Reactive Adsorption for the Selective Dehydration of Sugars to Furans: Modeling and Experiments

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5-hydroxymethylfurfural (HMF) can be produced from the acid-catalyzed dehydration of fructose, but its yield is limited due to subsequent HMF degradation to side products. A reactive adsorption process is proposed to improve the yield to HMF. Separate experimental single-component isotherms of fructose, HMF, formic acid, and levulinic acid on carbon BP2000 and reaction kinetics of the fructose dehydration to HMF in aqueous solution of HCl are presented to develop empirical isotherms and kinetic rate constants, respectively. These submodels are subsequently integrated in an adsorptive reactor at a range of temperatures (100–150°C) with different loadings of adsorbent. It is shown that the adsorbent improves HMF yield compared to the single-solution phase (adsorbent-free case). Low temperatures and high-adsorbent loadings improve HMF yield. Under certain conditions both reactive adsorption and the commonly used reactive extraction can result in a similar improvement in HMF yield. HMF recovery from the solid adsorbent has been identified as a major challenge that can be ameliorated through adsorbent and solvent selection. The framework outlined here can be applied to any aqueous phase chemistry where the desired product is an intermediate in a reaction cascade. *AIChE J*, 59: 3378-3390, 2013

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Introduction

Furans, a class of chemicals that can be obtained from biomass, have the potential to replace or supplement petroleum-derived intermediates as a feedstock in the production of fuels, plastics, and pharmaceuticals.[1] In particular, 5-hydroxymethylfurfural (HMF) can be produced directly from the acid-catalyzed dehydration of hexose sugars, such as fructose and glucose, which in turn can be produced from cellulose. Under these same acidic conditions, HMF and the hexose can polymerize to humins, while HMF can also rehydrate to levulinic acid (LA) and formic acid (FA), as shown in Scheme 1. Sugar losses to side reactions result in low HMF yields and significantly (negatively) impacted economics of HMF production.[2] As a result, it is imperative to improve the yield of HMF production in order to make HMF-based chemicals and fuels cost-competitive with those derived from petroleum.

Various approaches for improving the yield of HMF from sugar dehydration have been investigated. The first general approach entails suppression of side reactions via manipulation of the solvent, i.e., through utilization of nonaqueous solvents. For example, aprotic co-solvents, such as dimethyl sulfoxide (DMSO),[3] have been shown to significantly reduce the formation of side products, although isolation of HMF from these high-boiling additives is challenging for industrial use. Aside from aprotic solvents, ionic liquids have also been found to increase HMF yield.[4–6] Many other homogeneous and heterogeneous catalytic systems have been investigated, but it has not been possible to find a catalyst in water that promotes fructose dehydration without also promoting the formation of humins and the rehydration products.[7–13]

The second popular approach is the removal of HMF from the reaction medium as it is produced. This is usually achieved using biphasic aqueous—organic solvent systems, in which the HMF is extracted from water to the organic phase, minimizing HMF rehydration and humin formation. This reactive extraction concept was originally introduced in a biphasic water-organic solvent (methylisobutylketone (MIBK)) mixture.[14] More recently, Dumesic and coworkers improved reaction selectivity and HMF partitioning using additives in each phase.[15] Higher than 70% HMF molar

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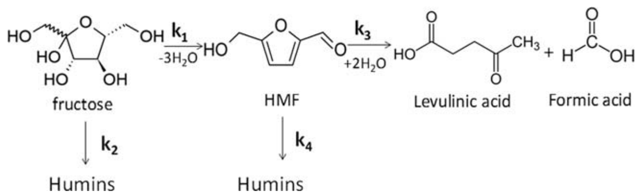

Scheme 1. Reaction network used to describe the dehydration of fructose to HMF and subsequent degradation reactions.

yield was achieved with initial concentrations of fructose up to 50 wt %, using HCl as a catalyst and a mixture of 2-butanol and MIBK as an extracting phase.[15] In many cases a significant fraction of HMF remains in the aqueous phase due to poor partitioning between the two phases. It was later demonstrated that a saturated aqueous phase solution of NaCl greatly increases the partition coefficient of HMF, leading to more efficient separations.[16] Even with these favorable partition coefficients, economic analysis by Torres et al. has shown that HMF is more expensive than petroleum-based polymer precursors,[2] suggesting that alternative processes are necessary to improve fructose utilization. Reactive adsorption is one such process that may prove more effective than reactive extraction.

Several groups have studied the use of adsorbents (zeolites,[17] carbons,[18,19] and polymers[20]) for removal of furans from hydrolyzed sugar solutions, motivated from the fact that furans are toxic to the biological processes used for ethanol production.[17,20] Much like the biphasic systems, the hydrophobicity of HMF drives it preferentially onto the adsorbent from the aqueous phase. Vinke and van Bekkum demonstrated the feasibility of adsorbing HMF in significant quantities, although they did not examine the effect of reaction temperature on the efficacy of the adsorbent.[21] Rajabbeigi et al. have demonstrated that activated carbon (BP2000) has a high HMF/fructose separation factor, which is desirable for a reactive adsorption process.[22] Coupling adsorption and reaction in a single adsorptive reactor generates a host of challenges when implemented at the industrial scale including adsorbent regeneration as well as raising the question of how to optimize reactive adsorption.[23,24] The optimum conditions for reaction and adsorption do not necessarily coincide, so a rigorous approach is necessary to evaluate the performance due to adding an adsorbent to the reactor.

The framework for analysis of a coupled reaction and adsorption operation has been well-developed.[25–33] The selectivity of gas-phase reactions, such as steam methane reforming,[31,33] and liquid phase esterification reactions,[34,35] has been shown to benefit from the incorporation of an adsorbent in the reactor. A similar process has been developed for the aqueous phase isomerization of glucose to fructose.[36] In all these systems, adsorption was employed to remove the product of an equilibrium-limited reaction from the reactive medium, leading to conversions greater than the equilibrium one.

Prior work has not examined the efficacy of reactive adsorption to selectively produce an intermediate product in a sequence of reactions. The goal of this study is to investigate whether reactive adsorption can increase HMF yield in fructose dehydration. We develop a continuum reaction/adsorption model consisting of two sub-models whose parameters are estimated from new experimental data of reaction and adsorption. To the best of our knowledge, the application of such a model for the selective production of an intermediate product in a series of irreversible reactions is conducted for the first time. To implement such a model, it is important to account for multicomponent adsorption, reaction kinetics, and possible transport/mixing effects at reaction conditions (Figure 1). In particular, we present data for single-component adsorption isotherms of fructose, HMF, levulinic acid, and formic acid on carbon BP2000 at different temperatures and use ideal adsorbed solution theory (IAST) to estimate multicomponent adsorption equilibria. The kinetic parameters of the reaction network (Scheme 1) are determined by fitting fructose dehydration and HMF rehydration kinetics at different temperatures. Additional experiments at different operating conditions were carried out and compared to model predictions. We then analyze the reactive adsorption process and compare it to new experimental data. The ability to recover the HMF from the adsorbent is also considered. Finally, the overall performance of the reactive adsorption process is compared to that of reactive extraction.

Experiments and Data Analysis

Materials

Fructose 99% (Sigma Aldrich), 5-(Hydroxymethyl)furfural (HMF) 98% (Sigma Aldrich), levulinic acid (LA) 98% (Sigma Aldrich liquid form), formic acid (FA) 88% (Fisher Scientific), sulfuric acid 5 M (Fluka), hydrochloric acid 1 M (Sigma Aldrich), potassium chloride 98% (Merck) and distilled water were used for solution preparation.

