



Supporting Information

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Supporting Information for

Direct, High-Yield Conversion of Cellulose to Biofuel

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Experimental Section

Conversion of cellulose into furanic products. 1,2-Dichloroethane (500 mL) was introduced into the extraction chamber of a standard apparatus for continuous extraction with a solvent heavier than water. A homogeneous suspension of microcrystalline cellulose (2.05 g, 5% water by mass) was prepared in a solution of lithium chloride (10 g) in concentrated hydrochloric acid (150 mL), and this was added to the extraction chamber. A boiling flask containing 1,2-dichloroethane (150 mL) and anhydrous sodium sulfate was attached to the apparatus and the solvent was heated to reflux. The aqueous slurry was heated at 65 °C with continuous mechanical stirring and subjected to continuous extraction for 18 h. At this point, further LiCl (5 g) in concentrated hydrochloric acid (75 mL) was added to the extraction chamber and extraction was continued for another 12 h. During the extraction the boiling flask was emptied every 6 h and replaced with fresh 1,2-dichloroethane (150 mL). The combined organic extracts were distilled to recover the solvent, and the residual oil (1.469 g) was chromatographed (silica gel, CH₂Cl₂:Et₂O, 2:1 gradated to CH₂Cl₂:MeOH, 95:5) to give 5-(chloromethyl)furfural (**2**) (1.233 g, 71 %), ¹H NMR (CDCl₃) δ 4.36 (s, 2H), 6.32 (d, 1H), 6.95 (d, 1H), 9.25 (s, 1H), ¹³C NMR (CDCl₃) δ 36.1, 111.6, 122.1, 152.2, 155.3, 177.1; 2-(2-hydroxyacetyl)furan (**3**) (0.116 g, 8 %), ¹H NMR (CDCl₃) δ 3.26 (brs, 1H), 4.71 (s, 2H), 6.56 (t, 1H), 7.26 (d, 1H), 7.60 (d, 1H), ¹³C NMR (CDCl₃) δ: 65.2, 112.7, 118.02, 147.2, 150.3, 187.8; 5-(hydroxymethyl)furfural (**1**) (0.082 g, 5 %), ¹H NMR (CDCl₃) δ 3.51 (brs, 1H), 4.66 (s, 2H), 6.50 (d, 1H), 7.21 (d, 1H), 9.51 (s, 1H), ¹³C NMR (CDCl₃) δ: 56.9, 110.1, 123.9, 151.8, 162.0, 178.1; and levulinic acid (**4**) (0.011 g, 1%), ¹H NMR (CDCl₃) δ 2.17 (s, 3H), 2.59 (t, 2H), 2.73 (t, 2H), ¹³C NMR (CDCl₃) δ: 27.9, 29.9, 37.8, 178.2, 207.0. Filtration of the remaining aqueous layer gave a fine, black humic material (0.10 g).

Conversion of glucose into furanic products. Using the general procedure described above, glucose (2.01 g) gave crude product (1.425 g) which was chromatographed to give 5-

(chloromethyl)furfural (**2**) (1.145 g, 71 %), 2-(2-hydroxyacetyl)furan (**3**) (0.103 g, 7 %), 5-(hydroxymethyl)furfural (**1**) (0.116 g, 8 %), levulinic acid (**4**) (0.032 g, 3%), and humic material (0.090 g).

Conversion of sucrose into furanic products. Using the general procedure described above, sucrose (2.06 g) gave crude product (1.543 g) which was chromatographed to give 5-(chloromethyl)furfural (**2**) (1.322 g, 76 %), 2-(2-hydroxyacetyl)furan (**3**) (0.090 g, 6 %), 5-(hydroxymethyl)furfural (**1**) (0.055 g, 4 %), levulinic acid (**4**) (0.064 g, 5%), and humic material (0.070 g).

