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Experimental studies towards optimization of the production of 5-(chloromethyl)furfural (CMF) from glucose in a two-phase reactor

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ABSTRACT

5-(Chloromethyl)furfural (CMF) is rapidly being established as a renewable platform chemical of great promise. The effects of mass transfer, reaction temperature, Hansen solvent parameters, solvent fraction, and initial glucose concentrations on yields of CMF, 5-(hydroxymethyl)furfural (HMF), 2-(hydroxyacetyl)furan (HAF), levulinic acid (LA), and humic matter were investigated in a two-phase system of 6 M HCl and an organic solvent. The ability of the solvent to extract HMF from the aqueous phase is found to be critical to achieving high CMF yields. Effective solvents must possess at least a small degree of Hansen hydrogen bonding capacity, and a high polarity is beneficial. Yields of CMF and HAF decrease with increasing glucose concentration but the yield of HMF is largely unaffected. The maximum productivity of CMF is achieved at a glucose loading of ca. 1.5 M across all solvent fractions tested.

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1. Introduction

At present, fossil hydrocarbon resources constitute the overwhelming majority of feedstocks for production of liquid fuels and commodity organic chemicals. As these limited resources are depleted, it will become necessary to transition to renewable feedstocks as replacements. Ideally, these would be derived from abundant cellulosic materials found in agricultural and forestry waste [1], urban green waste [2], and purpose-grown crops [3,4]. Furanic compounds based on 5-(hydroxymethyl)furfural (HMF) **1** and its derivatives have recently been advanced as highly promising platform compounds for gaining access to a range of renewable chemical and materials markets [5–8]. Unfortunately, HMF has only been produced at pilot scales from fructose, and to date no scalable approach to its synthesis from raw biomass has been reported. This is mainly due to its high water solubility, high boiling point, and sensitivity to the acidic conditions under which it is formed from carbohydrates. A potentially disruptive innovation in the renewable chemical field has recently been introduced in the form of the HMF analog 5-(chloromethyl)furfural (CMF) **2** [9–11]. Unlike HMF **1**, compound **2** can be accessed in high yield from glucose or even directly from cellulosic biomass and, since it is hydrophobic, it presents no problems in its isolation from acidic

aqueous reaction media. The synthesis of CMF has been reviewed in detail [12].

Although there have been recent studies on the kinetics of HMF formation [13] and on the effect of aqueous phase modifiers [14,15] and type of organic solvent [14] used in the production of HMF in two-phase systems, corresponding studies on the effects of reaction parameters on the yield of CMF are lacking. The most comprehensive investigation of this type was published in 1981 by Szmant and Chundury, who examined the individual effects of solvent type, HCl/substrate ratio, reaction temperature, reaction time, surfactant type, and substrate on CMF yields [16]. However, the many possible interactions between these variables were not explored.

The purpose of the present work is to determine the effect of key reaction parameters on the production of CMF so as to guide further development work toward the design of an industrial scale process. As such, the conditions under which these data were obtained may differ from those that would be typically chosen for production of CMF. For example, in a typical batch reaction operation, the reactants, solvent and acid are combined and brought to the reaction temperature for the desired amount of time, then cooled and worked up. This approach however has the drawback of imposing a thermal history on the reactants that is subject to adventitious variation and complicates interpretation of the data. To eliminate these issues, this study was conducted under isothermal conditions by adding the substrate to a preheated mixture of the remaining

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components in an open vessel. Furthermore, most of the prior work for producing halomethylfurfurals has involved the use of concentrated HCl (or HBr) in order to achieve high yields over short time frames [12]. Since the boiling point of 12 M HCl is *ca.* 50 °C, opening the hot vessel to transfer materials would result in the loss of an unknown amount of the volatile acid, which would render the data unreliable. A higher boiling reaction medium was thus required. Therefore, the experiments were conducted using 6 M HCl (bp 108 °C). This azeotropic composition allowed operation in an open system without the loss of acid.

