Solvothermal Production of Biofuels from Fructose

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STRUCTURE

- Biofuel components: definition & advantages.
- Production of 2,5-DMF from HMF.
- Production of HMF from C6 sugars.
- Future Work.
Asymmetric Transfer Hydrogenation

fructose

5-hydroxymethylfurfural

2,5-dimethylfuran

Dehydration
Why 2,5 DMF?

- High boiling point [92°C]; 14°C higher than ethanol’s (78°C).
- High energy density [30 kJ cm\(^{-3}\)]; 40% higher than ethanol’s.
- High Octane Number [RON = 119]; close to that of gasoline.
- Immiscible with water: no absorption of moisture & easier to blend with gasoline than ethanol.
- Similar combustion properties to gasoline; thus adoptable with current spark-ignition engine technologies.
- Dual-injection strategy offers efficient and flexible use of biofuels, whilst still using gasoline.
- Production of DMF does not require energy crops.
Catalytic Hydrogenation of 5-HMF in Formic acid – Triethylamine Mixture to produce 2,5 Dimethyl furan (DMF).
Selection of Catalyst & Reagents

- Ru, Rh & Ir are best catalysts for Asymmetric Transfer Hydrogenation (ATH). Ru (II) proved most successful for aldehydes & ketones.

- Metal catalyzed ATH reactions were conducted in the mixture of HCOOH (FA) & tri-ethylamine (NET<sub>3</sub>), where the mix acts both as solvent & reductant.

- FA/NET<sub>3</sub> mix forms a complex with Ru(II), which improves conversion and accelerates the reaction.

- This work extends the use of catalyst/reagents combination from aldehydes & ketones reactions to the ATH of 5-HMF.
### Experimental Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ( T, , ^\circ C )</td>
<td>100 - 240</td>
</tr>
<tr>
<td>Reaction Time ( t, , h )</td>
<td>1 - 10</td>
</tr>
<tr>
<td>( FA: Et_3 ) ratio</td>
<td>1:1 – 4:1</td>
</tr>
<tr>
<td>Ru/C catalyst dosage, g</td>
<td>0.05 – 5.0</td>
</tr>
<tr>
<td>([HMF]_0, , M)</td>
<td>0.2 – 1.4</td>
</tr>
<tr>
<td>Agitation speed, rpm</td>
<td>100 - 700</td>
</tr>
</tbody>
</table>

\([HMF]_0 = 0.8 \, M, \, t = 4 \, h; \, Ru/C (5 \, wt%) = 0.1g; \, FA+Et_3 \, volume = 25mL; \, FA:TEA = 5:2, \, rpm = 300, \, T = 210 \, ^\circ C\)
The observed decrease after 210°C was attributed to further conversion of DMF to other side-products.

- T = 210°C gave the best HMF conversion of 97.3% & DMF yield of 90.6%.
The Effect of FA/Et₃ Ratio

- **FA** is the H donor in this reaction.
- **Et₃** is a base, used in organic synthesis.
- **FA/Et₃** mix facilitated the H transfer process by acting as reductant.

- 5:2 ratio gave 93.8% HMF conversion & 92.1% DMF yield.
**The Effect of Ru/C Dosage**

- Ru (II) forms a complex with FA/Et₃ mix, thus excess Ru (II) offers no advantage.

- DMF yield is a function of [HMF]/unit mass of catalyst. Thus, as mass of catalyst increases above 0.1g, HMF/DMF ratio decreases and so does the yield.
Conclusions (1)

- 97.3% HMF conversion, giving DMF yield of 92.1% was successfully achieved in a batch reactor operating at optimum reaction conditions.

- Best reaction conditions are: 210°C, 0.8 M HMF, $FA/Et_3$ molar ratio of 5/2 using 0.1 g of $Ru (II)$, 300rpm, for 4h reaction time.

- $FA/Et_3$ mixture combined with $Ru (II)$ form a green solvent-catalyst mix to enhance the production of DMF from HMF by ATH.
Hydration of Fructose to produce 5-HMF using Deep Eutectic Mixture $p$-TSA+ChCl ($p$-toluene sulfonic acid + Choline Chloride)
Selection of Catalyst & Reagents

- Brønsted acidic deep-eutectic mixture dehydration of fructose to 5-HMF.

- The use of ChCl/$p$-TSA played a dual role both as hydrogen bond donor & catalyst for the dehydration reaction, thus obviating the addition of an external acid.
# Experimental Conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>50 - 110</td>
</tr>
<tr>
<td>Reaction time, min</td>
<td>10 - 120</td>
</tr>
<tr>
<td>Feed mass ratio, %</td>
<td>2.5 - 100</td>
</tr>
<tr>
<td>DES ratio, %</td>
<td>1:0.5, 1:1, 1:1.5, 1:2</td>
</tr>
</tbody>
</table>

1. $T = 80^\circ$C, $t = 60$ min, Feed mass ratio = 5 %, DES ratio = 1:1.
2. Weight percentage fructose in feed.
3. Mixing molar ratio [ChCl:p-TSA].
Effect of mass feed ratio

- 5HMF yield % decreased with increased fructose mass ratio.
- 5HMF is rehydrated by the presence of water produced from the dehydration of fructose.

- The lowest yield was 20.5% at feed ratio of 100%. High fructose concentration could result in unwanted side reactions.

- Change of the sample colour to a darker brown by increasing fructose ratio was observed.
**Effect of temperature**

- Fructose conversion increased with temperature from 77.1% at 50 °C to 99% at 110 °C.

- 5HMF yield remained steady ~ 65% up till 70 °C then increased to 70.6% at 80 °C.

- 5HMF selectivity decreased with temperature, from 84.3% at 50 °C to 51.1% at 110 °C. This is subsequent to decrease in yield caused by formation of side products at higher temperatures.
- maximum 5HMF yield of 90.7% was obtained at 1:1 DES molar mixing ratio. It decreased to 58.4% when the DES molar mixing ratio was increased to 1:1.5.
Conclusions (2)

- DES mix of ChCl/$p$-TSA is a promising catalytic solvent mixture for the dehydration of fructose to 5HMF, giving high yields and selectivity.

- The best yield was obtained 90.7%; at feed ratio of 2.5w%, DES mixing molar ratio of 1:1, 80 °C and 1h.
Future Plans

- **Science-based investigations**
  - Investigations into the reaction pathway(s) for ATH and hydration.
  - Catalyst reusability studies.

- **Engineering-based investigations**
  - From batch to continuous systems.
  - Product separation & purification.
  - Combining both processes in one continuous process.
  - Product characterisation studies (combustion characteristics & engine performance, etc…)
Thanks for your attention! Questions?