Hydrothermal Conversion of Lignocellulosic Biomass to Biofuels and Valuable Chemicals
Hydrothermal Conversion

HTC 101

Biomass

Water

Heating
Hydrothermal Conversion

- At 200-400 °C, 4-20MPa, water is still liquid.
- At this state, water can catalyze both acidic and basic reactions because self-dissociation of water to H+ and OH- is enhanced.

- When the temperature of water is close to supercritical point (374 °C), the phase boundary between liquid and gas disappears, and then all reactions are enhanced by the homogenous media.
- Due to these special catalytic properties of hot water, biomass HTC to bio-oil calls a great interest, but still not well studied.
- Critical Point at 374°C
- In the subcritical region, ionic reactions are enhanced, while in the supercritical region – free radical reactions are enhanced.
Advantages of Hydrothermal Conversion of Lignocellulosic Biomass to biofuel

- Lignocellulosic biomass
  - Most abundant feedstock
  - Low cost feedstock compared, can be zero for waste biomass like wood residue, manure, etc.
  - High yield crops (e.g. energy crops) identified
- Wet feedstock without predrying
- A thermochemical process that does not need to separate cellulose from lignin
- Can produces biogas and biooil depending on conditions
Comparison of HTC with other technologies

<table>
<thead>
<tr>
<th>Technologies</th>
<th>Conditions</th>
<th>Time</th>
<th>Main Products</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic treatment</td>
<td>Ambient T and P</td>
<td>&gt; 20 days</td>
<td>CO₂, Nitrate, N₂O</td>
<td>No bioenergy</td>
</tr>
<tr>
<td>Anaerobic treatment</td>
<td>Ambient T and P</td>
<td>~15 days</td>
<td>CH₄, CO₂</td>
<td>Slowly</td>
</tr>
<tr>
<td>Gasification/pyrolysis</td>
<td>400~600 °C</td>
<td>Several minutes</td>
<td>CH₄, H₂, CO, CO₂</td>
<td>Predrying required</td>
</tr>
<tr>
<td>HTC</td>
<td>250 to 350 °C</td>
<td>0 to 60 min</td>
<td>Bio-oil and CH₄ &amp; H₂</td>
<td>Without predrying</td>
</tr>
</tbody>
</table>
Hydrothermal Conversion of Cattle Manure to Biofuels
Much cattle manure in Canada

• In Canada, cattle manure production: 0.5 million tons per day \(^\text{[1]}\).
• Meanwhile, more cattle manure is produced in per hectare land.

**Air Pollution from Cattle Manure**

- **Toxic gas---Ammonia**
- **Greenhouse gases--- CH\textsubscript{4} & N\textsubscript{2}O**

**Ammonia emission sources in Canada, 2005**
(Envirenment Canada, Ammonia, 2009).

CH\textsubscript{4} and N\textsubscript{2}O emission from cattle manure in Canada.

Water pollution from cattle manure

- Pollutants---- Ammonia, Nitrate, and Phosphorus

- Water pollution---- Eutrophication [5]

Cattle manure

Ammonia

Nitrate

Phosphorus

Surface water

Underground water

Eutrophication

Soil pollution from cattle manure

- Soil pollution--- Acidification

Overall Objectives of the Research Program

- Cattle manure waste
  - Hydrothermal conversion
    - To produce bioenergy (biogas and bio-oil)
    - To reduce pollution and odor

- Literatures have shown that swine manure, wood and grass can be converted to bio-oil by hydrothermal conversion (HTC) [7-8].

- *No report on cattle manure in public literature*
Overall Experimental Procedures

Cattle manure → Aqueous solutions

1.8 L reactor (260~340 °C)

Gases

Liquid products

Solids

Micro-GC

Compositions (H₂, CO, CO₂, <C₅)

Glucose /Cellulose → Aqueous solutions (with catalysts)

70 mL tubular reactor (275~320 °C)

Micro-GC

Compositions

GC/MS

Yields

Bio-oil

Extraction

Yields

GC/FID

Compositions
Hydrothermal Gasification of Cellulose and Cattle Manure
Effects of Alkalinity and Phase Behaviour
Cellulose

