FeCl₃ and acetic acid co-catalyzed hydrolysis of corncob for improving furfural production and lignin removal from residue

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HIGHLIGHTS

- FeCl₃ and acetic acid were used to co-catalyze the hydrolysis of corncob.
- Lignin could be removed by the solvation effect of acetic acid in FeCl₃ medium.
- Destroyed fibrous structure of corncob leads to a great pressure drop in the system.

GRAPHICAL ABSTRACT

Acetic acid and FeCl₃ co-catalyzed hydrolysis of corncob not only promoted the furfural yield, but also enhanced the lignin removal. In addition, FeCl₃ was more effective in cellulose degradation while acetic acid favored the lignin removal. A maximum furfural yield of 67.89% was obtained within 30 min, combined with a lignin and cellulose removal rates of 54.79% and 25.71%, respectively, at 3% of acetic acid and 20 mM of FeCl₃ and 180 °C of reaction temperature.

ARTICLE INFO

Article history:
Received 9 May 2012
Received in revised form 13 July 2012
Accepted 16 July 2012
Available online 25 July 2012

Keywords:
Acetic acid
Corncob
FeCl₃
Furfural
Mass heat transfer

ABSTRACT

In order to increase furfural yield and lignin removal, both FeCl₃ and acetic acid were used to co-catalyze the hydrolysis of corncob. A series of experiments were carried out to investigate the effects of acetic acid, FeCl₃ concentrations and temperatures on furfural production and residue characteristics. The results showed that high FeCl₃ concentrations caused serious cellulose degradation while acetic acid was more effective for lignin removal. A maximum furfural yield of 67.89% (35.74% higher than that in conventional sulfuric acid-catalyzed process) was obtained at 180 °C in the presence of 20 mM of FeCl₃ and 3% of acetic acid. Simultaneously, lignin removal reached 54.79%, and 74.29% of the cellulose was remained for further utilization. Acetic acid and FeCl₃ co-catalyzed hydrolysis was not only a high efficiency and environmental friendly technique, but also provided a possibility to utilize the furfural residue for ethanol production and other industries.

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1. Introduction

As one of the most important and valuable chemicals, furfural is produced from lignocellulosic biomass by dehydrating pentoses which are present in the hemicellulose of the agriculture residues, such as corn cob, corn stock, rice hull, and olive stones (Lichtenthaler, 1998; Zeitsch, 2000). The current output of furfural is about 700,000 t yr⁻¹ around the world with a market price of around $2000 t⁻¹. Commercially, furfural is produced using sulfuric acid as homogeneous catalyst. First, the feedstock is mixed with an aqueous solution of sulfuric acid and loaded to the digester. The system is
maintained at the desired reaction temperature by injecting steam to the digester. Xylan is hydrolyzed to xylose and other monosaccharide, and further dehydration reactions of the pentoses yield furfural. Furfural is continuously stripped out from the reaction system by steam distillation (Montané et al., 2002). Although this process technology has been commonly used in more than 400 furfural plants in China for decades, some problems were encountered, such as large amount of furfural loss (nearly account for 40–50% of the potential furfural yield), corrosion of pipelines and valves at high temperature, safety issues and environmental problems due to toxic waste effluents (Tellería et al., 2011). For those reasons, the development of appropriate technology remains great interests for lignocellulosic hydrolysis and the growth of furfural industry.