Reaction kinetics

Experiments with different initial compositions of fructose, HMF and LA were carried out in a pH~1.1 buffer solution (Table 1). This solution was prepared by mixing 50 mL of potassium chloride 0.2 M with 26.8 mL of hydrochloric acid 1 M in a 200 mL volumetric flask and filled with distilled water. This buffer solution was added to a 100 mL volumetric flask containing the appropriate amounts of the reactants. Thirteen 5 mL glass reactors with an internal conical bottom and a conical magnetic stirring bar were preheated in an aluminum heating block filled with silicon oil. The high temperature experiment (138°C) was performed in

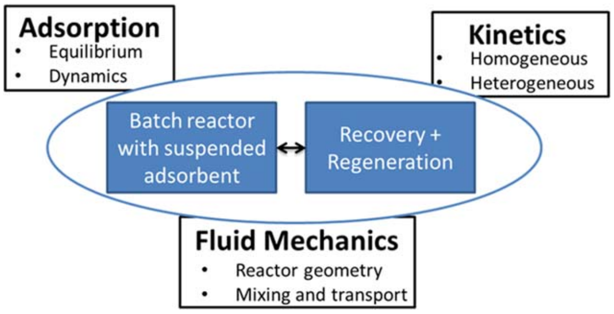

Figure 1. Schematic of information required in reactive adsorption.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1. Compositions and Temperatures of Experiments Carried Out in pH~1.1 Buffer Solution

No	Initial composition	Temperatures tested, °C
1	10 w/v% fructose	84, 86, 95, 104, 109, 112, 120, 126, and 138
2	5 w/v% fructose	111
3	20 w/v % fructose	111
4	5 w/v% HMF	88, 89, 99, 110, 114, 120, 121, 130, and 141
5	10 w/v% fructose and 5 w/v% HMF	111
6	5 w/v% fructose and 2.5 w/v% LA	111

20 mL round-bottom microwave reactors in an aluminum heating block filled with mineral oil. Other experimental temperatures were investigated using this setup to ensure consistency between reactors. The temperature was monitored with an external thermometer and a thermocouple inserted into a sealed reactor with the studied solution. An aliquot portion of the reaction solution was added to each of the preheated glass reactors. The time at which the test solution was added to the glass reactor was considered the starting point for data collection. Reactor vials were removed at regular time intervals and immediately quenched in an ice-bath before collecting sample for analysis. Experiments were carried out at nine reaction temperatures: 84, 86, 95, 104, 109, 112, 120, 126, and 138°C. The temperature variation during each experiment was ±2–3°C.

Fructose dehydration with reactive adsorption was carried out in an oil bath using 20 mL microwave reaction vials with aluminum crimp lids and silicone/PTFE septa by VWR. Typically, 37.3 mg of KCl, 132 mg of 37% HCl, and 1.12 g fructose were added to 9.92 g of deionized water. The oil bath temperature ranged from 105°C to 125°C with a stirring rate of 1000 rpm. For reactive adsorption tests, 200 mg (20 g/L) to 600 mg (60 g/L) of BP2000 were added. The reaction was run for 5 h at 105°C and 2 h at 125°C. HMF and other products were extracted from the BP2000 at room temperature. A more detailed description of the extraction procedure is given in the section of adsorption measurements. For all species we assumed 100% extraction efficiency, and the reported yields are based on the measured concentrations.

Analytical methods

Samples from the reactors were further diluted in 1 to 10 ratio with distilled water and analyzed with HPLC (2695 Waters) using an Aminex HPX-87H ion exchange column and a refractive index detector (RI 2414). A 5 mM solution of sulfuric acid was used as mobile phase with a flow rate 0.65 mL/min. The temperature of the column oven was 65°C and the temperature of the RI was 35°C. Calibration curves were built of all the known compounds and used for the quantification reactants and products.

Adsorption

HMF, levulinic acid, formic acid, and fructose adsorption on the BP2000 carbon black was carried out at different temperatures with a concentration of adsorbates ranging from 1 to 15 mg/mL. For measurements up to 90°C, 32 mg of BP2000 were added to 1.6 g of adsorbate solution in a 2 mL septum-sealed vial. For the room temperature (25°C) adsorption, the vials were placed on a stir-plate at 1000 rpm for 6 h. Adsorption measurements at 55 and 90°C were performed in oil baths placed on hot-plates at 1000 rpm for 6 h. The solutions were filtered as they were taken out from the vials with syringe filters preheated to 100°C to prevent the samples from cooling. Adsorption measurements at 150°C were performed in a Parr reactor. 1.00 g of BP2000 carbon black was added to 50 g of HMF solution. The solution was given 1 h for equilibrium at 150°C with a stirring rate of 600 rpm. The solution sample was taken with a two-stage sampling system. The first stage used glass wool and 420 mesh membrane (McMaster) to filter the BP2000 carbon black from the solution. The effluent was moved to a second stage where it was cooled down with ice water. This effluent was not exposed to atmosphere until it was cooled. The concentration of adsorbates in the solution was measured by HPLC (Shimadzu). Two control experiments were run to confirm that there is minimal reaction of HMF under the measurement conditions. Frist, 50 g of 2.00 mg/mL HMF solution with 1.00 g BP2000 was reacted at 150°C for 1 h. After the reaction, the wet carbon was separated from the solution by centrifugation. The HMF left in the solution was measured by HPLC. HMF adsorbed on the BP2000 was extracted by ethanol using the procedure developed before.[21] Approximately 30 g of ethanol were added to the carbon and stirred for 1 h. The carbon was centrifuged and re-washed with fresh ethanol for a total of 4 washings with the forth washing going overnight by a Soxphlet extraction device. In total, 91.3% of the initial HMF was recovered at the end. The HMF extraction efficiency from activated carbon using ethanol is around 90%,[21] so it is concluded that there is limited reaction of HMF under the measurement conditions. Another test was carried out using a 2.00 mg/mL HMF solution at 150°C for 1 h. HMF conversion of 1.6% was observed. For the fructose dehydration with reactive adsorption, all components were extracted from carbon using the method described above. Given the affinity of the fructose and levulinic acid to the carbon is much weaker than that of HMF, and the extraction efficiency of HMF is higher than 90% (obtained from the single component adsorption/desorption study), 100% extraction efficiency is assumed and reported yields are based on the measured concentrations.

Determination of kinetic rate constants

The analysis of our kinetic data was carried out using the simplified reaction network of fructose dehydration in acidic medium proposed by Kuster, as shown in Scheme 1.[37] Based on this network the following reactions take place (1) fructose dehydration to HMF, (2) fructose degradation/reversion reaction to soluble polymers, humins or other unknown products, (3) HMF rehydration to levulinic acid, and (4) HMF degradation to humins or other unknown products. All reactions were assumed to be irreversible and first-order.

Some reactions that lead to side products may not be well-described by first-order kinetics. Such reactions are not well-understood and are the subject of ongoing research. The assumption of first-order kinetics has been used in the past to analyze fructose[38–40] and glucose[41–45] dehydration kinetic experiments, so is considered adequate for this study.

The reaction rate constants at each temperature were estimated using the following procedure. k_3 and k_4 were fitted to the HMF rehydration experimental data (No. 4 in Table 1). In this case the rate equations have the following analytical solution

$$[HMF]=[HMF]_0\exp(-k_Ht) \tag{1}$$

$$[LA]=\frac{k_3}{k_H}[HMF]_0[1-\exp(k_H)]t \tag{2}$$

The reaction rate $k_H = k_3 + k_4$ of HMF disappearance was fitted to the HMF concentration profile measured experimentally using Eq. 1. Equation 2 was fitted to the concentration profile of LA to estimate the value of k_3 (reaction rate constant for the conversion of HMF to LA and FA). These values were assumed to be constant in the subsequent analysis of the experiments of fructose dehydration. The rate equations of the overall reaction network shown in Scheme 1 have also analytical solutions

$$[F]=[F]_0\exp(-k_Ft) \tag{3}$$

$$[HMF]=\frac{k_1[F]_0}{(k_F-k_H)}[\exp(-k_Ht)-\exp(-k_Ft)] \tag{4}$$

$$[LA]=\frac{k_1k_3[F]_0}{k_Fk_H}\left[1-\frac{k_F}{(k_F-k_H)}\exp(-k_Ht)+\frac{k_H}{(k_F-k_H)}\exp(-k_Ft)\right] \tag{5}$$

The reaction rate of fructose disappearance $k_F = k_1 + k_2$ was fitted to the fructose concentration profile (Eq. 3). The reaction rate constant for the dehydration of fructose to HMF (k_1) was estimated by fitting Eq. 4 to the HMF concentration profile and k_2 is then obtained by subtraction.

