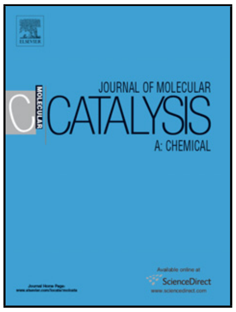

Title: Conversion of xylose, xylan and rice husk into furfural
via betaine and formic acid mixture as novel homogeneous
catalyst in biphasic system by microwave-assisted dehydration

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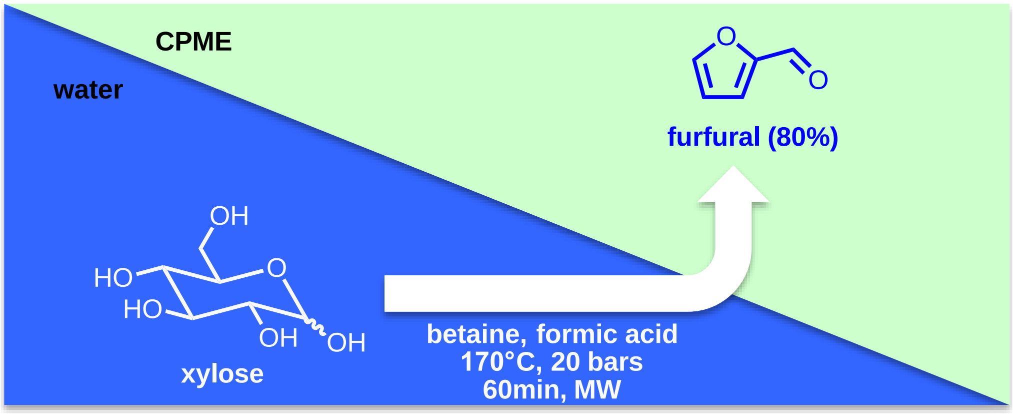
Highlights

- Microwave activation for the dehydration of D-xylose to furfural.
- Water-CPME as biphasic system to limit the production of humin.
- Betaine-formic acid mixture is an efficient acid catalyst system for the synthesis of furfural.
- The reusability of the catalyst was efficient during ten cycles.
- Application to xylan and rice husk gave the furfural in good yields.


CPME
water
OH
HO
O
HO
OH
OH
xylose
betaine, formic acid
170°C, 20 bars
60min, MW
O
O
furfural (80%)

Conversion of xylose, xylan and rice husk into furfural via betaine and formic acid mixture as novel homogeneous catalyst in biphasic system by microwave-assisted dehydration

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Abstract: Dehydration of D-xylose and direct transformation of xylan into furfural were achieved by means of betaine-formic acid (HCOOH) catalytic system. All reactions were microwave-assisted and carried out in a CPME-water biphasic system. At 170°C, in a pH range between 1.9 and 2.3, highest yields of 80 % and 76 % were obtained respectively for the pentose and the polysaccharide. Time dependence of the dehydration and influence of the temperature on the reaction kinetics were studied. Besides, at 190°C, using the optimized condition of the reaction, rice husk was also employed as a source of furfural with a single stage reaction.

Keywords: Furfural, biphasic system, microwave-assisted dehydration, xylan, rice husk.