In last decades, plenty of efforts have been made to improve the furfural yield. Although the furfural yield higher than 80% was achieved when pure xylose was used as a substrate (Dias et al., 2005; Montané et al., 2002), the furfural yield rarely exceeded 60% when it was produced from lignocellulosic biomass via one step process (Montané et al., 2002; Yemis and Mazza, 2011). In previous studies, many acidic heterogeneous catalysts (i.e. NaCl, MgCl2, CaCl2, Fe(acac)3, FeCl3.6H2O, FeSO4.7H2O, FeCl2.4H2O, MnCl2, Cu(OAc)2, and CuCl2.2H2O) were applied to obtain a mild and homogeneous hydrolysis reaction in the dehydration of xylose (Garrote et al., 1999; Xing et al., 2011), and FeCl3.6H2O was found to display a superior performance on hydrolysis of lignocellulosic biomass (Bayramoglu et al., 2012; Bu et al., 2011; Montané et al., 2002; Weingarten et al., 2010). Furthermore, it was also observed that the reaction of xylose catalyzed by FeCl3 was much faster than that by strong acid (i.e. HCl) and other chlorine salts (i.e. CaCl2, NaCl, KCl and KBr) (Marmotullio and Jong, 2010). So far, there are limited researches focusing on both promoting furfural production and the residue characteristics of lignocellulosic biomass, which may contain large amount of cellulose for bioethanol production and paper industry. An integrated use of cellulose, hemicellulose and lignin is very important for economical feasibility of biorefining industry. Due to technology and cost barriers (Chandra et al., 2007), currently, only hemicellulose (xylan) that contained in the raw stuff was utilized and converted to furfural in industrial process, and the waste residue was often used for solid fuel after drying. It was estimated that about 12–15 t of hydrolysis residue was discharged if 1 t of furfural is produced (Bu et al., 2011; Sun et al., 2008). The furfural residue contained large portion of cellulose that could be converted into glucose for ethanol fermentation (Bu et al., 2011), single cell protein production (Parajó et al., 1995) or for paper pulp (Grethlein and Converse, 1991). The largest obstacle to utilizing cellulose biomass or residual residue was cost-effectively to release sugars from recalcitrant lignocelluloses (Bu et al., 2011; Lynd et al., 2008; Rollin et al., 2011). It was rather difficult to digest the furfural residue with a low loading of enzymes because of the presence of a large amount of lignin (Bu et al., 2011). Therefore, a pre-treatment to remove lignin is a crucial step for an effective enzymatic hydrolysis (Bu et al., 2011). However, there is little research about the optimization of the catalysts and hydrolysis conditions for promoting furfural production and economically utilizing the furfural residue.

Acetic acid as a modest, low corrosive and environmental friendly catalyst was proved effective in catalyzing lignocellulosic biomass to produce furfural (Dallinger and Kappe, 2007; Garrote et al., 1999; Lowry, 1927; Zeitsch, 2000). In those studies, acetic acid was mixed lignocellulosic biomass in aqueous phase for hydrolysis and furfural production (Abad et al., 1997; Yemis and Mazza, 2011), but there was limited information about utilizing acetic acid steam as catalyst for furfural production. In addition, acetic acid was found to be an effective agent for fractionation of lignocellulosic biomass. For example, it caused an extensive delignification with simultaneous hemicellulose degradation at a high pulp yield (Dallinger and Kappe, 2007; Ligero et al., 2008; Vandergheem et al., 2011; Zhao and Liu, 2010).

In this study, FeCl3 and acetic acid (in steam form) were used to co-catalyze the hydrolysis of corncob for promoting furfural production. Another special focus was put on the effects of FeCl3 and acetic acid on cellulose recovery and delignification, which is important for value-added utilization of furfural residue. Specifically, we systematically investigated the separate and combined effect of FeCl3 and acetic acid on furfural yield, cellulose and lignin removals at different concentrations and temperatures. Based on experimental results, the mechanism of FeCl3 and acetic acid stimulating the furfural production was tentatively proposed.

2. Methods

2.1. Materials

Corncob was obtained from Changtu County Furfural Plant, Liaoning Province, China. The corncob was sieved to a size between 5 and 10 mm, air-dried, homogenized in a single lot, and stored for further use. Acetic acid, furfural standard, FeCl3.6H2O, sulfuric acid (Tianjin Keweiz Co., China) used in the experiments were analytical reagents without further purification. Distilled water was used to prepare the solutions and dilute the samples.

2.2. Reactor system and experiment procedure

A series of experiments were carried in a semi-batch tubing-bomb reactor system (see Fig. 1), which was designed according to industrial furfural production process. The reactor was a 47 mm of I.D. (Internal Diameter) stainless-steel vessel with a volume of 2.1 L. K-type thermocouple and pressure transducer were mounted inside the reactor to record the temperature and pressure, respectively. The feedstock was firstly mixed with varying concentrations of FeCl3 and then loaded to the digester. Varying concentrations of acetic acid solution was firstly loaded into a tailor-made electric boiler (Jinxin Petrochemical Equipment Co., Ltd., Weihai, China) and then heated to a desired pressure. The high-pressure steam that contained acetic acid was continuously injected into the reactor to supply catalysts and maintain the system at the desired reaction temperature. Furfural was continuously extracted from the digester by steam distillation. In order to collect the liquid products completely, the exhausted steam was condensed by the liquid nitrogen.

