Catalytic Microwave-Assisted Biomass Pyrolysis for Distributed Biofuels and Chemicals Production

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OUTLINE

• Brief background and introduction – why microwave-assisted pyrolysis
• Mobile microwave-assisted pyrolysis system development
• Catalytic microwave assisted pyrolysis
• Non-thermal assisted catalytic reforming
Nature of Current Cellulosic Biomass Production

• Distributed production
• Transporting bulky biomass from scattering production sites to a central processing facility has been a key barrier to biomass utilization
Cellulosic Ethanol

- 40-50 million gallons/year cellulosic ethanol plants: cost over $300 million to build, need over 2,000 tons biomass per day.

- Furthermore, compared with corn ethanol production, additional processing costs are needed to convert cellulosic feedstock to fermentable sugars, which would raise feedstock-associated costs to as high as 70–80% of the final product cost, in addition to other technical and management challenges.
Gasification and Fischer–Tropsch Liquid Biofuels

- 40-50 million gallons/year liquid fuel plants: cost about $1 billion to build, need over 3,000-4,000 tons biomass per day, and expensive to operate due to catalyst cost and safety issue related to high pressure and high temperature of the process, in additional other technical and management challenges.
Large Scale Processes

• High capital investment
• High operation technicality
• High feedstock transportation and storage costs
Distributed Biomass Conversion Systems (DBCS) - A “Smaller” Solution
Bale to Barrel DBCS

One round hay bale
diameter = 5ft
length = 5ft

As fertilizer back to field for biomass production

Power for conversion

Char
1,500,000BTU

H₂, CO, CH₄
Gas
2,250,000BTU

Biocrude
1.2 barrel
500lb, 6.7ft³,
75lb/ft³
3,750,000BTU
562,500BTU/ft³

1,000lb, 100ft³
10lb/ft³
7,500,000BTU
75,000BTU/ft³

Can be implemented on average size farms or small villages
Distributed Biomass Processing Scheme
Microwave Assisted Pyrolysis (MAP) System

Non-condensable gas

Feedstock

Feedstock

Power Generator

Microwave Generator

Char

Bio-oil
Microwave-Assisted Pyrolysis (MAP) System
Why MAP?

- Microwave heating is uniform and easy to control;
- It does not require high degree of feedstock grinding (e.g., large chunk of wood logs) and can handle mixed feedstock (e.g., municipal solid wastes);
- The conversion products (pyrolytic gas and bio-oils) are cleaner than those from gasification and conventional pyrolysis because our process does not have to use biomass powder and does not require agitation and fluidization;
- The syngas produced has higher heating value since it is not diluted by the carrying gas for fluidizing the biomass materials;
- Exothermic reactions (chemical reaction that releases energy and microwave plasma effect) can be maintained through careful control of the process parameters and therefore MAP is energy efficient; and
- Microwave heating is a mature technology and development of microwave heating system for biomass pyrolysis is of low cost.
- Scalable, portable, mobile – distributed conversion of biomass
Microwave Pyrolysis of Aspen
Canola Seed Press Cake
a. conventional heating approach

b. Microwave heating approach

c. Pyrolysis front development with conventional heating  d. Pyrolysis front development with microwave heating
Particle size effect in MAP

<table>
<thead>
<tr>
<th>Size (diameter, inch)</th>
<th>1/8</th>
<th>3/8</th>
<th>1/2</th>
<th>5/8</th>
<th>3/4</th>
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<tbody>
<tr>
<td>Oil yield (wt%)</td>
<td>55.15</td>
<td>60.40</td>
<td>60.52</td>
<td>55.06</td>
<td>54.25</td>
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<td>Char yield (wt%)</td>
<td>18.96</td>
<td>16.94</td>
<td>18.91</td>
<td>15.36</td>
<td>17.11</td>
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</table>

Note:
Feedstock: Poplar Wood
Microwave Power: 1250 Watt
Municipal Solid Wastes
MSW Pyrolysis Products
Microwave heating characteristics for different materials:
Power level calibration:

