A Novel Ionic Liquid Process for Conversion of Renewable Biomass into Petrochemical Intermediate

Wei Liu
Pacific Northwest National Lab
Richland, WA

Presentation at the 13th Annual Green Chemistry & Engineering Conference
College Park, MD
June 25th, 2009
Acknowledgment

▸ Colleague at Pacific Northwest National Lab
  John Holladay, Allan Cooper, Heather Brown, Richard Zheng

▸ CRADA partner – UOP LLC
  Timothy Brandvold, Joseph Kocal, Sharry Lynch

▸ Financial support by USDA under grant #68-3A75-7-613
Objective

- Develop an economically-viable process for direct catalytic conversion of biomass to 5-hydroxymethylfurfural (HMF) as a key intermediate and a flexible platform for producing chemicals and fuels

- Feedstock with increasing technical complexity
  - Fructose
  - Raw sugars
  - Cellulose
Background – why 5-hydroxymethylfurfural (HMF)?

- HMF has an aromatic-type ring structure and active functional groups on two sides
- A number of hydrocarbon molecules can be derived from HMF
- An important analogue to today’s petrochemical industry is paraxylene (PX) to terephthalic-acid (TA) product chain

\[ \text{PX} \xrightarrow{O_2 - H_2O} \text{TA} \]

2,5-furandicarboxylic acid (FDCA)
HMF is an extremely attractive bio-based platform for chemicals and fuels

- HMF is of interest since the 1890’s and a lot of synthesis work has been done. *Kunz (1993) and Lewkowski (2001)*
- Products derived from HMF have a wide range of value from fuels, petrochemicals, to specialty chemicals. *Bicker et al. 2003; Werpy & Petersen 2004; Gruter & Dautzenberg 2007; Huber et al. 2005.*

**Diagram:**
- **Biomass** → **Raw sugar** → **HMF**
  - + Chemical
  - + H₂
  - + O₂ + organic acids, anhydride or alcohol

**Products:**
- **Furandicarboxylic acid (FDCA)**
- **Terephthalic acid**
- **Hydroxymethylfuran**
- **Esters or ethers**
- **Hydrocarbons**
- Specialty chemicals in agricultural, consumer, and pharmaceutical industries
- Thermo-resistant polymers
  - *Polyester*
  - *Polyamide* (Others)
- Fuel additives
- Liquid fuel (gasoline, diesel)
Advantage and challenge to make HMF from biomass feedstock

Simple, efficient conversion stoichiometry:

HMF is produced by dehydration of three H2O molecules from sugar

There are many possible byproducts:

HMF has to be separated out of the mixture in an efficient way
Sugar was dissolved by an ionic liquid (IL).

High HMF yield was obtained by addition of a soluble catalyst into IL under atmospheric pressure and moderate temperatures (80-140°C) at reasonable reaction time (~h).

CrCl2 catalyst was the most effective for conversion of glucose to HMF.
HPLC separation of water extract of a reacted product mixture

- HMF is the dominating reaction product
- Ionic liquid is eluted out first
Innovations to address some fundamental problems for a practical ionic liquid process

Benefits with ionic liquid:

- regarded as a green solvent because of its low volatility
- ability to dissolve sugars at certain solubility levels and present some unique catalysis attribute

Challenges associated with ionic liquid:

- high cost, very high compared to the solvents being used in current commodity production processes, such as aromatics extraction in refinery.
- high viscosity, low mass transfer rate

Current approaches:

- Discover low-cost ionic liquids
- Improve reactor designs to achieve high yield and high throughput
- Develop an efficient separation process scheme to produce pure HMF and recover ionic liquid (>99%) for reuse
Process flow diagram of a nearly complete “green” process for continuous HMF production

Ionic liquid and water are used as primary working solvents

Feedstock
Fructose
Glucose
or Cellulose

Reactor I

Reactor II

Mixer

Filtration

Adsorption separation column

Drying

Clear solution

Rejected heavy byproduct (ionic liquid + catalyst loss)

Recovered water

Purge gas

Recovered water

Byproduct

HMF

Make up IL + catalyst

Refrigerated stream

IL + catalyst + un-converted feed

Water to recovery

Mixer

Adsorption separation column

Drying

Recovered water

Recycle stream

IL + catalyst + un-converted feed

Water to recycle

Recovered water

Reactor I

Reactor II

Drying

Drying

Drying

Drying

Mixer

Drying

Drying

Drying

Make up IL + catalyst

Ionic liquid and water are used as primary working solvents
Production and application chains of aromatics (BTX) and \textit{para}-xylene (PX) from petroleum

- Petroleum → Fractionation → Desulfurization → Catalytic reforming → Chemical feedstock
- Aromatic separation → Benzene → Zeolite catalytic conversion → Toluene
- C8 aromatic → Xylene isomer
- Paraxylene + O2 → High octane gasoline blend
- PTA → Thermo-resistant polymers

