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The Effect of Water on Furan Conversion over ZSM-5

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Catalytic fast pyrolysis is a method for converting lignocellulosic biomass into renewable aromatics and olefins. Water is a byproduct of this reaction and is also present in the biomass feed. As the water partial pressure is increased from 0 to 212 Torr (0 to 28 kPa), there is an increase in furan conversion from 43.8 to 84.8% over ZSM-5. The CO_2 and propylene yields also increase from 0.7 to 16.4% and 2.9 to 44.9%, respectively, as the water partial pressure increases. Water partial pressures in an industrial catalytic fast pyrolysis reactor should be within the range of water partial pressures used in this study. These results demonstrate that the presence of water promotes hydrolysis reactions in the gas-phase conversion of furanic pyrolysis vapors over zeolite catalysts.

Lignocellulosic biomass is an inexpensive and renewable feedstock that can be used to produce renewable fuels and chemicals.[1] Several processes for biomass conversion are currently under development.[1a] One approach is catalytic fast pyrolysis (CFP), which converts lignocellulosic biomass into aromatics in a single-step reaction that uses zeolite catalysts[2] and a fluidized bed reactor.[2c,e,f] Previously, it has been reported[2a,b,3] that during CFP the biomass first undergoes pyrolysis reactions to produce anhydrosugars (such as levoglucosan), followed by dehydration, decarbonylation, and decarboxylation reactions, which produce furanic intermediate species that are further converted into aromatic species through acid-catalyzed reactions. The conversion of furans over HZSM-5 has been used as a model reaction for the CFP of real biomass[2c,4] in an attempt to elucidate the reaction chemistry. Water is a byproduct of the CFP process produced in the dehydration reactions. In addition, water is present with the biomass and therefore fed into the process with the biomass. The objective of this paper is to study the effect of water on the CFP chemistry.

There are a few studies in the literature that have reported on the role of water in conversion of pyrolysis vapors over zeolite catalysts. Horne et al.[5] examined the effect of co-feeding water [at a partial pressure of 74 Torr (1 Torr = 0.13 kPa)] with biomass during pyrolysis, and then upgrading the pyrolytic vapors over a bed of ZSM-5. The water was found to double the yields of all gaseous product species (CO, CO_2, H_2, methane, and C_2 and C_3 alkanes and olefins) at all temperatures investigated (400–550 °C). The addition of steam to the catalytic pyrolysis of lipids produced by the algae *Chlorella pyrenoidosa* (the main fatty acids contained in this algae are oleic acid, linoleic acid, and palmitic acid) over ZSM-5 has been shown to shift product selectivity towards CO, CO_2, and C_2–C_4 olefins, as well as decreasing selectivity towards alkanes and coke.[6]

Table 1 and Figure 1 a–c show the effect of increasing the water partial pressure for furan conversion over ZSM-5 at 600 °C. These experiments were done by co-feeding water and furan over a ZSM-5 catalyst (H-form, obtained from Zeolyst, Inc.; $SiO_2/Al_2O_3 = 30$). As shown in Figure 1 a the furan conversion increased with increasing water partial pressure. The CO_2 and propylene yields also increased with increasing water partial pressure, as shown in Figure 1 b and c. These results show that increasing the water partial pressure increases the overall furan conversion, and that water catalyzes the hydrolysis of furan into CO_2 and propylene. Therefore, water has an important role in CFP.

The product yields and selectivities for individual species are shown in Table 1. The results obtained in the absence of a water co-feed are comparable to those that have been reported previously under similar reaction conditions.[4b,c] The overall aromatic yield decreased with increasing water partial pressure. The yield of CO did not change with increasing water partial pressure. Coke yield did not change appreciably until the water partial pressure was increased to 212 Torr; a decrease in the coke yield was observed at that pressure relative to lower pressures. The increase in olefin yield is almost entirely due to the increase in propylene. The toluene and xylene selectivity increases with water partial pressure. Cheng and Huber have previously shown that toluene can be produced from a reaction of furan with propylene by Diels–Alder condensation in the vapor phase over ZSM-5.[4c] These authors also showed a decrease in the selectivity towards heavier aromatics (e.g., styrene, ethylbenzene, indene, naphthalene) upon co-feeding propylene with furan at a propylene/furan molar ratio of 2.4:1. The increase in the toluene and xylene selectivity is probably related to an increase in the propylene concentration that is produced by the hydrolysis of furan with water. The yield of the polycyclic aromatics decreased with increasing water content, which again, is probably related to the increase in propylene yield. The yield of oxygenates did not show a major change with water content. However, among oxygenates, there is a shift in selectivity towards acetone and acetal-

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Table 1. The effect of co-feeding water on the overall product yields and individual product selectivities.[a]