- Microwave Power 1250 Watt
  - Level 10, 100%
  - Water: 1000 grams
  - Slope=4.16 Sec./K(°C)

- Microwave Power 1250 Watt
  - Level 6, 80%
  - Water: 1000 grams
  - Slope=5.74 Sec./K(°C)

- Microwave Power 1250 Watt
  - Level 6, 60%
  - Water: 1000 grams
  - Slope=7.82 Sec./K(°C)

- Microwave Power 1250 Watt
  - Level 4, 40%
  - Water: 1000 grams
  - Slope=17.30 Sec./K(°C)
Temperature profile of bulk corn stover during microwave-induced pyrolysis
Continuous microwave assisted pyrolysis system development
Mobile Microwave Assisted Biomass Pyrolysis System
Old MacDonald Had a Pyrolysis Doohickey

Mobile biofuel refineries provide sustainable energy for farms

A hundred years ago, threshing machines chugged from farm to farm across the plains, separating stalk from grain and turning raw crops into valuable commodities. By sharing the machine, farmers could boost productivity without owning the prohibitively pricey equipment. Today, that business model could work for a new product: biofuel.

Biofuel from farm waste is a promising alternative to oil, but it’s too expensive for any one farmer to make alone. Manufacturing cellulosic ethanol, the most common biofuel made from waste, costs up to $3 a gallon—going mostly to shipping raw materials and the enzymes used to break them down. Six years ago, Roger Ruan, a biosystems engineer at the University of Minnesota, began designing a smaller, simpler way to convert biomass to biofuel, using a process called pyrolysis.

The technique usually involves grinding biomass into a powder and heating it to break it into its chemical components, which are then turned into fuel. The pulverizing ensures that the material heats evenly but is energy-hungry and slow. To eliminate the grinding step, Ruan added a microwave generator, which nukes chunks of organic material from the inside out. Off-the-shelf tech helps keep the price below that of conventional systems.

Ruan commissioned a Chinese factory to build a camper-size prototype, and this fall he’ll hitch it to a pickup and hit the roads of rural Minnesota to conduct a field study. “We’ve got the choir signed on,” says Linda Meschke, a Minnesota farmer who is lining up farms for the pilot study, “and a tentative congregation watching to see what happens next.”

—MAGGIE KOERTH-BAKER

HOW TO TURN TRASH INTO POWER

1. TURN UP THE HEAT
   Biomass is sealed inside an oxygen-free chamber and heated with microwaves to 800°F, breaking the material into solid and gas components.

2. CLEAN OUT THE DUSTBIN
   The burned solids, called char, collect in a tray and can be used as fertilizer. The remaining mix of gases flows up into a condenser column.

3. SQUEEZE THE GAS
   Half of the gas is condensed into a liquid bio-oil, which can substitute for heating oil or industrial petroleum.

4. START AGAIN
   The remaining gas is stepped off and burned to produce electricity to power the system. For every pound of biomass, farmers get half a pound of bio-oil and a quarter pound of char, both combustible gas.

June 11: The World Cup of soccer begins, featuring broadcasts in 3-D for the first time. Put on your special glasses and tune in to ESPN to watch up to 25 3-D matches.
Pyrolytic biooil differential yields

microwave power 1250 Watt
Feedstock: corn stover
Retention time effect in MAP

Feedstock: Corn Stover, Power level: 1250 Watt
GC-MS analysis
Biorefining of Biooils and Liquefied Biomass