1. Introduction

Furfural or furan-2-carbaldehyde is a compound easily produced from xylose or directly from the hemicellulosic biomass dehydration. Due to its composition, rich in D-xylose, xylan should also become a good model for the direct conversion into furfural before starting the experiments with xylose-rich feedstock. Furfural is now recognized as a top-value bio-based chemical and expresses good potential as a selective solvent for diesel fuels, resins and lubricating oils. It could be also employed as precursor in the chemical industry for the preparation of various solvents such as tetrahydrofuran (THF), methyltetrahydrofuran (MeTHF), but also for the transformation into furfuryl alcohol, a well-known commercial available monomer. Its industrial production is currently carried out by using strong mineral acid such as HCl [1,2] or H_2SO_4 [3] in batch or continuous reactions against pentosan containing lignocellulosic biomass. However, these mineral acids are responsible for serious corrosion, safety problems, difficulty for separation and excessive waste, especially in monophasic systems, when the reactions are carried out in water only. In this case the product requires being distillated progressively during the process in order to avoid the generation of black insoluble carbonaceous material called humin. Furfural recovery is also clearly a cause of high energy consumption. To remedy to this problem and for improving the yield of the formed furfural, the target compound has to be extracted as soon as possible with a non-miscible hydrophobic solvent such as methylisobutylketone (MIBK), toluene or nitrotoluene. Thus, biphasic system demonstrated potential for improving the selectivity of furfural. Recently, De Oliveira Vigier et al. developped a strategy to produce 5-hydroxymethylfurfural (HMF) from D-fructose using betaine hydrochloride catalyst [4]. HMF was obtained under conventional heating with a maximum yield of 84% using an atypical biphasic system consisting of choline chloride, a deep eutectic solvent and MIBK as the active extraction solvent. On the other hand, other betaine based acid ionic liquids (ILs) obtained by equimolar addition of inorganic acid to the *N*-base material, have already proved their efficiency to promote the esterification of organic materials [5]. Currently, zwitterionic glycine betaine or *N*, *N*, *N*-trimethylglycine is widely produced in the carbohydrate industry and, in our opinion, it appeared to be interesting to determine both impact on the sugar dehydration and synergistic effect of an IL immerged in a Bronsted acid. Besides, in the literature, several works reported the employ of formic acid to accomplish dehydration of the pentose [6-8]. Moreover formic acid is an organic acid and now it is easily recovered from reaction by modern extraction methods. Unfortunately, if the reaction is realized in water without addition of extraction solvent, the cross-polymerization currently observed between D-xylose and furfural during the process limits the furfural selectivity. For our study, an eco-friendly solvent, the cyclopentylmethyl ether (CPME), was our first choice in regards its lower miscibility with water, its stability in presence of strong acids and it is not a peroxide-forming liquid. One of our recent work reports the successful employ of CPME as the furfural extractive solvent in a biphasic system for D-xylose and xylan dehydration in presence of $FeCl_3$ and NaCl under microwave irradiation [9]. To the best of our knowledge, there is no study about zwitterionic betaine-formic acid combined catalyst employed in a biphasic system for the conversion of D-xylose into furfural. More recently, microwave-assisted dehydration gave promising results for increasing yield of dehydration products from D-xylose [2, 9, 10], xylan and feedstocks. The residence time of the substrate could be shortened and only a few humin are formed. The main purpose of this work is to determine the effect of reaction temperature, the reaction time, pH and betaine-formic acid ratio and the CPME volume percentage on the yield and selectivity of formed furfural for each sample of interest.

2. Materials and methods

2.1. Materials

Furfural (99% minimum), D(+)-xylose L-arabinose and anhydrous betaine 98% were purchased from Acros Organic. Cyclopentylmethyl ether was supplied by Sigma Aldrich. Xylan (from benchwood >90 % (HPLC)) was obtained from Sigma Life Sciences). Rice husk was furnished from the Fukui city in Japan. The water used in all experiments was a Millipore Milli-Q grade.

2.2. General procedure for the synthesis of furfural in water-CPME as biphasic media from D-xylose, xylan and rice husk

In a typical experiment, 0.15 g (1.0 mmol) of D(+)-xylose, 0.07 g (0.59 mmol) of betaine and 0.25 g of HCOOH were introduced in a 10 mL vial closed with a septum, followed by the addition of water (1 mL) and CPME (3 mL). Biphasic batch reactions were carried out by way of microwave heating apparatus (AntonPaar Monowave 300) and stirred under magnetic stirring (600 rpm) for the desired time. Temperature in the reaction vessel was measured by means of an IR sensor and the vial was pressurized due to the normal vapor pressure of the solution at defined reaction temperature. At the end of the reaction, each sample was diluted with acetonitrile to obtain 100 mL of diluted solution and filtered prior to analysis through a syringe filter (PTFE, 0.45 μm, VWR). Identical procedure was done starting from 0.15 g of xylan and 0.15 g of rice husk.

2.3. Product analysis

Each sample of the reaction mixture was analyzed separately by means of a Shimadzu Prominence HPLC. D-Xylose was detected with a low temperature evaporative light scattering detector (ELSD-LTII) and products were detected with a UV-Vis detector (SPD-M20A) at a wavelength of 275 nm. The column used was a Grace C18 column (250 x 4.6 mm 5μm). The mobile phase was MeOH-H_2O (90:10) solution flowing at rate of 0.5 mL.min^{-1}. The column oven was set at 40°C. Regularly, the calibration was checked out in order to avoid eventual experimental errors associated with all measurements reported below.

D-Xylose conversion (*X*), furfural yield (*Yi*) and furfural selectivity (*Si*) were calculated by the following equations:

$$X = \frac{(Initial\ xylose\ amount\ (mol) - Final\ xylose\ amount\ (mol))}{Initial\ xylose\ amount\ (mol)}\ x\ 100$$

$$Yi = \frac{Final\ furfural\ amount\ (mol)}{Initial\ xylose\ amount\ (mol)}\ x\ 100$$

$$Si = \frac{Furfural\ yield}{Conversion\ of xylose}\ x\ 100$$

A second and fast dual-wavelength spectroscopic method found in the literature was employed to confirm the D-xylose concentration in the prehydrozylate from xylan hydrolysis [19,20]. The procedure involves the preparation of a color agent as follow: 2 grams (15.8 mmol) of phloroglucinol were dissolved in 110 mL of glacial acetic acid, followed by the addition of 10 mL of anhydrous alcohol and 2 mL of 36 % HCl aqueous solution. For each sample 1 mL of the aqueous layer containing the sugar were added to 10 mL of the previous color agent and heated up at 100°C for 10 minutes. After returned to the room temperature, 50 μL of each solution was introduced in 3.0 mL of deionized water before the spectral scanning conducted in a wavelength found between 380 and 700 nm. UV-Vis absorption spectra were recorded using a Jasco V530 UV-vis absorption spectrophotometer. In acidic media, the furfural formed is allowed to react with phloroglucinol to generate a derivative showing absorbance at 553 nm.