- Cellulose (a polymer of glucose) is the most abundant biopolymer globally, accounting for $1.5 \times 10^{12}$ tonnes of annually available biomass. (Klemm et al, 2005)

\[
\begin{align*}
6CO_2 + 6H_2O &\rightarrow 6O_2 + C_6H_{12}O_6 & \text{Photosynthesis} \\
C_6H_{12}O_6 + 6H_2O &\rightarrow 12H_2 + 6CO_2 & \text{Steam Reforming} \\
12H_2O &\rightarrow 12H_2 + 6O_2
\end{align*}
\]
Hydrothermal Gasification

Effects

Catalysts
- Alkali salts (Control pH)
- Pt group metals (Steam Reforming)

Physical effects
- Heating Speed → Gas Yield
- Supercritical > Subcritical
Cellulose Decomposition

Pathway I

Pathway II

Pathway III

OH⁻: Alkali Catalyzed reaction
H⁺: Acid Catalyzed reaction
LD: Low density reaction
HD: High density reaction
Results by Knezivic et al (2009) show not all intermediates gasified as easily…
Research Objectives and Overview

• Determine effects of alkali salt (Na$_2$CO$_3$) concentration on the gasification of cellulose in the presence of a Platinum group metal.
• Determine effect of headspace fraction on the hydrothermal gasification of cellulose in the presence of a Platinum group metal.
• Effect of alkali and a Pt group metal on the hydrothermal gasification of a mixed biomass, cattle manure.
Experimental Setup I

- Two batch reactors were constructed from SS 316 tubing. The reactor volume was 69mL.
- Reactors heated by Muffle Furnace

- Gas composition determined by micro gas chromatography (micro-GC)

- Liquid phase composition determined by gas chromatography with a flame ionization detector (GC-FID)
Effects of Alkalinity with 5% Pt/Al₂O₃ catalyst

\[ Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \]
Sodium Carbonate (alkaline pH) increase both carbon dioxide and hydrogen production.
As more acetic acid was produced, increasing amounts of methane were found in the solution.

Highest yields of acetic acid (and methane) were found in 0.1M sodium carbonate solution.
Liquid Phase Analysis

0M Na$_2$CO$_3$ – More Furfural Alcohol (HMF)

500 mM Na$_2$CO$_3$ – More Dihydroxyacetone and Lactic Acid
Similar but more variable results were obtained using a 5% Pt/SiO₂ catalyst.
Alkalinity Effects with 1% Pt/Al₂O₃

With a higher loading of 1% Pt/Al₂O₃, carbon monoxide became an important product under low alkalinity.
Effect of Headspace Fraction

- As headspace fraction increased, hydrogen increased.
- Magnitude of increase was dampened when sodium carbonate was added.
- HMF suppressed as the headspace fraction increased
- At highest headspace fraction, butyric acid most abundant
Experimental Setup II

- 1.8 L batch reactor (SS316), Parr Instrument Company
- Gas composition was analyzed by micro-GC
Experiments with Cattle Manure show synergy between the RuCl₃ and the basic NaOH catalysts.
Discussion – Effects of Alkalinity

• Three Distinct Regions of Alkalinity
  1. Region I – HMF suppression
  2. Region II – Change to Basic Solution pH
  3. Region III – Formation of Bicarbonates from Carbon Dioxide
• Peak in Hydrogen when using Pt/SiO$_2$ catalyst occurred at higher alkalinity (200 mM as opposed to 75 mM)
• Liquid Phase changes from HMF (0M Na$_2$CO$_3$), to lactic acid and dihydroxyacetone
• Methane likely to be related to the decarboxylation of acetic acid
• Significant interaction between RuCl$_3$ and NaOH catalysts
Discussion – Effects of Headspace Fraction

• Higher headspace fractions (vapour fractions) enhanced gas production, the effect was most significant without the addition of sodium carbonate.
• In general, decreasing headspace fraction resulted in a decreased concentration of detected chemicals.
• Under the most successful conditions (92.8% headspace fraction, no Na$_2$CO$_3$), butyric acid relatively significant chemical in the liquid phase.
Conclusions

• More facile pathways for gasification available under high headscape fraction, without the addition of alkali salt sodium carbonate.
• Acetic Acid appears to be a likely source for produced Methane
• Decomposition of Cellulose through HMF produces little gas
• Decomposition pathway has large impact on gasification yield and composition
Hydrothermal Conversion of Cattle Manure to Biooil
Laboratory Procedure