Single-component isotherms

Accurate modeling of an adsorptive reactor requires adsorption isotherms. We have considered the Freundlich, Langmuir, Sips, Redlich-Peterson, Dubinin-Radushkevich, Toth, and Temkin isotherms (procedure and quality of fit included in Supplemental Information) for analysis of single-component experimental data. Based on its low χ^2 value, the Redlich-Peterson isotherm was used to model HMF and fructose adsorption, Henry's law for LA adsorption, and the Freundlich isotherm for FA adsorption:

$$Redlich-Peterson\quad Isotherm: q_i^{Eq}=\frac{K_iC_i}{1+b_iC_i^{n_i}} \tag{6}$$

$$Henry\prime s\,Law: q_i^{Eq}=K_i^HC_i \tag{7}$$

$$Freundlich\quad Isotherm: q_i^{Eq}=K_i^FC_i^{n_i^F} \tag{8}$$

Here q is the adsorbate loading in mol/g and q^{Eq} is the equilibrium adsorbate loading. The adsorption parameters, including K (all isotherms), n (Redlich-Peterson and Freundlich), and b (Redlich-Peterson) for each material were estimated by minimizing the χ^2 value for a series of experimental isotherms obtained at different temperatures. Data at each temperature were fitted independently to determine the appropriate isotherm. Once the form of the isotherm was chosen, the data were refitted by keeping the exponential $n_{i,}$ constant. It was found that the K and b parameters determined using this method followed the van't Hoff form, allowing the estimation of the parameters at temperatures not directly examined through adsorption experiments. These values are given in Table 3.

Multicomponent adsorption

The dehydration of fructose results in a multicomponent solution with fructose, HMF, formic and levulinic acids. The presence of multicomponent mixtures is expected to affect HMF adsorption due to competition for adsorption sites. Gathering experimental data on multicomponent adsorption is impractical due to the wide range of possible solute concentrations. It is, therefore, advantageous to model multicomponent adsorption using single-component experimental data.

Ideal adsorbed solution theory (IAST) was originally developed[46] for adsorption of multicomponent gases and then extended to liquid mixtures.[47] The mathematical models, which have been outlined elsewhere[17,47,48] and in the Supplement, result in a series of equations that were solved using Newton's method. Analytical expressions for determining the spreading pressure by integrating the isotherm equations were used whenever possible. Otherwise, numerical integration was performed using the trapezoidal rule.

Reactive Adsorption Model

Model development

It is assumed that the adsorbent is uniformly suspended in the batch reactor using a stirrer. The analysis to estimate the stirrer speed necessary for suspension is shown in the Supplement. At this rate of stirring, the reactor can be considered spatially homogeneous, with much faster rates of mixing than reaction. Furthermore, it is assumed that the reactor is isothermal. Preliminary analysis[49] suggested that these conditions can be met under industrially relevant operating conditions. The molar balances in the aqueous phase are given in Eqs. 9–12

$$\frac{dC_F}{dt}=-(k_1+k_2)C_F-\hat{m}\frac{dq_F}{dt} \tag{9}$$

$$\frac{dC_H}{dt}=k_1C_F-(k_3+k_4)C_H-\hat{m}\frac{dq_H}{dt} \tag{10}$$

$$\frac{dC_{LA}}{dt}=k_3C_H-\hat{m}\frac{dq_{LA}}{dt} \tag{11}$$

$$\frac{dC_{FA}}{dt}=k_3C_H-\hat{m}\frac{dq_{FA}}{dt} \tag{12}$$

Here $\hat{m}$ is the loading of adsorbent in grams of adsorbent per liter of solvent. The righthand side of each of these equations includes a reaction term and an adsorption term. The adsorption term accounts for the removal of solute from the aqueous phase and depends both on the equilibrium as well as the dynamics of the system. Azizian determined that pseudo first-order kinetics is an appropriate description for adsorption when the concentration in the aqueous phase is high relative to that in the adsorbed phase; this form remains applicable even as the concentration approaches equilibrium.[50] The differential equations for the adsorbed phase are, therefore, represented by the following equations

$$\frac{dq_F}{dt}=k_F^L\left(q_F^{Eq}-q_F\right) \tag{13}$$

$$\frac{dq_H}{dt}=k_H^L\left(q_H^{Eq}-q_H\right) \tag{14}$$

$$\frac{dq_{LA}}{dt}=k_{LA}^L\left(q_{LA}^{Eq}-q_{LA}\right) \tag{15}$$

$$\frac{dq_{FA}}{dt}=k_{FA}^L\left(q_{FA}^{Eq}-q_{FA}\right) \tag{16}$$

Here k_i^L is the linear driving force mass-transfer coefficient of species i. Humins were treated implicitly, as we assumed their formation to be irreversible and that they neither

Table 2. Experimentally Determined Kinetic Parameters, at Buffered pH=1.1, of the Reactions Shown in Scheme 1; ($k_i=k_{i,o}*\exp(-E_a/RT)$) (the range Shown Corresponds to the 95% Confidence Interval)

Rate constant	$k_{i,o}$, $\min^{-1}$	E_a, kJ/mol
k_1	$3.64\text{x}10^{14} \pm 126$	124 ± 15
k_2	$1.54\text{x}10^{12} \pm 1.48\text{x}10^{4}$	107 ± 30
k_3	$8.12\text{x}10^{9} \pm 764$	91 ± 21
k_4	$8.87\text{x}10^{7} \pm 436$	81 ± 19

participate in any further reactions nor adsorb. The initial conditions were set based on the experimental concentrations. The nondimensionalization is discussed in the Supplemental Information.

It is desired to be in the kinetically-limited regime rather than the adsorption-limited regime because this maximizes the utility of the adsorbent. This occurs when $k_i^L >> k_1$, i.e., when the rate of adsorption is much faster than the rate of reaction. The exact value of the adsorption rate constant depends on the material as well as the temperature, but was not directly measured in this study. For this preliminary study k_i^L was arbitrarily set to $k_i^L=1000k_1$; for higher values of adsorption rate constant, the reactor performance did not exhibit any dependence on k_i^L, suggesting that the system can be considered kinetically controlled. Further study is needed to provide quantitative insights into the extent to which these adsorption rate limits affect reactor performance. All calculations are carried out using Matlab R2010.

The equilibrium concentration of each species was evaluated by solving the IAST equations using Newton's method. The equilibrium concentrations were used to find the rate of change of the adsorbed phase concentrations and aqueous phase concentrations. Integration was performed using Matlab's built-in initial value problem solver *ode15s*. The optimum yield was determined by a simple method, i.e., by allowing the reaction to run to completion and then finding the time that maximizes the total amount of HMF in the adsorbent and aqueous phases.

Results and Discussion

Chemical kinetics

The rate constants of the reactions shown in Scheme 1 were estimated at nine different temperatures using the procedure described earlier. The Arrhenius plots and the corresponding fits are shown in Figure SI-1, while the fitted pre-exponential factors and the apparent activation energies are shown in Table 2. These parameters were compared to those of earlier studies. Ashgari and Yoshida analyzed fructose decomposition kinetic data in subcritical water and estimated the activation energy of fructose dehydration to HMF to be equal to 160 kJ/mol.[40] Nibkin et al. used first principle microkinetic modeling and predicted an activation energy of 159 kJ/mol for the same reaction.[51] Both of these values are larger than the activation energy of fructose dehydration to HMF of this work (124 ± 15 kJ/mol). The discrepancy can be attributed to the following reasons. First, previous studies were carried out at significantly higher temperature range (190–240°C), and the data were fitted to a more complicated reaction network that considered LA and FA decomposition to side products as well as the direct formation of FA from fructose. At the conditions of our experiments, LA or FA decomposition to side products was not observed. In the experiments starting from HMF, the FA/LA molar ratio was very close to 1 indicating that both of them are formed primarily from HMF rehydration. On the other hand in the experiments starting from fructose, the molar ratio FA/LA was higher than 1 indicating that an additional path for FA formation exists. We believe that the additional paths considered by Ashgari and Yosida might be active at higher reaction temperatures.[40] In addition, the initial pH of their solutions was 1.8 instead of ~1 used here. Work of Kuster and Temmink as well as preliminary experiments from our group show that the pH has an effect on the reaction rates.[39] Other groups reported the apparent activation energy of fructose overall conversion. Bicker et al.[52] who studied the dehydration of fructose in acetone—water between 180–300°C, reported apparent activation energies between 98 and 158 kJ/mol depending on the H_2SO_4 catalyst concentration. Qi et al. also reported an activation energy of 103.4 kJ/mol for a 70–30 w:w acetone:water mixture.[53] These values are slightly larger than that of Bicker et al. (96 kJ/mol) for the degradation of fructose in subcritical water.[54] The activation energy of fructose conversion of our experiments (reactions 1 and 2 combined) was estimated to be 115.6 kJ/mol, a value that is close to these literature reported values despite the differences in types and amounts of acid catalysts and use of acetone.