In each experiment, the reactor was loaded with an amount of corncob equivalent to 400 g of dry matter. In order to reduce interstitial water and ensure the feeding steam distribute homogeneously into the granular corncob, a liquid: solid ratio of 0.6:1 (slightly below saturated water content of corncob) was used. Based on our previous optimization (data not shown), the reaction time was chosen to be 30 min. It must be noted that, in order to obtain a constant and homogeneous content of acetic acid in the reaction system, acetic acid was continuously carried into the reactor by feeding steam rather than directly mixing with feedstock before the reaction occurred.

2.3. Product analysis

The main fractions (cellulose, hemicelluloses and lignin) were analyzed after a quantitative acid hydrolysis under standard conditions (Parajó et al., 1993). The main compositions of the corncob were 34 ± 1% of cellulose, 31 ± 1% of hemicelluloses, and 18 ± 1% of lignin. Liquid was extracted and filtered through a 0.22 μm syringe filter. The residues were firstly immersed in 1% of NaOH solu-
tion for half an hour and then washed with fresh distilled water until neutral. The samples were dried at 50°C for 12 h and milled to a size under 40 meshes. The xylan was determined using NREL LAP “Determination of Structural Carbohydrates and Lignin in Biomass” (Sluiter et al., 2008). For this method, a two-step acid hydrolysis was used to hydrolyze the remaining xylan into forms of xylose, which is then quantified by HPLC. The concentrations of furfural in the liquid were also analyzed by HPLC with a Bio-Rad HPX 87H column at 40°C. The mobile phase was a mixture of 0.005 M H2SO4 and HPLC-grade acetonitrile (84%/16% vol/vol) at a flow rate of 0.5 mL min⁻¹ (Yuan and Chen, 1999).

The furfural yield, remaining cellulose and xylan, and xylan loss were calculated according to the following equations, respectively. Theoretical yield of furfural yield was obtained by multiplying the amount of xylan by 0.7272 (Zeitsch, 2000).

\[
\text{Furfural yield} = \frac{\text{furfural yield} \times \text{g in concentrate}}{\text{theoretical production of furfural} \times 100}
\]

\[
\text{Remaining cellulose} = \frac{\text{cellulose} \times \text{g in residue}}{\text{cellulose} \times \text{g in dry, untreated corncob} \times 100}
\]

\[
\text{Remaining xylan} = \frac{\text{xylan} \times \text{g in residue}}{\text{xylan} \times \text{g in dry, untreated corncob} \times 100}
\]

\[
\text{Xylan loss} = 1 - \text{Remaining xylan} - \text{Furfural yield}
\]

Corncob and residue were submitted to SEM (Scanning Electron Microscopy) analysis. The samples were prepared by abiding them on a specimen stub using a double-coated tape, and were sputter coated with AuPd prior to imaging with a KYKY-2800 scanning electron microscope (KYKY Technology Development Ltd., China) using 15 kV accelerating voltage.

3. Results and discussion

3.1. Impact of acetic acid or FeCl₃ on hydrolysis of corncob

Fig. 2A shows the effects of acetic acid concentrations on furfural yield, hemicellulose degradation, and lignin and cellulose removals. It was observed that the furfural yields firstly increased from 17.45% to 41.29% as acetic acid concentrations in the feeding steam increased from 1% to 3%, and then declined to 38.98% at 4% of acetic acid concentration. The xylan loss was found to continuously increase from 24.88% to 43.59%, indicating that high concentrations of acetic acid caused more xylan loss. Acetic acid exerted different effects on the lignin and cellulose removals during furfural process. For instance, the removals of lignin and cellulose increased from 7.82% and 5.83% to 41.54% and 18.02%, respectively, as acetic acid concentrations in the feeding steam increased from 1% to 4%. These results suggested that acetic acid exerted stronger effect on lignin removal than that of cellulose when using as catalyst for corncob hydrolysis.