2. Experimental

2.1. Materials

Food grade glucose was obtained from The Original Home Brew Outlet Inc., Sacramento, CA. Dichloromethane (DCM) was obtained from EMD Chemicals USA. Perchloroethylene (PCE) and 1,1,2-trichloroethane (TCA) were obtained from Acros Organics. 1,1,2,2-Tetrachloroethane (4CA) was obtained from Sigma–Aldrich. Deuterated chloroform (99.8% atom d) was obtained from Cambridge Isotope Laboratories. Toluene (Tol), 1,2-dichloroethane (DCE) and concentrated hydrochloric acid were obtained from Fischer Scientific. All chemicals were used as received.

2.2. Experimental methods

2.2.1. Extraction study

For this study, a stock solution of furanic products was prepared by addition of 25 g of fructose to 0.5 L of 6 M HCl at 79 °C. The reaction mixture was stirred with heating for 30 min during which time the temperature rose slightly to 83 °C. The mixture was then rapidly cooled in an ice-water bath and the humic matter removed by vacuum filtration. The dark, homogeneous filtrate was stored in an ice bath to slow decomposition.

All extractions were carried out within *ca.* 3 h from the time that the stock solution was prepared. Extractions were performed at room temperature by contacting 40 mL portions of the stock solution with 80 mL of solvent in a separatory funnel followed by vigorous shaking for 1 min. The solvents comprised a representative group of chloroalkanes (DCM, DCE, TCA, and 4CA), a chloroalkene (PCE), and a non-halogenated aromatic solvent (Tol). The organic phase was separated and dried over MgSO₄, and the solvent was removed under vacuum. The crude product mixture was then weighed and analyzed by ¹H NMR spectroscopy using a known mass of anisaldehyde as an internal standard.

2.2.2. Standard reaction procedures for the processing of glucose in a two-phase reaction with aqueous hydrochloric acid and an organic solvent

The reaction conditions and procedures for the parameter experiments were chosen to be consistent with those used for related studies in our laboratory [11]. Reactions were conducted under air in a 500 mL, three-necked flask equipped with a thermometer, reflux condenser, and a Teflon-coated magnetic stir bar and heated by means of an oil bath mounted on a stirrer hot plate. The flask was charged with solvent and sufficient 6 M HCl to bring the total volume of liquid to 210 mL, minus about 5 mL acid reserved for aiding the transfer of glucose, and the mixture was then heated with vigorous stirring. Once the desired reaction temperature was achieved, a weighed portion of glucose was added all at once and rinsed into the flask with the reserved acid. The reaction temperature typically recovered within about 30 s after glucose addition. The reaction was allowed to continue for 1 h, at which time the flask was removed from the oil bath and immediately cooled by

swirling in an ice-water bath. The reaction mixture typically reached 20 °C within 2 min after removal from the oil bath.

All yields were calculated based on the amount of product recovered by extraction, and no analysis was performed on the aqueous phase. Solid humic matter was removed from the cooled reaction mixture by vacuum filtration through Whatman grade #1 filter paper using a water aspirator, and the organic phase was separated. The aqueous phase was re-extracted once with a volume of fresh solvent equal in volume to that used in the reaction, the combined organic layers were dried over MgSO₄ and the solvent was evaporated. The dark, oily product was transferred to a tared vial. After weighing, the relative molar abundance of products was determined by ¹H NMR spectroscopy. Full details of the analysis are given in the [Supplementary Information](#).

3. Results

3.1. Reaction products

Following the standard reaction procedures described in Section 2.2.2 gives a mixture of four major, isolable products, i.e. HMF **1**, CMF **2**, 2-(hydroxyacetyl)furan (HAF) **3**, levulinic acid (LA) **4** plus solid humic material, as has been described previously [9]. The reaction is rendered graphically in [Scheme 1](#).