Polyester + DGG Composite

Polyester film

Polyester + fibers Composite

Polyurethane foam

Wood Adhesive

Biofuel
Catalytic pyrolysis

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<tr>
<th>Catalyst Group</th>
<th>Light Oil</th>
<th>Heavy Oil</th>
<th>Water Phase Residue</th>
<th>Char</th>
<th>Gas</th>
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<td>Nitrates</td>
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<td>28.00</td>
<td>29.72</td>
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<td>Metal-oxides</td>
<td>21.08</td>
<td>16.95</td>
<td>16.57</td>
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<td>Kalium chloride</td>
<td>9.05</td>
<td>12.93</td>
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<td>Nickel (II) nitrate</td>
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<td>10.04</td>
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<td>Magnesium sulfate</td>
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<td>No catalyst</td>
<td>33.54</td>
<td>32.01</td>
<td>32.01</td>
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Pyrolysis fraction yields (mass% of total biomass input) from runs with different catalysts and catalyst groups added to the *aspen* pellets.
Typical Compositions by Nitrates such as \((\text{MgNO}_3)_2, \text{Fe(NO}_3)_3\)

Chlorides help to improve and simplify the composition of bio-oil, compared with nitrates and sulfates.

Typical Compositions by Sulfates such as \(\text{Na}_2\text{SO}_4, \text{MgSO}_4\)

Typical Compositions by Chlorides such as \(\text{AlCl}_3, \text{MgCl}_2, \text{ZnCl}_2\) and \(\text{FeCl}_3\)
Total ion chromatograms from GC-MS analysis of pyrolytic oils from corn stover when different catalysts were used (8g/100g biomass). FF: furfural.
Microwave Pyrolysis in a Continuous System

Effect of temperature and catalyst on products (Dry basis)

<table>
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<tr>
<th>Temperature /°C</th>
<th>Catalyst</th>
<th>Bio-oil /%</th>
<th>Char /%</th>
<th>Gas /%</th>
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<td>475</td>
<td>-</td>
<td>42.0</td>
<td>35.1</td>
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<td>375</td>
<td>-</td>
<td>39.6</td>
<td>38.9</td>
<td>21.5</td>
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<tr>
<td>325</td>
<td>-</td>
<td>38.5</td>
<td>43.6</td>
<td>17.9</td>
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<tr>
<td>375</td>
<td>Catalyst A2</td>
<td>38.8</td>
<td>41.3</td>
<td>19.9</td>
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Sample: Corn cob
Feeding rate: 20Kg/h
Size: <1.2cm

Addition of catalyst A2 helps corn cob pyrolysis to produce a chemical-furfural.
Co-pyrolysis of corn stover and scrap tire

Corn stover : tire = 1:1
Sun Dried Algae
## Comparison of fossil oil and bio-oils from MAP of *Chlorella* sp. algae and wood

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<thead>
<tr>
<th>Properties</th>
<th>Bio-oils</th>
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<td></td>
<td><em>Chlorella</em> sp.</td>
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<td>Elemental analysis (wt.%)</td>
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<tr>
<td>C</td>
<td>65.40</td>
</tr>
<tr>
<td>H</td>
<td>7.84</td>
</tr>
<tr>
<td>N</td>
<td>10.28</td>
</tr>
<tr>
<td>O</td>
<td>16.48&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>30.7&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Density (kg/L)</td>
<td>0.98&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Viscosity, at 40 °C (Pa s)</td>
<td>0.06</td>
</tr>
<tr>
<td>pH</td>
<td>7-9.5</td>
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</tbody>
</table>

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<sup>a</sup> Data from other sources.  

<sup>b</sup> Calculated from elemental analysis.  

<sup>c</sup> Measured experimentally.  

<sup>d</sup> Density measured at room temperature.
# Elemental composition of algae bio-oil

## Sample Info:

<table>
<thead>
<tr>
<th>Client Name</th>
<th>New Generation Biofuels</th>
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<tbody>
<tr>
<td>Sample Description</td>
<td>Algae Biodiesel</td>
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<td>NABL Identification #</td>
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## Test Conditions

<table>
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<th>Date Analyzed</th>
<th>Sept 15 2010</th>
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<tr>
<td>Instrument</td>
<td>CE Elantech FlashEA 1112 CHNS/O Analyzer</td>
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<td>Reference Standard</td>
<td>BBOT</td>
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## Results