For rice husk, the furfural yields have been calculated from the measured HPLC value according to the following equation:

$$Yi = \frac{Final\ furfural\ concentration\ (mg/mL)}{Initial\ substrat\ concentration\ (mg/mL)}\ x\ 100$$

3. Results and discussion

Currently, betaine hydrochloride (BHC) is recognized for its catalytic activity, but as the best of our knowledge, its natural zwitterionic form was never employed as a catalyst for dehydrating C5 or C6 sugars. Before starting our experiments, betaine (0.07 g, 0.59 eq) was introduced in an aqueous solution of D-xylose (0.15 M). The resulted transparent solution was stirred for 1 hour at 170°C in presence of 3 mL of CPME upon microwave irradiation. In the case of the previous water-CPME ratio, for 1.0 mmol of furfural the partition coefficient of furfural between water and CPME was determinated using this formula $Kp = [furfural]_{water}/[furfural]_{CPME}$ and gave a value of 4. Interestingly, furfural was produced with a yield of 37 %. However even multiplied by two the amount of betaine, the yield never exceeded 41 %. In the literature, some ILs holding an acid moiety are reported to express potential for the dehydration of hexoses or pentoses in water using conventional heating in batch reactors.[11, 12] Inspired by these results, and also by some recent studies of formic acid catalytic activity for converting D-xylose into furfural, a combination of both catalysts appeared for us to be a good opportunity to develop a new homogeneous catalytic system. Addition of a small volume of formic acid to a betaine aqueous solution was expected to improve the fundamental activity of the betaine. Herein, IL [HBet][HCOO] is expected to bind to the released water during the dehydration mechanism.

3.1. Influence of measured pH on the furfural yield

For dehydrating D-xylose, the best betaine-formic acid ratio was investigated at 170°C using the best ratio of water-CPME (1:3; v/v) (Table 1) [8].

Table 1

Various ratio of betaine-formic acid, their relative pH and furfural yields.[a]

Entry	Formic acid ($g.mL^{-1}$)	Betaine (g)	pH	Furfural (%)
1	0.5	0	1.72	53
2	0.5	0.07	1.88	75
3	0.25	0.07	2.08	81
4	0.125	0.07	2.30	80

[a] Reaction conditions: D-xylose (150 mg), formic acid, betaine, water-CPME, 1:3, v/v, MW, 170°C, 1 h.

Without addition of the zwitterionic betaine (Table 1, entry 1), the reaction mixture was too acidic and only 53 % of furfural was produced during the procedure with a complete conversion of the D-xylose. In our opinion, betaine should be responsible of intermediate isomerization of xylose into xylulose, a species recognized to be more sensitive to dehydration in acidic condition, but not detected by HPLC. This result was compatible with the current conclusions about the relation existing between acid concentration and furfural selectivity [13, 14]. When added to 1 mL of aqueous formic acid solution (0.125-0.5M), betaine (0.07 g) is able to reduce the pH of each solution (Table 1, entries 2-4). For aqueous solutions of betaine (0.125 and 0.25 M), pH values were 2.30 and 2.08 respectively. These values were compatible with D-xylose dehydration and the yields of formed furfural reached 80 % in both cases (Table 1, entries 3 and 4). By increasing the concentration of formic acid using the same amount of betaine, the value of pH fell to 1.88 and only a small drop of yield was recorded. In many cases, in the literature the dehydration of the pentose is carried out at pH inferior or equal to 1. Without betaine, using a formic acid diluted aqueous solution of pH = 2.1, 48 % of furfural yield was obtained in the same above condition. At the lower pH, using mineral inorganic acids such as HCl, the acidity is a negative factor for getting high yield of furfural. Due to the formation of by-products generated by the resinification of the furfural contents, the dehydration shows low selectivity of furfural especially at the higher temperatures and promoted by the strong acidity of the catalyst.

3.2. Influence of the temperature on the furfural yield

Next, keeping the best condition of pH (Table 1, entry 3), influence of the temperature was studied (Fig 1). Maximum of furfural yield was obtained at 170°C with no trace of D-xylose contents remaining in the hydrophilic layer. Other higher yields were provided at 160 and 180°C with values of 72 and 76 % respectively. Unfortunately, the amount of produced humine was most significant at 180°C, one more time it became evidence of possible furfural degradation even in presence of a potent extraction solvent. However at 150°C, the selectivity of furfural showed a lowest value of 57 %. This result points out the thermal control of the pentose dehydration also confirmed by the mild furfural yield of 60 % obtained from L-arabinose when heated at190°C in the same condition [15].

