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Highly efficient and selective CO_2-adjuncted dehydration of xylose to furfural in aqueous media with THF

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Abstract

The selective dehydration of xylose into furfural using high-pressure CO_2 as effective and more sustainable catalyst in H_2O/THF system is for the first time reported. The conversion of D-xylose into furfural above 83 mol % with furfural yield of 70 mol % and the selectivity of 84 % was achieved with only 50 bar of CO_2 pressure within 1 hour at 180 °C.

Furfural is one of building blocks[1] which can be used as biomass-originated substitute of fossil-based pivot chemicals in the production of diverse chemicals (*e.g.* tetrahydrofuran (THF)).[2-5] Currently, furfural is exclusively produced by mineral acid catalysed dehydration of C_5-sugars present in the hemicelluloses of agricultural residues and hardwoods. It has been reported that at industrial practice, the furfural yield originated in batch processes has remained at or below 50 mol % of theoretical[6] due to occurrence of undesired parallel reactions leading to formation of humins.[7,8]

Up to date, the production of furfural from hemicellulose-derived sugars has been reported to be carried out in both monophasic and biphasic systems.[5,9,10] It is highly desired to produce furfural *via in-situ* generated acid catalyst conditions, without typical drawbacks for both homogeneous and heterogeneous catalysts. The basics of inorganic chemistry teach that CO_2 is little soluble in water, however even this negligible solubility forms unstable carbonic acid making the aqueous phase more acidic. This weak acid promotes the medium acidification helping biomass processing[11-15] and dehydration of sugars into furans as presented in this work. The proposed approach has great environmental benefits since the acidity of the medium can be easily turned off by simple depressurisation and removal of CO_2 from environment allowing its recovery and reuse.[14]

In this work, D-xylose was converted into furfural. The examined approach examines the benefits from the use of high-pressure CO_2 in the auto-generated acidic environment and the aqueous/THF reaction phase splitting guiding to the enhancement of final furfural yield and reaction selectivity.

Series of runs presented in Table 1 were carried out to scrutinise the role of THF (entries 1 and 2), CO_2 (*e.g.* entries 2 and 7) and temperature in the range of 160 - 180 °C for 30 and 60 min of reaction time (entries 3 - 6). Additionally, variation of water ($V_{aq.}$) and THF (V_{THF}) volumetric ratios were scrutinised (entries 7 - 9) in an effort to decrease the reactor headspace to analyse the effect of the CO_2 amount loaded into the reactor.

The analysis of results obtained in entries 1 and 2 confirms the expected adjunctive effect of THF presence. This data demonstrates that albeit lower xylose concentration was examined in entry 2, the furfural yield and selectivity of reaction raised expressively reaching values of 65.2 mol % and 41.4 %, respectively. This is in a good agreement with previous reports about THF effect on furfural production. For example, Wyman and co-workers found that in acid catalysed reaction with THF as co-solvent, furfural yield was as high as 86 mol % due to THF "protecting" effect of furfural from degradation.[16] However, it is important to state that Wyman and co-workers did not clarify how THF, as co-solvent in a monophasic system, is able to protect furfural from further degradation reactions. Beyond THF, another equally important agent in the formation of furfural is CO_2. The comparison of results obtained in entries 2 and 7 demonstrates that the presence of CO_2 enhances the furfural yield by 2/3. It indicates that in the presence of water, high-pressure CO_2 produces unstable carbonic acid leading to generation of acidic environment and consequently to more favourable xylose dehydration boosting the furfural yields in comparison to reactions without CO_2 (entries 2 and 7).

