Furfural (FF) is a typical dehydration product of pentose, and it can be converted into a series of novel liquid fuels and fuel additives, such as γ-valerolactone (GVL), 2-methyltetrahydrofuran (MTHF), and 2-methylfuran (MF) [1, 2]. GVL can be used directly as a liquid fuel or as an additive to current petroleum fuels, similarly to ethanol [3]. MTHF is a component of the P-fuel series, and recently MF has also been brought to the attention of fuel researchers [4, 5].

Pentoses make up around 60% of hemicellulose, which is one of the three major components in lignocellulosic biomass [6]. Hence, hemicellulose is a main source of substrates for FF production. The production process of FF comprises two main steps: hemicellulose is first hydrolyzed to pentoses such as xylose, and secondly the pentoses are dehydrated to form FF. Considering the complicated composition of biomass, xylose, a pentose found at high levels in hemicellulose, has been extensively used to study the formation of FF and to develop novel reaction systems [7]. In current commercial technologies for FF production, wheat straw and corn cob are usually chosen as substrates, and the common catalyst is a mineral acid such as sulfuric acid, hydrochloric acid, etc. [8, 9]. However, the commercial production process is still associated with several problems, such as low FF yield (around 50%) and equipment corrosion [8, 9]. De Jong obtained a good FF yield of 85% from straw in aqueous solution [10]. However, this yield was estimated from a model. Mandalika and Runge [11] used poplar wood chips as feedstock and achieved an FF yield (55.81%). Addition of an appropriate amount of NaCl further increased the yield to 69.20%. Other carbohydrates (arabinose and xylan) were also tested in the same reaction system and modest results were obtained.

Abstract

A novel green reaction system of CO₂–water–isopropanol has been developed for the production of furfural (FF) from xylose. Initially, a simple CO₂–water system was investigated, and the results showed that the formation of FF from xylose was greatly enhanced. CO₂ at high pressure could increase the acidity of the reaction system, and thus the FF yield was improved. By raising the reaction temperature, the conversion of xylose was remarkably accelerated in the CO₂–water–isopropanol system, leading to an acceptable conversion rate (94.41%) and FF yield (55.81%). Addition of an appropriate amount of NaCl further increased the yield to 69.20%. Other carbohydrates (arabinose and xylan) were also tested in the same reaction system and modest results were obtained.
concentrated seawater (10 ×), and acetic acid steam. The calculated yield was the actual FF yield divided by the theoretical FF yield, which was based on multiplying the amount of xylan by 0.7272. In this way, the yield could be higher than the true yield. Besides, it is possible that other compounds, such as oligosaccharides containing uronic acid and xylose units, which are not usually identified using traditional methods of xylan quantification such as HPLC, may have become potential sources of FF [5]. Thus, the development of a green reaction system with high efficiency has been the focus of much research in recent years.

Solvent and catalyst are two critical factors that must be taken into account when designing a reaction system for FF production. Solvent effects inevitably influence the thermodynamics and kinetics of the reaction, and they vary among different kinds of solvent [14]. The solvents used for FF production can be divided into three categories: single-phase systems, biphasic systems, and ionic liquids. Pure water is a typical green reaction medium that is extensively utilized in large-scale FF production [15]. However, water is also a polar protic solvent, which can easily induce side reactions and the formation of insoluble humin, and therefore aqueous reaction systems could result in lower FF yields compared with those based on a polar aprotic solvent [16–18]. Therefore, an organic solvent that is immiscible with water is added to prepare a biphasic solvent system, in which the newly formed FF in the aqueous phase can be simultaneously extracted into the organic phase [19]. Ionic liquids show excellent performance for the production of FF, but their high cost, undesirable viscosity, as well as the need to devise efficient product separation protocols limit their large-scale utilization [7]. Thus, the current reaction systems for FF production need to be made greener and more economical. In particular, the development of a renewable organic solvent as a single-phase system has received a great deal of attention [20–23]. Isopropanol, an organic alcohol solvent with low boiling point, is environmentally friendly, inexpensive, and easily recyclable [24]. Research has shown that isopropanol has the capacity to suppress the polymerization of FF, and as such appears highly promising for utilization in the production of FF from pentoses [16].