3.2. Effect of stirring rates

Since the reaction occurs in a two-phase system it is important to operate under conditions in which mass transfer between the phases is not limiting. The effect of stirring rate was studied at reflux in a mixture of 70 mL of 6 M HCl and 140 mL of 4CA with 3.5 g of glucose as substrate. Stirring rates were measured by observation of a magnetic stir bar at the integral settings of the stirrer hotplate using a stroboscopic tachometer.

The combined yield of all soluble products is unaffected by the stirring rate throughout the available range of 0 to *ca.* 30 revolutions per second (s^{−1}) ([Fig. 1a](#)). At low stirring rates the yield of CMF is lower and that of LA is higher than at high stirring rates ([Fig. 1b](#)). The lower rates of mass transfer between the phases lead to decreased yields of CMF due to decomposition into secondary products. The LA/CMF mole ratio is a sensitive measure of the extent to which mass transfer is a limiting factor in the production of CMF, as shown in [Fig. 1c](#).

A total of 7 replicate runs were performed at high stirring rates ranging from 14 to 27 s^{−1} (2 at 14 s^{−1}, 3 at 21 s^{−1} and 2 at 27 s^{−1}) where mass transfer is not limiting. Both the CMF yield and the LA/CMF mole ratio are constant over this range. The dashed lines in [Fig. 1b](#) and [c](#) indicate ± 1 standard deviation from the mean percent yields of CMF ($29.04 \pm 1.24\%$) and LA ($5.68 \pm 1.13\%$) and of the LA/CMF mole ratio (0.195 ± 0.033) at stirring rates between 14 s^{−1} and 27 s^{−1}. All subsequent experiments were therefore conducted in the range of 23–27 s^{−1} where the process is reaction rate limited and not mass transfer limited.

It was also found that the mass ratio of humic matter to LA is constant at *ca.* 0.34 throughout the whole stirring rate range (not shown), indicating that the relative rates of the pathways leading to these two decomposition products are unaffected by changes in the mass transfer rate and that the formation of humic acid is reaction rate controlled.

3.3. Solvent effects

The reflux temperature of the reaction mixtures was lower than the boiling points of either 6 M HCl (108 °C) or the solvents but tended to increase with increasing boiling point of the solvent.

Scheme 1. Reaction products of the acidic processing of glucose under conditions described in Section 2.2.2.

Fig. 1. (a–c) Yield of products as a function of stirring rate (s^{-1}). Glucose (3.5 g) heated at reflux for 1 h in a mixture of 6 M HCl (0.07 L) and 4CA (0.140 L). Dashed lines in Fig. 1b and c show the mean ± 1 standard deviation: 1a) Total yield of all products vs. stirring rate; 1b) CMF and LA yields vs. stirring rate; 1c) Molar LA/CMF ratio vs. stirring rate.

Fig. 2. Dependence of %CMF yield on solvent and reaction temperature. Glucose (3.5 g) heated in a mixture of 6 M HCl (0.07 L) and solvent (0.14 L) for 1 h.

Fig. 2 illustrates the effect of reaction temperature on CMF yield when different organic solvents were used.

The percent yield of CMF increased in a roughly linear manner with temperature. The chloroalkane solvents all gave similar CMF yields but the use of toluene and particularly PCE gave markedly lower yields. In order to explore the possibility that this effect might be due to reduced extraction of CMF, the relative ability of various solvents to extract furanic products from aqueous acid was tested. Fig. 3 shows a comparison of the amount of CMF and HMF extracted from the stock solution (Section 2.2.1) by each solvent, ordered by amount of HMF extracted. The quantity of CMF extracted in these experiments was less than that obtained in reactions in acid-solvent mixtures. Nevertheless, the extraction of products from the stock solution should accurately model the extraction of products in the mixed acid-solvent experiments. As can be seen, CMF is extracted well by all of the solvents, although PCE is somewhat less effective. However, this difference is not commensurate with the poor performance of PCE in the biphasic reactions.

Fig. 3. Relative extraction of CMF and HMF from stock solution by various solvents.