Table 1. Furfural production by dehydration of D-xylose using high-pressure CO_2 as catalyst.[a]

Entry	T (°C)	t (min)	[Xylose] (g/L)	$V_{aq.}$ mL	V_{THF} mL	X_{Xylose} (mol %)[b]	$Y_{furfural}$ (mol %)[b]	$S_{furfural}$ (%)[b]
1[c]	180	60	18.8	15	0	54.0	24.5	45.5
2[c]	180	60	12.5	10	5	65.2	41.4	63.5
3	160	30	18.8	25	0	42.1	21.0	49.9
4	160	60	18.8	25	0	44.8	25.1	56.0
5	180	30	18.8	25	0	73.1	31.2	42.7
6	180	60	18.8	25	0	88.0	42.7	48.6
7	180	60	12.5	10	5	82.9	69.4	83.7
8	180	60	12.5	20	10	81.9	66.9	81.7
9	180	60	12.5	40	20	68.3	17.9	26.3

[a] All CO_2-assisted dehydration experiments were carried out at 50 bar of initial CO_2 pressure. [b] For xylose conversion (X_{xylose}), furfural yield ($Y_{furfural}$) and reaction selectivity to furfural ($S_{furfural}$) definitions please refer to Electronic Supplementary Information (ESI). [c] Reactions performed without CO_2.

Also the selectivity of xylose dehydration is driven by the presence of CO_2. A maximum 83.7 % selectivity was achieved when CO_2 and THF were used together (entry 7). This result again confirms the dual adjunctive character of CO_2 and THF on dehydration of xylose to furfural. The formed carbonic acid accelerated the conversion of sugars and THF acting as extracting solvent reduces the occurrence of secondary loss reactions (*e.g.* products of condensation –

humins).[17] It is possible because as little as 30 bar of CO_2 makes a phase splitting separating furfural from water to THF-expanded CO_2-rich phase.[18] This, due to an advantageous partition of furfural between THF- and water-phases, helps to extract furfural from aqueous to organic gaseous phase protecting furfural from further conversion and degradation reactions in aqueous phase.

The preliminary tests showed that the reaction temperature is another important factor influencing the furfural production. Considering the results from entries 3-6, the xylose conversion doubled and furfural yield increased from 25.1 mol % to 42.7 mol % with an increase of temperature by only 20 °C from 160 °C (entry 4) to 180 °C (entry 6) for 1 h reaction. One the other hand, the increase of furfural yield was accompanied by a decrease of reaction selectivity to furfural from 56.0 % to 48.6 %. The obtained results indicate that higher reaction temperature increased the xylose conversion, either to furfural or other products (*i.e.* formic acid and/or humins) often reported in literature.[17]

Entries 7-9 show that either furfural yield or selectivity of the reaction is sensitive on the amount of feed charged in the reactor. It seems to be obvious, because the headspace of the reactor diminishes by increasing the amount of feed. Hence, at fixed initial temperature and pressure, less CO_2 was charged into the reactor and consequently less acidic environment could be generated. The highest furfural yield was obtained for the lowest feed charged (69.4 mol % and 83.7 % of furfural yield and reaction selectivity, respectively). Increasing 4 times the amount of feed charged into reactor either furfural yield or selectivity decreased to only 17.9 mol % and 26.3 %, respectively.

The effect of volumetric aqueous to organic ratio on the CO_2-assisted dehydration of D-xylose to furfural was investigated as is shown in Table 2. Varying the amount of H_2O and THF notable changes in composition of system occur, which influences the composition of both gaseous and liquid phases. The analysis of these changes and the knowledge of phase behaviour of H_2O:THF:CO_2 system (the phase envelopes for examined systems were obtained following the modelling of the reaction mixture according to procedure given in the ESI) confirm that the increase of V_{THF} in the reactive system favours CO_2 solubility in aqueous phase. This promotes more favourable conditions of acid-catalysed dehydration of xylose into furfural. For the highest $V_{aq.}/V_{THF}$ ratio (entry 11), the xylose conversion was relatively high (73.8 mol %) but the furfural yield was only 45 mol %. Decreasing the $V_{aq.}/V_{THF}$ ratio from 12:3 to 10:5 (entry 11 and 7), both xylose conversion and furfural yield increased up to 82.9 mol % and 69.4 mol %, respectively. Conversion of xylose reached its maximum of 100 mol % when $V_{aq.}/V_{THF}$ ratio was 3:12 (entry 14) but simultaneously only 45.4 mol % of furfural yield was achieved. Hence, higher V_{THF} in reactive system adjuncts to achieve higher xylose conversion, however about certain value the excessive amount of THF has negative effect on furfural yield and reaction selectivity as both decreases. Similar observation was made by Li et al. who found that when the amount of organic phase was higher than the aqueous phase, the production of humins was increased.[19]