The activation energy of HMF rehydration to LA and FA is 91 ± 21 kJ/mol. This value is within the range (57–111 kJ/mol) reported by several groups.[41–45] The biggest discrepancy with the previous studies is related to the activation energy of the reactions leading to humins from fructose and from HMF. We found values of 107 ± 30 kJ/mol and 81 ± 19 kJ/mol, respectively. For the degradation of HMF to humins, the value reported varies from 142 kJ/mol[42] to 95.6 kJ/mol.[40] The term humins usually refers to a large number of products like fructose fragmentation products, fructose reversion products as well as HMF polymers and HMF-fructose polymers. Depending on the reaction conditions a different reaction path might be dominant, explaining the differences in the observed activation energies. The difference in apparent activation energies between in various works underscores a clear need of developing more reliable reaction networks. This task will require advances in both analytical methods and computational techniques that can account for solvent effects.

Figure 2 compares the predicted concentration profiles to fructose dehydration experiments carried out under a range of conditions. The fructose dehydration profiles at four different temperatures are shown in Figure 2a–d (No. 1. in Table 1). Fructose dehydration in mixtures that contain also HMF or LA are shown in Figure 2e and f (No. 5 and 6 in

Table 3. Fitted Adsorption Parameters for Different Compounds on BP2000; Non-Exponential Parameters, Including *K* and *b* Parameters, are Fitted to the Form $p=p_0\exp(\delta H/RT)$, Where *p* is Either *b* or *K*

Adsorbate	Parameter	Pre-exponential, P_0	δ H, $\frac{\text{kJ}}{\text{mol}}$
Fructose	K, L/g	$4.63\text{x}10^{-2}$	13 ± 7
	b, $\left(\frac{L}{mol}\right)^n$	172	9 ± 9
	n	0.7685	
HMF	K, L/g	$9.15\text{x}10^{-7}$	47 ± 8
	b, $\left(\frac{L}{mol}\right)^n$	$1.54\text{x}10^{-3}$	41 ± 7
	n	0.7739	
LA	K, L/g	$5.14\text{x}10^{-5}$	20 ± 1
FA	K^F, $\frac{mol}{g}\left(\frac{L^n}{mol^n}\right)$	0.0011	4 ± 3
	n^F	0.6067	

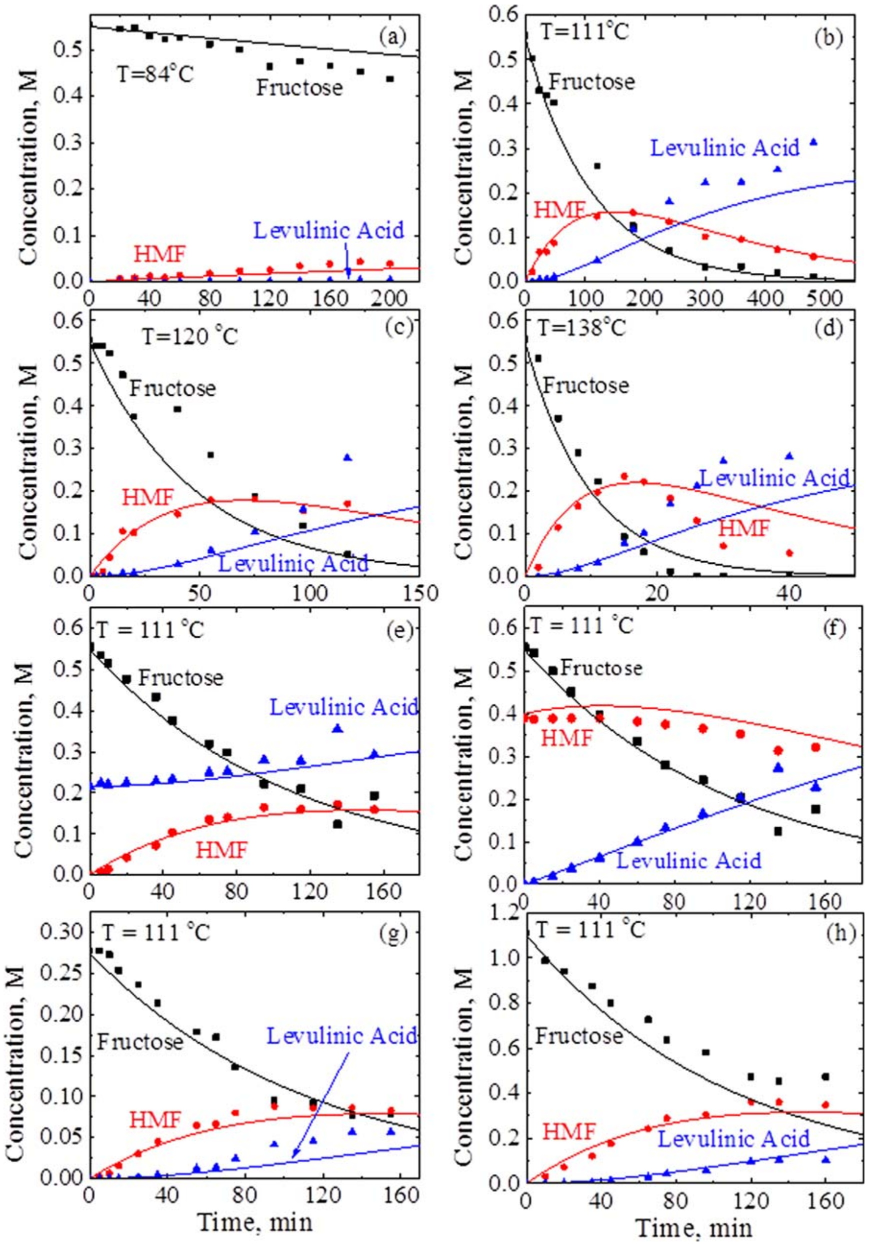

Figure 2. Experimentally observed fructose (squares), HMF (circles), and levulinic acid (LA) (triangles) concentrations as a function of time compared to model prediction (solid lines) starting with 10 wt % fructose at 84, 111, 120, 138°C (a-d), a mixture of 10 wt % fructose and 2.5 wt % LA at 111°C (e), a mixture of 10 wt % fructose and 5 wt % HMF at 111°C (f), 5 wt % fructose at 111°C, and 20 wt % fructose at 111°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 1), while the effect of initial fructose concentration is shown in Figure 2g and 2 h (No. 2–3 in Table 1). Since data No. 1 and 4 in Table 1 were used to estimate the parameters, the quality of fit in the other cases demonstrates the robustness of the model. It also indicates that considering all of reactions as first-order is a reasonable approximation, for the conditions of this study. Figure 2b–d shows that the model underpredicts the concentration of LA and overpredicts the concentration of HMF at long times. Such deviations are considered acceptable because subsequent analysis of reactive adsorption only uses model predictions before the time at which HMF yield peaks, which is before the deviations become large. Thus, the predicted concentration profiles are in satisfactory agreement with the experimental data, indicating that despite uncertainties in the reaction path, the kinetic model is able to quantitatively capture the concentrations profiles within the temperature range considered.

