heated catalyst bed, forming the desired product, furfural, along with humins. The water from the feed and the water from carbohydrate dehydration went into the vapor phase and aided in the removal of furfural from the reactive zone via a water:furfural azeotrope. The vapors were then condensed and collected in a glass flask (250 mL, Chemglass Inc., Catalog No. CG-1559-10) surrounded by an ice bath to ensure complete condensation of the product. One of the necks of this flask was sealed with a rubber septum. A 10 mL plastic syringe with Luer-Lock® tip (BD, Catalog No. 309604) was connected to a needle, which was introduced through the septum. This syringe was used to collect the distillate sample at regular intervals. The reaction was carried out under atmospheric pressure.

The reactive distillation unit was also equipped with a reflux valve, which was closed (reflux ratio = 0) to minimize humin formation from subsequent side reactions of furfural. The unreacted feed containing xylose and sulfolane along with the humins formed during the reaction were collected in a receiver (subsequently referred to as 'pot' in this paper) located below the reactor. The pot was a 3-necked 250 mL round-bottom glass flask (Chemglass Inc., Catalog No. CG-1530-01). A 20 mL plastic syringe with Luer-Lock® tip (BD, Catalog No. 309661) was connected to a needle which was pierced through a rubber septum used to seal one of the necks of the round bottom flask. This syringe was used to collect the pot sample at regular intervals. Another neck of the round bottom flask was sealed with a rubber septum, and 1/8" PTFE tubing (Chemglass Inc., Catalog No. CG-1037-10) was inserted through the septum into the pot. A digital syringe pump (KD Scientific, Model No. KDS KEGATO 270, Catalog No. 78-8270) was used to pump water through this tubing and into the pot at a constant rate of 0.50 mL/min. The pot was kept heated at a temperature of 160 ^{o}C to convert the water to steam, which then traveled up through the catalyst bed and helped to effectively remove furfural from the reaction zone (by forming the water:furfural azeotrope). Nitrogen was also introduced in one of the necks of the pot for further removal of furfural from the reaction zone. Initial experiments were carried out without additional steam generation.

Product Analysis

The pot samples were analyzed by HPLC on a calibrated Bio-Rad Aminex (HPX-87H) column using a refractive index detector (RID) (column heated to 65 °C, 0.01 N H_2SO_4 isocratic mobile phase at 0.6 mL/min, RID set at 55 °C, 60 min run time). The distillate (top) samples were analyzed by an Agilent 6890 GC equipped with a 30 meter DB-1 capillary column (J&W, 125-1032). Five microliters of the solution were injected into an injector port set at 175 °C, with a split ratio of 5:1, a total helium flow rate of 55.2 mL/min, a split flow rate of 44.4 mL/min and a head pressure of 6.25 psi. The oven temperature was held at 50 °C for 2 min, and then the temperature was increased to 110 °C at 10 °C/min ramp rate, followed by a second increase to 240 °C at a ramp rate of 20 °C/min. The flame ionization detector was set at 250 °C. A measured amount of the internal standard (1-pentanol) was added for the GC analysis, and the detected amount of furfural was recorded. The following equations were used for calulating (molar) yield, conversion and selectivity. [Note – molar yields are reported throughout this manuscript].

$$\%\ \text{Xylose conversion} = \frac{\text{Xylose reacted}}{\text{Xylose fed}} \times 100 \tag{1}$$

$$\%\ \text{Furfural yield} = \frac{\text{Furfural produced}}{\text{Xylose fed}} \times \frac{\text{mol wt. Xylose}}{\text{mol wt. Furfural}} \times 100 \tag{2}$$

$$\%\ \text{Furfural selectivity} = \frac{\text{Furfural produced}}{\text{Xylose reacted}} \times \frac{\text{mol wt. Xylose}}{\text{mol wt. Furfural}} \times 100 \tag{3}$$

Catalysts

Different types of ammonium forms of zeolite powders (or extrudates) with either beta (BEA), ZSM-5 (MFI), or mordenite (MOR) aluminosilicate frameworks were obtained from

Zeolyst International (more details are provided in **Table 1**). The Y (FAU) zeolite was obtained in H-form. The zeolite catalysts were calcined in air (at 550 ^{o}C for 8 h) to obtain the H-form of the zeolite. Most of the experiments were carried out with catalyst granules (without any binder). To prepare granules, the zeolite powder was loaded into a stainless steel die and pressed at 1.82 x 10^5 kPa using a Preco® hydraulic press. The resulting pressed-pellets (25 mm diameter x 25 mm thick) were crushed and sieved to produce granules of -12/+14 mesh (1.40 mm - 1.70 mm) that were calcined in air (at 550 ^{o}C for 8 h) before use in the reaction zone (as a catalyst bed). A few non-zeolite catalyst extrudates were also used in this study. These included *gamma*-alumina, titania, zirconia, and silica.

Catalyst Characterization

The catalyst samples were analyzed using several characterization techniques including inductively coupled plasma (ICP), thermogravimetric analysis (TGA), pore volume distribution (PVD), and X-ray diffraction (XRD). For ICP, the samples were analyzed on a PerkinElmer's Optima Radial View 5300 ICP-OES. A TA Instruments' Q500 TGA was used for the TGA analysis (TGA method - Equilibrate at 30 °C (air), ramp rate of 10 °C/min to 800 °C (air) and isothermal for 120 min (air)). Pore volume distributions in the region 2-150 nm were determined by nitrogen adsorption using a Micromeritics ASAP 2420. Samples were pretreated in vacuum at 150 °C for 12 h to remove adsorbed moisture, transferred to the instrument, and then evacuated and cooled to -196 ^{o}C (77 K) in a liquid nitrogen dewar. Nitrogen gas was admitted to the sample cell in doses from 50 Torr to 755 Torr and back to 50 Torr, while adsorption was recorded *via* differential pressure measurements. The catalyst characterization results are provided below.

Results and Discussion

Catalyst Screening and Reaction Optimization

Commercially available solid acid catalysts (listed in **Table 1**) were tested for their ability to produce furfural from xylose in the small scale reactive distillation apparatus described above. Our earlier catalyst screening study in a batch reactor helped to guide the zeolite selection (and Si/Al ratio) in this current investigation.[44] The selection of sulfolane as the preferred high boiling solvent for this work was based on prior work done by Fagan *et al*.[45] It has been reported in the literature that sulfolane is both thermally stable at elevated temperatures and chemically stable in the presence of strong acids and bases, making it useful in a variety of reaction conditions.[46] Fagan *et al*. carried out batch scouting experiments at small scale using sulfuric acid as a homogenous acid catalyst to test various high boiling, water miscible solvents.[45] Among the various solvents studied (such as polyethylene glycols, sulfolane, propylene carbonate, adipic acid, etc.), it was found that sulfolane provided a reaction medium that afforded the highest furfural yields.