Table 2. Furfural production by dehydration of D-xylose using high-pressure CO_2 as catalyst at various volumetric aqueous to organic solvent ratios.[a]

Entry	$V_{aq.}$	V_{THF}	X_{Xylose}	$Y_{furfural}$	$S_{furfural}$
	mL		(mol %)[b]	(mol %)[b]	(%)[b]
10	15.0	0.0	60.6	28.4	46.9
11	12.0	3.0	73.8	45.0	60.9
7	10.0	5.0	82.9	69.4	83.7
12	7.5	7.5	86.2	54.8	63.6
13	5.0	10.0	87.8	51.0	58.1
14	3.0	12.0	100.0	45.4	45.4

[a] All experiments were performed at the following conditions: 50 bar of initial CO_2 pressure, 12.5 g/L of xylose concentration in the feed, at 180 °C during 60 min of reaction time. [b] For xylose conversion (X_{xylose}), furfural yield ($Y_{furfural}$) and reaction selectivity to furfural ($S_{furfural}$) definitions please refer to Electronic Supplementary Information (ESI).

The behaviours found for 12.5 g/L of xylose concentration in the feed were similar also for two other studied (9.4 and 6.3 g/L) xylose concentrations as can be seen in Figure 1.

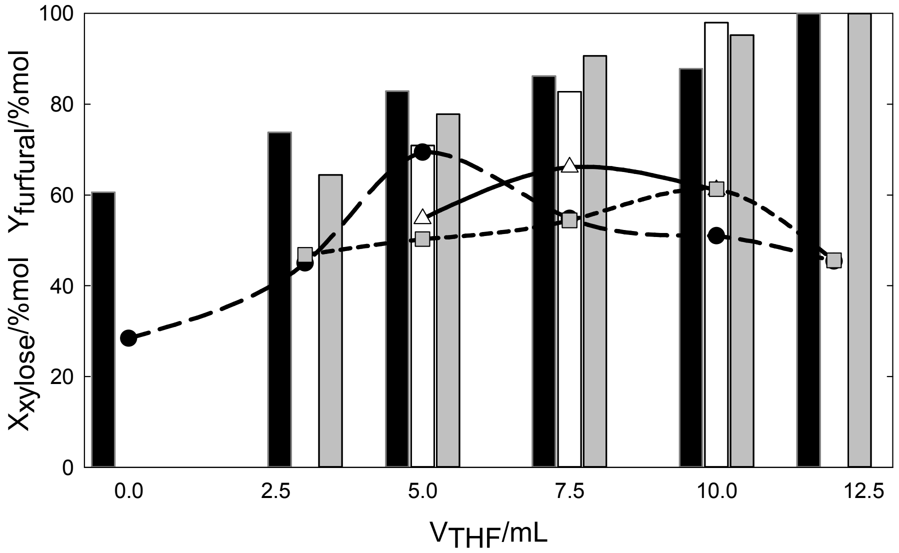

Figure 1. The evolution of xylose conversion (bars) and furfural yield (symbols) for various V_{THF} as a function of initial xylose concentration in the feed (black – 12.5 g/L, white – 9.4 g/L, grey – 6.3 g/L). All experiments were performed at the following conditions: 50 bar of initial CO_2 pressure, at 180 °C during 60 min of reaction time and at total volume ($V_{aq.}$+V_{THF}) of 15 mL. Lines are given as guide for the eye.