Adsorption isotherms

The single-component isotherm parameters were assumed to follow the van't Hoff relationship. The estimated parameters are shown in Table 3. The HMF and fructose heat of adsorption is determined from the low-concentration limit, where the contribution of *b* and concentration is not

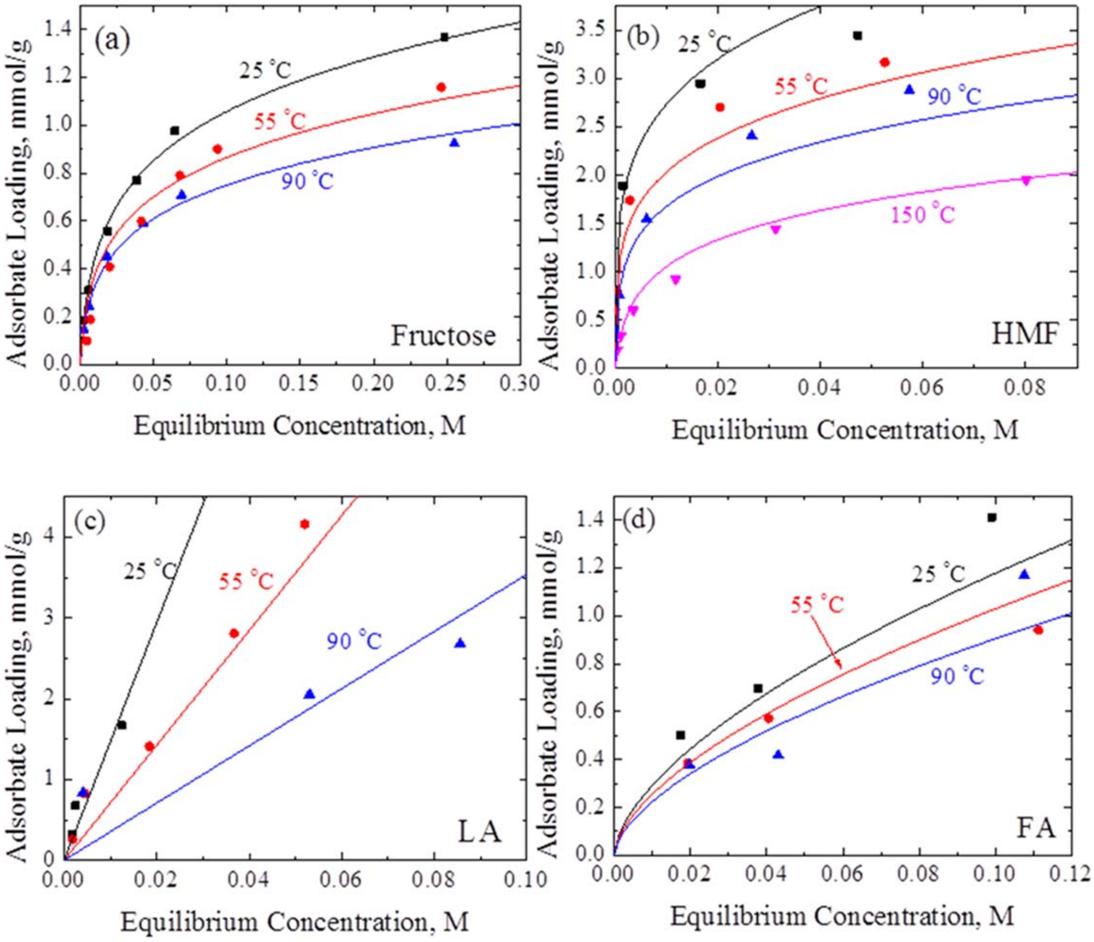

Figure 3. Experimental adsorption data fits of fructose (a), HMF (b), levulinic acid (LA) (c), and formic acid (FA) (d) in BP2000 at 25°C (black), 55°C (red), 90°C (blue), and 150°C (magenta, HMF only).

Points are data and lines are fits. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

significant, and the Redlich-Peterson isotherm (Eq. 6) reduces to Henry's law (Eq. 7). The estimated heat of adsorption of 41 kJ/mol for HMF adsorption is close to the heat of adsorption of phenol (47.5 kJ/mol) on bagasse fly ash,[55] which has structural parallels to adsorption of HMF on activated carbon. Moreover, HMF has a higher heat of adsorption than both FA and LA, with LA adsorbing more strongly than FA. Our finding is consistent with that of Vinke and van Bekkum who observed that HMF adsorbs more strongly than LA on the gas-activated ROX carbon.[21] FA, with fewer carbon atoms, should be more hydrophilic than either LA or HMF and adsorb less strongly. The exponents of HMF and FA adsorption, 0.7739 and 0.6067, are physically realistic (<1 and greater than 0), as expected on an energetically heterogeneous surface.[48,56]

Figure 3 compares the modeling isotherms vs. the experimental data used to generate that model. The single-component isotherm measurements span a range of temperatures comprising 25, 55, 90, and 150°C for HMF only. For HMF (Figure 3b), the fit is good at low concentrations at all temperatures. The quality of fit at high concentrations improves with increasing temperature. At the highest temperature, 150°C, the model is accurate across the entire concentration range. Good fits at elevated temperatures are important because these are the conditions where the reaction occurs. The model is then considered adequate for describing HMF adsorption under reaction conditions. LA adsorption is accurately predicted using Henry's law at each of the temperatures studied. Even though in the Henry regime, the loading of LA is comparable to the loading of HMF with a similar concentration, and it is therefore likely that LA and HMF compete for adsorption sites. Competitive adsorption between HMF and furfural has been previously studied,[17] and it was found that IAST effectively predicted experimental multicomponent adsorption in silicalite-1. Due to the quality of fit for each of the temperatures studied, single-component adsorption of LA is well-described by this adsorption model. While the Freundlich isotherm does not reduce to Henry's law at low concentrations, it performs better than Henry's law in approximating FA adsorption in BP2000. The fit is not in quantitative agreement but can suffice as an approximation at these concentrations. One explanation of the difficulties describing the experimental data is that FA adsorbs weakly and so it is subject to more experimental error, including the possibility that competitive adsorption with water is affecting the experimental isotherms. Regardless, it is not expected that the adsorption of FA has a large effect on HMF adsorption because, even at higher concentrations in the aqueous phase, it has a much lower loading than HMF. It is, therefore, concluded that this adsorption model can adequately describe the multicomponent adsorption of HMF on BP2000 to gain

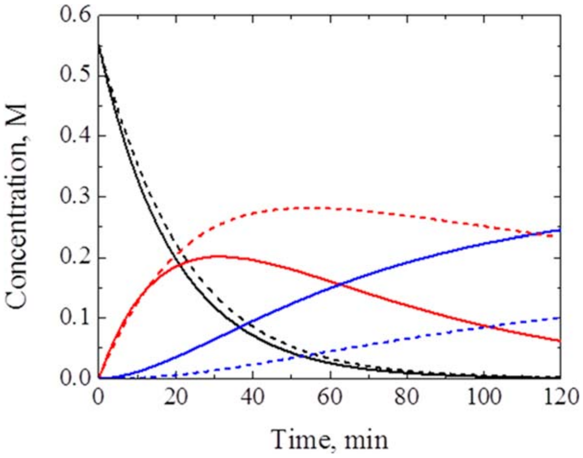

Figure 4. Comparison in the concentration profiles of fructose (black), HMF (red), and levulinic acid (blue) in a batch reactor at pH = 1.1 and 130°C between adsorbent-free reactor (solid) and reactive adsorber with 100 g/L of BP2000 (dashed).

The concentration denotes the total of both the adsorbed and aqueous phases. Reactive adsorption leads to enhanced yield compared to an adsorbent-free reactor. Long times lead to HMF yield loss due to side reactions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

insight into the performance and feasibility of a reactive adsorber.