Initial experiments were carried out with catalysts in the form of cylindrical extrudates (~1.5 mm x 5 mm). H-beta zeolite (Si/Al=12.5) and H-mordenite (Si/Al=10) catalysts containing 20 wt% alumina as a binder were used with the synthetic feed. From the data obtained for a 5 h run at 170 °C (with H-beta), it was apparent that the furfural yield was low (only 15%), even though the xylose conversion was significant (75-80%). This indicated that there were large amounts of undesired byproducts being formed during the reaction. For this experiment, no water was added to the pot for additional steam generation (for steam-stripping of furfural). Analysis of the pot samples (by HPLC) indicated that most of the furfural was being collected in the pot. This showed that the furfural formed was not effectively distilled out of the reaction zone. Instead, the product furfural travelled down the reaction zone and into the pot, where it underwent unwanted side reactions. A similar study was carried out using the same H-beta zeolite extrudates at a temperature of 180 ^{o}C. This higher temperature resulted in slightly higher xylose conversion (~88-90%) and higher furfural yield (~20%), but again, most of the furfural was collected in the pot.

Another set of experiments using H-mordenite (Si/Al=10) extrudates was carried out under the same conditions. In these experiments, the catalyst performance was monitored as a function of reaction temperature. From the results reported in **Table 2**, it was clear that both the xylose conversion and the furfural yield increased with temperature. However, even the highest furfural yield (21%) was still relatively low, and nearly half of that furfural was observed in the pot.

From the results obtained thus far, it was observed that the xylose conversion was significantly high (> 80%), but the furfural yields were quite low (~20%). This could be mainly due to two reasons: 1) xylose was getting converted to furfural, which was further converted into byproducts (oligomers/polymers of furfural) because of inefficient removal of furfural from the reaction zone, and 2) the catalyst was very active and immediately converted xylose (and furfural) into byproducts.

A few additional experiments were carried out with *gamma*-alumina catalyst (extrudates of 0.16 cm O.D.). One experiment was performed with synthetic feed for 4 h, and the products were sampled every 30 min. No additional water was introduced into the pot to generate additional steam in these experiments. The reaction temperature was maintained between 170-180 ^{o}C. During the first 60 min of the reaction, the catalyst color changed from white to black (pictures of the catalyst taken at different times during the reaction are shown in the Electronic

Supplementary Information (ESI)). Analyses of experimental data showed that the furfural yield was ~ 1%. The conversion of xylose was greater than 80%, which meant that the selectivity to furfural was extremely low under these conditions. A similar experiment was performed at a lower temperature range (140-160 ^{o}C), where again a very low yield of furfural was obtained. A large number of uncharacterized byproducts (humins), believed to have been formed through various dehydration and condensation reactions involving furfural, xylose or various intermediate species, appeared to form a black tar that coated the catalyst. The results showed that the *gamma*-alumina catalyst used in this study was highly active but not at all effective (or selective) in producing furfural.

Steam Stripping for Effective Furfural Separation

In the results reported so far, only N_2 alone was used to strip furfural from the reaction zone. However, as shown, just N_2 was not sufficient for this purpose as significant amount of furfural was detected in the pot. Furfural is known to form an azeotrope with water that boils at 97.85 ^{o}C and has a composition of 65 wt% water, or 10 moles water to 1 mole of furfural.[14] To enhance the effective separation of furfural from the reactive zone, it was hypothesized that additional steam would be necessary, and hence steam-stripping was introduced in the experiments discussed below.

To produce steam for effective furfural stripping, water was added to the pot at the bottom of the reaction zone at 0.5 mL/min throughout the reaction. The pot was maintained at a constant temperature of 160 ^{o}C, so that water could be converted into steam, which then traversed up through the reaction zone and then finally collected in the top flask along with other volatile compounds (mainly furfural).

This study was performed with H-beta zeolite (Si/Al=12.5) extrudates under the same operating conditions (temperature of 170 ^{o}C) as before but with added steam. This reaction was run for several hours with the same catalyst over a course of 3 days, with start up and shut down every day. From the results (summarized in **Table 3)** obtained during this study, it was found that the furfural yield increased to 25% (day 1) compared to the 15%, obtained without additional steam stripping. The pot furfural yield decreased, but the overall furfural yield was still quite low and was very similar to that obtained without steam stripping. The results indicated that steam stripping alone was not sufficient, and a more selective catalyst was needed to improve yield. At the end of the second and third day, the furfural yield dropped below that of day 1, but the furfural amount in the pot remained low on both days. A similar investigation was performed with and without steam stripping using H-mordenite (Si/Al=10) extrudates (data not shown). Again, the overall furfural yield was low, but the additional steam helped to drive the furfural to the top of the column.

All the catalysts discussed above were in the form of extrudates and contained some amount of alumina, which was added as a binder to provide adequate crush strength. A maximum furfural yield of ~25% was achieved using these catalysts, which was not sufficient to have an economical process for commercial furfural production. It was suspected that the alumina could be responsible for the lack of selectivity towards furfural. So, it was decided to investigate catalysts without any binder and to use catalyst granules of several zeolite samples (**Table 1**) for further study.

Figure 2 shows the results obtained with H-beta zeolite (Si/Al=12.5) granulated catalyst studied under the same experimental conditions as described earlier. From the experiment carried out for 12 h, it was observed that there was a significant improvement in the furfural yield compared to that obtained with H-beta zeolite extrudates containing alumina binder. The average furfural yield obtained with H-beta zeolite granules was 70%, supporting the hypothesis that the alumina binder was responsible for lower furfural selectivity (which could be due to the formation of oligomeric byproducts). Furfural yield and xylose conversion remained relatively constant during this 12 h run.

A similar study was carried out with H-mordenite granules (Si/Al=10). Furfural yields obtained with this H-mordenite catalyst were slightly higher (~75-80%) than with the H-beta zeolite catalyst. Xylose conversion was about 98% with a furfural seletivity in the range of 75-80%. A very small amount of furfural was detected in the pot. **Figure 3** summarizes the results for various catalysts studied for xylose dehydration under similar operating conditions as described before. Among all the catalysts screened in this study, H-mordenite (Si/Al=10) outperformed the rest of the catalysts and resulted in furfural yield of > 75%. The catalyst screening exercise helped in selecting H-mordenite as the preferred catalyst for further studies with real feed. These results are discussed below [H-beta zeolite (Si/Al=12.5) catalyst was also studied with real feed. These results are reported in the ESI].

As mentioned before, it was observed that steam stripping played a key role in the effective separation of furfural from the reaction zone. Most of the experiments were carried out by adding 0.5 mL/min of water in the pot (maintained at 160 ^{o}C). A separate study, using H-mordenite granules, was carried out to determine the efficacy of steam stripping on furfural yield. Water was added to the pot at flowrates of 0, 0.1 and 0.5 mL/min. **Figure 4** delineates the xylose conversion and furfural yield, as a function of time on stream and parametric in the flowrate of water added to the flask. The furfural yield decreased (as a function of time) rapidly in the absence of steam stripping (0 mL/min), yet the xylose conversion remained high. The yield of furfural was almost identical when 0.1 or 0.5 mL/min of water was added into the pot.

These data confirmed the hypothesis that, indeed, the furfural yield increases with steam stripping. It is important to note that a minimal amount of additional water would be the most economical option, due to the energy requirement to boil water. However, in the current study, the rate of water addition was kept constant at 0.5 mL/min for subsequent experiments.

Furfural from Pre-Hydrolysate Liquor (PHL) Feed

One of the key objectives of this study was to explore the feasibility of using real liquid feedstocks containing xylose to make furfural. There is an abundant supply of aqueous sugar streams available from several dissolving wood pulp mills containing prehydrolysis unit operations in the pulp milling processes. The prehydrolysis step involves autohydrolysis of the wood with the intent of removing some of the hemicelluloses in the biomass. [47-49] These relatively dilute carbohydrate streams are of little value to the pulp mills, but the C_5 sugars contained therein could potentially be useful for the production of furfural. In light of this fact, a representative sample of PHL was studied in this research endeavor. The composition of the PHL feed used in this study is reported in **Table 4**.