When high yield of furfural was recovered as the primary product from corncob hydrolysis, it was expected to obtain high delignification and low cellulose degradation for the residue. So, furfural residue can be further utilized in bioethanol production or paper industry. Fig. 3 illustrates the effects of temperatures, concentrations of acetic acid and FeCl₃ on the furfural yield, lignin and cellulose degradation during the hydrolysis of corncob at diverse and combination conditions.

3.2. Effect of temperatures on the xylan degradation, lignin and cellulose removals in the presence of FeCl₃ and acetic acid

Fig. 2B shows the effects of FeCl₃ as a substitute of strong acid on furfural production, xylan loss, and lignin and cellulose removals during furfural production process. It was observed that furfural yield firstly increased from 32.47% to 55.98% as FeCl₃ concentrations increased from 20 to 60 mM, but further increase of FeCl₃ concentration to 100 mM caused the lower yield (44.67%). Similarly as acetic acid, the xylan loss continuously increased from 21.55% to 53.95% when FeCl₃ concentrations increased from 20 to 100 mM. These results indicated that increasing FeCl₃ concentrations favored the furfural formation, but an excessive FeCl₃ caused more furfural loss. Liu and Wyman (2006) also reported that FeCl₃ not only catalyzed furfural formation but also accelerated furfural resinification and condensation. The lignin removal increased from 6.81% to 19.14%, while the cellulose removal increased from 9.71% to 51.06% as FeCl₃ concentrations increased from 20 to 100 mM. Based on these results, it was concluded that FeCl₃ was more effective in the cellulose degradation than that of lignin removal.

3.2.1. Experiments at 170°C

Fig. 3A shows the effects of FeCl₃ and acetic acid concentrations on the xylan degradation, lignin and cellulose removals at 170°C. At 1% of acetic acid concentration, the furfural yields increased...
Fig. 2. Influences of acetic acid or FeCl₃ concentration on xylan degradation, lignin removal and remaining cellulose. (A) Only acetic acid was used and (B) only FeCl₃ was used.

Fig. 3. Effects of FeCl₃ and acetic acid concentration on xylan degradation, lignin removal and remaining cellulose. (A) 170 °C; (B) 180 °C; (C) 190 °C; and (D) 200 °C. (1) 20 mM of FeCl₃; (2) 40 mM of FeCl₃; (3) 60 mM of FeCl₃; (4) 80 mM of FeCl₃.
from 32.25% to 52.19% as FeCl₃ concentrations increased from 20 to 80 mM. Simultaneously, the remaining xylan decreased from 41.27% to 8.98%, and the xylan loss increased from 26.48% to 38.83%. Remaining cellulose and lignin decreased from 87.54% and 92.19% to 69.98% and 80.37%, respectively. These results suggested that FeCl₃ not only promoted the hydrolysis of hemicellulose but also favored the condensation of furfural and intermediates causing the loss of furfural (Liu et al., 2009). When acetic acid was 2%, the furfural yields first increased from 48.59% to 61.27% as the FeCl₃ concentrations increased from 20 to 60 mM, and then decreased to 57.98% at 80 mM of FeCl₃. At the same time, xylan loss first decreased from 31.74% to 25.85% as FeCl₃ concentrations increased from 20 to 40 mM, and then increased to 36.41% at 80 mM of FeCl₃. The remaining lignin and cellulose continuously decreased from 76.24% and 85.22% to 49.85% and 65.54%, respectively, when FeCl₃ concentrations increased from 20 to 80 mM. Interestingly, at acetic acid concentration of 3%, the furfural yields continuously decreased from 64.27% to 50.24% as the FeCl₃ concentrations increased from 20 to 80 mM. This difference might be due to the fact that at high acetic acid concentrations, the increased FeCl₃ concentrations caused much stronger side reactions between furfural, cellulose, lignin and glucose. Simultaneously, the xylan loss also increased from 31.52% to 48.77%, and the remaining lignin and cellulose decreased from 47.28% and 84.27% to 32.25% and 63.44%, respectively, as the FeCl₃ concentrations increased from 20 to 80 mM. These results confirmed that acetic acid played an essential role on lignin removal, and the high FeCl₃ caused serious cellulose degradation. In addition, the combination of acetic acid and FeCl₃ showed synergistic effects on furfural yield and xylose loss.

