



## Carbon–carbon bond formation for biomass-derived furfurals and ketones by aldol condensation in a biphasic system

Ryan M. West, Zhen Y. Liu, Maximilian Peter, Christian A. Gärtner, James A. Dumesic\*

University of Wisconsin–Madison, Department of Chemical and Biological Engineering, 1415 Engineering Drive, Madison, WI 53706, USA

### ARTICLE INFO

#### Article history:

Received 1 May 2008

Received in revised form 25 August 2008

Accepted 1 September 2008

Available online 7 September 2008

#### Keywords:

Aldol condensation

Base catalysis

Biomass

Biphasic

Renewable fuels

### ABSTRACT

Production of liquid alkanes in the range of C<sub>8</sub>–C<sub>15</sub> from renewable sources, such as xylose and fructose (C<sub>5</sub> and C<sub>6</sub>), requires the formation of C–C bonds between the carbon chains. We have investigated aldol condensation as a catalytic route for this conversion in a biphasic system between various furfurals (furaldehyde (FUR), methyl furfural, and 5-hydroxymethyl furfural (HMF)) and ketones (acetone, acetol, dihydroxyacetone, 2-hexanone, and 3-hexanone) derived from biomass. This system employs a reactive aqueous phase containing a basic NaOH catalyst, an organic extracting phase to remove the aldol-adducts from the homogeneous catalyst, with the addition of salt (NaCl) to the aqueous phase employed to expand the miscibility gap between the aqueous and organic phases. The effect of reagent ratios and reaction conditions on the final product distribution, such as ketone to furfural and base to furfural ratio, was investigated and a simple first order model was used to gain insight into the reaction network. High yields to single and double condensation products can be achieved for acetone condensation with furfural compounds by proper choice of reagent ratios. Degradation of HMF appears to be catalyzed by base, leading to the formation of organic acids that subsequently neutralize the base catalyst. This degradation process limits the recycling of the aqueous phase and also decreases the condensation yield of species such as hexanones that do not readily dissolve in the aqueous phase. FUR, which does not readily degrade, is more completely condensed to form products; however, because FUR is less soluble in the reactive aqueous phase compared to HMF, high concentrations of base must be used to increase the rate of reaction.

© 2008 Elsevier B.V. All rights reserved.

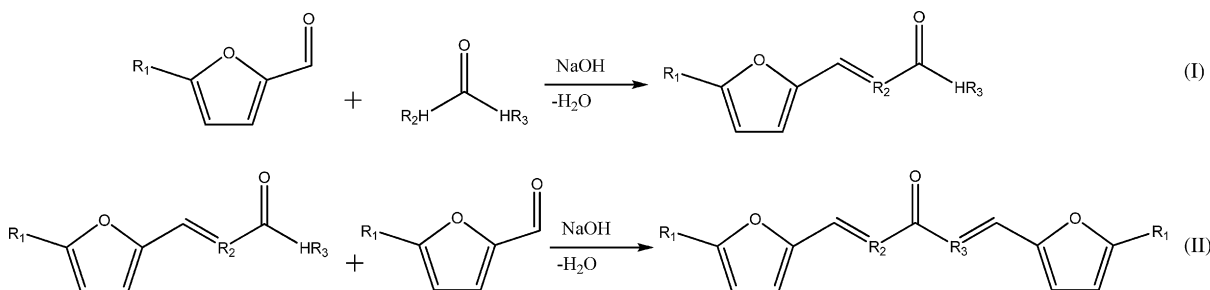
### 1. Introduction

The amount of biomass that can be grown globally on a sustainable basis could provide approximately 100EJ of energy per year [1], a value comparable to the annual worldwide use of energy by the transportation sector [2]. While it is currently possible to convert a hexose to *n*-hexane with high yields [3], this molecule is at the lower limit of molecular weight for use in liquid alkane transportation fuels [4,5]. In a recent paper, it was shown that the targeted synthesis of specific alkanes with molecular weights higher than hexane can be achieved from fructose by first dehydrating the sugar to produce furfurals, followed by the formation of C–C bonds via aldol condensation with ketones, and completed by subsequent removal of oxygen atoms to form alkanes by a combination of hydrogenation and dehydration reactions [6]. The first step in this process, the formation of furfurals such as 2-furaldehyde (FUR) and hydroxymethylfurfural (HMF), can be accomplished using chemical catalysts by acid-catalyzed dehydration of xylose and fructose

in high yields [6–9]. In addition, the final two steps in this alkane production process, hydrogenation and dehydration, are readily performed in flow reactors over solid catalysts with high yields [6]. In the present paper, we focus on the critical intermediate process involving C–C coupling reactions via aldol condensation.

The formation of C–C bonds by aldol condensation occurs between two carbonyl groups with reactive  $\alpha$ -hydrogens on at least one of the carbonyls, catalyzed under acid or basic conditions, although the present paper focuses on the latter. Scheme 1 shows reactions between the aldehyde group of furfural compounds (F) and the  $\alpha$ -hydrogen of ketone molecules (K). A single condensation occurs when the enolate form of the ketone created via base-catalyzed  $\alpha$ -hydrogen abstraction attacks the aldehyde of the furfural compound. These C–C coupling reactions are accompanied by dehydration, leading to the formation of conjugated systems of C=C and C=O double bonds, as shown in Scheme 1, (I). For ketones with a reactive  $\alpha$ -hydrogen on either side of the carbonyl group, a second condensation with the furfural is possible producing an F–K–F compound (Scheme 1, (II)). This formation of F–K and F–K–F compounds can be carried out with high selectivity versus the formation of F–F and K–K adducts. In particular, F–F bonds are not formed because furfural compounds do not possess a hydrogen

\* Corresponding author. Tel.: +1 608 262 1095; fax: +1 608 262 5434.  
E-mail address: [dumesic@engr.wisc.edu](mailto:dumesic@engr.wisc.edu) (J.A. Dumesic).



**Scheme 1.** Single and double condensation of a furfural and ketone model. (I) Formation of single condensation, F–K molecule. (II) Formation of double condensation, F–K–F molecule.

atom that is alpha to the carbonyl group, and reactions between two ketone molecules to form K–K compounds are slower compared to reactions of an aldehyde with a ketone [10].

Aldol condensation of acetone with 2-furaldehyde has been studied in homogeneously catalyzed mono-phasic systems, using water, methanol/water or ethanol/water solution as solvent [11–13]. Mono-phasic homogeneously catalyzed systems have several drawbacks, including the eventual need to neutralize the catalyst and remove high volumes of water. Accordingly, in the present study we have employed a biphasic catalytic system consisting of a reactive aqueous phase and an organic extracting phase. The aqueous phase contains the basic catalyst (e.g. sodium hydroxide, NaOH), while the organic phase consists of a low boiling point organic solvent (e.g., tetrahydrofuran, THF) that continuously extracts the hydrophobic condensation products. Salt is added to the aqueous phase (e.g. sodium chloride, NaCl) to improve the miscibility gap between the two phases by salting-out organic components from the aqueous phase. The use of an organic solvent with a low boiling point and latent heat improves the energetics for removing and recycling the solvent from the aldol-adduct products. Compared to water, THF as a solvent has a lower boiling point (339 K compared to 373 K at atmospheric pressure) and lower latent heat of vaporization (30 kJ/mol compared to 41 kJ/mol at their normal boiling point temperatures).

## 2. Experimental

### 2.1. Reactive compounds

Acetone was chosen as a model compound for ketones, while FUR and HMF were chosen as furfural compounds. Acetone and FUR were purchased from Sigma–Aldrich, while HMF was produced by fructose dehydration in a biphasic system, as described in an earlier work [6]. The resulting solution of 6 wt% HMF in THF was used directly, or it was concentrated using a rotary evaporator. In addition to the aforementioned model compounds, we studied aldol condensation of 5-methyl-furfural (MeFur), which is formed from dehydration of methyl-pentoses that are present in varying concentrations with pentoses in biomass feedstocks used to make FUR [9]. In addition, we studied condensation of 2-hexanone and 3-hexanone, which can be made via the dehydration/hydrogenation of sorbitol [14]. We also investigated condensation of dihydroxyacetone, and glyceraldehyde, which can be formed by retro-aldol reactions of glucose [15]; and, we studied the condensation of acetol, which can be made from the dehydration of glycerol [16].