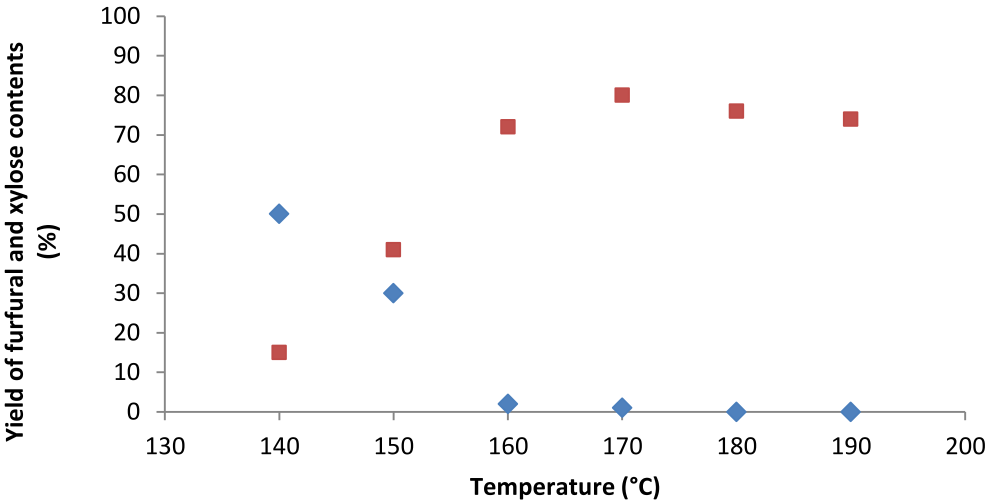


Fig. 1. Reaction profile for the D-xylose dehydration in presence of betaine-HCOOH. Xylose contents (blue dots) and furfural yield (red dots). Reaction conditions: D-xylose (150 mg), betaine (0.07 g), HCOOH (0.25 g), water-CPME, 1:3, v/v, MW, 1 h.

3.3. Influence of the xylose loadings on the furfural yield

In the third part, a screening of different xylose loadings was also operated (Table 2). Except the variation of the C5 sugar concentration, all parameters remained unchanged.

Table 2. Various loadings of xylose versus furfural yields.[a]

Entry	D-Xylose (mg.mL^{-1})	Furfural (%)
1	100	81
2	150	80
3	200	76
4	250	73
5	300	72

6	400	71
7	600	65

[a] Reaction conditions: D-xylose, betaine (0.07 g), HCOOH (0.25 g), water-CPME, 1:3, v/v, MW, 170°C, 1 h.

Usually, by increasing the contents of the pentose, yield of furfural became inversely proportional to the pentose loading. Once the D-xylose concentration reached a value of 600 $g.L^{-1}$, yield began to decline because of the enhanced viscosity of the aqueous layer (Table 2, entry 7). Furthermore, the viscous state prevent of the efficient extraction of furfural by CPME, the product remaining entrapped in the sugar excess. More exactly, higher viscosity is reported to be the main cause of high rate of cross-polymerization and by the way the formation of large amount of black humine, mostly when D-xylose conversion is not quantitative. Despite our efforts, in each case, it was difficult to isolate the sugar from the humine even tritured and no trace of D-xylose was detected from the aqueous layer by the spectroscopic method

3.4. Influence of the residence time on the furfural yield

For this following purpose the study was realized at 3 defined temperatures (160, 170 and 180°C) (Fig 2). Each sample was heated up and the reaction was stopped at a defined period of time before determine their furfural concentrations by HPLC.