The real feed solution was used to study furfural production in the reactive distillation unit using H-mordenite (Si/Al=10) and H-beta zeolite (Si/Al=12.5) granulated catalysts. Results obtained with the H-mordenite catalyst are shown in **Figure 5**. During a 10 h run, C5-sugar conversion, furfural yield, and selectivity dropped significantly. These results were quite different from the results obtained using synthetic feed on the same H-mordenite catalyst, in which no appreciable drop in the performance was observed at a comparable reaction time. A similar study carried out on H-beta zeolite catalyst showed significant decline in both furfural yield and sugar conversion (data are shown in the ESI). PVD analysis was performed to investigate the root cause for the rapid deactivation of the catalysts when PHL solution was used as a feed.

Pore Volume Distribution (PVD) Analysis

Zeolites have high surface areas and large pore volumes. Reduction in surface area (and/or pore volume) could potentially be one of the reasons for the catalyst deactivation. It was hypothesized that the activity of the catalysts tested in the reactive distillation process declined over time due to reduction in surface area (or pore volume), as a result of organic compounds (coke or possibly humins) building up inside the pores and/or on the surface of the solid acid catalysts as is commonly observed in a variety of catalytic and separation processes using zeolites.[50] In this study, different zeolites were analyzed before (“fresh”) and after reaction (“used”) to determine their BET surface area and pore volume. The results are summarized in **Table 5**. A fresh catalyst sample (H-mordenite) was found to have a surface area of 552 m^2/g. When a “used” catalyst tested with synthetic feed was analyzed, the surface area decreased to 19.5 m^2/g. A similar reduction in surface area was also observed for the catalyst used with the real feed. It was discovered that the maxium degassing temperature in the PVD test was only 150 ^oC, which was not high enough to remove the sulfolane solvent from the pores (boiling point = 285 ^oC). To remove these high boilers from the catalyst, the catalyst was degassed at 300 ^oC for 12 h. It was observed that the surface area was largely recovered (~ 400 m^2/g) after degassing at high temperature. The catalysts were thencalcined in air at 500 ^oC (for 1 h), and the surface areas of these calcined catalysts were remeasured. The resulting surface areas of calcined catalysts were comparable to that of the fresh catalyst. Therefore, it was inferred that there was no permanent reduction in surface area (and pore volume) of the catalysts, either when synthetic or real feed was used. Since the PVD analysis was not completely conclusive about the nature of the species present on the catalyst surface or the reason behind catalyst deactivation, TGA analysis was carried out as described below.

Thermogravimetric Analysis (TGA)

To develop further understanding of the nature of the species present on the catalyst surface, TGA was carried out on the catalysts used with the synthetic and real feeds. **Figure 6a** shows the results obtained with a used H-mordenite catalyst after exposure to the synthetic feed. The TGA was performed in the presence of air and nitrogen in two separate experiments. The presence of oxygen in the TGA run under air appeared to accelerate the rate of weight loss above ~400 °C but did not appear to introduce new thermal oxidative decomposition pathways, because the total weight loss after heating to 800 °C was about the same in both (air and N_2) atmospheres Similar results (see ESI) were obtained for the catalyst studied with real feed. This shows that the material deposited on the catalyst run under synthetic/real feed conditions was mainly in the form of a volatile material, which could be removed over a certain temperature. One would expect significantly different slopes (and also higher weight loss for the TGA carried out in air) for the curves obtained in **Figure 6a** if carbonaceous material were present on the catalyst. This is because air/O_2 oxidizes these carbonaceous materials (coke) at a certain temperature range (300-400 ^{o}C). It can be inferred from these results that the organic moieties present on the surface of the catalysts were not carbonaceous material/coke.

A similar TGA analysis was carried out on the catalyst used under real feed conditions. These data are presented in **Figure 6b** and are compared with those of the catalyst used with the synthetic feed. This comparison shows that the weight loss curves for a given catalyst type were nearly identical (above 150 °C, after water loss). The results suggested that materials (other than water and sulfolane) that were present in the used catalyst were probably of similar type and amount, regardless of whether a real or synthetic feed was used. This was an important finding as it suggested that the real (PHL) feed used in this study did not have any specific chemical substance which led to carbonaceous deposit on the catalyst surface, thereby deactivating the catalyst. This led us to speculate that there might have been a different deactivation mechanism in play here. Further catalyst characterization study was carried out to investigate the possible mechanism for catalyst deactivation, and this is discussed below.

Inductively Coupled Plasma (ICP) Analysis

ICP analysis was performed on both the fresh and used H-mordenite catalyst samples [H-beta zeolite data are available in the ESI] subjected to both synthetic and real feeds. The objective of the ICP analysis was to investigate the change in metal composition of these catalysts, before and after the reaction. The concentration profile (ICP data) of various elements present in the starting real feed and the molar ratio (with respect to the Al) of various elements present in the H-mordenite tested under different feed conditions are presented in **Table 6**. The catalyst tested with the synthetic feed had metal content similar to that of the fresh catalyst. The used catalyst, tested with the real feed, not only decreased in activity over time (**Figure 5**), but also showed much higher levels of calcium, potassium and magnesium (reported as molar ratio with respect to Al) than the catalyst tested with synthetic feed. The real feed was also analyzed by ICP, and the data are reported in **Figure 7** (elemental analysis) and **Table 6**. The most prevalent metal ions in the real feed were calcium, potassium and magnesium, suggesting that these metals were removed from the real feed by the catalyst. It was hypothsized that the cations present in the real feed solution exchanged with the H^+ ions in the zeolitic micro-structure, causing it to lose its acidic properties and hence, activity.

To validate this hypothesis, an attempt was made to remove these cations from the feed solution. To do this, the original PHL was first filtered with 0.20 μm filter media to remove any undissolved solids. Subsequently, the filtered PHL was treated with Dowex^{TM} Marathon^{TM} C ion exchange resin (IER) (10% V/V, an acidic IER) that exchanged H^+ in the IER with the soluble metal cations in the PHL feed. The initial pH of this filtered solution was about 3.4, but after stirring it for 2 h with the IER, the pH dropped to ~2. The drop in pH clearly indicated that the cations in the feed solution were being exchanged with the resin while H^+ ions were released into the solution, as expected. The resin/PHL mixture was mixed for a total of 20 h and then filtered through a coarse frit to separate the IER treated PHL from the resin. The comparison of the ICP analyses (**Figure 7**) of the untreated PHL vs 1x-IER (one time IER) treated PHL, indicated that most of the metals were removed from the PHL after IER treatment, leaving behind only a small amount of alkali metals (e.g., K, Na, etc.).

This 1x-IER treated PHL (mixed with 80 wt% sulfolane) feed was used next to test the efficacy of the granulated H-mordenite (Si/Al=10) catalyst. The reactor temperature was maintained at approximately 175 ^{o}C. This particular experiment was carried out for 52 h over 7 days. The xylose conversion obtained in this experiment is compared with that of an earlier experiment carried out with the filtered PHL feed (without IER treatment) in **Figure 8a**. The average furfural yield, selectivity and xylose conversions on each day of this 7 day run, are plotted in **Figure 8b**. From these data, it was clear that the removal of salts/metals from the PHL significantly improved the xylose conversion, furfural yield, and catalyst life. These data supported the hypothesis that the presence of salts in the PHL was the primary reason for the deactivation of the acidic catalyst and that the removal of salts, significantly improved the catalyst performance.