### 2.2. Experimental setup

Typical experiments for aldol condensation were carried out by mixing an organic feed solution and an aqueous feed solution in a 25 mL batch reactor. The organic phase was created by adding

the desired reactants (furfurals and ketones) to THF, or by adding the desired ketones to the solution of HMF in THF produced from the dehydration of fructose. The aqueous phase contained 6–27 wt% NaOH, and it was saturated with NaCl. The mass ratio of the organic and aqueous phase was kept at 2:1, except for several runs where a ratio of 20:1 was used. The stirring speed during reaction was set at 1180 rotations per minute (rpm), which was sufficient to achieve good mixing of the two phases, such that the results were not significantly affected by stirring speed.

Scaled-up reactions were performed in a 500-mL flask, employing 300 mL of solution. These experiments produced yields similar to those obtained using 25-mL reactors. These larger volumes of condensation products were then concentrated in a rotary evaporator, and subsequently hydrogenated over a Pd-based catalyst, and finally deoxygenated to produce alkanes by dehydration/hydrogenation over a bifunctional Pt/NbOPO<sub>4</sub> catalyst in tubular flow reactors. The alkane products were quantified by GC-FID detection, using standards obtained from Sigma. Because most of the condensation products were unavailable commercially for making standards, the composition of the final alkane products was used to back-calculate the relative amounts of single-step/double-step aldol condensation products [6].

### 2.3. Analysis method

The compositions of the aqueous and organic phases were analyzed using HPLC (Waters 2690 system equipped with PDA 960 UV (320 nm) detector) and GC (Shimadzu GC-2010 with an FID detector and a DB-5 column from Alltech). To monitor the progress of the reaction versus time, samples were taken more frequently at the beginning when the rate was most rapid and less frequently towards the end when the rate was slower. For other runs, only the feed and final solutions were analyzed. Hydrochloric acid was added immediately after sampling to neutralize the small amount of base catalyst and quench the reaction in all cases, except for studies of the change in pH with reaction for which the pH was measured before the sample was neutralized.

## 3. Results

### 3.1. Reactive system properties

#### 3.1.1. Biphasic system/salting out effect

The addition of a salt to the aqueous phase improves the separation of the two phases via the salting out effect. Without salt, THF and water are fully miscible. With concentrated salt, the two phases that form are not fully immiscible and contain small quantities of the other phase. Using water saturated with NaCl, it was determined that the THF layer contained  $0.079 \pm 0.009$  g water/g THF, while the water layer contained  $0.053 \pm 0.007$  g THF/g water at room temperature and pressure.

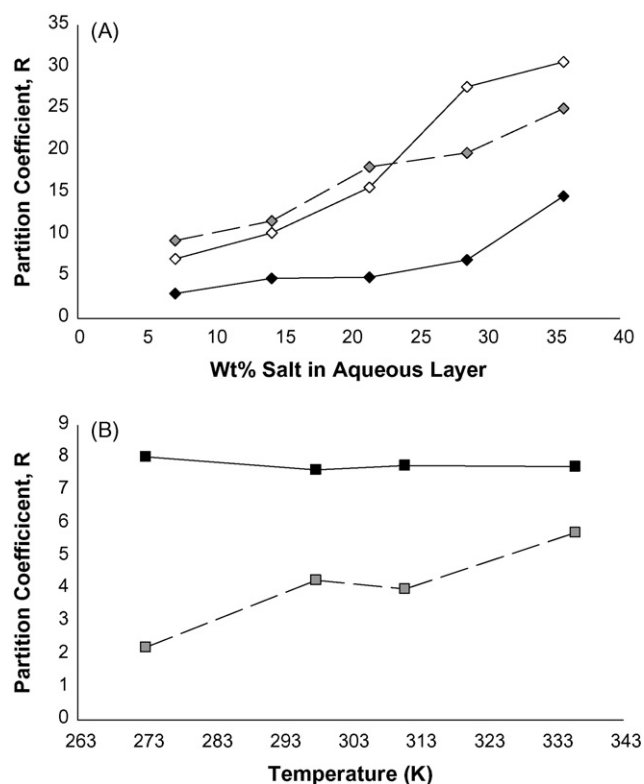


Fig. 1. Partition coefficients in THF/water. (A)  $T=298$  K; (◆) HMF; (◇) MeFur; (◊) FUR. (B) 30 wt% NaCl; (■) HMF; (▣) acetone.

### 3.1.2. Partition coefficients

The partition coefficient,  $R$ , is defined as the concentration (g/mL) of the species in organic layer divided by the concentration (g/mL) in aqueous layer at reaction conditions. Because the base catalyst is present in the aqueous phase, a compound with a higher  $R$  value would be expected to react at a slower rate. The value of  $R$  can be increased by the addition of salt to the aqueous phase, which helps to expel less soluble species into the organic phase by “salting out” these species [7]. Fig. 1A demonstrates the effect of salt concentration in the aqueous phase on the partition coefficients of HMF, MeFur and FUR in THF and water. As the concentration of salt increases to the saturation point of 36 wt% NaCl, the value of  $R$  increases to a maximum around 14, 25 and 31 for HMF, MeFur and FUR, respectively. As shown in Fig. 1B, temperature did not significantly affect the partitioning of HMF and acetone between phases.

The measured values of  $R$  for chemical species relevant to this investigation at typical reaction conditions are listed in Table 1. For reagents, the values were measured at initial reaction conditions without base (i.e. a NaCl saturated aqueous phase in contact with extracting solvent, THF at room temperature and pressure). For products, these values are given for post reaction conditions. The values of  $R$  for post reaction conditions are slightly lower than the initial  $R$  values due to the decrease in salt concentration from the formation of water, a byproduct of condensation. It is apparent that the additional hydrophilic hydroxyl group of HMF increases its solubility in the aqueous layer relative to both FUR and MeFur, resulting in a lower  $R$  value. The  $R$  value of acetol is lower than acetone due to its additional hydroxyl group. In a similar manner, values of  $R$  for the hexanones are larger than that of acetone, due to the longer hydrophobic alkane chains that increase their organic solubility. The aldol products undergo dehydration to form long conjugated species. Accordingly, these conjugated products are more soluble

Table 1  
Partition coefficients for species at different conditions

	Species	Partition coefficient	
		Saturated NaCl	Post-reaction
Furfurals	HMF	14.3	5.8–8.1
	FUR	30.6	26.7
	MeFur	25.0	19.7
Ketones	Acetone	4.0	4.0
	2-Hexanone	>180 <sup>a</sup>	>180 <sup>a</sup>
	3-Hexanone	>80 <sup>a</sup>	>80 <sup>a</sup>
	Acetol	0.06	0.06
Condensation products	F-A (HMF)	–	59
	F-A-F (HMF)	–	44
	F-A (FUR)	–	>100 <sup>a</sup>
	F-A-F (FUR)	–	>100 <sup>a</sup>

<sup>a</sup> Aqueous phase concentration below detection limit and thus estimated at the detection limit.

in the organic phase than their corresponding reactants. The HMF derived products are more soluble in the aqueous phase than the corresponding FUR products due to the additional hydroxyl group. The FUR derived products partitioned so strongly into the organic phase that their concentration in the aqueous phase was below the detection limits for both HPLC and GC analyses.

### 3.2. HMF-based reactions

HMF prepared from the biphasic dehydration of fructose with THF [6] was used for all HMF-based experiments. A typical dehydration run yielded a product solution containing  $6.0 \pm 0.6$  wt% ( $420 \pm 40$   $\mu\text{mol/mL}$ ) HMF in THF. For studies using more concentrated HMF, this 6 wt% solution was concentrated in a rotary evaporator to the desired concentration. The results for all runs are included in Table 2, along with the varied parameters for each run. The values given in Table 2 were taken after either HMF could no longer be detected in the sample, or after the concentration of products and reactants remained constant with time as determined by HPLC. The distribution of single (F–K) and double condensation products (F–K–F) in Table 2 is given as the molar ratio of single products to double condensation products. The condensate yield is the relative amount of initial HMF that is converted into single and double condensation products. Total carbon balance is the condensate yield plus any unreacted HMF.