H_2O partial pressure [Torr]	0	21	130	212
Water/furan molar ratio	0	3.5	24.4	47.7
Furan conversion [%]	43.8	51.8 ± 2.6	72.5 ± 6.7	84.8 ± 1.2
Coke on catalyst [wt.%]	7.8	6.7 ± 0.2	8.1 ± 1.5	3.7 ± 0.4
Product		*Yield [%]*		
aromatics	8.1	6.3 ± 0.3	6.9 ± 0.8	5.2 ± 0.5
olefins	8.2	14.5 ± 1.2	30.6 ± 3.4	53.9 ± 1.6
oxygenates[b]	1.3	1.3 ± 0.0	1.7 ± 0.4	1.9 ± 0.0
CO	5.8	5.4 ± 0.6	6.1 ± 1.1	5.2 ± 0.1
CO_2	0.7	3.6 ± 0.6	8.9 ± 1.5	16.4 ± 1.2
methane	0.0	0.1 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
coke	11.9	10.2 ± 0.3	12.4 ± 2.2	5.6 ± 0.6
Aromatics		*Selectivity [%]*		
benzene	32.4	37.9 ± 1.4	33.6 ± 0.7	27.6 ± 0.2
toluene	27.0	36.1 ± 1.7	42.3 ± 2.6	51.2 ± 2.0
ethylbenzene	0.1	1.2 ± 0.1	1.1 ± 0.0	1.2 ± 0.3
xylenes[c]	3.4	4.3 ± 0.5	6.6 ± 0.5	9.0 ± 0.6
styrene	6.8	5.9 ± 1.2	4.9 ± 1.0	4.0 ± 0.4
indene	15.5	6.8 ± 0.5	4.5 ± 0.9	3.2 ± 0.7
naphthalene	9.7	5.2 ± 2.6	4.5 ± 1.8	2.7 ± 0.9
2-methylnaphthalene	3.8	2.4 ± 1.7	2.2 ± 1.1	1.1 ± 0.1
1-methylnaphthalene	0.0	0.3 ± 0.2	0.3 ± 0.1	0.2 ± 0.0
Olefins				
ethylene	40.1	18.7 ± 3.9	13.4 ± 3.4	8.0 ± 1.0
propylene	35.0	60.3 ± 2.9	74.1 ± 2.9	83.2 ± 1.3
butenes[d]	4.2	8.4 ± 1.1	8.2 ± 0.2	8.1 ± 0.2
allene	6.0	4.8 ± 0.8	1.1 ± 0.4	0.4 ± 0.1
cyclopentadiene[e]	14.7	7.8 ± 0.9	3.2 ± 0.1	0.3 ± 0.1
Oxygenates				
benzofuran	37.6	36.3 ± 7.7	9.4 ± 6.3	3.3 ± 2.0
acetaldehyde	28.6	27.1 ± 1.3	47.4 ± 1.1	48.0 ± 2.3
acetone	n.a.[f]	11.5 ± 0.6	28.0 ± 1.9	42.7 ± 4.2
2-methylfuran	24.7	16.2 ± 5.8	6.8 ± 1.2	1.3 ± 0.0
phenol	9.2	8.9 ± 1.1	8.4 ± 2.1	4.7 ± 0.0

[a] Reaction conditions: $T = 600\,^{\circ}C$, furan WHSV = 9.3 h^{-1}, furan partial pressure = 6 Torr, $t = 6$ min, total system pressure = 760 Torr. Values shown include one standard deviation ($n \pm SD$) whenever possible. [b] Defined as any oxygen-containing molecule other than CO or CO_2. [c] Includes all three xylene isomers. [d] Includes 1-butene, 2-butene, isobutene, and butadiene. [e] Only C_5 olefin detected in significant quantities. [f] Not quantified under these conditions.