Reactive adsorption

Figure 4 shows the concentration profile in the batch reactor as a function of time with and without adsorbent. Without adsorbent, after around 30 min, HMF concentration passes through a maximum. At this point, the rate of fructose dehydration is equal to the rate of HMF degradation; beyond this time, fructose has been sufficiently depleted, and the rate of HMF degradation overtakes fructose dehydration. The LA and FA concentrations monotonically increase and eventually become the dominant non-humin components (after around 150 min in the absence of adsorbent). Since it is assumed that FA and LA are formed due to the stoichiometric decomposition of HMF and do not participate in any further degradation reactions, their concentrations are equal. The dashed line in Figure 4 shows the effect of the adsorbent on the concentration profile. The total HMF concentration (total number of moles of HMF per liter of aqueous solvent) passes through a maximum later in time than in the adsorbent-free case. Since a large fraction of the HMF is in the adsorbed phase, the concentration of HMF in the aqueous phase is much lower than in the case of the adsorbent-free system decreasing the rate of HMF degradation to FA, LA, and humins. Consequently, the rate of fructose dehydration and HMF degradation are equal at a later time resulting in higher HMF yields. An adsorbent with the properties of BP2000 does not affect the selectivity of fructose consumption, but reduces the rate of HMF degradation, which is one of the routes of carbohydrate carbon loss to undesired products. The results of Figure 4 clearly show that combining reaction with adsorption can be effective at improving HMF yield.

Figure 5 shows the selectivity and yield to HMF as a function of time for various adsorbent loadings (no adsorbent, 20, and 60 g/L of adsorbent). Zlokarnik found that a suspension can be treated as a homogeneous mixture with volume fractions up to 0.30,[49] which corresponds to a solid loading of approximately 100 g/L for the low specific gravity of BP2000. Our experiments showed that the maximum adsorbent loading that can form a homogeneous suspension is ~60 g/L, since higher loadings resulted in difficulties in stirring and filtration. However, the highest loading of 100 g/L was also considered since it might be achievable with other adsorbent materials. At low conversions, the selectivity to HMF is the same with or without adsorbent. This indicates that, as expected, the adsorbent has little effect on fructose dehydration or humin formation from fructose. At longer times, the selectivity to HMF drops off rapidly in the adsorbent-free case, whereas it remains fairly high in the high-adsorbent case. The effect of adsorbent is dominant at longer times (near and after the maximum peak), where high concentrations of HMF have formed. In practice one would likely stop the reaction around the maximum yield.

The model accurately captures the HMF yield enhancement when compared to experimental data. Table 4 compares the predicted and experimental fructose conversions, HMF yields, and LA yields for a reactive adsorption process with 0, 20, and 60 g/L of BP2000 at 125°C after 2 h. The model qualitatively captures the experimental trends, which can be seen in Figure 6. Even without adsorbent, the model predicts higher conversion than observed, as well as different HMF and LA yields. A slight decrease in fructose conversion from 89 to 84–85% is observed experimentally that is not predicted by the model, i.e., the addition of the carbon slows down slightly the fructose conversion. We also compared the HMF yield predicted by the model at the same conversion as that of the experiments, rather than the yield at the end of 2 h. Table 5 shows that the predicted HMF yield differs from experimental values even with this adjustment, but the model overestimation of HMF yield remains constant at 2–4%. One possible cause of this disagreement is the blocking of surface adsorption sites by humins or humin

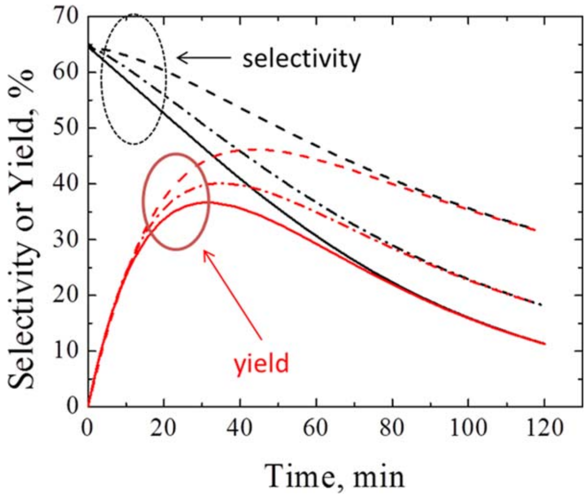

Figure 5. Selectivity and yield to HMF at 130°C as a function of reaction time with 0 g/L (solid), 20 g/L (dot-dash), and 60 g/L (dash) of BP2000 adsorbent. As the adsorbent loading increases, the yield to HMF improves.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table 4. Comparison Between Experiments and Model Predictions for HMF and LA Yield after 2 Hours at 125°C Using HCl Catalyst (pH = 1.1)

	Fructose Conversion, %		HMF Yield, %		LA Yield, %	
Solid Loading	Calculations	Experiments	Calculations	Experiments	Calculations	Experiments
0 g/L	98.1	89.0	20.1	29.6	34.9	34.0
20 g/L	98.0	84.2	26.9	33.7	29.2	31.9
60 g/L	97.8	84.5	38.9	40.7	19.1	15.8

precursors. This effect should be small as humins should not be able to diffuse to the interior of the carbon adsorbent. Yet, humin formation may explain why the model overestimates HMF yield. Still, the model does predict semiquantitatively the change in HMF yield and the suppression of LA formation. These results suggest that the model can be useful in estimating the adsorbent-induced enhancement.

Although the adsorbent improves the selectivity toward HMF, its effect is expected to decrease at higher temperatures due to decreased adsorption. Figure 7a shows the optimum yield of HMF, and Figure 7b shows the fraction of HMF in the adsorbent as a function of temperature. Figure 7a shows an increase in the optimum yield of HMF as temperature increases. This result is counterintuitive because HMF adsorption is reduced at high temperatures, as demonstrated in Figure 7b. As temperature increases, the fraction of HMF in the adsorbed phase is gradually reduced, from 69% at 100°C to 47% at 150°C for the 60 g/L case. However, the optimum HMF yield increases due to the chemical kinetics. This effect can be seen in the increase in HMF yield when no adsorbent is present. The adsorbent is still beneficial, allowing high HMF yields at lower temperatures.

After the end of the reaction, HMF has to be recovered from the aqueous phase, containing unreacted fructose and HMF, humins, and FA/LA, and the adsorbent, which contains primarily adsorbed HMF and some LA. The adsorbent has to be separated from the reaction mixture using an appropriate unit operation (e.g., filtration or centrifugation), and then brought in contact with fresh solvent for HMF to desorb. Recovering the adsorbate by increasing the temperature of the vessel over the reaction temperature runs the risk of allowing uncatalyzed thermal degradation of HMF known to occur at temperatures of 165°C.[57] Although the exact time to equilibration is not considered explicitly, such a process may take several hours, which would be long enough for reaction to occur at high-recovery temperatures.

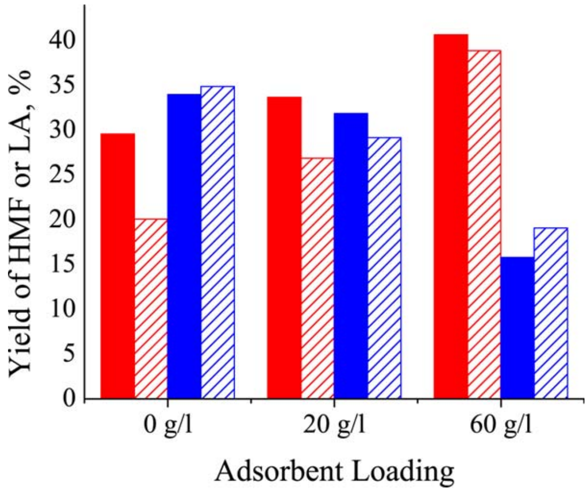

Figure 6. Comparison between experimental (solid), and model (hashed) yields of HMF (red), and LA (blue) with different adsorbent loadings after 2 h of reaction at 125°C with pH = 1.1.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8 shows the fraction of HMF recovered at three different temperatures as a function of the ratio of the volume of solvent used in recovery to the volume of solvent used in reaction. The pre-recovery concentrations of adsorbed HMF were determined by stopping the reaction at the time corresponding to the optimum HMF yield at each temperature. Even at 130°C, 63.0% of the HMF remains adsorbed with a 3:1 recovery: reaction solvent ratio. Evidently, a large quantity of solvent is required to desorb HMF. Alternate configurations such as continuous adsorbent washing may improve the time scale of the process, but would not reduce the total amount of solvent required. Clearly, both the temperature of the recovery and the amount of solvent are key parameters. Substantial improvements could be achieved by using an alternative solvent. Alcohols, in particular, are widely used for regenerating adsorbents saturated with furans[20,58,59] and should be effective in recovering a much higher fraction of HMF.