#### 3.2.1. HMF to acetone ratio

Fig. 2 shows the change in product distribution, given as the ratio of single to double condensation products, for a range of reactant molar ratios. All other reaction conditions were kept constant for the two data sets at different amounts of base. As the amount of acetone is increased relative to the amount of HMF, more single products are formed for both cases. As shown in Fig. 2, at lower acetone:HMF ratios, the final product distribution contained unreacted HMF, while at higher ratios, the total recovered carbon decreased. The maximum yield to products therefore occurred at moderate acetone:HMF levels for the given base levels (1.6 and 2.0) and a temperature of 298 K.

#### 3.2.2. HMF to base ratio

Results in Table 2 and Fig. 3 show the influence of the amount of catalyst on the final yield and composition. When acetone is in excess relative to HMF, more catalyst (a higher NaOH:HMF molar ratio) results in a lower single:double product ratio as shown Fig. 3 (◆). The same effect can also be seen by comparing Table 2 entries 3 and 11 (acetone:HMF = 1.63), single:double equal to 4.31 and 2.23 at NaOH:HMF of 1.63 and 2.27, respectively, and for entries

**Table 2**

Final composition, yield and carbon balance of HMF and condensation products in a biphasic THF/saltwater reactor with organic:aqueous mass ratio = 2.0

#	Batch size (mL)	Ketone	Initial HMF concentration ( $\mu\text{mol/mL}$ )	Ketone:HMF	NaOH:HMF	Temperature (K)	Steps	Single:double molar ratio	Condensate yield (%)	Total carbon balance (%)
1	300	Acetone	401	0.50	1.00	298	6	0.72	87.1	89.0
2	300	Acetone	296	0.52	1.56	298	1	1.23	48.1	76.0
3	300	Acetone	429	1.63	1.63	298	1	4.31	62.1	64.8
4	300	Acetone	452	8.02	1.61	298	1	9.20	68.6	68.6
5	300	Acetone	450	24.13	1.61	298	1	21.67	41.7	41.7
6	300	Acetone	319	0.67	1.98	298	1	1.19	85.0	93.6
7	300	Acetone	321	1.00	1.99	298	1	2.45	83.4	90.3
8	300	Acetone	398	2.00	1.96	298	1	4.24	87.0	87.0
9	300	Acetone	418	2.00	2.48	298	1	3.33	74.7	75.4
10	300	Acetone	322	0.67	0.97	298	1	1.17	86.7	95.9
11	300	Acetone	517	1.63	2.27	298	1	2.23	59.7	60.1
12	25	Acetone	423	2.00	0.50	298	1	4.72	73.8	73.8
13	25	Acetone	396	2.00	0.10	333	1	15.52	27.7	77.0
14	25	Acetone	420	2.00	0.25	333	1	13.96	30.5	74.4
15	25	Acetone	396	2.00	0.50	333	1	5.63	65.4	69.6
16	25	Acetone	396	2.00	0.75	333	1	5.58	70.3	70.3
17	25	Acetone	424	2.00	1.00	333	1	4.84	66.3	66.3
18	25	Acetone	424	2.00	0.25	353	1	7.35	62.5	87.9
19	25	Acetone	445	1.00	0.75	298	6	1.28	78.9	78.9
20	25	Acetone	414	0.50	1.00	298	6	0.64	81.9	81.9
21	25	Acetone	406	0.50	2.00	298	6	0.53	75.5	75.5
22	25	Acetone	422	0.50	1.00	298	1	0.82	79.1	79.1
23	25	Acetone	437	0.50	1.00	298	12	0.50	74.9	74.9
24	25	–	440	–	0.25	298	–	–	–	87.1
25	25	–	456	–	0.25	333	–	–	–	84.0
26	25	–	437	–	0.35	298	–	–	–	89.4
27	25	–	403	–	0.50	333	–	–	–	78.3
28	25	–	434	–	0.71	298	–	–	–	82.8
29	25	–	296	–	1.41	298	–	–	–	41.9
30	25	–	434	–	2.00	298	–	–	–	14.0
31	25	Acetone	424	2.00	0.50	313	1	5.43	71.5	71.5
32	25	Acetone	424	2.00	0.50	353	1	5.26	70.5	70.5
33	25	Acetone	406	0.50	1.00	333	1	0.94	66.6	68.7
34	25	Acetone	440	2.00	2.00	298	1	3.17	71.9	71.9
35 <sup>a</sup>	25	Acetone	446	2.00	0.50	298	1	2.61	83.1	83.1
36 <sup>a</sup>	25	Acetone	446	0.50	1.00	298	6	0.44	63.0	63.0
37 <sup>a</sup>	25	Acetone	446	0.50	0.50	298	6	0.84	65.5	83.6
38	25	Acetone	2280	2.00	0.10	333	1	$\infty$	17.5	58.8
39	25	Acetone	1143	2.00	0.50	298	1	4.07	76.6	76.6
40	25	Acetone	2322	2.00	0.50	333	1	15.33	26.1	26.1
41	25	Acetone	1161	2.00	0.50	333	1	3.76	56.6	56.6
42	25	Acetone	2280	2.00	0.10	298	1	2.07	27.8	43.0
43	25	Acetone	1143	2.00	0.25	298	1	4.85	63.4	69.1
44	300	2-hexanone	426	2.00	2.00	298	1	–	22.0	22.0
45	25	2-hexanone	445	2.00	2.00	298	1	–	31.4	31.4
46	25	2-hexanone	434	2.00	2.00	313	1	–	28.1	28.1
47	25	3-hexanone	434	2.00	2.00	298	1	–	12.3	15.8
48	25	Acetol	434	2.00	2.00	298	1	–	21.0	21.0
49	25	Acetol	421	0.50	1.00	298	6	–	4.6	8.7
50	25	Dihydroxyacetone	421	2.00	2.00	298	1	–	0.0	0.0
51	25	Glyceraldehyde	421	2.00	2.00	298	1	–	7.8	7.8

<sup>a</sup> Organic:aqueous mass ratio = 20.

8 and 9 (acetone:HMF = 2.0), single:double equal to 4.24 and 3.33 at NaOH:HMF of 1.96 and 2.48, respectively. When HMF is in excess relative to acetone, use of more catalyst has little effect as shown by comparing entries 10 and 6 (acetone:HMF = 0.67), single:double equal to 1.17 and 1.19 at NaOH:HMF of 0.97 and 1.98, respectively, and entries 20 and 21 (acetone:HMF = 0.5), single:double equal to 0.64 and 0.53 at NaOH:HMF of 1.00 and 2.00, respectively.

The total carbon balance in all cases decreases as the NaOH:HMF ratio increases as shown in Fig. 3 ( $\diamond$ ) and Table 2 for all above listed cases. When acetone is in excess to HMF, the yield of single and double condensation products reaches a maximum at intermediate values of the base ratio, while at lower base ratios unreacted HMF is present in the final solution as shown by comparing ( $\diamond$ ) and ( $\blacklozenge$ ) in Fig. 3. At a NaOH:HMF ratio of 0.1–0.5, a significant difference between the total carbon (HMF plus products) and the product car-

bon can be seen. Above a ratio of 0.5, however, all the HMF is reacted to products.

### 3.2.3. HMF temperature effects

Increasing the temperature only slightly impacted the final distributions. When acetone was in excess (acetone:HMF = 2.0, NaOH:HMF = 0.5), Fig. 4 shows a slight decrease in total carbon with increasing temperature and little variation in the distribution of single and double condensation products. When HMF was in excess, entries 22 and 33 in Table 2 show that increasing temperature from 298 to 333 K had a mild impact on the single/double ratio 0.82–0.94, while also decreasing the total carbon recovered from 79.1 to 68.7%.