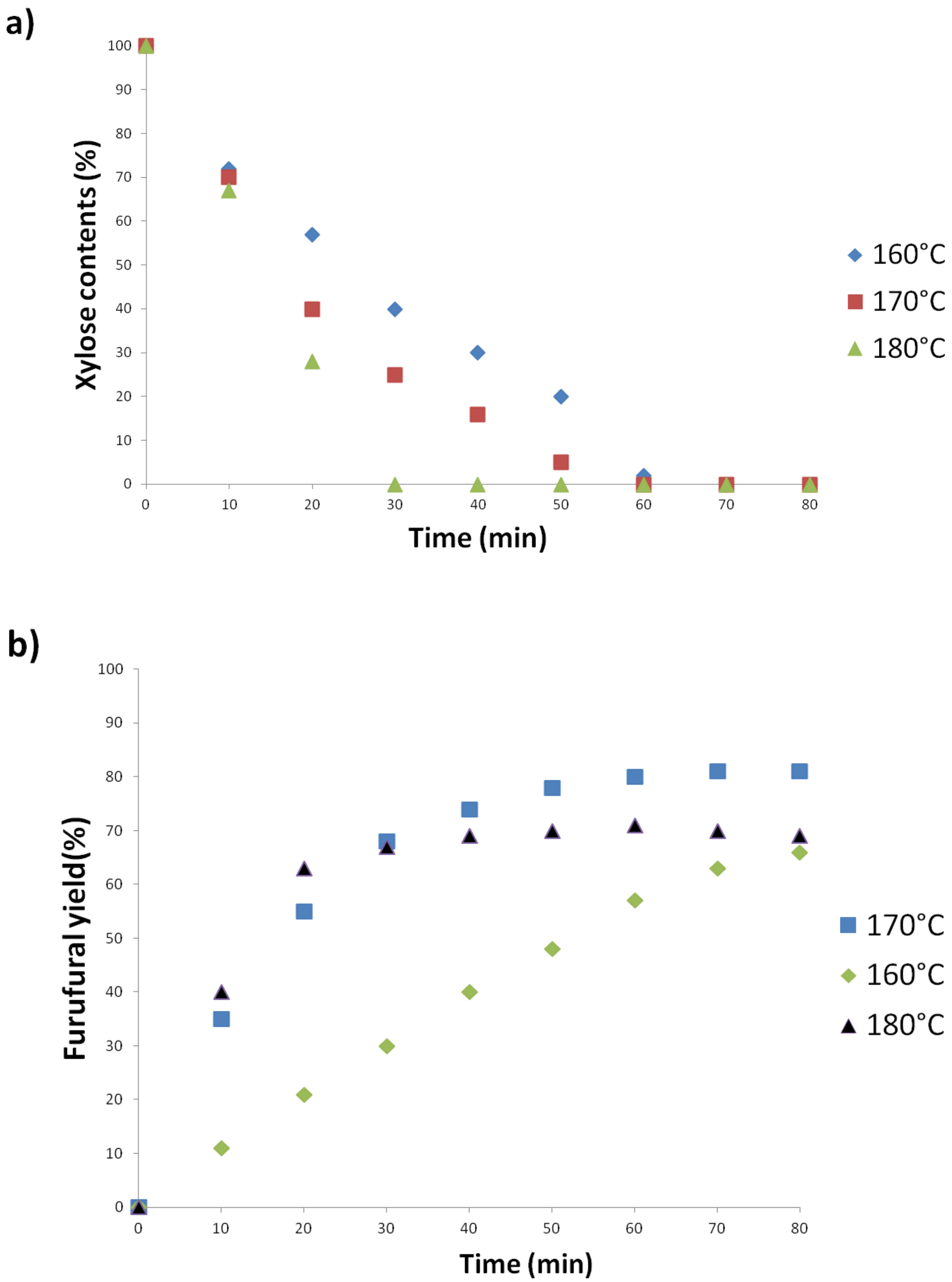


Fig. 2. Reaction profile for dehydration of D-xylose in presence of betaine-HCOOH at

varying temperatures a) xylose contents; b) furfural yields. Reaction conditions: D-xylose (150 mg), betaine (0.07 g), HCOOH (0.25 g), water-CPME, 1:3, v/v, MW.

At 160°C, the yield increase appeared to be quite linear and both yield and selectivity of furfural increased progressively until they finally reached a maximum value of 66 % after 80 minutes of stirring. Even the conversion of D-xylose was complete after 60 minutes, the reaction afforded a few humin in the vessel when heated for longer periods. If a similar sample is heated at 170°C, the maximum of yield of 80% was observed just after 60 minutes and remained constant beyond this time. On the above graphic, the conversion of xylose at 170°C followed a typical pattern, complete from 60 minutes, then the value of selectivity was definitively limited to 80 % for this condition. At this temperature, with no surprise, CPME confirmed its good ability to extract furfural product and this hydrophobic furfural content was not subjected to undesired second-type of side-reaction usually observed between furfural itself. In our opinion, at 170°C the cross-polymerization could be the main cause of the humin formation. This theory was reinforced by means of a simple test carried out in a biphasic system consisting of 1 mL of water containing 0.07 g of betaine and 0.25 g of formic acid brought in contact with 32 $g.L^{-1}$ furfural solution in CPME. Herein, warmed up at 170°C in microwave oven, even for period longer than 80 minutes, the concentration of furfural remained almost unchanged. By opposite, for temperature superior to 170°C, furfural is currently degraded *via* second type of side-reaction catalyzed by acid despite the moderate pH of 2.3. Thus in the normal way, at 180°C, after 20 minutes of stirring 63 % of yield was higher than the value obtained at 170°C for the same period. Unfortunately, the furfural selectivity was clearly inferior with a value of 87 %. After 20 minutes of stirring, the selectively was closed to 92 % at 170°C. Furthermore, if the reaction is carried out at 180°C after 20 minutes, both yields and selectively decreased jointly and the final value of selectivity was 69 % From 180°C, in a pressurized vessel, the dielectric constant of water decreases in parallel to its polarity, the solvent becoming more compatible with the less polar furfural. This phenomenon could also explain the limit of selectivity expressed at this temperature.