Even though the IER treatment helped to remove most of the salts/cations from the PHL feed and lowered the catalyst deactivation rate, there were still some salts left behind (**Figure 7**) after the first IER treatment, which led to eventual deactivation of the catalyst. To completely remove these salts/cations from the PHL feed, the IER treatment was performed twice (referred to as ‘2x-IER’). ICP data were collected for the untreated, the 1x-IER, and the 2x-IER filtered PHL feeds (**Figure 7**). As seen from this chart, the cations that were not completely removed by the first IER pretreatment (i.e., calcium, potassium), were either completely removed (below detection limits) or nearly completely removed (sodium) after the second ion exchange.

The 2x-IER treated PHL feed was used next to ascertain if additional metal ion removal from the PHL feed would further improve the catalyst performance or not. The furfural yield obtained during a 25 h run (over 3 days) using this feed has been delineated in **Figure 9**. A constant furfural yield of ~76% was observed throughout this run. These results further supported and confirmed the earlier hypothesis that the cations present in the feed were responsible for catalyst deactivation and that a complete removal of these cations *via* IER treatment enabled sustained catalyst performance. [In the ESI, the declining furfural yield/sugar conversion has been compared to the amount of K^+ fed into the reactor. These data showed that there was a direct correlation between K^+ present in the feed and the catalyst deactivation.]

Catalyst Regeneration

Catalyst lifetime is critical in any chemical process.[51, 52] Even though the IER treatment offered a solution for reducing rapid catalyst deactivation and for maintaining high furfural yields in short-term tests, this method solely relies on the effective performance of the IER to eliminate deactivation. In a real industrial/commercial process with long times on stream, slow deactivation may eventually degrade the catalyst performance, cations may occasionally get through the resin, etc., thus making the development of an effective catalyst regeneration procedure necessary.

An accelerated aging test protocol was developed to ensure significant catalyst deactivation prior to regeneration tests. Initially, the H-mordenite (Si/Al=10) catalyst was tested with 2x-IER treated PHL feed, as was performed earlier (for experiments in **Figure 9**). This served as confirmation that the fresh catalyst was working (producing yields ~75%) as expected and did not deactivate during the first 7 h of reaction (day 1) (**Figure 10**). On the second day of the run, the catalyst was exposed to the untreated (filtered only) PHL feed, which still contained the dissolved cations. This experiment was carried out for about 8 h (day 2). As expected, the furfural yield decreased significantly from 75% to about 40%. Thus, the desired deactivated catalyst was obtained successfully.

During this experiment, the color of the catalyst changed from white to black (Please see ESI for pictures of the catalyst before and after calcination). This could be due to the deposition of several species (e.g., sulfolane, high molecular weight moieties, etc.) during the reaction. The black, deactivated catalyst was removed from the reactor and calcined (in air) at a temperature of 500 ^{o}C for 5 h. After calcination, much of the original white color of the catalyst was restored. This calcination procedure was not optimized. However, as hypothesized earlier, the dark color due to the deposition of sulfolane or other high molecular weight species was not the culprit in catalyst deactivation, but rather, the exchange of zeolitic protons with cations present in the PHL feed caused the rapid decline in catalyst activity. To remove these cations and restore the acidity of the H-mordenite, the catalyst was soaked in a 0.05 N sulfuric acid solution overnight. It was then washed with de-ionized water several times. ICP analysis was performed on this regenerated catalyst, and the results (molar ratio with respect to aluminum) are compared to those obtained from the used catalyst tested with untreated PHL feed (**Table 7**). As seen from these data, regeneration with dilute sulfuric acid successfully removed the undesired metal cations, presumably replacing them with H^+. This calcination and dilute acid regeneration appeared to remove more than 91% of the potassium from the used/deactivated catalyst. Overall, the catalyst was successfully regenerated by this procedure.

From the ICP data (**Table 7**), K^+ was found to be the major cation replacing the H^+ in the zeolite framework. Even though potassium and other cations replaced about 20% of the acidic sites, the drop in catalyst activity was more than 20% (**Figure 5**). This indicated that all the acidic sites present in the zeolite pores were probably not being effectively utilized, and the reaction was occurring mostly on the surface of the catalyst. This requires further investigation and a better understanding of the cation exchange procedure taking place in the zeolite pores and could potentially help in better design of a catalyst. To ensure that the regeneration procedure did not affect the zeolite structure, XRD (X-ray diffraction) analyses on both the fresh and regenerated catalyst were performed (diffraction patterns included in the ESI). The XRD patterns of the fresh and the regenerated catalyst were identical, confirming that the dilute acid treatment did not alter the zeolite micro-structure.

The above experiment (**Figure 10**) was then continued with the regenerated H-mordenite catalyst with the 2x-IER treated PHL feed (same as that used on day 1). This run was continued for 10 h on day 3. The regenerated catalyst, which was deactivated on day 2, was successfully regenerated and produced ~75% yields throughout this run, very similar to the yields observed with the fresh catalyst on day 1. This proved that the deactivated catalyst could be regenerated by this relatively simple but robust unoptimized procedure.

In situ **Catalyst Regeneration**

The above study showed that the catalyst can be completely regenerated using high temperature calcination and dilute sulfuric acid treatment. Here, the used catalyst was removed from the reactor and was calcined in a furnace at 500 ^{o}C. However, if frequent catalyst regeneration would be necessary in an industrial process, one would prefer an *in situ* regeneration process to avoid productivity loss due to reactor downtime [Note: *In situ* regeneration refers to a process in which catalyst is regenerated in place without being removed from the reactor]. Also, in an industrial scale reactor, it would be difficult to achieve such a high temperature uniformly across the reactor, and attempts to achieve this goal would likely lead to unattractive capital investment. Therefore, an *in situ* catalyst regeneration procedure without the calcination step was investigated.

One experiment was performed with the used H-mordenite catalyst from the 51 h run (**Figure 8**). After this 51 h run, an attempt was made to regenerate the catalyst *in situ* by dilute acid treatment. This catalyst was not calcined but was soaked (*in situ*) in 0.05N sulfuric acid for 24 h. After acid treatment, it was thoroughly washed with de-ionized water. This regenerated catalyst was then reused with the 2x-IER treated PHL feed in an 8 h reaction (**Figure 11**). It was found that the furfural yield increased to 65%, which was 11-13% higher than that for the catalyst before *in situ* regeneration, but still 10-12% lower than that for the catalyst that was regenerated with calcination and dilute acid soaking (**Figure 10**). Therefore, it was inferred that for maximum catalyst performance enhancement, calcination followed by dilute acid soaking would be necessary.