*5-(Ethoxymethyl)furfural (**5**).* 5-(Chloromethyl)furfural (**2**) (1.24 g, 8.58 mmol) was dissolved in absolute ethanol (60 mL) and the solution was stirred at room temperature for 8 h. The excess ethanol was recovered by distillation and the residue was chromatographed (silica gel, CH₂Cl:Et₂O, 2:1) to give **5** (1.26 g, 95 %) as a pale yellow liquid, ¹H NMR (CDCl₃) δ 1.04 (t, 3H), 3.39 (q, 2H), 4.32 (s, 2H), 6.34 (d, 1H), 7.06 (d, 1H), 9.40 (s, 1H), ¹³C NMR (CDCl₃) δ 14.1, 63.6, 65.3, 110.3, 121.8, 151.8, 157.9, 176.7.

*5-Methylfurfural (**6**).* The method of Hamada, et al.¹ was used: A mixture of 5-(chloromethyl)furfural (**2**) (1.17 g, 8.09 mmol) and PdCl₂ (0.030 g) in N,N-dimethylformamide (5 mL) was introduced into a flask which was evacuated, back filled with hydrogen, and kept under a positive pressure of hydrogen with a balloon. The reaction mixture was stirred at 40 °C for 3 h and then filtered through Celite. CH₂Cl₂ (150 mL) was added to the filtrate and the resulting solution was washed with 1M HCl (50 mL), 5 % aq. NaHCO₃ (50 mL), and finally water (50 mL). The organic layer was dried over anhydrous MgSO₄. Evaporation of solvent and chromatography (silica gel, CH₂Cl₂:Et₂O, 2:1) gave **6** (0.78 g, 87%) as a colorless liquid, ¹H NMR (CDCl₃) δ: 2.45, (s, 3H), 6.08 (d, 1H), 7.22 (d, 1H), 9.56 (s, 1H), ¹³C NMR (CDCl₃) δ: 14.0, 110.2, 124.4, 151.9, 159.8, 176.8.

Reference

- (1) K. Hamada, G. Suzukamo, K. Fujisawa, *Eur. Pat. Appl.* **1982**, 44186A1.

Material and Energy Balance Analysis for Flow Through Reactor

Background

We will take as our reactor a well-mixed CSFR (continuously stirred flow through reactor). We consider two input streams and one exit stream as shown in the following flow sheet

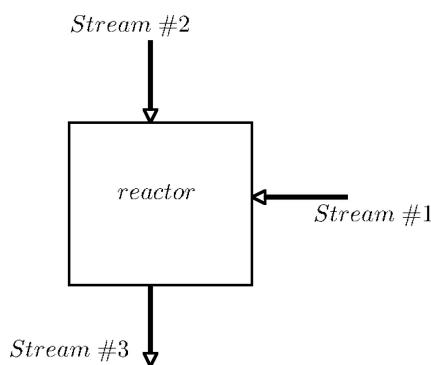


Fig. 1 : Reactor flow sheet

Stream # 1 contains HCl (species A), cellulose ($C_6 H_{10} O_5$, species B), water ($H_2 O$, species C) and LiCl (species D). which does not react. Stream # 2 contains a pure solvent stream ($C_2 H_2 Cl_2$ species E) which also does not react. The exit stream #3 contains $H_2 O$, $C_6 H_{10} O_5$, $C_6 H_5 Cl O_2$ (species F, also known as CMF), HCl, LiCl and $C_2 H_4 Cl_2$

Material Balance

The species balance for any species i for the above reactor shown in Fig 1 is

$$-(M_i)_1 - (M_i)_2 + (M_i)_3 = R_i, \quad i = A, B, \dots, F \quad (1)$$

Here R_i is the rate of production of species i . The notation $(M_i)_j$ is the molar flow rate of species i in the j^{th} stream. Based on experimental data we conservatively estimate that the fractional conversion of cellulose (species B) is

$$\xi_B = \frac{(M_B)_1 - (M_B)_3}{(M_B)_1} = 0.66 \quad (2)$$

The constraints on the stoichiometry are given by

$$\sum_{j=1}^5 N_{ji} R_j = 0 \quad (3)$$

where N_{ji} is the composition matrix for the *reacting species* given by

$$N_{j,i} = \begin{pmatrix} 0 & 6 & 0 & 6 \\ 1 & 10 & 2 & 5 \\ 0 & 5 & 1 & 2 \\ 1 & 0 & 0 & 1 \end{pmatrix} \quad (4)$$