Cattle manure

+ water

HTC reaction system
(1.8L; 310 °C; 15min)

Liquid Products

Extraction

CH₂Cl₂
C₄H₁₀O
CHCl₃

Evaporation

Bio-oil
Bio-oil
Bio-oil

Separation

Comparison

Yields
Heating values
Structures
Effects of solvents on bio-oil yields

(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of CO)
Effects of solvents on elemental compositions of bio-oil

(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of CO)
### Effects of solvents on heating values of bio-oil

<table>
<thead>
<tr>
<th>Bio-oil</th>
<th>Heating value (MJ/kg)</th>
<th>Standard derivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil (extracted by CH₂Cl₂)</td>
<td>36.08</td>
<td>2.06</td>
</tr>
<tr>
<td>Bio-oil (extracted by CHCl₃)</td>
<td>35.55</td>
<td>0.99</td>
</tr>
<tr>
<td>Bio-oil (extracted by C₄H₁₀O)</td>
<td>36.56</td>
<td>0.18</td>
</tr>
<tr>
<td>Cattle manure</td>
<td>15.2</td>
<td>0.73</td>
</tr>
</tbody>
</table>
Effects of solvents on structures of bio-oil

UV-VIS analysis spectra of bio-oil extracted by different solvents

(Conditions: 125g of cattle manure, 500mL of water, 6g of NaOH, process gas of 0 psig of CO, and residence time of 15 min)
Effects of temperatures on bio-oil/bio-gas yields

(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of N$_2$)
Effects of pressures on bio-oil yields

Figure 5. Effect of initial conversion pressure on biooil yield
(Conditions: 125 g of cattle manure, 500 g of water, 0.5 mol of NaOH, temperature of 310 °C, residence time of 15 min, and process gas of N2)
Effects of processing gases on bio-oil yields

Figure 6. Effect of process gases on bio-oil yield

(Conditions: 125g of cattle manure, 500g of water, 0.5 mol of NaOH, temperature of 310 °C, and 0 psig process gas)
Effects of mass ratios of cattle manure to water on bio-oil yields

Figure 7. Effect of cattle manure to water mass ratios on bio-oil yields

(Conditions: T = 310 °C, 0.5 mol of NaOH, residence time of 15 min, and 0 psig initial pressure of CO)
Effects of processing gas

![Graph showing the effects of processing gas on bio-oil yield across different temperatures. The graph plots bio-oil yield (mass % of volatile content of cattle manure) against temperature (°C). The graph includes lines for CO, H₂, N₂, and Air, each with a different symbol.]
## High heating values of bio-oils

<table>
<thead>
<tr>
<th>Energy types</th>
<th>Heating value (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-oil from HTC</td>
<td></td>
</tr>
<tr>
<td>290 °C</td>
<td>35.07</td>
</tr>
<tr>
<td>300 °C</td>
<td>36.10</td>
</tr>
<tr>
<td>310 °C</td>
<td>35.74</td>
</tr>
<tr>
<td>325 °C</td>
<td>34.28</td>
</tr>
<tr>
<td>Bio-ethanol</td>
<td>29.8</td>
</tr>
<tr>
<td>Coal</td>
<td>32.5</td>
</tr>
<tr>
<td>Gasohol E85</td>
<td>33.1</td>
</tr>
<tr>
<td>Bio-diesel</td>
<td>41</td>
</tr>
</tbody>
</table>
Bio-oil from cattle manure: Comparison with petro liquid fuels

The main components of HTC bio-oil were carboxylic acids, aldehydes, and phenol derivatives.

The main components of petroleum are alkanes.

GC analysis of HTC bio-oil and fossil liquid fuels
Bio-oil from cattle manure: Stability

- The color of HTC bio-oil became darker with time.
- More residual solids were formed over time.
- During storage, the concentrations of aromatic chemicals and phenol derivatives decreased, while aldehydes and ketones increased.