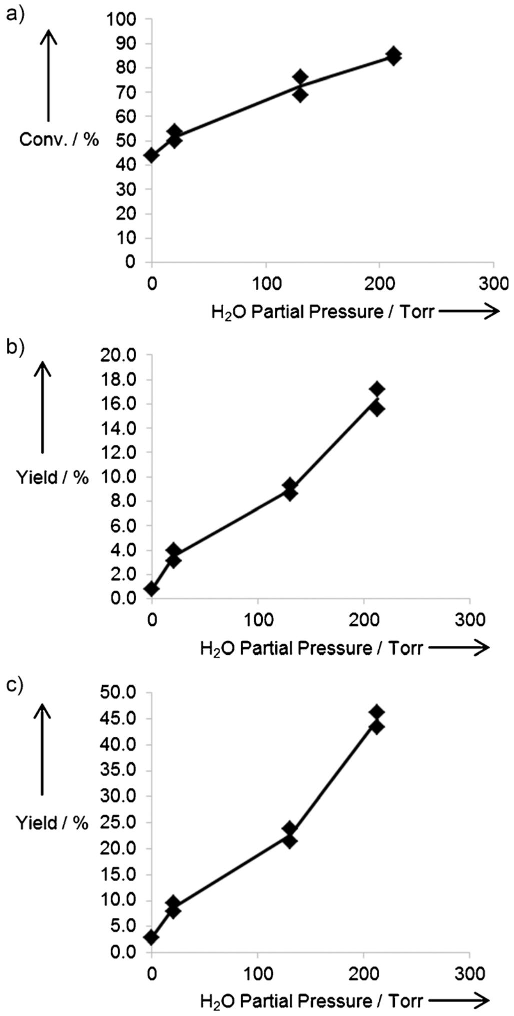
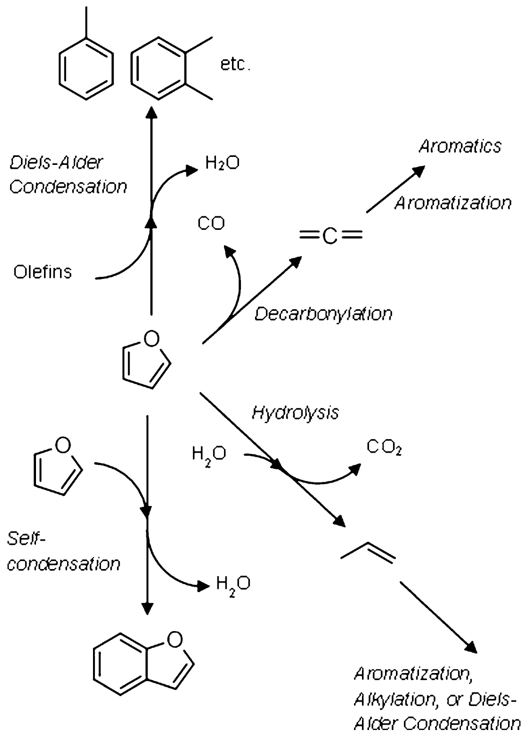


Figure 1. The effect of water partial pressure on a) the conversion of furan, b) the yield of CO_2, and c) the yield of propylene. Reaction conditions: temperature = 600 °C, furan WHSV = 9.3 h^{-1}, furan partial pressure = 6 Torr, reaction time = 6 min, total system pressure = 760 Torr.

dehyde and a decrease in benzofuran as the partial pressure of water co-feed increases.

We have previously reported that furan undergoes three initial reactions over ZSM-5:[4c] 1) Decarbonylation to produce allene and CO, 2) Diels–Alder reaction with another furan to produce benzofuran and water, and 3) Diels–Alder condensation with an olefin to produce aromatics and water. The results herein demonstrate that there is another pathway for furan conversion that involves the hydrolysis of furan with water to produce propylene and CO_2. Thus, there are four reactions for the initial conversion of furan, as illustrated in Scheme 1. This shows that the products in CFP will be influenced by 1) the concentration of furan and other oxygenated pyrolysis vapors, 2) the concentration of olefins, and 3) the concentration of water. The data in Table 1 indicate that increasing the water partial pressure will increase the rate of furan hydrolysis into propylene and CO_2. However, water did not change the CO yield, thus suggesting that water has little impact on the rate of decarbonylation.

It is useful to consider the effect of water in an industrial CFP reactor. The actual water concentration in the reactor will depend on several factors, including the moisture content of the initial biomass, the overall stoichiometric reaction, the reactor pressure, and the amount of moisture that is present in the fluidization recycle gas stream. Jae et al. estimated the water yield to be 19.3 wt.% using a gallium-promoted ZSM-5 catalyst for the CFP of pine wood.[7] Equation (1) has been developed to calculate the amount of water that may be produced during the CFP of biomass (where *x* is the moles of water present in the biomass). Equation (1) was adapted from the stoichiometry proposed by Carlson et al.,[2c] and the coefficients were calculated by fitting experimental yields obtained from Jae et al.[7] for the conditions with highest aromatic yield: 600 °C, with a weight hourly space velocity (WHSV) of 0.3 h^{-1}. Equation (1) uses toluene (C_7H_8) as a proxy for all aromatics, propyl-



Scheme 1. Proposed reaction network for furan conversion over ZSM-5 in the presence of water, adapted from Cheng and Huber.[4c] Reactions include Diels–Alder condensation with olefins to produce aromatics and water, furan decarbonylation to produce CO and allene, furan hydrolysis and decomposition to produce CO_2 and propylene, and furan Diels–Alder self-condensation to produce benzofuran and water.