• Polyester
## Comparison of proposed HMF production to incumbent para-xylene (PX) production

<table>
<thead>
<tr>
<th></th>
<th>PX production</th>
<th>Proposed HMF process</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock</strong></td>
<td>Heavy (C7-C9) Naphtha</td>
<td>Raw sugars, non-food grade</td>
</tr>
<tr>
<td><strong>Catalytic conversion</strong></td>
<td>1) Catalytic reforming (naphtha→aromatics)</td>
<td>Sugars to HMF in ionic liquid with soluble catalysts</td>
</tr>
<tr>
<td></td>
<td>2) Xylene isomerization and ethylbenzene (EB) conversion (both at 20 - 40bar of H₂ gas, 300-500°C)</td>
<td>(80-200°C, atmospheric)</td>
</tr>
<tr>
<td><strong>Separation</strong></td>
<td>PX from xylene isomers and EB</td>
<td>HMF from the catalyst/ionic liquid, and un-converted sugar</td>
</tr>
<tr>
<td><strong>Separation technology</strong></td>
<td>Distillation + crystallization or distillation + SMB (chromatographic separation)</td>
<td>Filtration and adsorption (chromatographic separation)</td>
</tr>
<tr>
<td><strong>Main challenge</strong></td>
<td>Separation of xylene isomers</td>
<td>Recovery of catalyst and ionic liquid</td>
</tr>
<tr>
<td><strong>Recycle</strong></td>
<td>H₂ gas, meta-xylene, ortho-xylene, EB</td>
<td>Catalyst/ionic liquid, unconverted sugar</td>
</tr>
<tr>
<td><strong>Key Equipment</strong></td>
<td>2 high T and high P reactors</td>
<td>1 low T and ambient P reactors</td>
</tr>
<tr>
<td></td>
<td>1 Distillation column</td>
<td>1 Swing bed Adsorption</td>
</tr>
<tr>
<td></td>
<td>1 crystallization or SMB</td>
<td></td>
</tr>
</tbody>
</table>
Potential impact of HMF as substitute for petroleum-derived paraxylene

- There is a much larger gross margin for sugar-derived HMF than aromatics-derived PX
- Aromatics is valuable for high-octane gasoline blend
- During the PNNL-UOP CRADA, we will look at overall techno-economics of the process including sensitivity analysis of feedstock, catalysts, solvents, etc.

- If all polyester and polyamide product can be made of HMF,
  - Saving of 12 billion gallons/year of aromatics from petroleum-derived gasoline
  - One $billion/year CO₂ emission credit (at $35 per ton).
Fructose conversion profiles at different temperatures in a batch reactor

~10 wt % fructose loading in ionic liquid at start
- Fast reaction kinetics, 95% fructose disappeared in a few minutes at 110oC
- HMF is the dominating product and increases with fructose conversion
Most fructose is converted within a few minutes

HMF content in reacted mixture increases with initial fructose loading
## Screening of solid adsorbents on high throughput combinatorial test apparatus

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Simulated mixture with [EMIM]Cl ionic liquid</th>
<th>Simulated mixture with new ionic liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Zeolite series (Z)</td>
<td><a href="#">Feed A: 1% Glucose / 0.5% Levulinic acid / 3.5% HMF / 95% ionic liquid.</a></td>
<td><a href="#">Feed A: 7.3% HMF, 12.7% H₂O, 80% ionic liquid.</a></td>
</tr>
<tr>
<td>• Carbon series (C)</td>
<td><a href="#">Feed B: 1% Fructose / 0.5% Levulinic acid / 3.5% HMF / 95% ionic liquid.</a></td>
<td><a href="#">Feed B: 0.5% glucose, 19.4% H₂O, 80% ionic liquid.</a></td>
</tr>
<tr>
<td>• Silica series (S)</td>
<td><a href="#">Feed C: 0.5% Fructose / 0.25% Levulinic acid / 1.75% HMF / 50% water / ionic liquid.</a></td>
<td></td>
</tr>
<tr>
<td>• Polymeric resin series(R)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

*Note: [EMIM]Cl (1-ethyl-3-methylimidazolium chloride) is a common ionic liquid used in organic synthesis.*
Adsorption breakthrough curve of adsorbent column
a model mixture of HMF, Fructose, and ionic liquid

Selecting HMF adsorption

Fructose
HMF

Time (min.)

wt%
Production of HMF from raw sugars is an attractive conversion route to substitute petroleum-derived petrochemicals with renewable biomass

- Efficient conversion chemistry - “Simple” dehydration reaction
- Higher product value than fuels
- Significant impact on reduction of foreign oil dependence and greenhouse gas emission

A lower cost ionic liquid system has been discovered to provide fast reaction kinetics (~10 min) and high HMF selectivity (>90%) with fructose feedstock.

A promising adsorbent material has been identified for selective adsorption of HMF from the ionic liquid reaction mixture.

Development of an ionic liquid catalytic process for HMF production is on progress