### 3.2.4. Stepwise addition

From stoichiometry, an Acetone:HMF ratio of 0.5 is expected to yield the most double condensation product. Using less acetone

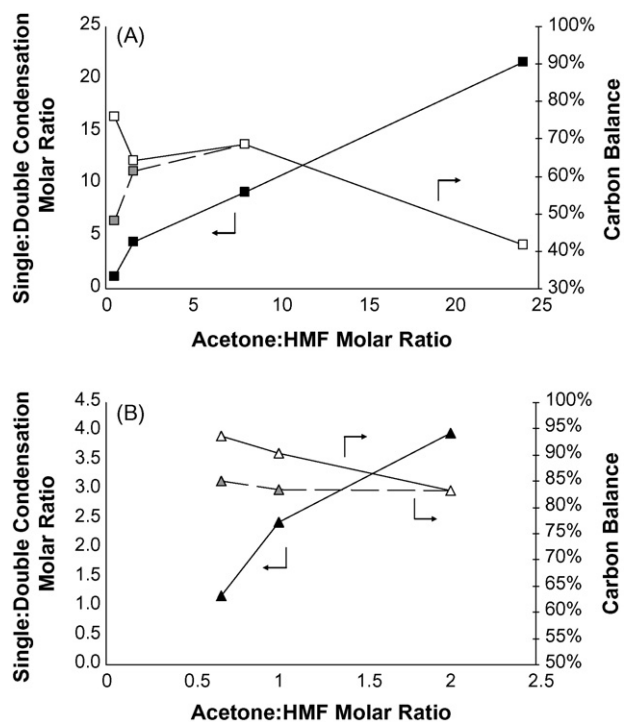


Fig. 2. Product distribution and carbon balance for different acetone:HMF molar ratios. (A) NaOH:HMF=1.6, 300-mL batch; (■) single:double condensation ratio; (□) carbon balance of single and double; (□) carbon balance of single, double and HMF. (B) NaOH:HMF=2.0, 300-mL batch; (▲) single:double condensation ratio; (▲) carbon balance of single and double; (▲) carbon balance of single, double and HMF.

would result in unreacted HMF, and using more acetone would result in more single condensation product. Since the formation of double condensation products results from a series of reactions, adding the acetone in steps to keep the acetone concentration low throughout the experiment might help maximize the yield of double condensation products. To test this idea, acetone was added either all at once (one step), in six equal additions, or in twelve equal additions over the course of 1 h to the stirred HMF solution (NaOH:HMF ratio=1 at 298 K). The final molar ratio of acetone/HMF was 0.5. As shown in Fig. 5, the single:double ratio is approximately constant as acetone is added with more steps. The total carbon yield decreases, however, as acetone is added in steps.

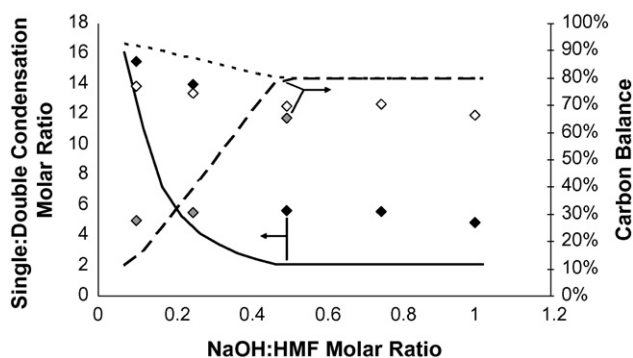


Fig. 3. Product distribution and carbon balance for different NaOH:HMF molar ratios. Acetone:HMF=2.0, temperature 333 K, 25-mL batch; (◆) single:double condensation ratio; (◆) carbon balance of single and double; (◇) carbon balance of single, double and HMF; (—) modeled ratio; (---) modeled carbon balance of single and double; (·) carbon balance of single, double and HMF.

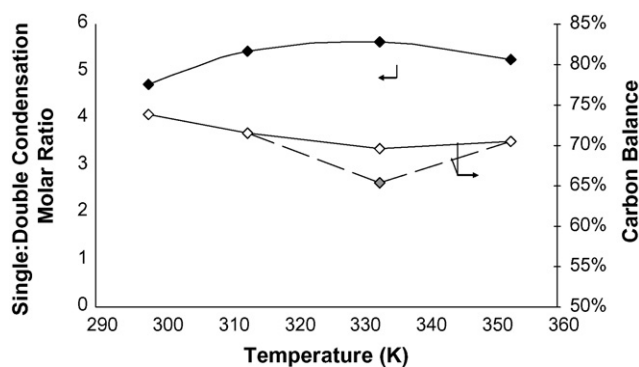


Fig. 4. Product distribution and carbon balance with changes in temperature. Acetone:HMF=2.0, NaOH:HMF=0.5, 1 step addition; (◆) single:double condensation ratio; (◆) carbon balance of single and double; (◇) carbon balance of single, double and HMF.

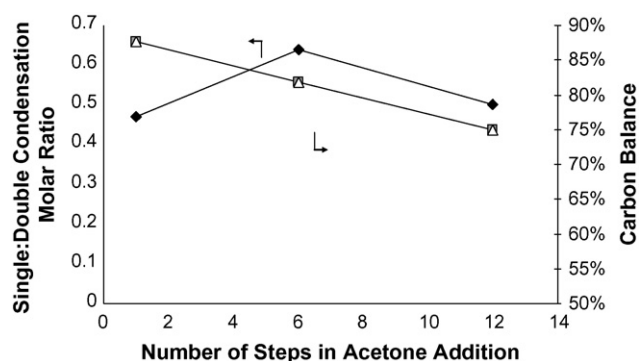


Fig. 5. Product distribution and carbon balance for the stepwise addition of acetone to HMF mixture at Acetone:HMF=0.5, Base:HMF=1.0, Temperature=298 K; (◆) single:double condensation ratio; (□) carbon balance of single and double; (△) carbon balance of single, double and HMF.

### 3.2.5. HMF degradation without ketones

HMF can react to form other chemicals such as levulinic and formic acids via reaction with water, or it can degrade to form humins [17]. To test the influence of the amount of base on the degradation of HMF, biphasic systems at different NaOH:HMF ratios were studied without ketones. The concentration of HMF decreased initially with time and reached a constant level, from which the extent of HMF degradation was calculated, and these values are reported in Fig. 6 for various base levels. The pH of the feed and samples was also measured to monitor the disappearance of NaOH. In all samples, a high initial pH (12–13.8) was recorded, but a relatively neutral final pH of 8–10 was seen. In Fig. 6, it can be seen that more

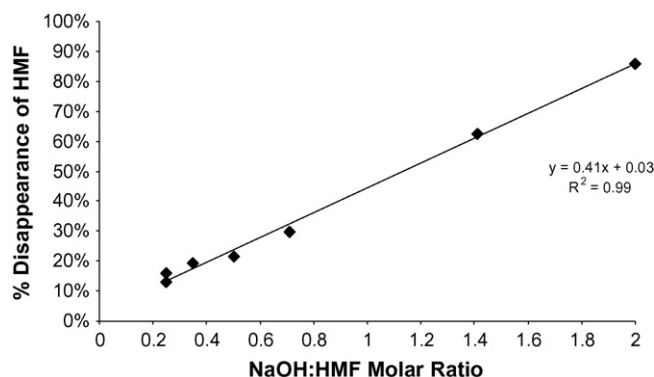
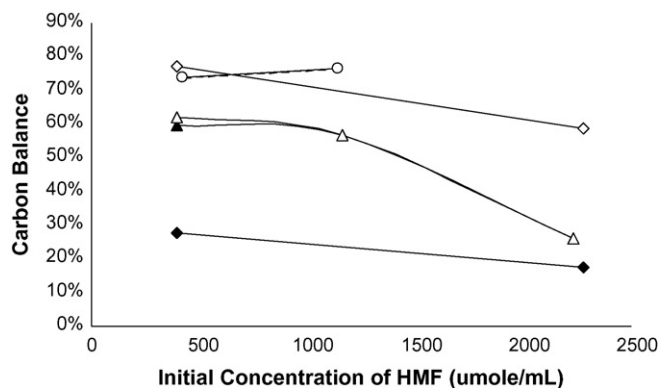


Fig. 6. Disappearance of HMF at different NaOH:HMF ratios without ketones.