3.2.2. Experiments at 180 °C

Fig. 3B shows the effects of FeCl₃ and acetic acid concentrations on the xylan degradation, lignin and cellulose removals at 180 °C. The results were similar with those obtained at 170 °C. At acetic acid concentration of 1%, furfural yields increased from 36.98% to 59.64% as the FeCl₃ concentrations increased from 20 to 60 mM, and further increase (80 mM) caused a lower yield (53.67%). Xylan loss also increased from 25.43% to 42.12% as above. At acetic acid concentration of 2%, the furfural yield first increased from 51.59% to 63.69% as FeCl₃ concentrations increased from 20 to 40 mM, and then declined to 59.45% at 80 mM of FeCl₃. Similarly, the xylan loss showed first decreasing trend, then increasing with the minimum value of 29.44% at 40 mM of FeCl₃. At acetic acid concentration of 3%, the furfural yield dropped from 67.89% to 55.21% and the xylan loss increased from 31.14% to 44.79% as FeCl₃ concentrations increased from 20 to 80 mM. The largest difference between the results at 180 °C and those at 170 °C was the degree of cellulose degradation. As the temperatures increased from 170 to 180 °C, much more cellulose was removed (Fig. 3A and B). For instance, at 3% of acetic acid concentration and 80 mM of FeCl₃, the remaining cellulose was decreased from 63.44% to 29.98%. In addition, it was found that the granular corn cob was destroyed and converted to muddy fluid under these conditions. There was a similar result in a previous work (Liu et al., 2009), where the remaining cellulose decreased from 73% to 20% as the temperatures increased from 160 to 180 °C at 100 mM of FeCl₃ concentration. By contrast, no significant change on lignin removal was found as the temperatures increased from 170 to 180 °C.

3.2.3. Experiments at 190 °C

The effects of FeCl₃ and acetic acid concentration on the xylan degradation, lignin and cellulose removal at 190 °C are shown in Fig. 3C. As the temperatures increased from 180 to 190 °C, the furfural yield generally increased when the acetic acid concentration was 1%. For instance, an increasing trend of furfural yield (from 59.64% to 62.35%) and a minor reduction of xylose loss (form 31.39% to 31.11%) were observed as temperatures increased from 180 to 190 °C when acetic acid and FeCl₃ concentration were 1% and 60 mM, respectively. This result indicated that furfural loss caused by side reactions could be reduced by increasing temperature in a mild condition. But when the acetic acid concentrations were 2% and 3%, the furfural yield generally declined with increasing temperatures. For example, xylan loss increased from 29.44% to 30.64% and furfural yield declined from 63.69% to 56.98% as temperatures increased from 180 to 190 °C when acetic acid and FeCl₃ concentration were 2% and 40 mM, respectively. In addition, the remaining lignin and cellulose gradually declined as the temperature increased from 180 to 190 °C. Although high lignin removal was achieved (20.37% of the lignin remained in the residue) at 190 °C at the conditions of 3% of acetic acid and 80 mM of FeCl₃. Only 18.01% of the cellulose was remained in the residue. The high cellulose loss was not desirable for further utilization of cellulose for bioethanol plant and other industries.

FeCl₃ not only promoted furfural formation, but also caused the cellulose degradation especially at high temperatures, which was the main cause of the cellulose loss during the pretreatment (Liu et al., 2009). Based on our experimental results, the concentrations of FeCl₃ should not exceed 20 mM so as to promote the furfural yield and simultaneously obtain a high cellulose yield in the residue.