Exploitation of a recyclable catalyst with high activity has been one of the key aims in the research on FF production. The catalysts most commonly used for the dehydration of carbohydrates to produce FF comprise homogeneous acids (organic acids, inorganic acids, salts, etc.), solid acids (acidic resins, zeolites, metal oxides, etc.), and acidic ionic liquids [7, 25, 26]. Nevertheless, there are still some problems associated with these acidic catalysts, such as the poor recyclability and high corrosivity of homogeneous acids, the deactivation of solid acids owing to humin deposition, and the high cost of ionic liquids. Compared to these catalysts, CO₂ as an acidic gas can easily overcome these various drawbacks because of its nontoxic and recyclable nature, and it can dissolve in water and numerous organic solvents to provide an acidic environment [27]. Besides, large amounts of CO₂ are being released from the combustion of fossil fuels all over the world, making it a widely accessible greenhouse gas. Pressurized CO₂–water reaction systems have frequently been used for the hydrothermal conversion of biomass under mild conditions, because the carbonic acid generated by the dissolution of CO₂ in water can greatly promote the hydrolysis of cellulose and hemicellulose therein [28, 29]. Recent research has shown the possibility of using CO₂ as a catalyst for the conversion of xylose and hemicellulose into FF [30]. Morais et al. [30] chose CO₂ as a catalyst and converted xylose into FF in a water–tetrahydrofuran–methyl isobutyl ketone (water–THF–MIBK) solvent system. A maximum FF yield of 56.6% and an acceptable selectivity of 62.3% were obtained at 180°C in a reaction time of 60 min. Kumar et al. [31] converted xylose into FF in a CO₂-enriched medium consisting of water and an ionic liquid. They found that CO₂ enhanced the acidity of the solution and therefore the reaction rate was increased. A 90.2% yield of FF was obtained at 160°C in a reaction time of 2 h (50 wt% ionic liquid in the medium).

Recently, the influence of halides on the dehydration of sugars to FF has been attracting much attention, since the presence of halide ions showed peculiar catalytic effects on this reaction [24, 32, 33]. In particular, metal chlorides were reported to accelerate the degradation of xylose and especially xylotriose at 180°C [34]. Marcotullio and De Jong [24] studied the reaction mechanism of xylose dehydration to FF and tested several chloride salts in dilute acidic solutions at temperatures between 170°C and 200°C. Significant improvements in FF yield and selectivity with the addition of chloride salts were observed in their research, and it was postulated that chloride ions favor the dehydration of xylose.

In general, the production of FF from xylose is an acid-catalyzed process, and in our previous research, the novel green reaction system of CO₂–water–isopropanol showed excellent performance for the production of 5-hydroxymethylfurfural (HMF) by fructose dehydration [21]. In this study, we have applied the system of CO₂–water–isopropanol in the production of FF, and the influence of CO₂ pressure, reaction temperature, water/isopropanol ratio, and amount of NaCl added on the conversion of xylose have been assessed. The feasibility
of using the same reaction system for the dehydration of other carbohydrates (arabinose and xylan) has also been tested.

Experimental Section

Materials

Xylose, arabinose, isopropanol, FF, and NaCl were purchased from Aladdin Industrial Corporation (Shanghai, China). Xylan extracted from beech wood was purchased from Sigma Corporation (St. Louis, MO, USA). All chemicals were of analytical grade and were directly used without purification. CO₂ with a purity of 99.995% was purchased from Hangzhou Jingong Special Gas Corporation (Hangzhou, China).

Procedure for conversion of carbohydrates to FF

A schematic representation of the reactor system used in this work is shown in Figure 1. In a typical reaction process, a mixture of xylose (3 g) and solvent (water or water-isopropanol at a specified volume ratio; 60 mL) was placed in the Parr reactor (100 mL; Parr Instruments, Moline, IL, USA). The reactor was then charged with CO₂ and pressurized to a specified level. Subsequently, mechanical agitation was applied at a stirring rate of 500 rpm for 1 h to make most of the CO₂ dissolve and to reduce CO₂ density variations due to changes in initial temperature. The pH of the solution in the reactor was measured and compared with that of a CO₂-saturated solution under atmospheric pressure to ensure that the solution was nearly saturated with CO₂. The conversion reactions were then carried out at the same stirring rate. The temperature was preprogrammed by means of a reactor controller (Parr Instruments) following a two-step process. The reactor was first heated from room temperature to 140°C at a rate of 12°C/min. Thereafter, it was heated to the desired temperature at a slower rate (5°C/min) to avoid overheating. After the reactor had been held at the designated temperature for the required duration, heating was stopped and the reactor was cooled to room temperature by an air flow. The liquid sample was collected from the reactor and filtered through a 0.22-mm syringe filter. It was then analyzed by high-performance liquid chromatography (HPLC). Each experiment was performed in triplicate.