**Fig. 7.** Influence of initial HMF concentration on final carbon distribution at constant NaOH:HMF ratio. NaOH:HMF=0.1, acetone:HMF=2.0, Temperature 333 K; (◆) carbon balance of single and double; (◇) carbon balance of single, double and HMF. NaOH:HMF=0.5, Acetone:HMF=2.0, Temperature 333 K; (▲) carbon balance of single and double; (△) carbon balance of single, double and HMF. NaOH:HMF=0.5, Acetone:HMF=2.0, Temperature 298 K; (●) carbon balance of single and double; (○) carbon balance of single, double and HMF.

HMF is degraded at higher concentrations of base. Approximately 1 mole of HMF degrades for every 2.4 moles of base. These trends suggest that HMF degradation into organic acids is catalyzed by the NaOH. The organic acids are in-turn neutralizing the NaOH such that eventually, HMF degradation stops leaving unreacted HMF and low concentrations of NaOH.

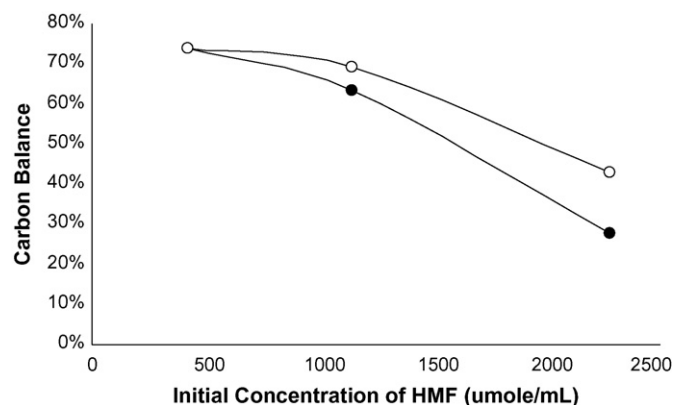
### 3.2.6. Initial concentration

Fig. 7 shows the influence of initial HMF concentration at constant NaOH:HMF ratios. Increasing the HMF concentration from 420 to 1120  $\mu\text{mol/mL}$  had little effect for NaOH:HMF=0.5 at both 298 and 333 K. However, increasing the concentration further to 2280  $\mu\text{mol/mL}$  decreased the carbon collected as both condensation products and HMF.

Increasing the concentration of HMF at a constant total amount of base in the aqueous phase was also investigated. Fig. 8 demonstrates that as the HMF concentration is increased, with constant total amount of NaOH, the carbon recovered both as products and as unreacted HMF decreases. More HMF remains unreacted at higher concentrations, and this behavior is likely due to neutralization of base.

### 3.2.7. Mass ratio (changing aqueous concentration)

Experiments were carried out to study the effect of changing the mass ratio of organic to aqueous layers, while keeping all other conditions constant. The organic feed contained 446  $\mu\text{mol/mL}$ , and by



**Fig. 8.** Influence of initial HMF concentration on final carbon distribution at constant total base at 600  $\mu\text{mol NaOH/mL}$  (Aqueous), Temperature 298 K; (●) carbon balance of single and double; (○) carbon balance of single, double and HMF.

increasing the organic to aqueous mass ratio, the concentration of base in the aqueous phase was increased to maintain a constant NaOH:HMF ratio. In both cases, increasing the organic:aqueous mass ratio from 2 to 20 decreased the molar ratio of the single to double condensation product. In the case of excess acetone, entries 12 and 35, (acetone:HMF=2.0, NaOH:HMF=0.5), all of the HMF was reacted and the yield of condensation products improved from 73.8 to 83.1%. In the case of excess HMF, entries 20 and 36, (acetone:HMF=0.5, NaOH:HMF=1.0), all of the HMF was reacted; however, the yield of condensation products dropped from 81.9 to 63.0% at the higher mass ratio.

### 3.2.8. HMF other ketones

Results for aldol condensation of HMF with 2- and 3-hexanone are shown in Table 2 entries 44–47. Yields of condensation products were from 22.0 to 31.4% for 2-hexanone, whereas lower yields near 15.8% were observed for 3-hexanone, which does not contain a primary  $\alpha$ -hydrogen. Aldol condensation of HMF with acetol, entries 48–49, formed a single condensation product, with a yield of 21.0% with excess acetol and very little product with excess HMF, 4.6%. In this case, the presence of a hydroxyl group on one of the primary carbon atoms inhibited the second condensation step. Consistent with this behavior, dihydroxyacetone, containing two primary hydroxyl groups, did not show evidence of condensation products with HMF, entry 50. Glyceraldehyde condensation with HMF, entry 51, formed a compound with a UV signature similar to a condensation product. However, the yield was quite low, 7.8%, and the exact nature of the product was not determined.

**Table 3**

Final composition, yield and carbon balance of other furfurals and condensation products in a biphasic THF/saltwater reactor with organic/aqueous mass ratio=2.0

#	Batch size (mL)	Ketone	Initial furfural concentration	Ketone:furfural	NaOH:furfural	Temperature (K)	Steps	Single:double molar ratio	Condensate yield (%)	Total carbon balance (%)
52 <sup>a</sup>	300	Acetone	1536	3.99	3.04	298	1	3.99	90.9	96.3
53 <sup>a</sup>	300	Acetone	2458	2.50	1.97	298	1	2.50	94.0	96.0
54 <sup>a</sup>	300	Acetone	2216	1.50	1.91	298	1	1.37	–	–
55 <sup>a</sup>	300	Acetone	1979	1.00	1.97	298	1	0.81	–	–
56 <sup>a</sup>	300	Acetone	1512	0.50	2.27	298	1	0.21	67.2	76.2
57 <sup>a</sup>	25	Acetone	2031	2.00	0.50	298	1	6.26	82.2	82.7
58 <sup>a</sup>	25	Acetone	1108	2.01	0.52	298	1	8.72	87.6	87.9
59 <sup>a</sup>	25	Acetone	1170	2.00	1.99	298	1	4.57	94.6	96.4
60 <sup>a</sup>	25	Acetone	1223	0.51	2.31	298	1	0.07	98.6	98.9
61 <sup>a</sup>	25	Acetone	2538	0.51	1.02	298	1	0.11	89.9	90.3
62 <sup>a</sup>	25	–	1100	–	2.00	298	1	–	–	59.3
63 <sup>b</sup>	300	Acetone	1419	1.50	1.97	298	1	1.46	91.9	96.3

<sup>a</sup> FUR.

<sup>b</sup> MeFur.

### 3.3. Other furfural-based reactions

In addition to hexose sugars, pentose and methyl pentose sugars are present in biomass-derived feed stocks. Accordingly, we have studied aldol condensation of furfurals derived from these sugars, namely 2-furaldehyde from xylose, and 5-methyl-2-furfural (MeFur) from methyl pentoses. As the production of FUR from xylose (and with it small amounts of MeFur) is already commercialized [9], these furfural compounds were purchased rather than made from the corresponding sugar. Results from studies of these compounds are included in Table 3.

#### 3.3.1. 2-Furaldehyde

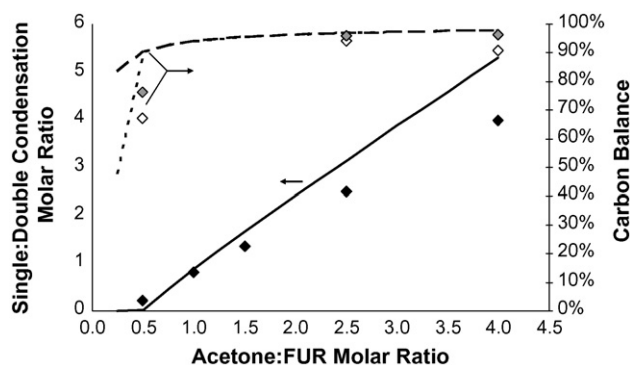
The biphasic condensation of FUR with acetone demonstrates similarities to the condensation of HMF with acetone, with several notable differences. First, degradation experiments conducted without ketones, show that FUR neither degrades as rapidly, nor does it degrade to the extent of HMF. For this reason, yields of FUR condensation products are higher than from HMF under the same conditions. Second, FUR does not contain a carbon atom attached to the 5 position of the furan ring, which allows FUR to undergo additional reactions at these and other sites [6,13,18]. The products resulting from additional condensation at this position were not detectable with our HPLC method, and are not included in Table 3. However, the presence of these species can be detected by subjecting the solution to subsequent hydrogenation followed by hydrodeoxygenation, leading to the formation of the corresponding C<sub>16</sub>–C<sub>23</sub> alkanes [6].