Besides the above discussed parameters, the furfural yield also depends on reaction time and initial xylose concentration in the feed as it is depicted in Figure 2. The obtained results show that at the initial stage of reaction, the furfural production was the fastest for the lowest xylose concentration; however the differences between concentrations especially for longer reaction times (*e.g.* 90 min) are negligible. However, prolonged reaction time had a negative effect on the furfural yield, especially for more concentrated solutions, because for 120 min of the reaction time, a decrease of furfural yield was observed mostly due to possible aforementioned side reactions.[7]

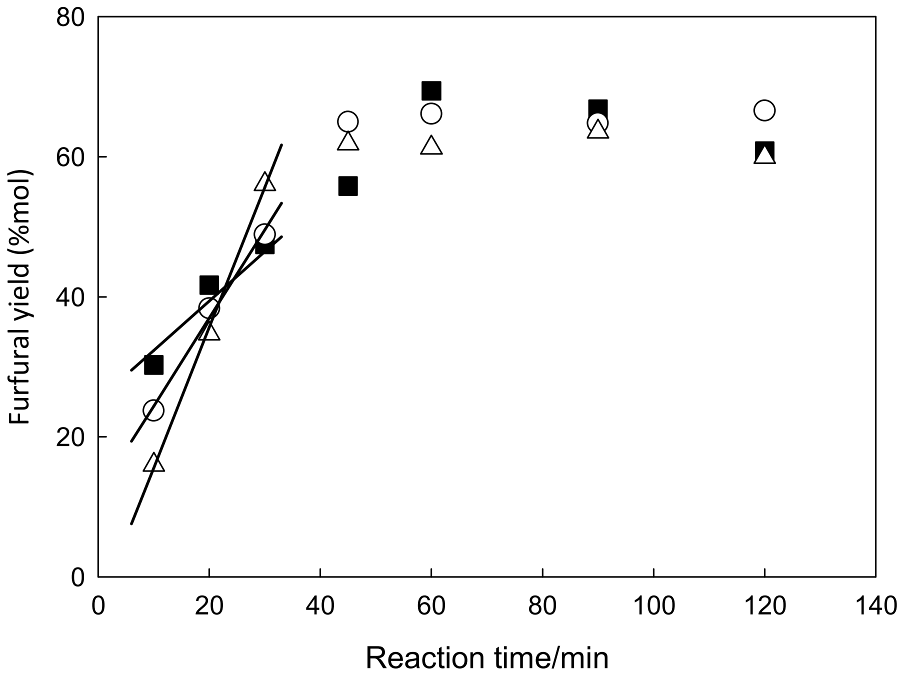

Figure 2. The evolution of furfural yield for various initial xylose concentrations (■ -12.5 g/L, ○ – 9.4 g/L, △ – 6.3 g/L) achieved over time in reactions performed at 50 bar of initial CO_2 pressure, 180 °C and $V_{aq.}/V_{THF}$ ratio of 10:5 mL/mL. Lines merely demonstrate the difference in the initial furfural production rate for various xylose concentrations.

The furfural yields presented in this work are in the similar range to those reported for xylose dehydration using mineral acid (HCl) as catalyst.[20] Gairola and Smirnova used different approach to investigate the hydrothermal dehydration of D-xylose to furfural with simultaneous furfural extraction with supercritical CO_2.[21] The maximal furfural yield from xylose was similar to those obtained in this work (68 mol % *vs.* 69 mol %) but it was achieved at severer reaction conditions (230 °C and 120 bar of CO_2 pressure) than those presented in this work.

Concluding, the efficient production of furfural in selective way using high-pressure CO_2 as catalyst in H_2O/THF system was reported. The combined adjunctive character of CO_2 in aqueous media and THF as extracting solvent enabled a simple operational procedure for xylose dehydration into furfural. This methodology led to obtain a xylose conversion above 83 mol % resulting in a final furfural yield of 70 mol %. The used approach does not require post-reaction neutralisation typical for acids and uses the most environmentally friendly solvents such as CO_2 and H_2O to obtain furfural yields similar to those with mineral acid and combined extraction systems.

Electronic Supporting Information

The electronic supporting information contains the experimental section, details of phase equilibrium prediction and reaction (heating and holding time) profiles.

Acknowledgments

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