As identified above, calcination of the catalyst appeared to be necessary for effective catalyst regeneration. But it was difficult to achieve a very high temperature (> 250 ^{o}C) in the lab reactor. Also, at industrial-scale, low temperature would be the preferred option for catalyst regeneration. Perhaps the calcination could be performed *in situ* at lower temperatures, achievable without additional reactor heating capabilities. An experiment was performed in which a used catalyst was calcined (in air) inside an oven for 24 h (see ESI for more details) at different temperatures (in the range of 200-500 ^{o}C), and the weight loss from the catalyst was observed as a function of temperature. There was a very small difference in the weight loss observed at 250 ^{o}C and 500 ^{o}C, suggesting that the low temperature calcination might be just as effective as the 500 ^{o}C calcination. These encouraging results prompted evaluation of the feasibility of low temperature calcination for *in situ* catalyst regeneration.

To determine the feasibility of low temperature calcination, another experiment was performed in which the H-mordenite catalyst was subjected to 2x-IER treated PHL feed. A furfural yield of ~75% was observed during this run (**Figure 12**). After establishing the base line yield with this short run, the catalyst was calcined *in situ* at 225 ^{o}C for 1 h. The purpose of the calcination was to remove the deposits from the surface of the catalyst. After this step, the catalyst was deliberately deactivated using the filtered PHL feed (without IER pretreatment). During this 3 h run, it was noticed that the catalyst activity decreased significantly as the furfural yield declined to ~ 42 %. This deactivated catalyst was then calcined *in situ* at 225 ^{o}C for 24 h. After calcination, the reactor was cooled down to room temperature, and the catalyst was soaked overnight in 0.05 N sulfuric acid. After this low temperature calcination/acid treatment regeneration, the catalyst was thoroughly washed with water. The regenerated catalyst was then tested with 2x-IER treated PHL feed. During this 5 h run, a furfural yield of ~75 % was obtained, and no detectable decline in the furfural yield was observed. The furfural yield obtained with the regenerated catalyst was identical to that observed earlier with a fresh catalyst. This experiment showed that the H-mordenite catalyst used in this study could be successfully regenerated *in situ* at low temperatures (< 250 ^{o}C) with dilute mineral acid treatment.

Conclusions

A comprehensive experimental study of furfural production from synthetic and real wood-based pre-hydrolysate liquor feeds containing xylose was carried out using a continuous reactive distillation process with solid acid catalysts. To the best of our knowledge, this is the first study demonstrating the concept of a continuous reactive distillation process for furfural production using solid acid catalysts and sulfolane as solvent. The technical feasibility of this process was successfully demonstrated with synthetic xylose feeds using an H-mordenite (Si/Al=10) zeolite catalyst where we obtained a furfural yield of ~75% at 175 ^{o}C. In this process, furfural was immediately separated from the reaction zone by steam-stripping of the furfural:water azeotrope, which minimized the formation of undesired high molecular weight by-products and improved the furfural yield. Furfural was collected as pure product with water in the distillate. Sulfolane helped to maintain catalyst activity by continuous catalyst cleaning (by solubilizing and removing high molecular weight byproducts), thus resulting in longer catalyst life.

The feasibility of furfural production from commercial PHL feeds (from a dissolving wood-pulp mill) was successfully demonstrated with the reactive distillation process. Salts (in the form of metal cations) present in these feeds replaced acid sites in zeolite catalysts and thus resulted in significant catalyst deactivation. This catalyst deactivation issue was resolved with effective pretreatment of the PHL with an acidic ion-exchange resin, and this resulted in extended catalyst lifetime and stable furfural yields, similar to that obtained with synthetic xylose feeds. Finally, an *in situ* catalyst regeneration method was demonstrated which could be used for commercial-scale furfural production from PHL feeds.

The concept of continuous reactive distillation for the production of furfural offers various advantages over the conventional batch (Quaker Oats[14]/ homogeneous steam-stripping) process currently used to manufacture furfural. These advantages include high yield, a non-corrosive environment (with the possible exception of *in situ* regeneration), continuous operation, lower humin formation, catalyst recyclability, etc. However, the process as described herein has only been demonstrated at lab scale, and further optimization would be required to solve potential issues (e.g., catalyst deactivation, solvent recycle, etc.) typically faced in industrial-scale operation.

Overall, the reactive distillation process proved to be a promising technique that could potentially be used in the chemical industry, transforming a renewably-sourced biomass to value-added chemicals. Such processes typically suffer from lower rates due to equilibrium limitations, poor selectivity of desired products, catalyst deactivation due to the formation of high molecular weight polymeric compounds formed by undesired series reactions, and require difficult and expensive separation and purification steps. The use of reactive distillation process in other applications awaits further exploration and exploitation.

Acknowledgements

The authors would like to thank Alan Allgeier, Kathy Lloyd, Jane Ramsey and Joseph Galperin for conducting the various characterization techniques used in this study, and Steve Breske for identifying an effective IER to remove problematic cations. We also thank Ben Hambleton, Joseph Nestlerode, Scott Hutchison, David Spritzer, and James Haliburton for their help and dedication in conducting the experiments reported in this paper. Special thanks are extended to Todd Hunt for his careful and diligent thermogravimetric analyses, which provided key insights into the catalyst deactivation and regeneration procedure. Finally, the authors thank E. I. DuPont de Nemours and Co. for support and permission to publish this work.

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Table 1: Catalysts used in this study. Reported catalyst properties were provided by supplier/s.

Catalyst type *	**Supplier**	**Product No.**	**Si/Al**	**Binder**	**BET Surface Area m^2/g**
H-mordenite (powder/granules)	Zeolyst	CBV21A	10	None	500
H-beta (powder/granules)	Zeolyst	CP814E	12.5	None	680
H-Y (powder/granules)	Zeolyst	CBV720	15	None	720
H-ZSM-5 (powder/granules)	Zeolyst	CBV3020	15	None	405
H-Y (extrudates)	Zeolyst	CBV720	15	γ-Alumina (20 wt.%)	720
H-mordenite (extrudates)	Zeolyst	CBV21A	10	γ-Alumina (20 wt.%)	500
H-beta (extrudates)	Zeolyst	CP814E	12.5	γ-Alumina (20 wt.%)	680
gamma-alumina (extrudates)	BASF	Al-3952	n/a	None	186
Titania (TiO_2) – Anatase (extrudates)	Evonik	Aerolyst® 7711	n/a	None	48
Silica (SiO_2) (extrudates)	Saint-Gobain NorPro	XS16080	n/a	None	250
Zirconia (ZrO_2) (extrudates)	Saint-Gobain NorPro	XZ16052	n/a	None	85

* Zeolite catalysts (except Y) were originally obtained in the ammonium form. They were calcined in air at 550 °C (for 8 h) to obtain H-form of zeolite.

Table 2: Results obtained with H-mordenite (Si/Al=10) extrudates. Experimental conditions: Feed: 5 wt% xylose, 15 wt% water, 80 wt% sulfolane, catalyst amount: 10 g, feed flow rate: 0.75 mL/min, reaction time: 2 h.

Temperature (˚C)	**Xylose conversion (%)**	**Total furfural yield (%)**	**Total furfural selectivity (%)**	**Top furfural yield (%)**	**Pot furfural yield (%)**
151	68	< 1	-	-	-
163	81	3	4	1	2
174	93	13	14	8	5
185	95	21	22	11	10

Table 3: Results obtained with H-beta zeolite (Si/Al=12.5) extrudates with enhanced steam stripping. Experimental conditions: Feed: 5 wt% xylose, 15 wt% water, 80 wt% sulfolane, catalyst amount: 10 g, feed flow rate: 0.75 mL/min, temperature: 175 ^{o}C.