3.2.4. Experiments at 200 °C

Fig. 3D showed a general up trend of xylan loss and corresponding down trend of furfural yield as the temperatures increased from 190 to 200 °C. For instance, furfural yield declined from 64.57% to 45.61% and xylan loss increased from 31.16% to 52.29% as temperatures increased from 190 to 200 °C at 2% of acetic acid and 60 mM of FeCl₃. Riera et al. (1991) also obtained a similar result that furfural yields decreased from 8.7 to 4.1 g/100 g dried corn cob as the temperatures increased from 180 to 200 °C at 0.16 mM of H₂SO₄. These results indicated that many side reactions (condensation of furfural with intermediates and self-resification of furfural) occurred at high temperatures especially in the presence of strong catalysts. Other side reactions, such as the esterification of cellulose with acetic acid and the polymerization of furfural with lignin could occur (Lam et al., 2009). The products, a kind of black, viscous polymerized resin attached to the surface of particle corn cob, which would prevent the diffusion of furfural and the further hydrolysis of corn cob. On the other hand, the viscous aqueous phase prevent the stripping out of furfural causing the long residence time, which further facilitated more side reactions.

In short, above results showed the differential effects of acetic acid and FeCl₃ on furfural yield, xylan loss, and lignin and cellulose degradation at different temperatures. In general, the combination of high temperature with high concentration of FeCl₃ in acetic acid media could not only accelerated cellulose and hemicellulose solubilization, but also promoted cellulose and xylose degradation. Therefore, the FeCl₃ could be employed but the concentrations should not exceed 20 mM for enhanced furfural production and a high level of remaining cellulose in the residue. Based on above results, balancing the furfural yield, xylan loss, lignin removal and cellulose degradation, the optimized conditions were 20 mM of FeCl₃ and 3% of acetic acid and 180 °C of reaction temperature. At the optimum conditions, a high furfural yield of 67.89% was achieved together with high lignin removal of 54.79% and high remaining cellulose of 74.29%.

3.3. Mechanism of FeCl₃ and acetic acid promoting furfural yield

In previous studies, the “proton transfer” theory of acid (Lowry, 1927), “stabilizing effect” (Marcotullio, 2010) and “salting out” ef-
fect of chlorine salts were adopted to explain the phenomena in hydrolysis of lignocellulosic materials, furfural production, degradation of lignin and cellulose. In this study, the theory of mass and heat transfer was tentatively employed to elucidate the mechanisms of strong promoting effect of FeCl₃ and acetic acid on the furfural production and other performances, such as xylose loss, lignin removal, and cellulose degradation.

Classical one-step method for the furfural production in a batch process involves six processes (Gámez et al., 2006): (I) diffusion of protons through the wet lignocellulosic matrix; (II) solvation of xylan from hemicellulose; (III) acid catalyzed hydrolysis of xylan to xylose; (IV) dehydration of xylose to form furfural catalyzed by acid; (V) diffusion of furfural in the liquid phase; (VI) distillation and stripping of furfural by feeding steam. Ideally, the theoretical yield of furfural was 100%, where xylose could be converted to furfural (Zeitsch, 2000). But in practice, the maximum furfural yields were between 45% and 55% of the potential (Montané et al., 2002). The relative low furfural yield could be mainly caused by two reasons. One was the low hydrolysis of lignocellulosic materials, and the other was ascribed to the furfural loss caused by the side reactions.

Previous results proved that the furfural yield was higher from smaller particle size due to the bigger surface area per unit volume of reacting solids (Riera et al., 1991). Since more energy was consumed to produce smaller particles, in industrial furfural plant, the granule was not too small (generally 1–2 cm). In this study, corncob particles were further destroyed to small size during the hydrolysis process when FeCl₃ and acetic acid were used as catalysts. SEM observation of microscopic structure of hydrolysis residues clearly showed that the corncob particles were greatly destroyed in acetic acid and FeCl₃ medium (data not shown). By contrast, an intact fibrous structure of the residue was observed when corncob was hydrolyzed by pure water. Furthermore, there were clear images indicating that crash severity of corncob increased with increasing the concentrations of FeCl₃ and acetic acid (data not shown). Consequently, the interior porosity of the corncob dramatically increased as the fibrous structure was damaged and fragmented during steps I-III. As a result, the dissolution and diffusion rate of xylan increased and the catalysts (Fe³⁺, Cl⁻, H⁺ and CH₃COOH) distributed more homogeneously into the liquid phase as schematically shown in Fig. 4. In addition, the entirely destroyed fibrous structure resulted in an increased specific surface area of the granular corncob. Therefore, the contacting area between distributed liquid and steam increased as shown in Fig. 4A, which also promoted the mass and heat transfer, and favored the furfural recovery by steam stripping. All these contributed to a milder and more homogeneous hydrolysis and dehydration reaction in the presence of FeCl₃ and acetic acid.