Analytical methods

The filtered solution was analyzed on a Dionex HPLC system (Dionex, Sunnyvale, CA, USA) equipped with a Bio-Rad Aminex HPX-87H column (Bio-Rad, Hercules, CA, USA) and an RI 2000 refractive index detector. H₂SO₄ solution (pH 2.5) was used as the mobile phase, and its flow rate and the corresponding column temperature were kept at 0.6 mL/min and 60°C, respectively. The concentrations of xylose, arabinose, and FF were determined by reference to standard calibration curves. The conversion rates of pentoses (xylose and arabinose) and the yields of FF were calculated as follows:

\[
\text{pentose conversion rate} = \frac{\text{moles of pentose reacted}}{\text{moles of starting pentose}} \times 100\%
\]

\[
\text{FF yield} = \frac{\text{moles of FF formed}}{\text{moles of starting pentose}} \times 100\%
\]

Figure 1. Schematic representation of the reactor system used for the production of furfural from carbohydrates.
Results and Discussion

Conversion of xylose in the CO₂–water system

As shown in Figure 2, the conversion rate of xylose and the corresponding FF yield increased notably with increasing CO₂ pressure. When xylose was treated at 180°C for 180 min, its conversion rate and the yield of FF increased from 66.78% and 31.71% at 0.1 MPa to 75.03% and 38.69% at 2.0 MPa, respectively. Besides, it was obvious that the increase in FF yield on going from 1.0 MPa to 2.0 MPa was more marked than that on going from 0.1 MPa to 1.0 MPa. High CO₂ pressure was beneficial for its dissolution in water, and in this way more carbonic acid was generated, leading to higher acidity of the solution, which favored the dehydration of xylose to form FF. By comparison with the acid-catalyzed production of FF, under neutral hydrothermal conditions, the reaction pathway of xylose primarily involves its thermal degradation to form FF, glycolaldehyde, glyceraldehyde, etc. [35, 36]. Cao et al. [35] conducted hydrothermal conversion of xylose for 10 min at 180°C and obtained a relatively low conversion rate and an FF yield of 15.68% and 3.73%, respectively. When the reaction temperature was increased to 240°C, the conversion rate and FF yield were significantly increased to 99.5% and 33.9%, respectively. Morais et al. [30] studied the conversion of xylose in pure water with CO₂ as the catalyst at a higher pressure of 5 MPa, whereupon an almost 100% conversion rate was achieved at 180°C within 60 min. In spite of this, the FF yield was rather low (16.5%), which may have been due to the occurrence of undesirable degradation reactions related to xylose under acidic hydrothermal conditions at high pressure.

Effect of isopropanol on the conversion of xylose in the CO₂–water system

Figure 3 shows the xylose conversion rates and FF yields in the reaction system of CO₂–water–isopropanol. It was
found that the conversion of xylose was slower with the addition of isopropanol than in pure water. Both the conversion rate of xylose and the yield of FF showed decreasing trends as the relative content of isopropanol was increased. When the reaction was conducted for 180 min at 180°C, the conversion rate of xylose decreased from 75.03% in pure water to 65.66% in water–isopropanol (1:2, v/v), and the corresponding FF yield decreased from 38.68% to 9.79%. Previously, we investigated the conversion of fructose in the CO₂–water–isopropanol system, and the results indicated that the introduction of isopropanol decreased the amount of dissolved CO₂ [21]. Hence, the acidity of the reaction system was reduced with increasing proportion of isopropanol, which resulted in decreases in xylose conversion and FF yield. Morais et al. [30] carried out xylose dehydration in a water–THF–MIBK solvent system at an initial CO₂ pressure of 2 MPa at 180°C. After 60 min of reaction, the xylose conversion rate and FF yield reached 85% and 35%, respectively. The xylose conversion in their research was better than that in our study; this was because water–THF–MIBK constitutes a biphasic system, providing ideal conditions for CO₂ to generate carbonic acid in water. Thus, the dehydration reaction could be better catalyzed. Moreover, the water-immiscible MIBK prevented degradation reactions of FF by extracting it from water, thus favoring its production.