3.5. Influence of CPME volume percentage on the furfural yield

Starting from the initial CPME-water ratio, different CPME volume percentages were tested for dehydrating 150 mg of D-xylose (Fig 3). Each sample was heated up at 170°C for one hour. Except with 4 mL of CPME, the conversions of D-xylose were quantitative and almost near to 100 % also confirmed by the spectroscopic method.

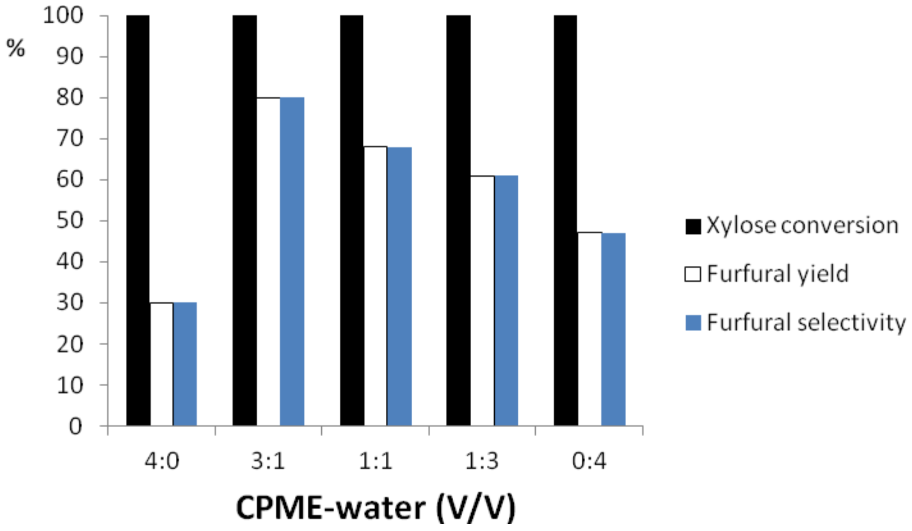


Fig. 3. Effect of the water to CPME phase ratio (v/v) on the furfural production. Reaction

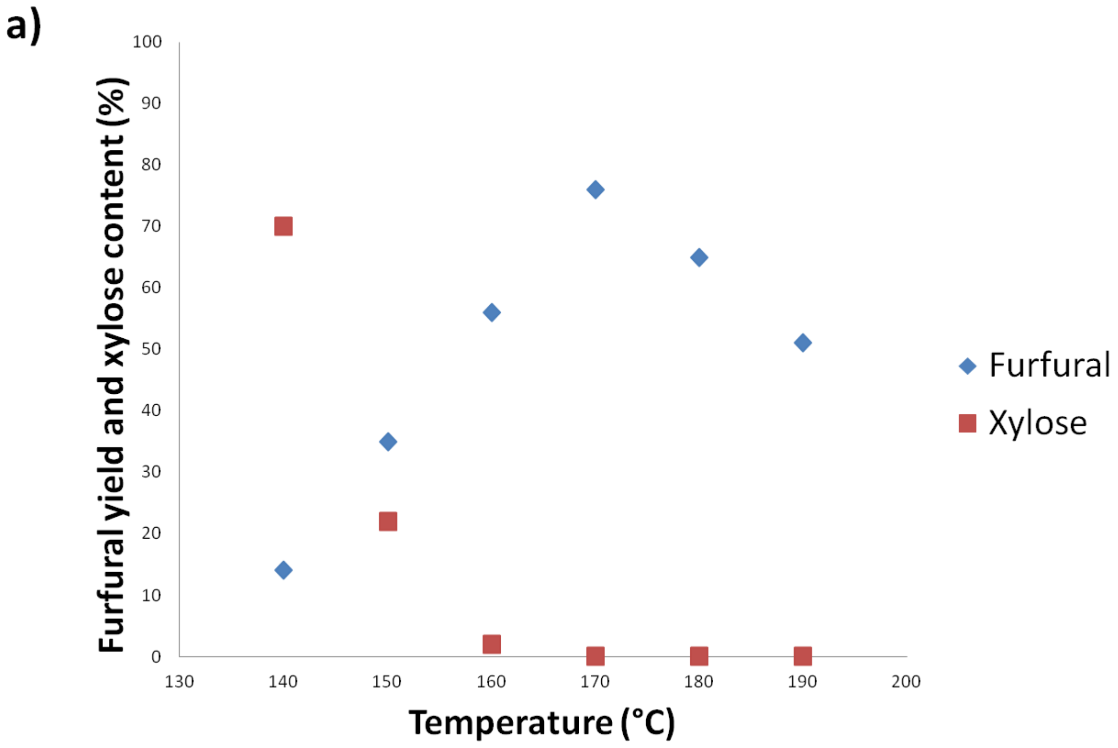
conditions: D-xylose (150 mg), betaine (0.07 g), HCOOH (0.25 g), water-CPME (4 mL), MW, 170°C, 1 h.