3.4. Effects of solvent fraction and initial glucose concentration

The effects of initial glucose concentration and organic solvent fraction of the reaction medium (*Sf*) were studied in a series of 53 experiments in which the mass of added glucose and *Sf* were varied independently in a constant total liquid volume of 210 mL, corresponding to the points shown in Fig. S2 in the [Supplementary Information](#) (SI). The initial aqueous concentration of glucose was a function of both the mass of glucose added and the *Sf*. To obtain plots of percent yield vs initial aqueous glucose concentration, the data were transformed as described in the [Supplementary Information](#). Reactions were performed at reflux with stirring in the range of 23–27 s^{−1}.

3.4.1. Primary products

Plots of percent yield of primary products as a function of solvent fraction and initial aqueous glucose concentrations from 0.5 to 5.0 M are shown in Fig. 4a–c. The percent yields of all primary products increase with increasing solvent fraction such that the curves are concave up.

The percent yield of CMF decreases with increasing initial glucose concentration. This decline was more pronounced at lower glucose concentrations. The yield of HAF also decreases with glucose concentration, but the distinction between the rate of decline at lower and higher loadings was more evident than for CMF, and this effect increased with increasing solvent fraction. In contrast, the percent yield of HMF was found to be less sensitive to glucose concentration and appeared to depend almost solely on the solvent fraction.

3.4.2. Secondary products

As with the primary products, the percent yield of LA increases with solvent fraction as shown in Fig. 4d. Since LA is highly soluble in water this may simply reflect more complete extraction of LA rather than an actual increase in LA formation. The yield of LA appears to be maximized at an initial glucose concentration of ca. 2 M. However, this trend is relatively weak compared with the general variation in LA yield.

The yield of humic matter has a strong dependence on solvent fraction as shown in Fig. 4e. At *Sf* < 0.5, humic matter yield increases linearly with glucose concentration. At *Sf* ≥ 0.5, humic matter production is negligible at initial glucose concentrations of ≤2 M. Higher initial glucose concentrations thus require higher *Sf* to reduce humic matter formation to low levels.

3.4.3. Absolute CMF yield

Percent yield of product is a common measure of process optimization, but there are situations where yield might be sacrificed in order to maximize the amount of product generated in a given reactor volume per unit time. The amount of CMF obtained with respect to solvent fraction and amount of glucose added is plotted in Fig. 5. The CMF vs. glucose curves at each solvent fraction were closely approximated by second order polynomials. The maximum amount of CMF was obtained with 0.30–0.35 mol of glucose in the 210 mL reaction volume across all solvent fractions tested. Thus, the factor determining the maximum amount of CMF produced at a given *Sf* was the amount of glucose in the total reaction volume rather than the concentration of glucose in the aqueous phase. Deviation from this behavior, resulting in lower CMF yields, occurred only when large amounts of glucose were used in conjunction with high solvent fractions, such that initial aqueous phase glucose concentrations were ≥4.4 M.

4. Discussion

4.1. Effect of solvents and temperature

The expectation was that increased reaction temperature would lead to increases in CMF yield per unit time, since the rate-limiting isomerization of glucose to fructose has an activation energy of approximately 106 kJ mol^{−1} [17]. This held true for DCE, TCA, and 4CA, however; toluene and PCE gave unexpectedly low yields.

The extraction experiments revealed that while there is some variation in the ability of the solvents to extract CMF, this is insufficient to account for the observed dependence of CMF yield on solvent. In contrast, there is a marked difference in the ability of the solvents to extract HMF. The solvents (DCM, DCE, TCA, and 4CA) all extract HMF well, but toluene and PCE extract about 16% and 1% as much as TCA, respectively. Thus, the ability of a solvent to extract HMF is clearly a key requirement for obtaining good yields of CMF.