**3.3.1.1. Acetone to FUR ratio.** Fig. 9 demonstrates the effects on the product distribution and yields of changing the acetone:FUR ratio. As with HMF, an increase in this ratio increases the single to double product ratio in a nearly linear fashion.

**3.3.1.2. Base to FUR ratio.** Increasing the NaOH:FUR ratio from 0.52 to 1.99 decreases the single to double product ratio in a similar manner to HMF, as shown by comparing entries 58 and 59 in Table 3 (single:double equal to 8.72 and 4.57). However, unlike HMF, increasing the NaOH:FUR ratio increased the amount of single and double products collected (from 87.6 to 94.6%).

#### 3.3.2. 5-Methyl-2-furfural (MeFur)

Aldol condensation of methyl furfural (MeFur) with acetone produced a carbon balance that was among the highest of any furfurals, with 91.9% of the carbon being present as products, and 96.3%



**Fig. 9.** Product distribution and carbon balance for different acetone:FUR molar ratios; NaOH:HMF=2.0, Temperature 298 K; (♦) single:double condensation ratio; (◇) carbon balance of single and double; (◇) carbon balance of single, double and FUR; (—) modeled ratio; (---) modeled carbon balance of single and double; (· ·) carbon balance of single, double and HMF.

present including MeFur. With a carbon at the 5 position of the furan ring, MeFur does not react to form larger chain species like FUR. In addition, MeFur does not rehydrate to form organic acids like HMF.

## 4. Discussion

### 4.1. Reaction model

The coupled effects of different variables on the final yield and distribution of the biphasic system make it difficult to develop a thorough understanding of the reaction kinetics. In this respect, analysis of the data using a simple reaction model helps to elucidate some of these effects. Accordingly, we employed the following simple nine-step model to explain the trends observed in our experimental studies:

- (1)  $F_o \leftrightarrow F_{aq}$
- (2)  $A_o \leftrightarrow A_{aq}$
- (3)  $F-A_o \leftrightarrow F-A_{aq}$
- (4)  $F-A-F_o \leftrightarrow F-A-F_{aq}$
- (5)  $F_{aq} + A_{aq} \rightarrow F-A_{aq}$
- (6)  $F-A_{aq} + F_{aq} \rightarrow F-A-F_{aq}$
- (7)  $F_{aq} + NaOH \rightarrow F_{degrade}$
- (8)  $F-A-F_{aq} + F-A-F_{aq} \rightarrow \text{polymer}$
- (9)  $F-A-F_{aq} + F-A_{aq} \rightarrow \text{polymer}$

The symbols  $F_o$ ,  $A_o$ ,  $F-A_o$  and  $F-A-F_o$  represent HMF (or FUR), acetone, single condensation product, and double condensation products, respectively, in the organic layer. Quantities with aq subscripts are the corresponding species in the aqueous layer.

The first four reactions in the model are the partitioning of furfural, ketone, single and double condensation products between the aqueous and organic phases. These reactions are reversible, and their rates are combinations of the forward and reverse reaction rates in the form of

$$r_1 = k_1 * [F_o] - k_1/K_1 * [F_{aq}]$$

$$r_2 = k_2 * [A_o] - k_2/K_2 * [A_{aq}]$$

$$\vdots$$

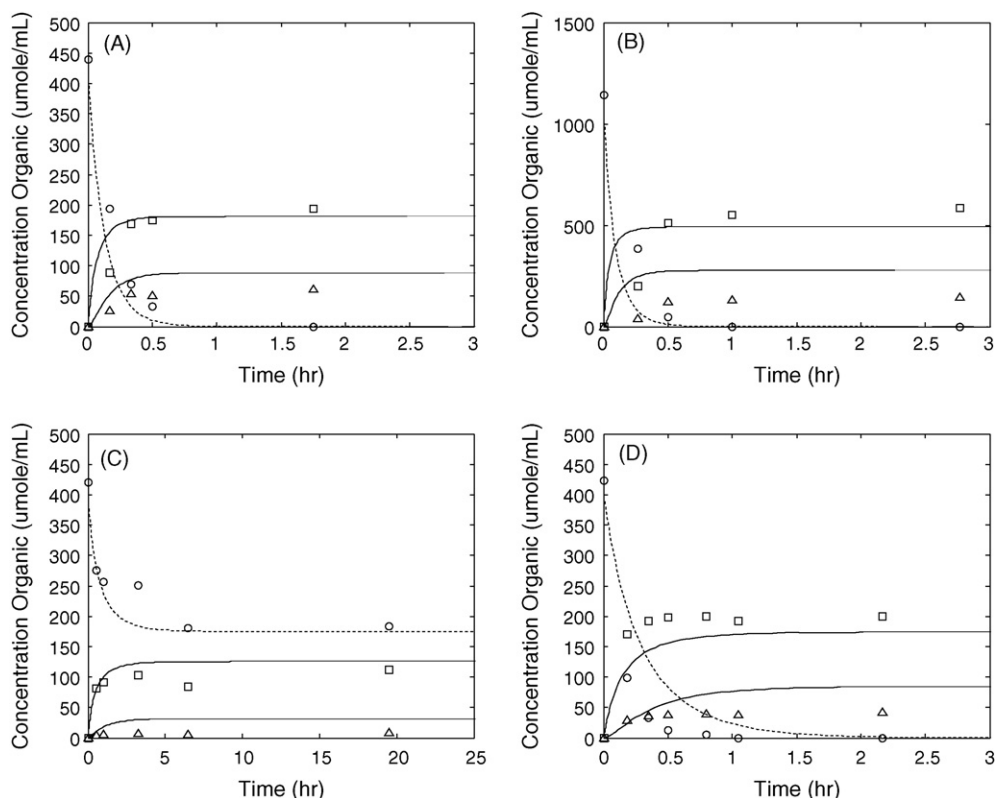
where  $k_1$  through  $k_4$  are the forwards rate constants and  $K_1$  through  $K_4$  are the equilibrium constants. The equilibrium values for these four reactions are taken to be the measured partition coefficients ( $R$ ) for the reacting species at the reaction conditions (Table 1, for HMF this value was taken as 7.3, the average for all runs). The forward rate constants for these steps were chosen to insure that these steps are quasi-equilibrated.

Steps (5) and (6) are the condensation reactions between a furfural and ketone or a single condensation product and ketone, respectively. Both of these condensation reactions are assumed to occur in the aqueous phase, because this phase contains the base catalyst. The rate of aldol condensation depends upon the concentrations of catalyst, furfural and ketone (or single condensation product) in the aqueous layer. After condensation, the aldol adduct eliminates a water molecule to form an extended conjugation system, which lowers the energy of the molecule. Accordingly, reactions (5) and (6) are modeled as irreversible steps that are first order in catalyst, ketone (or single condensation product) and furfural.

$$r_5 = k_5 * [NaOH] * [A_{aq}] * [F_{aq}], \quad k_5 [=](L^2/mol^2/s)$$

$$r_6 = k_6 * [NaOH] * [F-A_{aq}] * [F_{aq}], \quad k_6 [=](L^2/mol^2/s)$$

Results from our experiments indicate that HMF undergoes degradation reactions in the absence of ketones, accompanied by a



**Fig. 10.** Concentration versus time model fits for HMF; (○) experimental HMF; (□) experimental single condensation product; (△) experimental double condensation products; (---) Model HMF; (—) model single condensation; (- · -) model double condensation. (A) Acetone:HMF = 2.0, Temperature = 298 K, NaOH:HMF = 2.0. (B) Acetone:HMF = 2.0, Temperature = 298 K, NaOH:HMF = 0.50. (C) Acetone:HMF = 2.0, Temperature = 333 K, NaOH:HMF = 0.25. (D) Acetone:HMF = 2.0, Temperature = 333 K, NaOH:HMF = 1.0.