As expected, the yield of furfural increased with the volume of CPME. On the other hand, when reaction was performed only in water a large amount of humin was formed. According to these results, maximum of yield was certainly achieved with the CPME-H_2O (3/1) ratio. In a biphasic system, a minimum volume of polar solvent such as pure water or aqueous DMSO [16] is required to dehydrate effectively pentose derivatives. Curiously, the present betaine-HCOOH catalytic system is able to convert D-xylose into its furfural counterparts without any trace of water. Despite the lack of D-xylose solubility in the active extraction solvent, 30 % of furfural was produced in the sole organic layer.

3.6. Transformation of xylan and risk husk using optimized conditions

Direct transformation of amorphous xylan was operated using various ratio of betaine-HCOOH, the depolymerization of 1->4-β-xylopyranosyl linkages to monomers units is reported to be more active for pH near to 1. Furfural formation from xylan involves a two-steps mechanism. Basically, the polysaccharide backbone is depolymerized into single pentose monomer units before their own dehydration. However the furfural yield is known to be dependent of the real concentration of D-xylose released during the process. According the type of method employed and the pH of the mixture, xylo-oligomers of various length and numbers found in the hydrozylate liquor could influence the final yield of furfural. Using the optimized method described for the

D-xylose dehydration, 150 mg of the polymer introduced in 1 mL of water solution loaded in presence of betaine and formic acid furnished the target furfural in 58% yield. Later, with 0.5 g of HCOOH, at a lower pH of 1.9, the yield reached a value of 76 %. In the other hand, if the aqueous phase is loaded with 300 mg of xylan, at 170°C the resulting viscous hydrozylate afforded only 48 % of the desired furfural after one hour of microwave heating. In order to determine the best condition of temperature in parallel to the residence time study, all related experiments were successively realized at pH 1.9 (Fig 4).



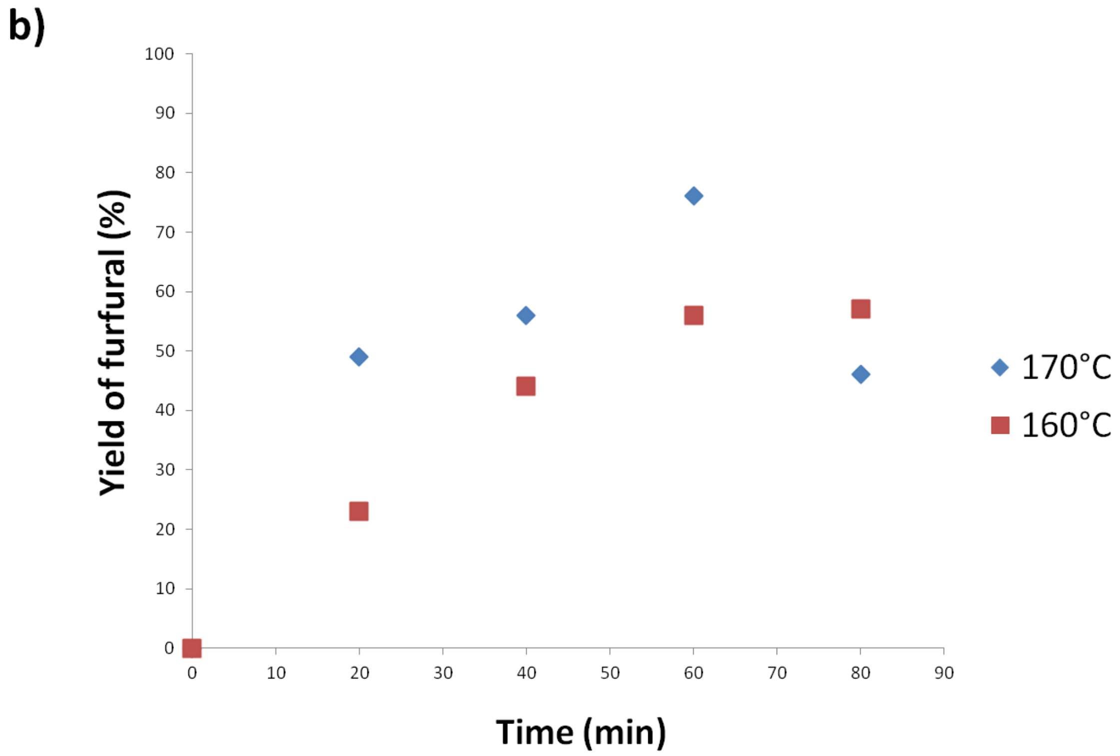


Fig. 4. a) Temperature reaction *vs* furfural yield and percentage of released D-xylose; b) Time residence *vs* furfural yield measured at 160 and 170°C. Reaction conditions: xylan (150 mg), betaine (0.07 g), HCOOH (0.25 g), water-CPME, 1:3, v/v, MW.