The columns represent species A,B,C,F, the rows represent atomic species C, H, O, Cl . Solving Eq. 3 we get the constraints on the production rates R_i which are

$$\begin{aligned} R_A &= -R_F \\ R_B &= -R_F \\ R_C &= 3 R_F \end{aligned} \quad (5)$$

The molar flow rates per unit time entering to the reactor are specified as follows

$$\begin{aligned} C_6 H_{10} O_5 : & 1.5 / 162 = 0.00925926 \\ HCl : & 98.235 / 36.46 = 2.69432 \\ H_2 O : & 167.28 / 18 = 9.29333 \\ LiCl : & 15 / 42.39 = 0.353857 \end{aligned} \quad (6)$$

The total molar flow rate is $(M_T)_1 = 12.350766$ mol/time

For our calculation we will assume basis for the inlet flow rate of 100 mol/hr. We can readily solve the species balances Eq. 6 in conjunction with Eq. 5 to obtain the following composition for stream #3

$$\begin{aligned} (M_A)_3 &= 21.7655 \text{ mol / hr} \\ (M_B)_3 &= 0.025489 \text{ mol / hr} \\ (M_C)_3 &= 75.3914 \text{ mol / hr} \\ (M_D)_3 &= 2.865 \text{ mol / hr} \\ (M_F)_3 &= 0.0494787 \text{ mol / hr} \end{aligned} \quad (7)$$

The species rates of production are

$$\begin{aligned} R_F &= 0.04948 \text{ mol / hr}, \quad R_A = R_B = -R_F \\ R_C &= 0.148436 \text{ mol / hr} \end{aligned} \quad (8)$$

Energy Balance

For our reactor we can write the following energy balance

$$\left(\sum_{i=1}^4 M_i H_i \right)_1 + (M_E H_E)_2 - \left(\sum_{i=1}^6 M_i H_i \right)_3 = -\dot{Q} \quad (9)$$

Here $(H_i)_j$ is the partial molar enthalpy of the i^{th} species in the j^{th} stream and $-\dot{Q}$ is the net rate of heat input into the reactor. Now the last term of the LHS of the energy balance can be rearranged using the species balances (see Eq. 1) to obtain

$$\sum_{i=1}^4 [(H_i)_1 - (H_i)_3] (M_i)_1 + [(H_E)_2 - (H_E)_3] (M_E)_2 - \Delta H_{rxn} R_F = -\dot{Q} \quad (10)$$

For simplicity we assume that all streams behave ideally and that the temperature of the streams is $T=65^\circ\text{C}$. Thus the energy balance becomes

$$-\Delta H_{rxn} R_F = -\dot{Q} \quad (11)$$

Here ΔH_{rxn} is the heat of reaction evaluated at T=65°C. To determine the heat of reaction we use the following heats of formation at standard conditions and ideal heat capacities at standard conditions.

Heats of formation

$$\begin{aligned} \text{HCl : } & \Delta H_A^0 (T = 25^\circ\text{C}) = -167.2 \text{ kJ/mol} \\ \text{C}_6 \text{H}_{12} \text{O}_6 : & \Delta H_B^0 (T = 25^\circ\text{C}) = -1267.8 \text{ kJ/mol} \\ \text{H}_2 \text{O} : & \Delta H_C^0 (T = 25^\circ\text{C}) = -285.8 \text{ kJ/mol} \\ \text{C}_6 \text{H}_5 \text{O}_2 \text{Cl} : & \Delta H_F^0 (T = 25^\circ\text{C}) = -227.05 \text{ kJ/mol} \end{aligned} \quad (12)$$