To maximize HMF recovery, we examined whether adsorbents with different adsorption properties could be more efficient. To achieve this we have performed a simple sensitivity analysis whereby we changed the parameters of the HMF adsorption isotherm, while keeping the isotherms of the other components as those for BP2000. Three different HMF adsorption isotherms, shown in Figure 9, were examined. These isotherms were constructed to have similar behavior in the high- and low-concentration regions of the isotherm, but very different shapes at the intermediate concentration region (see parameters in Table 6). The behavior at the intermediate region is adjusted by changing the magnitude of the exponent as well as the b coefficient. The "high b" case, obtained by increasing the exponent as well as the b parameter, corresponds to an adsorbent with a more energetically homogeneous surface than BP2000, i.e., each adsorption site has approximately the same heat of adsorption. When $n = 1$, the Redlich-Peterson isotherm reduces to the well-known Langmuir isotherm, which corresponds to an energetically homogeneous surface. The "low b" case corresponds to a more energetically heterogeneous distribution of adsorption sites. This case is expected to be advantageous for recovery because more of the adsorbate is weakly adsorbed. However, such a material would also adsorb less HMF during reaction. In other words, ease of recovery must be balanced with the effectiveness of the adsorbent.

Figure 10 shows the performance of the three different isotherms using three different metrics that reflect HMF yield enhancement during the reaction step (peak yield and

Table 5. Comparison Between Experiments and Model Predictions for HMF and LA Yield at Equal Conversions for T = 125°C and HCl Catalyst (pH = 1.1).

		HMF Yield, %		LA Yield, %	
Solid Loading	Fructose Conversion, %	Calculations	Experiments	Calculations	Experiments
0 g/L	89.0	32.3	29.6	19.9	34.0
20 g/L	84.2	38.1	33.7	12.5	31.9
60 g/L	84.5	44.4	40.7	7.2	15.8

percent adsorbed) as well as ease of recovery from the material (percent recovered using a volume of recovery solvent: volume of solvent in reaction ratio of 2:1). The high *b* case has an improved maximum HMF yield and a higher fraction of the HMF in the adsorbed phase, but makes recovery of HMF adsorbed on this material much more difficult to (fraction recovered is much less than the base case of BP2000). Conversely, the low *b* case results in a slightly lower peak HMF yield and adsorbed fraction, but the HMF is much more easily recovered than the other cases. This indicates that there is an optimum with respect to adsorbent selection, as a material that adsorbs HMF more strongly makes HMF recovery more difficult. Even though no such material has yet been identified, it is likely that this could improve the process for the production of HMF.

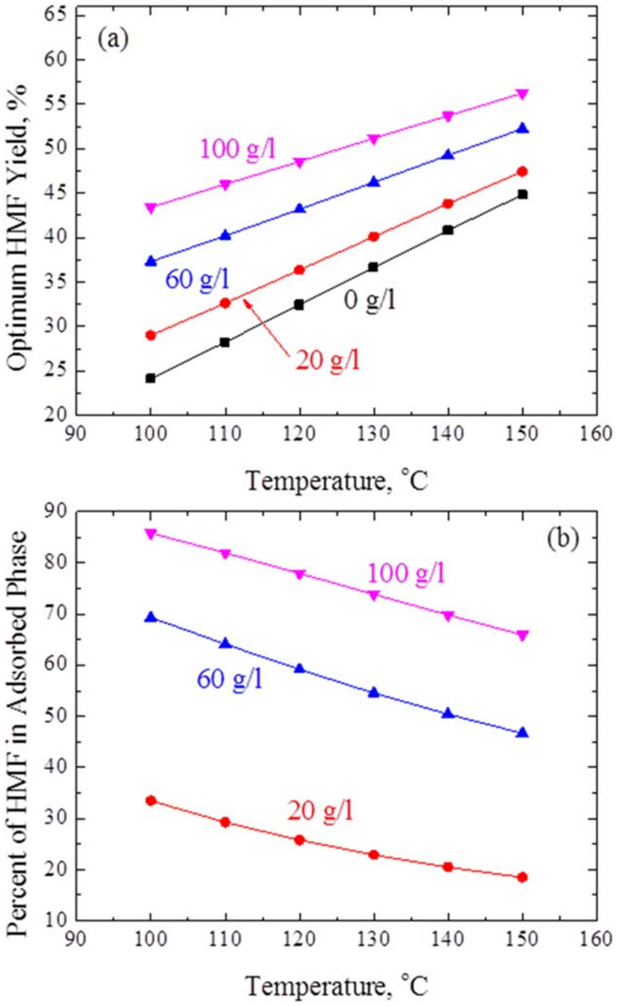

Figure 7. (a) Optimum yield as a function of reaction temperature for 0 (black), 20 (red), 60 (blue), and 100 g/L (magenta) BP2000, and (b) percent of HMF in adsorbed phase of the total present in solution at the optimum yield with BP2000 loadings indicated.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The efficacy of the proposed process must be compared to alternative processes. A biphasic reaction system is considered one of the more promising process alternatives.[2,60] Figure 11 compares the total HMF yield of reactive adsorption and reactive extraction. It is assumed that the partition coefficient of HMF between the organic and extractive phase is 1.65 and the organic:aqueous solvent ratio is 1.56. Both of these values were originally used in an economic analysis by Torres et al. and were, thus, considered realizable at an industrial scale.[2] The predicted reactive extraction results are roughly in line with previously observed HMF yields (between 31–70%) obtained after 35 min at 150°C with an HCl catalyst (pH = 0.6).[16] These values are typical of prior studies.[14,15,61] This does not include recovery from the organic solvent (evaporation/distillation) or the adsorbent (desorption), which needs to be addressed after the HMF recovery process has been optimized. At low temperatures, the two processes have very similar yields. At higher temperatures, reactive extraction provides higher yield. This is because the partition coefficient is assumed to be temperature-independent, while the adsorption parameters change. In

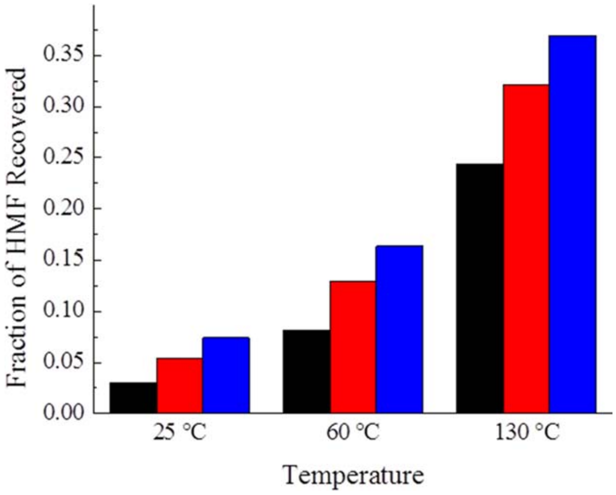

Figure 8. Fraction of adsorbed HMF recovered from 60 g/L of BP2000 adsorbent in a batch recovery process using water as the recovery solvent at 25, 60, and 130°C.