(It was stored at room temperature. HTC bio-oil was produced from cattle manure)
Hydrothermal Conversion of Cellulose to Biooil
Bio-oil from cellulose

- No alkanes were detected in HTC bio-oil from cellulose.
- The compositions of HTC bio-oils varied with the initial pH levels of aqueous reaction media.
  - At pH<7: HMF and levulinic acid
  - At pH=7: HMF, acetic acid and lactic acid
  - At pH>7: Carboxylic acids

GC analysis of HTC bio-oils produced from cellulose at pH=3, 7 and 14
**pH value changes vs. initial pH level**

- Reaction pathways of HTC changed during alkaline HTC

Comparison of initial and final pH levels of alkaline HTC of cellulose to bio-oil

- **A Zone**
  - Cellulose
  - Carboxylic acids
  - Weak alkaline solutions
  - Final pH < 7
  - Bio-oil: HMF + carboxylic acids

- **B Zone**
  - Cellulose
  - Carboxylic acids
  - Strong alkaline solutions
  - Final pH > 7
  - Bio-oil: carboxylic acids
Hydrothermal Conversion of Cellulose, Glucose to Alkanes
Motivation: Previous bio-oil from cattle manure or cellulose is not “oil”

<table>
<thead>
<tr>
<th></th>
<th>HTC bio-oil</th>
<th>Catalytic HTC bio-oil</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compositions</strong></td>
<td>Acids, aldehyes, aromatic chemicals</td>
<td>Alkanes (Petroleum)</td>
</tr>
<tr>
<td><strong>Chemical stability</strong></td>
<td>Unstable</td>
<td>Stable</td>
</tr>
<tr>
<td><strong>Separation</strong></td>
<td>Organic solvent extraction</td>
<td>Voluntary separation from aqueous solutions</td>
</tr>
<tr>
<td><strong>Use as a liquid fuel</strong></td>
<td>Upgrading needed</td>
<td>Directly used by car engine</td>
</tr>
</tbody>
</table>

- Need to improve the quality of HTC bio-oil by catalytic HTC
Alkanes from CHTC of glucose with hydrogen

- Alkane yields increased with increasing H$_2$ pressure.
- More heavy gaseous alkanes (C$_3$H$_8$, C$_4$H$_{10}$) were produced with higher H$_2$ pressure.
- The chemical composition was the same as that of liquefied petroleum gas (LPG)

0.5 g glucose, 3 g water, 0.5 g Pt/Al$_2$O$_3$, 1.5 h reaction time and at 265 °C.
C\textsubscript{5-9} liquid alkanes were detected in liquid products.

But, much more C\textsubscript{1-4} alkanes were formed than C\textsubscript{5-9} alkanes.
Alkanes from CHTC of glucose (cont...)

• Problems with CHTC of glucose to alkanes

• Few liquid alkanes were formed from glucose.

\[
\text{Glucose (C6)} \rightarrow \text{Gaseous alkanes (C< 5)}
\]

• External H\(_2\) was required for CHTC.

\[\text{H}_2 \text{ is required for hydrogenation reaction}\]
A new reaction process was proposed to produce liquid alkanes from cellulose with *in situ* $\text{H}_2$.
Illustration of In-situ-H$_2$-APR process

Before conversion at room temperatures:
- Reactor
- N$_2$
- Water
- Cellulose

During conversion at high temperatures (300 °C):
- Heating the reactor
- Steam

1. In situ H$_2$ produced by steam reforming of cellulose in steam phase.
   (catalyzed by pH>7)
   (catalyzed by pH<7)
3. In situ H$_2$ + Alkane precursors

Alkane bio-oil (liquid alkanes)
Results: Alkanes from CHTC of cellulose

- Effects of volumetric ratios of input water to reactor
  - Too little or too much water inhibited alkane bio-oil formation.
  - The alkane bio-oil mainly consisted of nonane, octane and heptane.
**Results: Alkanes from CHTC of cellulose**

- Effects of pH levels of aqueous reaction media
  - Alkane bio-oil yields were further increased by weak alkaline conditions.
  - pH/reaction pathway changes mainly led to this improvement.