<p>| | |</p>
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<tr>
<td>%Carbon:</td>
<td>64.12032318</td>
</tr>
<tr>
<td>%Hydrogen:</td>
<td>8.272509257</td>
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<tr>
<td>%Nitrogen:</td>
<td>9.7</td>
</tr>
<tr>
<td>%Sulfur:</td>
<td>0</td>
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<tr>
<td>%Oxygen:</td>
<td>12.01842054</td>
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</table>

## Data Interpretation

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<thead>
<tr>
<th>% Composition accounted for:</th>
<th>94.11125298</th>
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<tbody>
<tr>
<td><strong>Compound formula:</strong></td>
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<tr>
<td>Carbon</td>
<td>5.343</td>
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<tr>
<td>Hydrogen</td>
<td>8.205</td>
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<tr>
<td>Nitrogen</td>
<td>0.693</td>
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<tr>
<td>Sulfur</td>
<td>0.000</td>
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<tr>
<td>Oxygen</td>
<td>0.751</td>
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## Algae bio-oil and blend

<table>
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<th>Test Description</th>
<th>Test ID / Method</th>
<th>Result</th>
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<tr>
<td>10-140</td>
<td>pH</td>
<td>A23 / SOP 4-4-01-A23</td>
<td>8.37</td>
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<tr>
<td>10-140</td>
<td>Sulfated Ash</td>
<td>F6 / ASTM D874</td>
<td>0.0088%</td>
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<tr>
<td>10-140</td>
<td>Kinematic Viscosity @ 40°C*</td>
<td>A5 / ASTM D445</td>
<td>45.57 cSt</td>
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<td>10-140</td>
<td>Flash Point (Cleveland Open Cup)*</td>
<td>A1 / ASTM D92</td>
<td>80°C ▼</td>
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<tr>
<td>10-140</td>
<td>Pour Point*</td>
<td>A32 / ASTM D6749</td>
<td>-13°C</td>
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<td>Carbon Residue</td>
<td>F10 / ASTM 4530</td>
<td>8.22%</td>
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<td>Ultimate Analysis (CHONS)</td>
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<td>See attached sheet</td>
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<td>10-140</td>
<td>Specific Gravity @ 15.5°C/60°F</td>
<td>A40 / ASTM D1298</td>
<td>1.029</td>
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<td>10-140</td>
<td>Gross Heat of Combustion</td>
<td>A51 / ASTM D240</td>
<td>30.43 MJ/kg</td>
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<td>AN 10850</td>
<td>Water and Sediment</td>
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<td>Gross Heat of Combustion</td>
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<td>23.51 MJ/Kg</td>
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Hydrothermal pretreatment

- Reduce nitrogen contents in algal feedstock by hydrolysis of protein; reduce energy inputs required for algae dewatering and drying.
Continuous Hydrothermal Biomass Pyrolysis System
High Throughput Continuous Catalytic Hydrothermal Conversion System
<table>
<thead>
<tr>
<th>Pretreated algae</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Ash</th>
<th>C retention</th>
<th>N retention</th>
<th>HHV (MJ/kg)</th>
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<td>63.6</td>
<td>8.3</td>
<td>4.8</td>
<td>12.8</td>
<td>43.8</td>
<td>21.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>63.1</td>
<td>8.1</td>
<td>4.4</td>
<td>12.2</td>
<td>43.3</td>
<td>19.2</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>67.5</td>
<td>9.1</td>
<td>3.6</td>
<td>13.5</td>
<td>39.6</td>
<td>13.4</td>
</tr>
</tbody>
</table>

Pretreated algae samples had higher carbon contents and enhanced heating values under all reaction conditions and N removal of over 75% at 200 °C−225 °C for 30–60 min.
• 75% of N removal was achieved.
• 73%-99% of fatty acids retention was obtained, which means very minor amount of lipids loss during pretreatment.
• Pretreated algae were more hydrophobic, had much lower water holding capacity, and were much easier to be dried and stored with less biological deterioration.
The pyrolytic bio-oil from pretreated algae contained less N-containing compounds and the bio-oil contained mainly long-chain fatty acids (C14–C18, over 45%) which can be more readily converted into hydrocarbon fuels in the presence of simple catalysts.
Wastewater to algae to biofuels system
• Acquire Commercially Available Catalysts