After reactions of steps I–III, the furfural was formed by dehydration of xylose catalyzed by acid and/or FeCl₃ in step VI. Furfural contains three unsaturated bonds with the highly reactive characteristics. Chemically, furfural participates in the same kinds of reactions as other aldehydes and other aromatic compounds, which caused furfural loss. So, the step VI was very important for controlling the furfural recovery and furfural loss, where furfural was continuously extracted from the reactor by steam distillation. A short residence time of furfural in the aqueous phase was the key to avoid the side reactions. Ideally, 100% of the furfural could be...
Consequently, the pressure drop was dramatically affected by the mass and heat transfer efficiency of the reaction system (Tamir, 1994). In addition, the methods to increase pressure drop and obtain a subsequent increment of mass transfer driving force could be effective in accelerating the stripping of furfural and obtaining a higher furfural yield. In this study, the influences of pressure gradient on the furfural yield were analyzed quantitatively.

It was reported that the pressure drop $\Delta p$ depends on particle diameter $d_p$, porosity $\epsilon$, particle shape and fluid property (density $\rho_l$ and viscosity $\mu_l$) and flow velocity of the fluid ($\phi_0$) (Ergun, 1952). The pressure drop in a packed bed of porous medium can be calculated according to Eq. 5:

$$\Delta p = \frac{150(1-\epsilon)^2}{\epsilon^3} \frac{\mu_0 \phi_0}{d_p U_e} + 1.75 \frac{(1-\epsilon)}{\epsilon^3} \frac{\rho_1 \phi_0 \frac{\phi_0}{d_p}^{0.5}}{d_p}$$

where, $L$ is the height of the reactor. $\Phi$ is the shape factor. Obviously, the pressure drop $\Delta p$ is inversely proportional to porosity $\epsilon$ and particle diameter $d_p$. During the hydrolysis of corncob, the corn-cob particles were destroyed which led to a diminishing of $\epsilon$ and $d_p$. Consequently, the pressure drop $\Delta p$ increases. In order to investigate the relationship of pressure drop and the furfural yield, the pressure drop and the corresponding furfural yield at 180 °C with different catalysts were determined, and the experimental results are shown in Fig. 5.

It was found that the pressure drop was dramatically affected by the crash degree of corncob, which was catalyzed by different catalysts. When steam was used without any foreign acid, the fibrous structure in the residue remained intact and the pressure drop was 114 Pa. By contrast, the pressure drop reached 13,873 Pa at the conditions of 3% of acetic and 20 mM of FeCl₃. Additionally, when the pressure drop increased from 4785 Pa (at the conditions of 3% of acetic and 20 mM of FeCl₃) to 20,000 Pa at the temperatures of 180 °C to 13,873 Pa, the furfural yield increased from 36.25% to 67.89%. Simultaneously, the percentage of xylan loss of corncob also decreased from 54.91% to 32.91%. These results indicated that the pressure drop could reflect the furfural yield and furfural loss, and the high pressure drop correlated severe crash of corncob catalyzed by catalysts.

4. Conclusion

Acetic acid and FeCl₃ co-catalyzed hydrolysis of corncob not only promoted the furfural production, but also enhanced the lignin removal. The increased acetic acid concentrations exhibited higher lignin removal than that of cellulose removal, while the higher FeCl₃ exerted stronger effect on cellulose degradation than that of lignin removal. A maximum furfural yield of 67.89% was obtained within 30 min at 180 °C together with a 54.79% of lignin removal and a 25.71% of cellulose removal in the presence of 3% of acetic acid and 20 mM of FeCl₃.

Acknowledgement

The authors acknowledge the financial support from the National Natural Science Foundation of China (NSFC) (No. 511000618), National Water Pollution Control and Management Technology Major Projects (No. 2012ZX07020003-004), and Special Fund of Environmental Protection Research for Public Welfare of China (201109035).

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