Day	Time (min)	Xylose conversion (%)	Total furfural yield (%)	Total furfural selectivity (%)	Top furfural yield (%)	Pot furfural yield (%)
1	144	71	25	35	20	5
2	420	66	10	15	8	2
3	305	70	10	14	8	2

Table 4: Analysis of filtered pre-hydrolysate liquor feed obtained from hardwood digestion.

	wt % of liquid
Glucose (C_6)	0.74%
Xylose (C_5)	4.66%
Galactose (C_6)	0.46%
Arabinose (C_5)	0.00%
Mannose (C_6)	0.88%
Fructose (C_6)	0.00%
Formic Acid	0.44%
Acetic Acid	2.20%
HMF	0.06%
Furfural	0.27%
Total C5	**4.66%**
Total C6	2.09%
pH	3.39

Table 5: BET surface area of H-mordenite (Si/Al=10) catalysts

	BET surface area (m^2/g)
Fresh catalyst	552
Uncalcined - used catalyst with synthetic feed	19
Uncalcined - used catalyst with real feed	38
Calcined - used catalyst with synthetic feed	538
Calcined - used catalyst with real feed	535

Table 6: ICP data for real feed (ppm amounts of various elements in the real/PHL feed) and molar ratio (with respect to Al) of various elements present in fresh H-mordenite (Si/Al=10), H-mordenite used with synthetic feed, and H-mordenite used under real feed conditions.

Element	**PHL feed (elements in ppm)**	**Molar ratio**	**Fresh H-mordenite catalyst**	**H-mordenite catalyst with synthetic feed**	**H-mordenite catalyst with filtered PHL real feed**
Al	<1	Al/Al	1	1	1
Ca	560	Ca/Al	4.15E-04	3.25E-03	1.39E-02
Cr	< 1	Cr/Al	4.92E-04	6.45E-04	5.16E-04
Fe	21	Fe/Al	1.02E-02	1.22E-02	9.39E-03
K	908	K/Al	6.72E-04	2.60E-04	1.96E-01
Mg	172	Mg/Al	4.87E-03	5.02E-04	1.97E-02
Mn	62	Mn/Al	1.26E-04	1.85E-04	2.64E-03
Na	88	Na/Al	5.96E-03	1.25E-02	3.60E-02
Ni	< 1	Ni/Al	2.24E-04	5.54E-04	5.68E-04
Si	11	Si/Al	9.90	10.52	10.57

Table 7: ICP data (presented as molar ratio with respect to Al) for used H-mordenite (Si/Al=10) catalyst (tested with filtered PHL feed and the same catalyst then regenerated (with calcination and acid treatment))

	H-mordenite catalyst tested with filtered PHL feed	**Regenerated H-mordenite catalyst (calcined & acid treated)**
Si/Al	10.5700	10.6000
K/Al	0.19618	0.0165
Mg/Al	0.01969	0.0008
Mn/Al	0.00264	0.0001
Na/Al	0.03598	0.0094

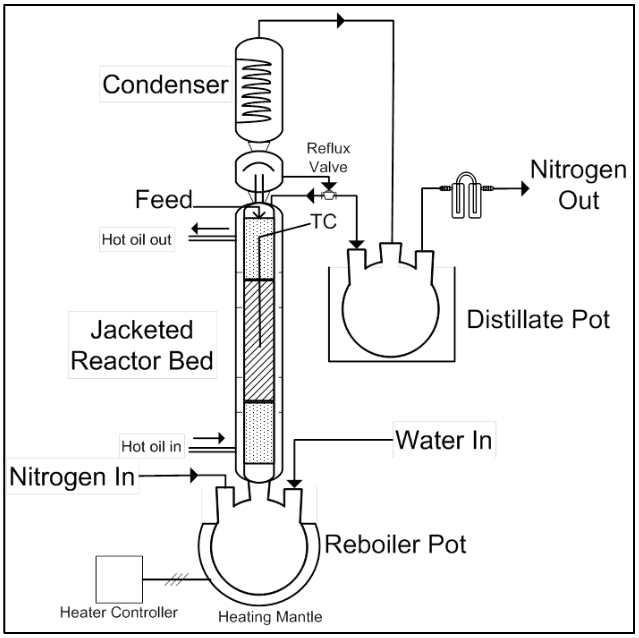

Figure 1: Schematic representation of lab-reactor set up used for the reactive distillation process.

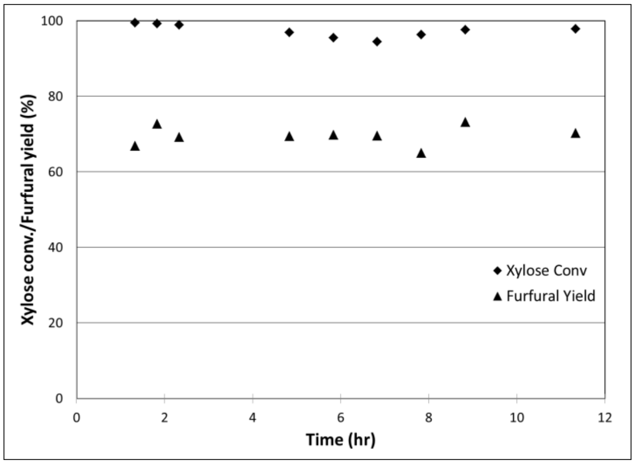

Figure 2: Xylose conversion and furfural yield obtained as a function of time using H-beta zeolite (Si/Al=12.5) granulated catalyst. Experimental conditions: feed: 5 wt% xylose, 15 wt% water, 80 wt% sulfolane, catalyst amount: 10 g, temperature: 170-175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot for steam generation: 0.5 mL/min.

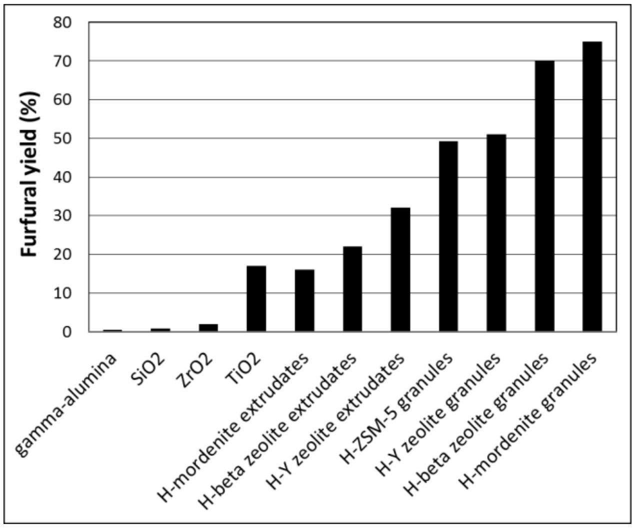

Figure 3: Furfural yield obtained during catalyst screening study on various catalysts. Experimental conditions: feed: 5 wt% xylose, 15 wt% water, 80 wt% sulfolane, catalyst amount: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot: 0.5 mL/min, total reaction time: 5 h.