One possible explanation for this effect is that by extracting HMF the solvent is able to sequester it into an environment where it is shielded from decomposition while at the same time lowering the effective concentration of HMF in the aqueous acid. Since the decomposition of HMF by acid has a reaction order greater than one, decreasing the aqueous concentration of HMF would lead to a disproportionately larger decrease in the rate of conversion of HMF into secondary products. Another possibility may be that HMF is actually converted into CMF in the organic phase. Although the solubility of both HCl and HMF in non-polar solvents is much lower than in water, the activity of each component is the same in all phases at equilibrium. This raises the possibility that an optimal system for producing CMF might contain little or no aqueous phase. In fact, in early work in this field, Fenton and Gostling produced BMF [18] and CMF [19] by simple treatment of fructose, sucrose and cellulose with ethereal HBr and HCl, respectively, at room temperature over a period of 12–48 h. Although the yields in these studies were low, no attempt to optimize the reaction under these conditions has been published.

It is useful to be able to predict the performance of extracting solvents in the carbohydrate-to-CMF process based on their physico-chemical properties. Fig. 6 shows the Hansen parameter values for solvents used in this study as well as DCM [20]. The solvents all have similar values for dispersion, but vary greatly in polarity and hydrogen bonding ability. A comparison of PCE, the poorest solvent, with 4CA, the best, reveals that they have very similar dispersion and polarity. But while 4CA has a hydrogen-bonding parameter on par with the other chloroalkane solvents, PCE has a hydrogen bonding parameter of 0.0. Thus, hydrogen-bonding ability appears to be a key feature of the solvents that perform well in this reaction.

Szmant and Chundury performed a study of solvent effects complimentary to that described here. Unlike the present work, in which the reactions were conducted at reflux, the temperature of which varied with the solvent, these authors examined the effect of solvent on CMF yield at a constant temperature [16]. Correlation of their results with the Hansen parameters of the solvents is shown in Table 1. Both isooctane and CCl₄ have polarities of 0.0, yet the CMF yield with the latter solvent is almost 3.5 times that obtained with the former. The key difference is that isooctane has a hydrogen bonding parameter of 0.0 while the value for CCl₄ is 0.6. If the data for isooctane are excluded, the correlation of yield with polarity for the remaining solvents is excellent ($R^2 = 0.98$) while the correlation with dispersion is somewhat lower (R^2 ca. 0.80). Thus, while a complete lack of hydrogen bonding ability renders a solvent a poor performer in this reaction, the effectiveness of solvents with even modest hydrogen bonding capacity appears to be mainly a function of their polarity, with dispersion playing a less important role.

Fig. 4. (a–e). Effect of varying the initial glucose concentration (M) and organic solvent fraction (Sf) on product yield on heating at reflux in mixtures of 6 M HCl and 4CA for 1 h: a) CMF 2; b) HMF 1; c) HAF 3; d) LA 4; e) humic matter.

These results explain why the CMF yields obtained with toluene and PCE are unusually low. The yield of CMF with PCE appears to be limited by this solvent's complete lack of hydrogen bonding ability, while the yield with toluene appears to be limited by its relatively low polarity in relation with the other solvents tested.

4.2. Effects of solvent fraction and initial glucose concentration

4.2.1. Primary products

The percent yields of both CMF and HAF decrease as the initial concentration of glucose increases. Studies have shown that the decomposition of glucose in acid is first order in glucose [21,22], so the observed dependence of CMF yield on initial glucose concentration, which would suggest a power law exponent of <1, requires an explanation. Kuster examined the loss of HMF from a 1 M solution in 2 M HCl at 95 °C and found that the rehydration of HMF was accelerated by 38% in the presence of either glucose or fructose [23,24]. Van Dam and coworkers found that the decomposition of

1 M HMF in 1 M aqueous HClO₄ at 88 °C was accelerated by use of 50% ethylene glycol as co-solvent, but not by addition of an equivalent volume of methanol [25]. Glycerol behaved similarly to ethylene glycol. The decreased stability of HMF toward hydrolysis in the presence of ethylene glycol and glycerol was explained by formation of cyclic HMF acetals, which apparently are rehydrated at a much higher rate than HMF itself. The possibility that HMF may form cyclic acetals with saccharides was raised as a possible explanation for the deleterious effect of high concentrations of sugars on HMF yield. In contrast to this, the insensitivity of HMF yields to initial glucose concentration in the present work runs counter to both literature precedent and the behavior of the other primary products.