To determine the heat of reaction at T=65°C, we use

$$\begin{aligned} \Delta H_{rxn} &= \Delta H_{rxn}^0 + \Delta C_p (65 - 25) \\ \Delta C_p &= (-C_{pA} - C_{pB} + 3 C_{pC} + C_{pF}) \end{aligned} \quad (13)$$

Ideal heat capacities

$$\begin{aligned} \text{HCl : } & C_{p,A} = 29.56 \text{ J/mol}\cdot\text{K} \\ \text{C}_6 \text{H}_{12} \text{O}_6 : & C_{p,B} = 198.2 \text{ J/mol}\cdot\text{K} \\ \text{H}_2 \text{O} : & C_{p,C} = 33.65 \text{ J/mol}\cdot\text{K} \\ \text{C}_6 \text{H}_5 \text{O}_2 \text{Cl} : & C_{p,F} = 132.95 \text{ J/mol}\cdot\text{K} \\ \text{O}_2 : & C_{p,O_2} = 29.36 \text{ J/mol}\cdot\text{K} \\ \text{CO}_2 : & C_{p,CO_2} = 39.41 \text{ J/mol}\cdot\text{K} \end{aligned} \quad (14)$$

Note : because of the uncertainty in determining the heat of formation for cellulose we have used glucose as a substitute for cellulose in the energy calculations.

From the energy balance Eq. 11, we find

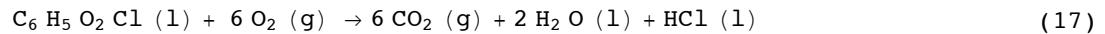
$$\dot{Q} = 18.6596 \text{ kJ/hr} \quad (15)$$

Thus from the heat balance gives

$$\dot{Q} = 18.6596 \text{ kJ/hr} \quad (16)$$

Since $\dot{Q} > 0$, this means that the reaction is endothermic and we need to supply heat to the reaction to maintain isothermal operation. It is of interest to determine if heat of combustion of the CMF in stream #3 exceeds this value, and if so by how much.

The heat of combustion of species F in stream #3 is given by



$$\Delta H_{c,CMF}^0 = 6 \Delta H_{f,CO_2}^0 + 2 \Delta H_{f,H_2O}^0 + \Delta H_{f,HCl}^0 - \Delta H_{f,CMF}^0 \quad (18)$$

Substituting in the heats of formation we find

$$\begin{aligned} \Delta H_{c,CMF}^{65^\circ\text{C}} &= \Delta H_{c,CMF}^0 + \Delta C_p (65 - 25) \\ &= -2871.78 \text{ kJ/mol} \end{aligned} \quad (19)$$

And based on our material balance the molar flow rate of CMF is

$$(M_F)_3 = 0.0494787 \text{ mol/hr} \quad (20)$$

Thus the potential thermodynamic energy in the form of CMF produced by the reaction is

$$\Delta H_{c, \text{CMF}}^{65^\circ\text{C}} (M_F)_3 = -142.092 \text{ kJ / hr} \quad (21)$$

Note a negative heat of combustion implies that energy is produced by the combustion reaction. The ratio of heat added to the reactor to energy potential of CMF is therefore

$$\frac{\text{Thermodynamic energy of CMF}}{\text{energy supplied to the reactor}} = \frac{142.092}{18.6} = 7.6393 \quad (22)$$

References

Thermodynamic data used in the above calculations was taken from several sources: Reklaitis(1983), Sandler(2006), and the software package ChemDraw. The calculations described above are routine in chemical engineering and are described by Sandler (2006).

G. V. Reklaitis, *Introduction to Material and Energy Balances*, John Wiley & Sons, 1983

S. I. Sandler, *Chemical, Biochemical and Engineering Thermodynamics*, John Wiley & Sons, 2006