corresponding decrease in pH such that for every one mole of HMF degraded, 2.4 moles of base are neutralized, as shown in Fig. 6. The rate of degradation increased at higher concentrations of base suggesting, that the base was catalyzing the degradation of HMF to acids. Step (7) models the degradation of HMF as a first order reaction with respect to HMF and NaOH, and the resulting organic acids are then assumed to neutralize 2.4 moles of base.

$$r_7 = k_7 * [\text{NaOH}] * [\text{F}_{\text{aq}}]$$

Our experiments also showed that FUR undergoes degradation, but at a slower rate compared to HMF. It was assumed that this degradation is similarly catalyzed by NaOH, and the degradation of FUR was then modeled separately. Steps (8) and (9) were included to model two possible polymerization reactions for FUR. These steps were not included for HMF runs, because polymer products were not observed from HMF. Polymerization is assumed to be irreversible and catalyzed by NaOH. Two possible polymerization reactions were considered, one between two double condensation products (to make a 26 carbon species) and one between a single and double condensation products (to form a 21 carbon species).

$$r_8 = k_8 * [\text{NaOH}] * [\text{F-A-F}_{\text{aq}}]^2$$

$$r_9 = k_9 * [\text{NaOH}] * [\text{F-A-F}_{\text{aq}}] * [\text{F-A}_{\text{aq}}]$$

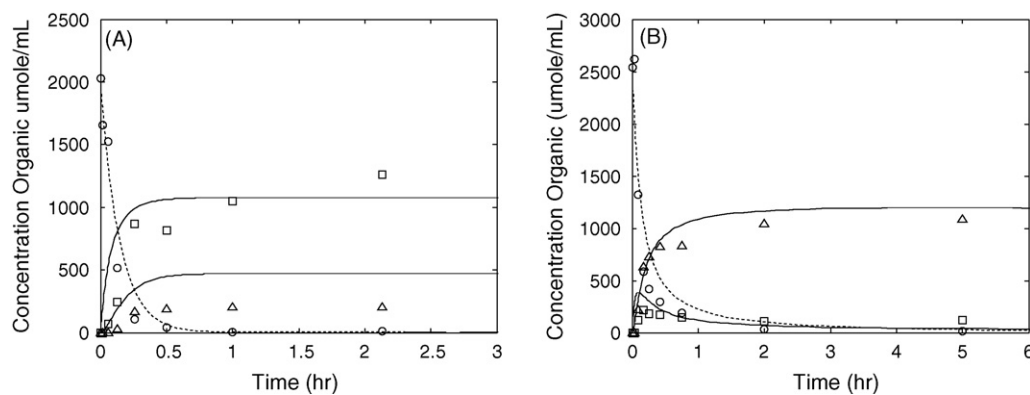
The reaction model was fit using the experimental data collected versus time in 25 mL reactors (see Tables 2 and 3), and employing the lsqnonlin function in Matlab. The results from degradation runs conducted in the absence of ketones were used first to fit the independent value of  $k_7$  for degradation of HMF

and FUR. These degradation parameters were then assumed to be the same for runs involving ketones and hence condensation reactions.

Typical examples of the trends with respect to time for the experimental data and the model fit for aldol condensation of HMF and FUR are given in Figs. 10 and 11, respectively. When modeling HMF, only small differences were seen between the data at 298 and 333 K, and the HMF data at 298 and 333 K were thus modeled together. Fig. 10 shows that the model describes the experimental data reasonable well over a large number of NaOH:HMF ratios at both temperatures. A possible explanation for this trend can be found in Fig. 1B. The partition coefficients of HMF and acetone change only slightly with a change in temperature from 298 to 333 K, suggesting that the available reactants in the aqueous phase might limit the reactivity. It is also possible that the variance in the data is too great to detect the differences between these two temperatures. Fig. 11 shows the experimental and model points for typical FUR runs at various NaOH:FUR and acetone:FUR ratios. Again, the model captures the essential trends exhibited by the experimental data for FUR.

The model parameters are listed in Table 4. The equilibrium and forward rate constants for the partitioning reactions, 1–4 are given but were not varied in the fitting of the model. The adjusted parameters,  $k_5$ – $k_9$ , are also given along with their sensitivities. The sensitivities are defined as the change in the sum of the concentrations of reactants and products (i.e., furfural, single and double products) due to the change in  $k_i$ , divided by the change in  $k_i$ , with this numerical derivative then divided by the sum of the concentrations and multiplied by the value of  $k_i$ , such that the sensitivity is dimensionless. The values of  $k_5$  and  $k_6$ , which control the rates of condensation, have large impacts in the reaction model. The con-





**Fig. 11.** Concentration versus time with model fits for FUR; (○) experimental FUR; (□) experimental single condensation product; (△) experimental double condensation products; (---) Model FUR; (—) model single condensation; (· · ·) model double condensation. (A) Acetone:FUR = 2.0, Temperature = 298 K, NaOH:FUR = 0.5. (B) Acetone:FUR = 0.5, Temperature = 298 K, NaOH:FUR = 1.0.

stant which controls the rate of degradation of HMF into acids,  $k_7$ , had a smaller impact.

For reactions involving FUR, the parameters that most affected the final distributions are the forward rate constants of condensation,  $k_5$ , and  $k_6$ . The degradation constant  $k_7$ , and second polymerization constant,  $k_9$ , have only a slight impact, while the first polymerization constant,  $k_8$  has a moderate influence on the model.

The results from the reaction model allow us to compare and contrast the reactivity of HMF versus FUR. HMF is known to degrade in aqueous medium to form organic acids. FUR can degrade to form other products other than acids [9]; however, an aqueous medium does not promote these degradations. Consequently, in the biphasic system, HMF degrades more rapidly than FUR, and the value of  $k_7$  is thus significantly higher for HMF than for FUR, equal to 3.8 and 0.026, respectively. FUR also polymerizes, leading to addition degradation processes in the aqueous phase, modeled with constants  $k_8$  and  $k_9$ . Because the concentration of FUR condensation products in the aqueous phase is low ( $K_3 = K_4 = 1/100$ ) these rates are relatively low. In spite of these differences between HMF and FUR, the aldol condensation rate constants are similar. The forward single condensation rates for FUR and HMF are 0.054 and 0.078, respectively, while the rate constants for the second condensation step are 1.82 and 2.28, respectively.

#### 4.2. Acetone to furfural

Changes in the acetone:furfural ratio at constant NaOH:furfural ratio for both HMF and FUR showed similar trends, as seen in Figs. 2 and 9. In both cases, the distribution of single and double products increased as the acetone:furfural ratio increased, and this trend is captured by the reaction model for both compounds and is shown in Fig. 9 for the FUR system.

#### 4.3. Base level effects

Because HMF degrades and neutralizes the base catalyst, the NaOH:HMF ratio influences the final distribution. Fig. 3 demonstrates that the model displays similar trends to those seen in experiments. At low NaOH:HMF ratios, the degradation of HMF completely neutralizes the base, which halts the condensation reaction, leaving unreacted HMF. The condensation follows a series path; the single condensation product is created first, followed by the double condensation product. Accordingly, neutralizing the base decreases the rate of the second condensation relative to the first. At low NaOH:HMF ratios, this effect increases the single to double condensation ratio. At higher NaOH:HMF ratios, sufficient base is present that all the HMF reacts, and the single to double product ratio decreases.