Operating at an optimally high Sf limits the amount of glucose that can be processed per unit volume of the reactor, which in turn limits the quantity of CMF that can be produced in a given yield/time relationship. One possible way around this would be to add the glucose, or other substrate, continuously over the course of the

Fig. 5. Absolute yield of CMF as a function of glucose added to a total reaction volume of 0.210 L, for different values of Sf.

Fig. 6. Hansen solubility parameters of solvents used in extraction experiments.

Table 1

Percent yield of CMF from High Fructose Corn Syrup at 75 °C and Hansen parameters of solvents, from data by Szmant and Chundury [16].

Solvent	%CMF yield	Dispersion	Polarity	Hydrogen bonding
Iso-octane	19.9	14.1	0.0	0.0
CCl ₄	68.8	17.8	0.0	0.6
Toluene	76.0	18.0	1.4	2.0
Trichloroethylene	81.5	18.0	3.1	5.3
Chlorobenzene	89.8	19.0	4.3	2.0

reaction. This mode of addition would allow maintaining a low aqueous sugar concentration, which in turn should lead to higher percent yields of CMF. Continuous addition of a reactive sugar, such as glucose or fructose, to a system containing a relatively small volume of aqueous acid should enable the synthesis of CMF in high yield and the optimization of output per unit time for a given size of reactor.

4.2.2. Secondary products

All of the primary products are known to decompose on heating in aqueous acid. Humic matter has been formed from both HMF [26] and HAF [27]. Additional decomposition pathways of HMF [28] and HAF [29] give a mixture of LA and formic acid. Heeres states that the formation of humic matter has a reaction order of 1.23 in

HMF [30]. Chuntanapum and Matsumura report a reaction order of 4.29 in HMF and state that soluble decomposition products such as 1,2,4-trihydroxybenzene also contribute to humic matter formation, with a reaction order of 1.21 [31]. More relevant to the present work, Heeres has shown that the formation of humic matter has a reaction order of 1.30 in glucose and 1.13 in acid [28]. In contrast, the formation of LA from HMF and glucose is reported to have reaction orders in substrate of 0.88 [30] and 1.09, [28] respectively. Further kinetic studies have been carried out on the formation of humic matter from cellulose [32] and water hyacinth [33], and the effects of the concentration of water [34], acid [24], and the initial concentration of saccharides have been investigated [24]. Despite these studies, the formation of humic matter remains poorly understood.

No data regarding the kinetics of CMF decomposition are available, however the fact that CMF is hydrolyzed to HMF quickly at elevated temperature [35] indicates that these two species must rapidly equilibrate in aqueous HCl under the reaction conditions. Thus, decomposition of HMF would be expected to also decrease the yield of CMF. One possible explanation for the observed insensitivity of HMF yields to glucose concentration in this work is that as HMF decomposes, its concentration may be maintained by virtue of its rapid dynamic equilibrium with the more abundant CMF product.

As noted above, the formation of humic matter has a reaction order in HMF greater than unity, so it is reasonable that extraction of HMF from the aqueous phase would markedly decrease humic matter formation. Humic matter has low economic value and is produced to some extent in most preparations of furanic compounds. Thus, a fuller understanding of its formation would be valuable.