According the graphic 4a, for temperatures found between 150 and 170°C, the furfural yield increased linearly, until it began to fall from 180°C, characteristic feature of furfural degradation encountered at the higher temperatures. In parallel to the phenomenon, for temperatures comprised between 140 and 160°C, the released D-xylose was not completely converted into furfural. In the Figure 4b, the influence of the reaction time was carefully studied at 160°C and 170°C. At 160°C, the furfural yield enhancement is more progressive and linear compared to the results recorded at 170°C. After 60 minutes, in both cases the degradation of furfural seems to be slow, but curiously at

170°C under microwave irradiation it became out of control. In our opinion, at the lower pH of 1.9, the concentration of the released xylose could be accelerated promoting the non desired cross-polymerization between xylose and furfural. Besides this result is also in agreement with the yield of 53 % obtained from the dehydration of the same mass of xylose in the same pH condition but this time without betaine.

The final purpose of our work involve the transfer of the optimized procedure to rice husk, a renewable, cheap and largely available feedstock rich in cellulosic and hemicellulosic biomass rich in complex polysaccharide backbone [17]. For this reason, rice husk could be employed directly as a furfural source, but the process to access to the top-value product requires various pretreatments such as sonication or boiling. At 190°C, compared to the two-stage process developed by Suxia et al. [18] leading to furfural yields of 9 %, our optimized procedure using dried rice husk (200 mg) in presence of betaine (0.08 g) and 1 mL of aqueous formic acid solution (50 g.mL^{-1}) in a typical biphasic microwave-assisted reaction yielded the target furfural in 6%.

3.7. Resusability of the catalytic system

Several consecutive reactions were performed with the optimized procedure. After one cycle the aqueous layer was recovered from the current reaction and loaded with D-xylose (150 mg), fresh CPME (3 mL) were also added each time as the extraction solvent. Finally, each cycle was carried out for 60 minutes at 170°C and starting from the fifth cycle the yield of formed furfural began to decrease and gave only a value of 75 %. The phenomenon could be explained by the pH measurement realized after each cycle. Indeed, the pH value moved from 2.08 to 2.75 but remained enough acidic to produce furfural. Interestingly, the system still remained active after ten cycle, however it appeared difficult to control the yields found between 69 and 75 %

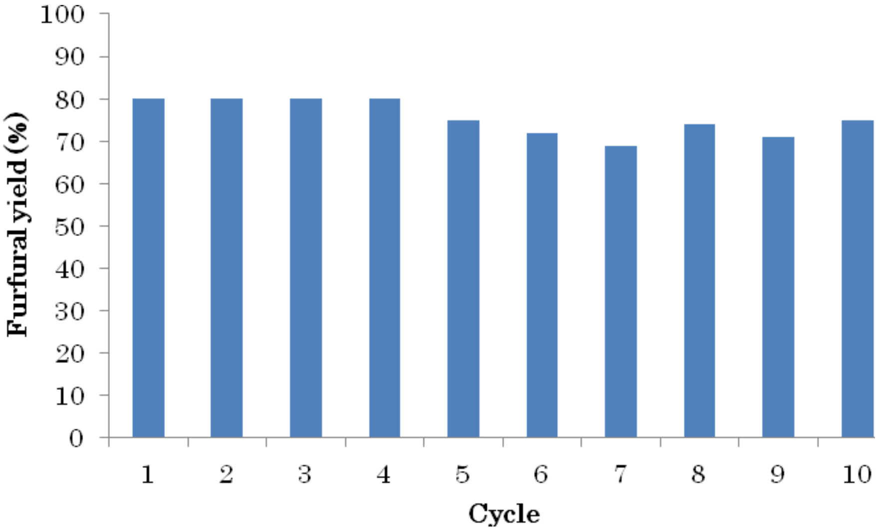


Fig. 5. Reusability of the aqueous phase containing betaine and HCOOH for the D-xylose dehydration to furfural. Reaction conditions: D-xylose (150 mg), betaine (0.07 g), HCOOH (0.25 g), water-CPME, 1:3, v/v, MW, 170°C, 1 h.

4. Conclusion

In summary, we have demonstrated the potential of betaine coupled with an excess of formic acid for the furfural production in a water-CPME biphasic system heated in a range of temperature between 160 and 180°C. The best yields were obtained at 170°C for 1 hour of stirring. This methodology was also suitable for producing furfural from xylan and rice husk. In the next stage of our study, this procedure should be transposed to hexoses and cellulose in order to produce 5-hydroxymethyl furfural (HMF) as the main target compound.

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