**Effect of reaction temperature on the conversion of xylose in the CO₂–water–isopropanol system**

Figure 4 shows the effect of reaction temperature on xylose conversion at a water–isopropanol ratio of 2:1. It is obvious that both the conversion rate of xylose and the yield of FF increased rapidly with increasing temperature. When the reaction was conducted for 180 min at 170°C, the conversion rate of xylose and the FF yield were 61.81% and 17.21%, respectively. When the reaction temperature was further increased to 180°C, 190°C, and 200°C, the corresponding conversion rates and yields increased to 72.51% and 32.51%, 83.17% and 38.50%, and 94.41% and 55.81%, respectively. The direct conversion of xylose to FF usually requires a high activation energy (around 30 kcal/mol), such that the reaction needs to be conducted at a temperature higher than 150°C [37]. The reaction system in this research was based on catalysis by carbonic acid produced by the dissolution of CO₂ in water. Carbonic acid has relatively weak acidity and therefore an even higher reaction temperature was required for the conversion of xylose to FF. Jing and Lu [36] studied the hydrothermal conversion of xylose at high temperatures (180–220°C), and the maximum FF yield of 50% and the highest conversion rate of 95.8% were obtained at 220°C. However, such high temperature could also lead to the occurrence of side reactions. In particular, under acidic conditions, the formed FF could undergo undesirable reactions such as Diels–Alder addition [38]. Under acidic conditions at high temperature, this reaction may easily be initiated by the formation of a hydrogen bond between the oxygen atom of the aldehyde group of FF and a hydroxonium ion (H₃O⁺), through which the electron density of the aldehyde group on FF is increased, while that of the furan is decreased. Diels–Alder reaction between two FF molecules would thereby be accelerated, leading to the formation of complex compounds [39]. Besides, high reaction temperature might also result in hydrolytic fission of the aldehyde group of FF to generate formic acid and direct degradation of xylose to form small-molecule products such as glyceraldehyde and glycolaldehyde [36, 39, 40]. Hence, it is of great importance to choose an appropriate reaction temperature to obtain the best compromise between the yield of targeted
Effect of NaCl addition on the conversion of xylose in the CO\textsubscript{2}–water–isopropanol system

From analysis of the above results, it could be inferred that xylose was efficiently converted into FF in the simple system of CO\textsubscript{2}–water–isopropanol. The highest FF yield (55.81%) and xylose conversion rate (94.41%) were obtained at 200°C with a CO\textsubscript{2} pressure of 2 MPa in a reaction time of 180 min. In the similar research performed by Morais et al., the reaction system of water–THF–MIBK was employed and the maximum FF yield of 56.5% and highest xylose conversion rate of 90.7% were achieved under the optimized conditions (2 MPa CO\textsubscript{2}, 180°C, 60 min) [30]. These moderate yields of FF suggest that the simple employment of CO\textsubscript{2} as an acidic catalyst for the conversion of xylose is not able to ensure high FF yields.

Chloride ion has been reported to accelerate the enolization of xylose, which should favor FF formation [24, 32]. With a view to further increasing the performance of the reaction system, NaCl was introduced into the solvent as an additive, and the obtained results are presented in Figure 5. It can be seen that although the addition of NaCl had little influence on the conversion rate of xylose, the yield of FF was dramatically increased. On adding 0.3 g, 0.9 g, and 1.8 g of NaCl, the FF yield increased from 55.81% (without NaCl) to 62.28%, 69.20%, and 67.00%, respectively. This indicated that the presence of NaCl selectively promoted the generation of FF. For the optimal case, whereby the maximum yield of FF was obtained (69.20%), we isolated the product from the reaction mixture in a rotary evaporator. The isolated yield of FF was calculated as 75 ± 5% (considering the total FF yield in the reaction as 100%). Bhaumik and Dhepe [41] reported the production of FF in a solvent system of water and toluene, and they obtained a similar isolated yield of 79% (based on 100% total FF yield) by means of distillation.

When the amount of NaCl added was increased to 1.8 g, the FF yield began to decrease. This unexpected trend was also found by Marcotullio et al. [24]. They concluded that an excess of chloride ions relative to hydrogen ions led to undesirable reactions caused by accumulated 1,2-enediol intermediates. Consequently, the FF yield showed a slight drop in the presence of much NaCl.

Hongsiri et al. [42, 43] obtained similar results for the acid-catalyzed conversion of xylose to FF at 200°C. Compared to conditions of catalysis by hydrochloric acid or oxalic acid without salt addition, they found that the introduction of NaCl improved the FF yields from 52.8% to 64.3% and from 50.5% to 59.3%, respectively.