**Table 4**  
Summary of the parameters used in the model

	Rate expressions	Units	2-Furaldehyde		HMF	
			Values	Sensitivity (%)	Values	Sensitivity (%)
$k_1$	$r_1 = k_1 * [F_0] - k_1 / K_1 * [F_{aq}]$	1/s	2.78	–	2.78	–
$K_1$		(unitless)	0.037	–	0.14	–
$k_2$	$r_2 = k_2 * [A_0] - k_2 / K_2 * [A_{aq}]$	1/s	2.78	–	2.78	–
$K_2$		(unitless)	0.25	–	0.25	–
$k_3$	$r_3 = k_3 * [F - A_0] - k_3 / K_3 * [F - A_{aq}]$	1/s	2.78	–	2.78	–
$K_3$		(unitless)	$1.00 \times 10^{-2}$	–	$1.69 \times 10^{-2}$	–
$k_4$	$r_4 = k_4 * [F - A - F_0] - k_4 / K_4 * [F - A - F_{aq}]$	1/s	2.78	–	2.78	–
$K_4$		(unitless)	$1.00 \times 10^{-2}$	–	$2.27 \times 10^{-2}$	–
$k_5$	$r_5 = k_5 * [NaOH] * [A_{aq}] * [F_{aq}]$	$L^2/mol^2/s$	$(5.4 \pm 1.1) \times 10^{-2}$	26.0	$(7.8 \pm 1.2) \times 10^{-2}$	24.6
$k_6$	$r_6 = k_6 * [NaOH] * [F - A_{aq}] * [F_{aq}]$	$L^2/mol^2/s$	$1.82 \pm 0.55$	32.9	$2.28 \pm 0.50$	31.0
$k_7$	$r_7 = k_7 * [NaOH] * [F_{aq}]$	$L/mol/s$	$2.5 \times 10^{-2}$	0.1	$3.8 \pm 1.4$	9.5
$k_8$	$r_8 = k_8 * [NaOH] * [F - A - F_{aq}]^2$	$L^2/mol^2/s$	$2.7 \times 10^{-2}$	7.6	(Not in model)	–
$k_9$	$r_9 = k_9 * [NaOH] * [F - A - F_{aq}] * [F - A_{aq}]$	$L^2/mol^2/s$	$8.2 \times 10^{-4}$	1.8	(Not in model)	–

Equilibrium constants,  $K_i = 1/R_i$  where  $R_i$  is the partition coefficient given in Table 1. Sensitivity of each parameter ( $S_i$ ) is calculated at time = 50 h by the following formula:

$$S_i = \frac{k_i}{\sum \varepsilon} \times \frac{\delta_{\varepsilon,i}}{\delta_{k,i}}$$

where  $k_i$  is the value of the parameter,  $\sum \varepsilon$  is the sum of all furfural, single and double condensation concentrations for a representative set of model conditions,  $\delta_{\varepsilon,i}$  is the change in  $\varepsilon$  when  $k_i$  is changed by  $\delta_{k,i}$  with  $\delta_{k,i} = 10\% k_i$ .

The degradation of FUR is slower than that of HMF, and FUR thus neutralizes less base (if any) than does HMF; therefore, only slight variations with changes in NaOH:FUR ratio are observed, as seen in by comparing entries 58 and 59. The reaction model shows these same trends. Additionally, because FUR does not readily partition to the reactive aqueous phase, relatively high NaOH:FUR ratios, 2–3, must be used to fully condense FUR at the same rate as HMF.

#### 4.4. Stepwise addition

The stepwise addition of acetone to HMF, as shown in Fig. 5, caused a decrease in the overall yield, with a slight variation in single to double product ratio. These trends were observed with the model as well and can be explained as follows. With stepwise addition of acetone, the concentration of acetone is lower initially, thereby decreasing the rate of aldol condensation. Because the rate of HMF degradation is not directly related to the acetone concentration, degradation proceeds faster than condensation when the acetone concentration is low. While the total amount of acetone added is the same, the step-wise addition of acetone leads to larger extents of HMF degradation, such that less HMF is available to form the second condensation product. At the same time, lower concentrations of acetone favor the formation of the second condensation product. These opposing trends keep the single to double condensation ratio approximately constant.

#### 4.5. Other ketone reactants

The condensation of HMF with ketones other than acetone was mostly unsuccessful, with low yields to the condensation products. The reason for these low yields is ultimately due to the degradation of HMF. For the hexanones, the measured partition coefficients were 180 and 80, for 2 and 3-hexanone, respectively, compared to a value of 4 for acetone. Because the hexanones did not readily dissolve in the reactive aqueous phase, the rate of aldol condensation with HMF was low, leading to high extents of HMF degradation. By changing the value of the partition coefficient in the model from 4 to 80 and 180, the modeled yield to condensation products drops from around 80% to 25% and 15% respectively.

Dihydroxyacetone did not condense at a measureable rate. The steric hindrance and electron donating properties of the attached hydroxyl groups prevent the formation of reactive enolate form of this species. The same behavior appears to be true for acetol and glyceraldehyde as no double condensation and only slight single condensation products were detected.

## 5. Conclusions

The condensation of HMF and FUR with various ketones was investigated in a biphasic system. The final distribution and yield of products can be controlled by adjusting the molar ratio of the ketone to furfural reactants and by changing the amount of the

basic NaOH catalyst relative to the furfural reactant. A simple first order model was used to gain insight into the reaction network. Increased ratios of ketones to furfurals yield more single condensation products, while lower ratios yield more double condensation products. HMF degradation appears to be catalyzed by base, leading to the formation of acidic byproducts which neutralize the base, thereby limiting the formation of condensation products. This neutralization process limits the recycling of the aqueous phase, and it also decreases the yields of aldol product species from such reactants as hexanones that do not readily dissolve in the aqueous phases. FUR, which does not readily degrade, is more completely condensed to form products; however, because FUR is less soluble in the reactive aqueous phase compared to HMF, high concentrations of base must be used to increase the rate of reaction.

Optimal yields of double condensation products are produced at the stoichiometric value of two furfurals to one ketone, while optimal single condensation products are made at high ketone to furfural ratios. In both cases, sufficient base must be employed to either offset its neutralization by HMF degradation or to overcome the low partitioning of FUR into the reactive aqueous phase.

## Acknowledgements

Supported by U.S. Department of Energy Office of Basic Energy Sciences and the National Science Foundation Chemical and Transport Systems Division of the Directorate for Engineering. We also thank Y. Roman, J. Chheda, and C. Barrett for discussions and technical assistance.

## References

- [1] M. Parikka, *Biomass and Bioenergy* 27 (2004) 613–620.
- [2] International Energy Outlook, in Technical report no. DOE/EIA-0484 (2007), Energy Information Administration, 2007.
- [3] G.W. Huber, R.D. Cortright, J.A. Dumesic, *Angewandte Chemie* 43 (12) (2004) 1549–1551.
- [4] K. Owen, T. Coley, *Automotive Fuels Handbook*, Society of Automotive Engineers, Warrendale, PA, 1990.
- [5] *Diesel Fuels Technical Review*, Chevron Corporation, 2007.
- [6] R.M. West, Z.Y. Liu, M. Peter, J.A. Dumesic, *Sustainable Chemistry* 1 (5) (2008) 417–424.
- [7] Y. Roman-Leshkov, et al., *Nature* 447 (7147) (2007) 982–985.
- [8] Y. Roman-Leshkov, J.N. Chheda, J.A. Dumesic, *Science* 312 (5782) (2006) 1933–1937.
- [9] K.J. Zeitsch, *The Chemistry and Technology of Furfural and its many By-products*, Elsevier Science, New York, 2000 (sugar series: 13).
- [10] G. Solomons, C. Fryhle, *Organic Chemistry*, 7th ed., 1999, 1264 pp.
- [11] K.I. Matsumoto, Toshiyuki, J. Mizuie, *Tetrahydrofurfuryl alcohols*. Jpn. Kokai Tokkyo Koho, Arakawa Chemical Industries, Ltd., Japan, 1986.
- [12] N. Fakhfakh, P. Cagnet, M. Cabassud, *Journal de la Societe Chimique de Tunisie* 8 (2) (2006) 203–218.
- [13] N. Fakhfakh, et al., *Chemical Engineering and Processing* 47 (3) (2008) 349–362.
- [14] E.L. Kunkes, et al., *Science* 322 (2008) 417–421.
- [15] M. Sasaki, et al., *Green Chemistry* 4 (3) (2002) 285–287.
- [16] C.-W. Chiu, et al., *AIChE Journal* 52 (10) (2006) 3543–3548.
- [17] B. Girisuta, L.P.B.M. Janssen, H.J. Jeeres, *Green Chemistry* 8 (2006) 701–709.
- [18] A. Gandini, *Advances in Polymer Science* 25 (1977) 47–93.