![Graph showing Alkane yields (carbon mmol) vs pH (3, 7, 7.5, 8, 9)]

- Initial pH > 7
- In situ H₂ (catalyzed by pH > 7)
- Alkane precursors (catalyzed by pH < 7)
- Final pH < 7

In-situ-H₂-APR of cellulose to alkane bio-oil under weak alkaline conditions
Possible explanation to petroleum formation

- In-situ-H$_2$-APR: a possible explanation for petroleum formation

<table>
<thead>
<tr>
<th>Observations</th>
<th>Petroleum formed in sea</th>
<th>Bio-oil formed by In-situ-H$_2$-APR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil Main components</td>
<td>alkanes</td>
<td>alkanes</td>
</tr>
<tr>
<td>Associated with natural gas?</td>
<td>Yes</td>
<td>Yes (syngas)</td>
</tr>
<tr>
<td>Environment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metals</td>
<td>Ni, Fe, V, Cu</td>
<td>Pt, Ni (catalysts)</td>
</tr>
<tr>
<td>Inorganic chemicals</td>
<td>SiO$_2$/Al$_2$O$_3$ (the main components of earth crust)</td>
<td>SiO$_2$/Al$_2$O$_3$ (catalyst supports)</td>
</tr>
<tr>
<td>pH</td>
<td>7.5-8.4 (sea)</td>
<td>7.5 (aqueous media)</td>
</tr>
<tr>
<td>Steam</td>
<td>Geothermal heating</td>
<td>External heating</td>
</tr>
<tr>
<td>Liquid water</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Conclusions

1. HTC bio-oil was different from petroleum, in terms of chemical composition.

2. HTC bio-oil compositions were unstable and changed with time.

3. But, by CHTC (especially, In-situ-H\textsubscript{2}-APR), alkane bio-oils were produced from glucose and cellulose. Their compositions are quite same as liquefied petroleum gas and gasoline, respectively.

4. Via catalytic HTC, therefore, a quick production of petroleum from renewable/carbon-neutral biomass would become feasible.
Biomass is Biological Material Derived from Living Organisms Recently

Absorb CO₂ and solar energy

Three types of biomass:

• Lignocellulosic and starch-based plants (e.g. Wood, grass, livestock manure)

• Triglyceride-producing plants: e.g. canola, soybeans, sunflower, safflower

• Algae are another source of triglycerides as well as carbohydrates and lignin.
Transportation Energy Needs to Remain Liquid to Fit in Existing Tanks and Be Transportable

- World has ~ 800 million vehicles, and adds 50 million vehicles per year
- Biomass is the only renewable source for renewable transportation fuel.
- Biofuel is the solution before electrical car becomes affordable and reliable.
- Biofuel may remain important since other sectors demands electricity rather than fuel.
Henry Ford originally designed the Ford Model T to run completely on ethanol. But then crude oil became more cheaply available.
Platforms for Biofuel Production

- **SynGas**: Syngas (CO + H₂)
- **BioOil**: Biofuel (Including tars, acids, chars, alcohols, aldehydes, esters, ketones and aromatic)
- **VFA**: VFA (Acetate, propionate, Butyrate and so on)
- **Sugar**: Glucose(C6), xylose(C5), sucrose and so on

**Ligno cellulosic Biomass**
- Gasification
  - Pilot
- Pyrolysis and Liquefaction
  - Pilot
- Hydrolysis
  - Commercial
- Anaerobic Digestion
  - Commercial

**Oily biomass**
- Extraction
  - Commercial
- Edible oil
- Transesterification
  - Biodiesel
- Hydrotreating
- Renewable diesel

**Commercial**
- Pilot
- Commercial
- Pilot

**SynGas and Sugar platform**: two actively researched field for the liquid fuel
## Challenges to existing biofuels

- Mostly from edible biomass
- High cost: 90% of $$$ goes to separation
- Mixed with petroleum gasoline

<table>
<thead>
<tr>
<th>Bio-oil</th>
<th>Feedstock</th>
<th>Pretreatment</th>
<th>Use as liquid fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-ethanol</td>
<td>Food crops</td>
<td>Not required</td>
<td>1. Needing to be mixed with petroleum before use</td>
</tr>
<tr>
<td></td>
<td>(e.g. Corn, wheat)</td>
<td></td>
<td>2. Not used in cold weather</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(low vapour pressure of ethanol)</td>
</tr>
<tr>
<td>Bio-diesel</td>
<td>Food crops</td>
<td>Predrying biomass</td>
<td>1. Not used in cold weather</td>
</tr>
<tr>
<td></td>
<td>(e.g. Canola oil)</td>
<td></td>
<td>(gelling at low temperatures &lt; -10 °C)</td>
</tr>
</tbody>
</table>
New Generation Biofuels: Cellulosic Feedstock...
Sustainable Production of Biofuels:
An Integrated Biomass Production System