• Acquire Raw Materials for Making Biorefining Catalysts

• Synthesize Biorefining Catalysts
  - Hydrotreating/Hydrocracking Catalysts
  - Metathesis Catalysts
Acquire/Catalysts Synthesis

Catalyst Used for Bio-oil Conversion
Catalysts Synthesis

Zeolite Precursor Synthesis

Zeolite Precursor Synthesis
Catalyst Screening Microreactor Setup
Pressurized hydro-processing system
# Catalyst Used for Bio-oil Conversion

<table>
<thead>
<tr>
<th>Catalyst A</th>
<th>Catalyst B</th>
<th>Catalyst C</th>
<th>Catalyst D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Ru / Al₂O₃ (self-prepared)</td>
<td>Ni-Co/C (self-prepared)</td>
<td>CBV-400 (Zeolyst International)</td>
<td>CBV-780 (Zeolyst International)</td>
</tr>
<tr>
<td>Catalyst E</td>
<td>Catalyst F</td>
<td>Catalyst G</td>
<td>Catalyst H</td>
</tr>
<tr>
<td>Ni/Alumina/Silica</td>
<td>Al₂O₃</td>
<td>Zeolite mixed with Al₂O₃</td>
<td>Cu-CBV 400 (Self prepared)</td>
</tr>
</tbody>
</table>
Canola oil with catalysts

- Co-Mo/Al₂O₃
- Co-Mo/ZSM-5
- Catalyst A

- 1-Pentene, 2-methyl-
Hydrotreating Canola oil

Gasoline

Co-Mo/C, 600°C, Canola Oil, 0.5 Hr
HDO of wood derived oil

Aspen biooil

Reaction temperature = 400°C

Reaction temperature = 500°C

Reaction temperature = 600°C

Benzene
Toluene
p-Xylene
Phenol
Phenol, 2-methyl
HDN/HDO of N-O containing compound

Feedstock

Reaction temperature=400°C

Reaction temperature=500°C

Reaction temperature=600°C
Hydrogenation of algal pyrolytic biooil

Catalyst: W-Mo/Al2O3
At 350 C, 1000 psi, 0.5-2 ml/min
HDO/HDN of algae derived oil

- Benzene
- Benzene, 1,3,5-trimethyl-
- Benzene, 1,2,4,5-tetramethyl-
- Benzene, 12,3,4-tetramethyl-
- Benzene, pentamethyl-
- Benzene, 3-ethyl-1,4,5-tetramethyl-
Catalytic upgrading

Co-pyrolysis oil from Corn stover : tire = 1:1

Catalyst: Ni-Mo/Al2O3
At 350 C, 1000 psi, 0.5-2 ml/min
Oleic acid conversion over catalysts

![Bar chart showing conversion of oleic acid over catalysts A1 to A26. The conversion values range from 80% to 100% for each catalyst.](chart.png)
Liquid product yield of Canola oil over various catalysts

![Bar chart showing the yield of Canola oil over various catalysts](chart.png)
HydroDeOxygenation (HDO) of Model Compounds

(Syn-Biooil and Aspen biooil+SynBiooil Mixture)
HDO of N-O containing compound solution
HDN of N-O containing compound
Heating values (HHV, measured by bomb calorimeter, Cal/g)

High heating value of feedstocks

<table>
<thead>
<tr>
<th>Oleic acid</th>
<th>Lineolic acid</th>
<th>Canola oil</th>
<th>JP-8</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>9446.5</td>
<td>9451.1</td>
<td>9310.2</td>
<td>10982.3</td>
<td>10794.6</td>
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</tbody>
</table>