Volume of solvent used in recovery: volume of solvent used in reaction of 1:1(black), 2:1 (red), and 3:1 (blue).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

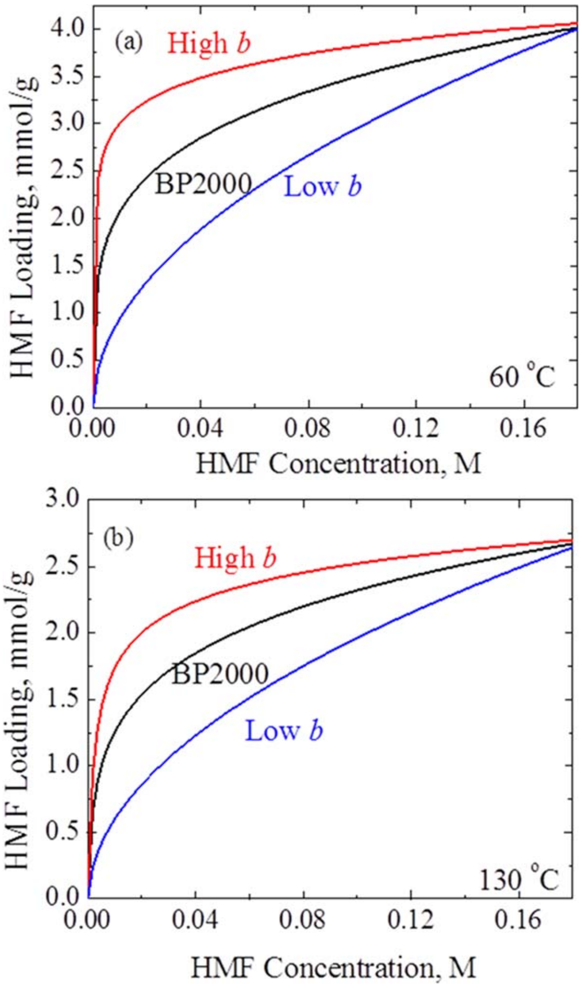

Figure 9. Two hypothetical HMF adsorption isotherms (red and blue) and that of BP2000 carbon (black) at 60°C (a) and 130°C (b) used to perform sensitivity analysis of the effect of different materials on the reactive adsorber performance.

The hypothetical isotherms are obtained using high *b* (red) and low *b* (blue) values. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

a real system, the partition coefficient depends on the activity coefficients of HMF in the organic and aqueous phases; temperature has similar effects on both activity coefficients, so the partition coefficient is probably only weakly dependent on temperature. What this comparison shows is that the reactive adsorption can be competitive on the basis of HMF yield. Economic analysis will be necessary to compare the two processes. Reactive adsorption may be preferable when downstream processes are considered. For instance, Román-Leshkov et al.,[62] propose using HMF as a substrate for the production of dimethylfuran. By using an adsorbent, the solvent choice for the downstream reaction would not be constrained by compatibility with a reactive extraction process, i.e., a water-miscible solvent like ethanol could be used as a solvent for the second reaction.

Table 6. Modified Adsorption Parameters of the Isotherms Used in Figures 9 and 10

	K, L/g		b, $(L/mol)^n$		
Temperature	60	130	60	130	n
Base	21.71	1.1366	3665	286	0.7739
High *b*	21.71	1.1366	4500	350	0.9
Low *b*	21.71	1.1366	2300	180	0.5

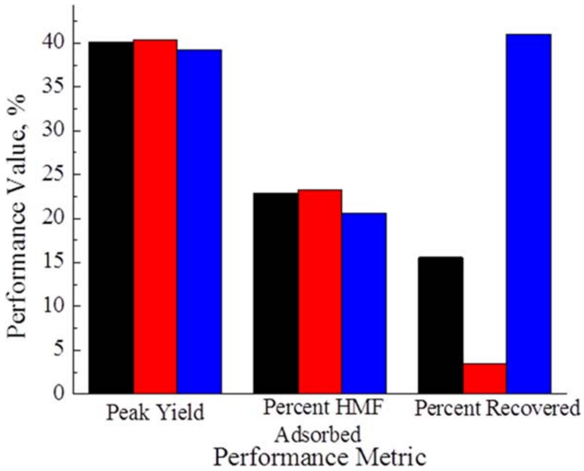

Figure 10. Comparison of the effect of material isotherm (see Figure 8) on performance: "high *b*" (red) and "low *b*" (blue) isotherm performance to 20 g/L BP2000 (black) using peak yield, percent of HMF in the adsorbed phase, and percent of HMF recovered with a 2:1 recovery:reaction solvent ratio and with both reaction and recovery at 130°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

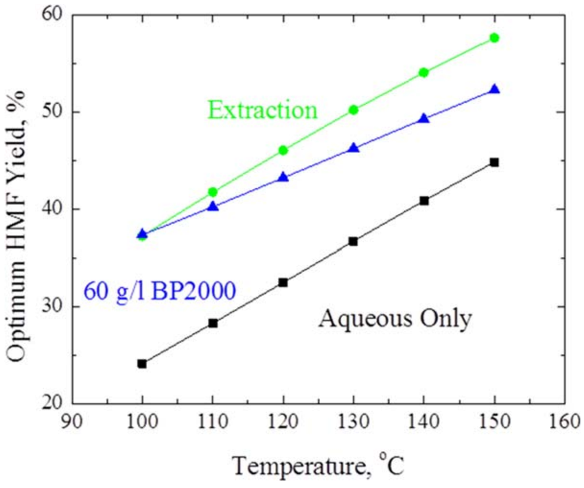

Figure 11. Comparison of HMF optimum yield without adsorbent (black), with 60 g/L of adsorbent (blue), and in a biphasic reactor (green) with an organic phase with a partition coefficient of 1.65 and an organic:aqueous volume ratio of 1.56.

The partition coefficient is taken to be temperature-independent, due to lack of experimental information.-Reactive extraction gives higher HMF yield than reactive adsorption at high temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Conclusions

Reactive adsorption has been studied for the first time as a means of improving the yield of a desirable (intermediate) product in a cascade of reactions where side reactions decrease its yield. The specific process studied herein was the production of 5-hydroxymethyl furfural (HMF) from the acid catalyzed dehydration of fructose. Kinetic measurements of the acid catalyzed chemistry and adsorption isotherms on BP2000 carbon were conducted separately over relevant process conditions. A reactive adsorption model was then built to describe the coupled reaction and separation process and assessed with experiments carried out in a batch reactive adsorber.

It was found that reactive adsorption can be a promising process for the selective production of HMF from acid-catalyzed fructose dehydration and can result in significant enhancement of maximum yield compared to a simple (non-adsorber) reactor at the same conditions. The reactive adsorption model qualitatively described the increase in adsorption performance when compared to experimental data. The adsorbent has greatest effect at low temperatures, while reaction energetics favors high temperatures. The adsorbent is able to improve HMF yields such that similar yields could be obtained at 120°C in the presence of adsorbent as were found at 150°C without adsorbent. Our model suggests that under certain conditions both the proposed reactive adsorption and the reactive extraction, introduced years ago, can result in a similar improvement in HMF yield. However, yield should not be the only metrics of comparison; the entire process economics should be considered in future work. Recovery of adsorbed HMF has been identified as a challenge, although one that could be addressed by using a more heterogeneous adsorbent and possibly a different solvent from water for recovery.

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Notation

Symbols

b_i = Redlich-Peterson constant, $\left(\frac{l}{mol}\right)^n$
C_i = concentration of component i, mol/l
k_i = rate constant of reaction i, min^{-1}
K_i^F, = Freundlich constant, $\left(\frac{l}{g}\right)^n$
K_i^H, = Henry constant of component i, l/mol
k_i^L, = mass-transfer coefficient of component i, min^{-1}
k_i^*, = dimensionless rate constant of reaction i
$\hat{m}$, = loading of adsorbent, $G_{\text{Adsorbent}}/^{l}{}_{\text{Solvent}}$
n_i = Redlich-Peterson exponential term
q_i = adsorbed concentration, mol/g
q_i^{Eq} = equilibrium adsorbed phase concentration,
q_i^M = measured adsorbed phase loading
t = reaction time, min^{-1}
y^2 = dimensionless concentration

Greek letters

χ^2 = chi-squared quality of fit measure

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