Conversion of other carbohydrates in the CO\textsubscript{2}–water–isopropanol system

The conversion results of arabinose and xylan in the CO\textsubscript{2}–water–isopropanol system are shown in Table 1. When no NaCl was added, the conversion rate of...
Table 1. Conversion results of xylose, arabinose, and xylan in the CO₂–water–isopropanol system.

| Feedstock | Temperature (°C) | Time (min) | Water–isopropanol ratio | NaCl addition (g) | FF yield (%) | Conversion rate (%) |
|-----------|------------------|------------|-------------------------|------------------|--------------|--------------------|
| Xylose    | 200              | 180        | 2:1                     | –                | 55.81        | 94.41              |
| Xylose    | 200              | 180        | 2:1                     | 0.9              | 69.20        | 93.64              |
| Arabinose | 200              | 180        | 2:1                     | –                | 15.63        | 95.67              |
| Arabinose | 200              | 180        | 2:1                     | 0.9              | 39.09        | 95.80              |
| Xylan     | 200              | 180        | 2:1                     | –                | 10.96        | –                  |
| Xylan     | 200              | 180        | 2:1                     | 0.9              | 15.60        | –                  |

Arabinose was already over 95%, but the corresponding FF yield of 15.63% was much lower than that from xylose under the same conditions, indicating an impediment for arabinose to be converted into FF. Gallo et al. [46] investigated the conversion of pentoses catalyzed by sulfuric acid, and they also found that the FF yield from arabinose was unsatisfactory, amounting to only half of that from xylose. Garrett analyzed the reaction kinetics for degradations of xylose and arabinose, and their results revealed that arabinose gave a lower rate constant than xylose, which was attributed to the different steric positioning of the hydroxyl groups in the reactive forms of these two pentoses [47]. Dussan et al. [48] further demonstrated that the distribution of tautomers of xylose and arabinose in an aqueous medium could affect their reactivities. Arabinose predominately exists in α-pyranose form (about 57%) in water, which gives low FF selectivity owing to its great thermal stability. In contrast, xylose exists in water mainly in its β-pyranose form (about 65%), which can be readily converted into FF.

With the addition of NaCl, the conversion rate of arabinose was still over 95% and remained almost unchanged, while the FF yield increased dramatically from 15.63% to 39.09%. It could be inferred that chloride ion was also important for the production of FF from arabinose, and a reaction mechanism akin to that for the enolization of xylose was likely to be involved. Hongsiri et al. [42, 43] applied hydrochloric acid and oxalic acid in the conversion of arabinose to FF at 200°C, and moderate FF yields of 24.5% and 44.7%, respectively, were obtained. When they added NaCl to the aqueous solvent, the yields of FF from arabinose catalyzed by hydrochloric acid or oxalic acid increased to 34.5% and 49.1%, respectively.

Xylans are polysaccharides composed of xylose units connected by β-1,4-glycosidic bonds. The conversion process from xylan to FF involves two steps: xylan is first hydrolyzed to form xylose, and then the xylose undergoes dehydration to generate FF. The data in Table 1 indicate that the FF yield from xylan was low, at just 10.96%. Even when NaCl was added, the yield only increased slightly to 15.60%. This could be attributed to insufficient cleavage of the β-1,4-glycosidic linkages in xylan due to the low acidity of the CO₂–water–isopropanol reaction system. Thus, the amount of reactive xylose was low, leading to a poor yield of FF. Meanwhile, some oligosaccharides formed from the slow hydrolysis process could cause side reactions unfavorable for the formation of FF. From a practical point of view, when dealing with raw biomass feedstocks, an autohydrolysis process is needed in order to deconstruct the biomass into soluble oligosaccharides [11, 49]. Further processing of the formed hemicellulosic sugars in the proposed system of CO₂–water–isopropanol would be much more desirable.

**Conclusion**

This research has mainly been focused on elucidating the conversion of xylose to produce FF in a reaction system of CO₂–water–isopropanol. In the simple CO₂–water system, the carbonic acid generated by CO₂ dissolution can catalyze the dehydration of xylose to form FF, and increasing the CO₂ pressure further enhances the acidity of the reaction system, thereby accelerating FF production. After the introduction of isopropanol, the acidity of the system was weakened, and therefore the conversion of xylose and the formation of FF were suppressed. By optimizing the reaction temperature, the highest FF yield obtained in the CO₂–water–isopropanol system was over 55%. When NaCl was added to the solvent, the conversion rate of xylose was almost unchanged, but the yield of FF was greatly improved to around 70%. Moreover, the conversion results for arabinose and xylan in the CO₂–water–isopropanol system indicated that the addition of NaCl considerably promoted the formation of FF, although the yields still remained at low levels.

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Conflict of Interest

The authors declare that they have no competing interests.

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