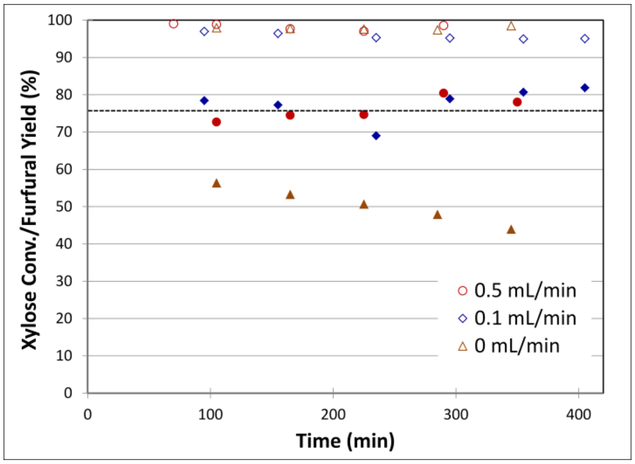

Figure 4: Xylose conversion and furfural yield obtained during experiments with various water flow rates (to generate steam) in the reboiler pot. Hollow symbols: xylose conversion, solid symbols: furfural yield. Experimental conditions: feed: 5 wt% xylose, 15 wt% water, 80 wt% sulfolane, H-mordenite (Si/Al=10) catalyst: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot for steam generation: 0-0.5 mL/min. (horizontal dashed line - 75 % yield).

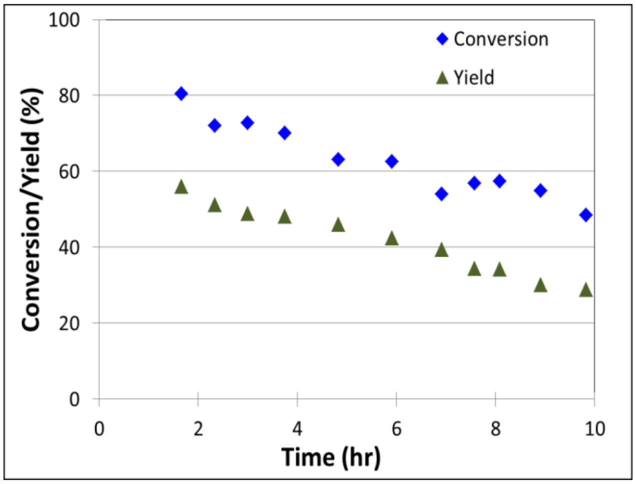

Figure 5: Xylose (C5-sugar) conversion and furfural yield obtained during experiments carried out on H-mordenite (Si/Al=10) granulated catalysts using real feed solution. Feed: 20 wt% filtered PHL, 80 wt% sulfolane, H-mordenite (Si/Al =10) catalyst: 10 g, temperature: 175 °C, feed flow rate: 0.75 mL/min, water flow rate in the pot for steam generation: 0.5 mL/min.

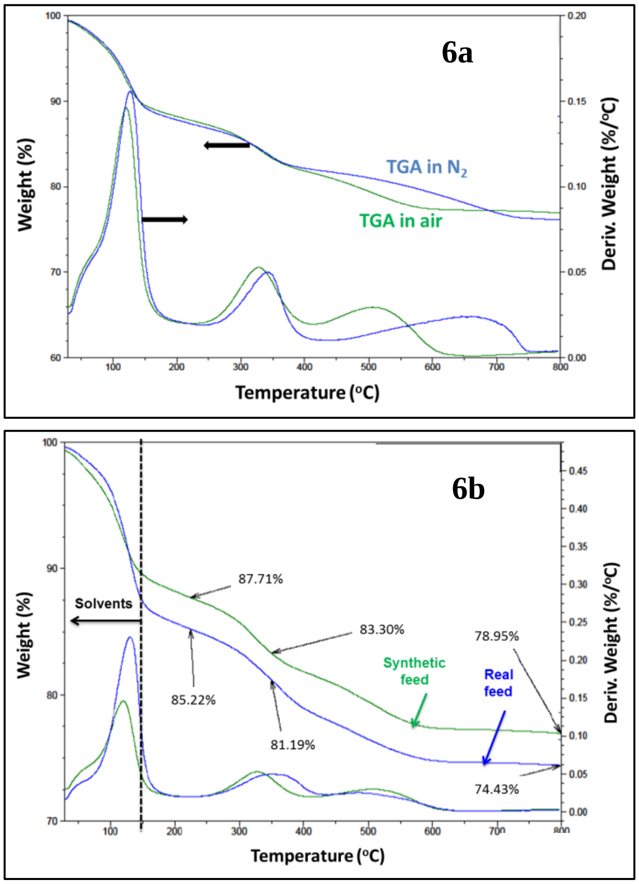

Figure 6: TGA carried out on the H-mordenite (Si/Al=10) catalyst granules a) used under synthetic feed conditions, in the presence of air (green curve) and N_2 (blue curve) and b) comparison of TGA (in air) data obtained on used H-mordenite catalyst tested under synthetic

and real feed conditions. The weight loss was identical for both the real and synthetic feeds, except for an intial difference of 2% attributed to the intial amount of solvent (water) on the catalyst surface. Both, % weight loss and derivatized weight loss (secondary Y-axis), are shown.

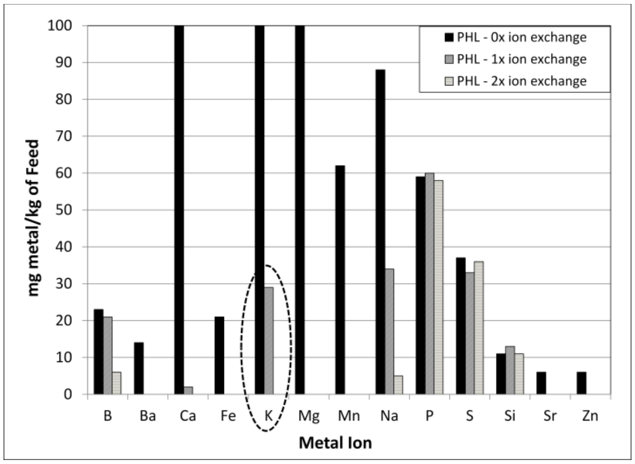

Figure 7: Comparison of metals present in the PHL feed, before and after ion-exchange resin (IER) treatment with Dowex^{TM} Marathon^{TM} C resin. The ICP data were collected before IER treatment, after 1x IER treatment and 2x IER treatment. The ion-exchange was performed using 10 vol% (of feed) resin at room temperature (time = 6h).