4.2.3. Effective partition coefficients

If the yield of each component was limited solely by its degree of extraction from aqueous acid, then the yield vs. Sf should be governed by the solvent/aqueous acid partition coefficient (Pc). The yield vs. Sf curve of HMF in 4CA is consistent with its having a Pc between 0.10 and 0.15. The curve for CMF is similar, varying slightly with initial glucose concentration, and would be consistent with a Pc of 0.15–0.30. The method by which these effective partition coefficients were determined is discussed in the [Supplementary Information](#). The partition coefficient for CMF would however be expected to be much greater than that for HMF. The Atom-Fragment Contribution method of Meylan and Howard [36] can be used to calculate the $\log_{10}$ (o/w) for compounds based on their structure. The calculated $\log_{10}$ (o/w) for HMF is -0.067 , while that of CMF is estimated to be 1.652. The fact that CMF behaves as if it had a Pc only slightly greater than that of HMF demonstrates that the yield of CMF is not limited by its ability to be extracted into the solvent and is consistent with our earlier observation that CMF yield is strongly influenced by the ability of the solvent to extract HMF.

5. Conclusions

The data generated in this parameter study allow us to draw the following conclusions:

- 1) Variation of the stirring rate in the range of 0–ca. 30 s⁻¹ does not affect total product yield, but strongly influences the product distribution. Low mass transfer rates lead to a decrease in CMF yield with concomitant increase in yield of the secondary product LA and, to a smaller extent, humic matter. Thus, experiments to study the formation of furanic compounds such as HMF and CMF should ensure that mass transfer effects are not limiting. Mass transfer limitations become negligible in the

present reactor configuration at stirring rates above $\sim 14\text{ s}^{-1}$. Faster stirring gives no changes in product distribution.

- 2) When glucose is heated in 2:1 mixtures of solvent with 6 M HCl, CMF yield increases in a roughly linear manner with increasing temperature. Yields with DCE, TCA and 4CA are similar, but toluene and particularly PCE give lower yields, demonstrating that the nature of the solvent plays a critical role in achieving high yields. At least some degree of hydrogen bonding ability is required and a high polarity is advantageous. These factors are closely associated with the ability of the solvent to extract HMF. The data predict that dichloromethane should also be a good solvent for this reaction, based on its physicochemical properties and low cost, although its low boiling point would require that the process be conducted in a sealed vessel.
- 3) The highest yields of CMF are obtained when the concentration of glucose in the aqueous phase is kept low. However, limiting the amount of glucose necessarily also limits the amount of CMF that can be produced in a given reactor volume. The results of this study suggest that the gradual addition of substrate throughout the course of the reaction may allow for a greater quantity of CMF to be produced per unit volume, while at the same time achieving a high yield. In this case it may be particularly advantageous to use a reactive saccharide such as glucose or fructose.
- 4) Multiple lines of evidence suggest that the yield of CMF is limited by decomposition of HMF. Whether the extraction of HMF into the organic phase increases CMF yields by protecting HMF from decomposition, lowering the aqueous phase concentration of HMF, providing a medium conducive to the conversion of HMF to CMF, or by some combination of these factors, the partitioning of HMF into the solvent appears to be critical to obtaining high CMF yields. Thus, adjustments to the reaction conditions that promote this effect should be beneficial. Besides using solvents having better HMF extracting properties, the solubility of HMF in the aqueous phase could be decreased by a salting out effect. If a chloride salt is used this would have the added advantage of shifting the HMF/CMF equilibrium in favor of CMF. Preliminary experiments in this direction have proved promising.
- 5) The percent yield of HMF is insensitive to initial glucose concentration in this system, in apparent contrast to literature precedent for decreasing HMF yield with increasing glucose concentration when CMF is not involved. This result establishes that CMF plays a key role in moderating the concentration of HMF. It is proposed that HMF lost through decomposition to LA and humic matter can be replenished by rapid equilibration between CMF and HMF, ultimately resulting in decreased yields of CMF.
- 6) Humic matter is formed in the aqueous phase from HMF and HAF and their decomposition products. Efficient extraction of these compounds into an organic solvent can suppress formation of humic matter to very low values, even at initial aqueous glucose concentrations as high as 4.4 M. The fact that at least some humic matter is formed even under conditions of low initial glucose concentration and high solvent fraction suggests that there may be more than one mechanism for producing it.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.renene.2015.07.032>.

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