ene (C_3H_6) as a proxy for all olefins, and pure carbon (C) as a proxy for coke. We estimate that the water partial pressure is 84 Torr for a CFP reactor that operates at 760 Torr, with a feed that has 8.5 wt.% moisture content, and a water yield of 23.4 wt.%. The water partial pressure could vary between 60 and 117 Torr (from dry biomass to a 20 wt.% moisture content, respectively; total pressure 760 Torr). If the reactor pressure increased to 1520 or 2180 Torr, then the water partial pressure would increase to 119 or 171 Torr, respectively, for an anhydrous feed.

$$\begin{aligned} C_{4.2}H_{6.1}O_{2.7}+x\,H_2O \rightarrow\; & 0.10\,C_7H_8+0.13\,C_3H_6+1.12\,CO \\ & +0.35\,CO_2+0.16\,CH_4+(0.91+x)\,H_2O \\ & +1.04\,H_2+1.50\,C \end{aligned} \tag{1}$$

As shown herein, this partial pressure value of water does cause a 45.4% increase in the conversion of furan (based on interpolation between the 21 and 130 Torr water partial pressure experiments) and an increase in the propylene and CO_2 yields. Whereas the CFP of real biomass does not selectively produce propylene and CO_2 in quantities as high as demonstrated herein, it is plausible that water does indeed have an effect on the reaction chemistry. This difference is likely due to the more complex nature of real biomass. It is also possible that water may preferentially react with these other species rather than with furan.

Water can cause dealumination and may also influence the catalyst stability.[8] Dealumination can result in a decrease in the number of Brønsted sites present on the catalyst, which can result in catalyst deactivation.[8] Zeolites can be stabilized to prevent dealumination by the addition of phosphorus.[9] However, during the course of our experiments, we did not observe any effects of dealumination. A catalyst sample examined after four experiments showed almost no change in the amount of Brønsted sites (determined by isopropylamine temperature programmed desorption;[10] 0.366 mmol g^{-1} before, 0.354 mmol g^{-1} after experiments) or surface area (measured by N_2 adsorption).

Water has a dramatic influence on the CFP chemistry with furan model compounds. As shown herein, water hydrolyzes furans to produce propylene and CO_2. This reaction is of importance in the design of realistic processes from biomass, and suggests that the water partial pressure will be important in designing a realistic CFP process. More work is necessary to determine if changing the water partial pressure will have an effect on the product distribution of CFP of real biomass.

Experimental Section

Reactions were performed in a continuous flow fixed bed reactor system capable of feeding a volatile reaction stream, as well dripping a second reaction stream into the furnace over the catalyst bed. The catalyst was supported by a quartz frit inside a tubular quartz reactor. Reaction temperature was monitored by a thermocouple inserted inside the furnace into a well located in the quartz reactor immediate above and to the side of the catalyst bed. Both streams were fed using syringe pumps (Fisher, KDS100). Helium (Airgas, UHP 5.0 grade) was used as a carrier gas, controlled by a mass-flow controller (Brooks) set at 400 mL min^{-1}. The catalyst used in all experiments was ZSM-5 (SiO_2/Al_2O_3 molar ratio = 30; NH_4 form; Zeolyst International), which was calcined in situ with a heating rate of 4 °C min^{-1} to 600 °C for at least 3 h before use under air (Airgas, industrial grade) at a nominal flow rate of 60 mL min^{-1} (controlled by a needle valve); the air was purified by passing it through a desiccant trap. The feed for the reactions was furan (99% purity; Sigma Aldrich, used without any modification). In-house deionized water was used as the aqueous feed. All reactions were performed at 600 °C, with a reaction time of 6 min. Gaseous products were collected by gas bags and quantified by GC-FID/TCD (FID column: Restek, Rtx-VMS 40 m × 0.25 mmID × 1.4 μm; TCD column: Supelco Analytics, 80/100 Hayesep D 30 ft × 1/8 in × 2.1 mm). Coke content was determined by combusting residual carbon and passing combustion products over a converter (13% CuO on Al_2O_3; Sigma–Aldrich) to convert any CO into CO_2. The CO_2 was captured by an Ascarite trap (NaOH supported on silica; Sigma Aldrich). Coke content was calculated from the mass difference of the Ascarite trap. No liquid products were recovered. Conversion was calculated based on the moles of furan present in the feed minus the moles of furan detected at the reactor effluent. Yield was calculated based on the amount of carbon present in the product species divided by the amount of carbon present in the furan feed. Selectivity was calculated based on the amount of carbon present in a product species divided by the amount of carbon present in all product species of that type.

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