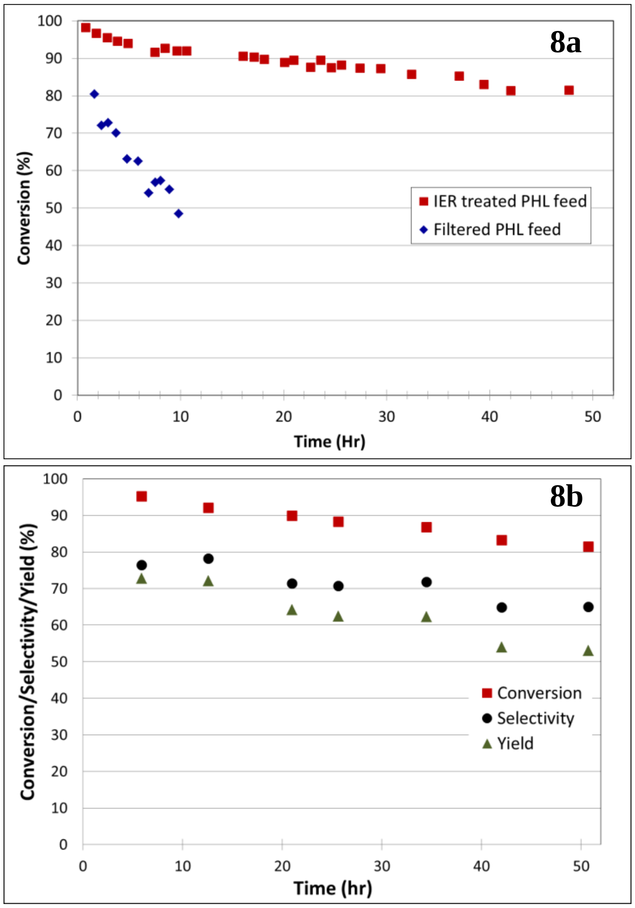

Figure 8: a) Comparison of xylose conversion obtained on H-mordenite (Si/Al=10) catalyst using filtered and Dowex^{TM} Marathon^{TM} C resin (1x IER) treated PHL feed. b) Average (of each day) conversion, furfural yield and selectivity obtained during 7 day run. Experimental conditions: feed: 20 wt% filtered/1x-IER treated PHL, 80 wt% sulfolane, catalyst: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot for steam generation: 0.5 mL/min.

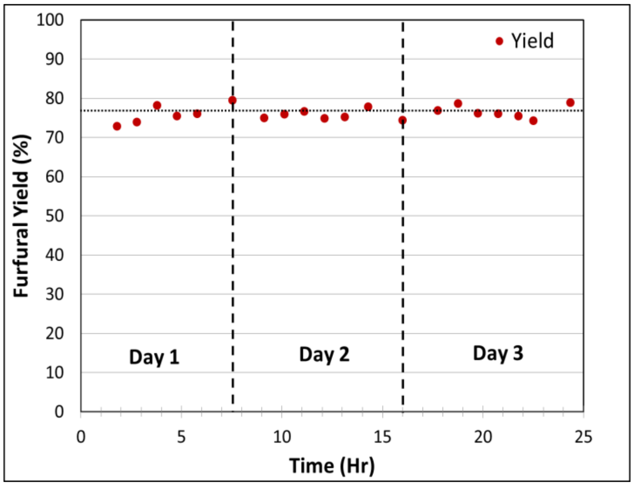

Figure 9: Furfural yield obtained during a reactive distillation study carried out on H-mordenite catalyst (Si/Al=10) using 2x IER treated PHL feed. Experimental conditions: 20 wt% PHL, 80 wt% sulfolane, catalyst: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot for steam generation: 0.5 mL/min (horizontal dashed line - 76% yield).

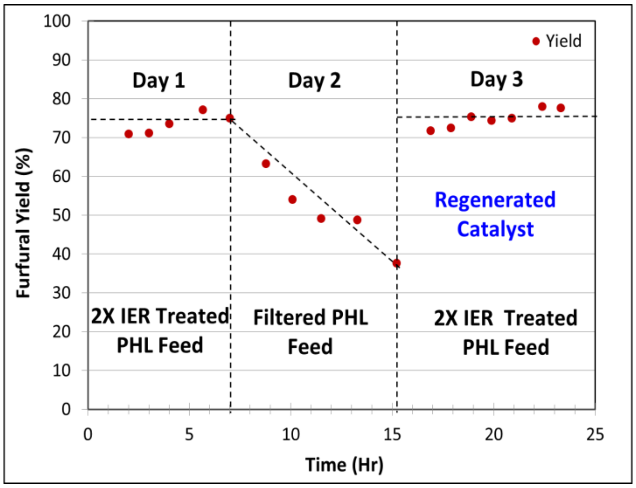

Figure 10: Furfural yield obtained during a reactive distillation process on H-mordenite (Si/Al=10) catalyst. On day 1 and day 3, Dowex^{TM} Marathon^{TM} C treated (2x IER) PHL feed was used. On day 2, filtered PHL feed without IER treatment was used. Experimental conditions: 20 wt% PHL, 80 wt% sulfolane, catalyst: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot for steam generation: 0.5 mL/min.

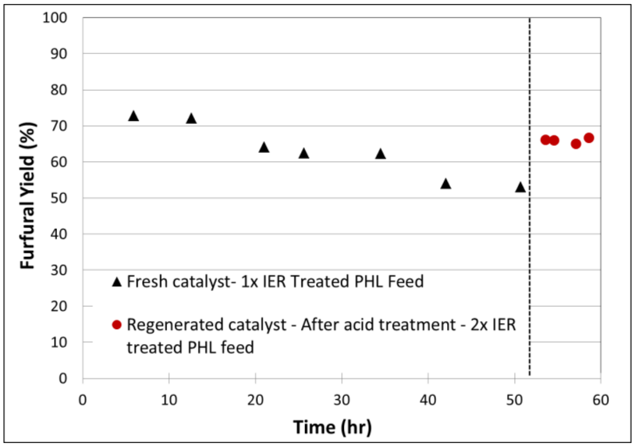

Figure 11: Furfural yield obtained during a reactive distillation run. Triangles: Fresh H-mordenite (Si/Al=10) catalyst with 1x IER treated PHL feed. circles: yield data obtained with catalyst regenerated *in situ* by soaking in 0.05 N sulfuric acid for 24 h, feed: 2x IER treated PHL feed. Experimental conditions: feed: 20 wt% PHL (1x/2x IER treated), 80 wt% sulfolane, catalyst: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot: 0.5 mL/min.

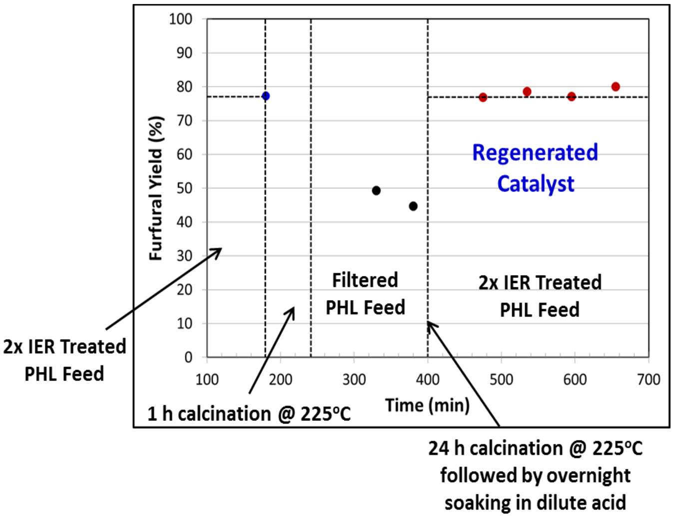

Figure 12: Furfural yield obtained during an experiment carried out with 2x IER treated PHL feed, filtered PHL feed, and 2x IER treated PHL feed. After the 1st step, the catalyst was calcined at 225 ^{o}C (for 1 h, in N_2) to remove sulfolane from the catalyst surface. After treating with filtered PHL feed, the catalyst was calcined at 225 ^{o}C (for 24 h, in N_2) and soaked overnight in 0.05 N sulfuric acid for regeneration. Experimental conditions: feed: 20 wt% PHL (filtered/2x IER treated), 80 wt% sulfolane, H-mordenite (Si/Al=10) catalyst: 10 g, temperature: 175 ^{o}C, feed flow rate: 0.75 mL/min, water flow rate in the pot: 0.5 mL/min.