High heating value of products

<table>
<thead>
<tr>
<th>A-6</th>
<th>A-7</th>
<th>A-8</th>
<th>A-23</th>
<th>A-27</th>
</tr>
</thead>
<tbody>
<tr>
<td>9651.7</td>
<td>10023.6</td>
<td>9856.5</td>
<td>9554.0</td>
<td>9609.4</td>
</tr>
</tbody>
</table>

Note: The heating value of gasoline from internet, the other were measured in the lab.
Biomass (yellow) is pyrolyzed in the quartz tube and vapors go through the catalysts bed (blue) and then analyzed by GC/MS.
Microwave Assisted Catalytic Pyrolysis
Direct catalytic pyrolysis of algae

- Aromatic hydrocarbons are the major pyrolysis products (74% yield) with the use of catalyst A.
- Acetic acid, furfural, N-containing compounds and fatty acids were converted to aromatics.
NTP-Assisted Catalytic Reforming

- Catalytic reforming has become a useful way to produce biofuels and other chemicals
- Conventional catalytic reforming usually requires high temperature and high pressure
- Catalysts can perform well at low temperature and pressure with assistance of Non-thermal Plasma (NTP).
NTP Reactor

Energetic electrons, ions, molecules, highly reactive radicals, etc. generated though electrical discharge in syngas to help synthesize liquid fuels and chemicals
Pulsed Corona Discharge Reactors

Silent discharge reactors

NTP Reactors
NTP Reactors for Catalytic Reforming
Cross section of the NTP reactor

- Cupper foil (ground)
- Quartz tube (dielectric barrier)
- Stainless steel tube (anode)
- Catalysts

FT-IR
GC-MS
Ionizations of Nitrogen and Hydrogen with NTP-Assisted Catalysis

- $N_2 \rightarrow 2N^+$
- $H_2 \rightarrow 2H^+$
- $N^+ + H^+ \rightarrow NH^+$
- $NH^+ + H^+ \rightarrow NH^2+$
- $NH^2+ + H^+ \rightarrow NH^3+$
Example - Ammonia Production

• 12% + ammonia produced at 150 °C and atmospheric pressure
• Potential to reach higher concentration with further optimization of catalysts and conditions
• Low capital, operation, and maintenance costs
NTP Ammonia synthesis different catalysts.

\( V_{N_2} : V_{H_2} = 1 : 3 \), \( N_2 \) and \( H_2 \) total flow rate 60ml/min, voltage 5000V, frequency 8000Hz.)
FT-IR spectrum of NTP reforming of N$_2$, CO, H$_2$ and/or H$_2$O vapor.
FT-IR spectroscopy of NTP reforming of CO and H₂O vapor.
Summary

- The microwave-assisted catalytic pyrolysis technology has great potential for large scale demonstration and commercialization.
- The innovative NTP assisted catalytic reforming processes show many advantages over conventional high temperature and high pressures processes.
- The pyrolysis time (i.e. retention time) plays an important role in oil quality and liquid product yield;
- Particle size is not a significant issue in terms of oil quality (composition) and product yield distribution;
- Co-pyrolysis of solid wastes such as scrap tires/plastics and biomass is practically feasible;
- With the aid of catalyst, the quality (heating value, O and N content, etc.) of the pyrolytic oil (bio-oil) can be significantly improved.
About the Center

The center is formed under the umbrella of IREE. Full Membership is open to the entire faculty of the University of Minnesota. Affiliate Membership is open to the biobased community outside the university.

Objectives

- To establish a network of multidisciplinary researchers, state and federal government officials, and private-sector organizations and entities who share the same interest in development and use of biobased production technologies
- To identify opportunities in production and marketing of bioenergy and biomaterials
- To identify public and private funding sources and facilitate research programs
- To incorporate biobased production information in existing courses and curricula
- To create a plan to educate the public and promote the use of bioenergy and biomaterials

Research
- Technology Innovation
- Outreach & Education

Bio-Economy

BioEnergy

BioMaterials

BioChemicals

Sustainability

Http://biorefining.cfans.umn.edu
Acknowledgments:


Funding Agencies:
Questions?

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