Pyrolysis of Lignocellulosic Materials for the Production of Bio-fuels, Bio-chemicals and Bio-char

Manuel Garcia-Perez

Washington State University

Northwest Wood-Based Biofuels + Co-Products Conference

Seattle, April 28-30, 2014
Pyrolysis Scheme to Produce Bio-char and Heat

Pyrolysis Scheme to Produce Bio-char and bio-oil

BUSINESS MODELS
Concept 1: Slow Pyrolysis to produce heat and bio-char

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Liquid</th>
<th>Char</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow heating rates, large particles, large residence time of vapors</td>
<td>30 - 45 %</td>
<td>25-35 %</td>
<td>25-35 %</td>
</tr>
</tbody>
</table>
Main Feedstock used: **Woody Biomass**.

Main product: **Gardening and tree care**. Biochar has not made a substantial entry into large scale agricultural operations.

Average retail price: **$ 2.48/kg**.

Main equipment used: Varies from **micro-scale cookstoves to large scale industrial facilities**.

**Scientific research:** Number of peer-reviewed bio-char related publications increased nearly five-fold over the last five years\(^1\).

**Pyrolysis Companies by Sectors and Countries (IBI Survey)**

**Services Provided to the Bio-char industry**

---

Despite the growing interest in producing bio-char and heat, the lack of available information on clean designs hinders those interested in developing this industry. The inadequate flow of information for potential users forces the design of pyrolysis units to remain an art.

SLOW PYROLYSIS

Frequency of Pyrolysis Technology (IBI Survey)

Intermediate Pyrolysis Reactors

- **Mobile multi-heath furnace**
- **Rotary drum**
- **Moving bed vacuum Pyrolysis**

<table>
<thead>
<tr>
<th>Black is Green Pty Ltd</th>
<th>Amaron rotary drum reactor (Coates Engineering)</th>
<th>Vacuum Pyrolysis Reactor (Pyrovac)</th>
</tr>
</thead>
</table>
# SLOW PYROLYSIS

## Intermediate Pyrolysis Reactors

<table>
<thead>
<tr>
<th>Reactor Type</th>
<th>Company/Location</th>
<th>Website</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auger Pyrolysis</td>
<td>BiogreenR</td>
<td><a href="http://www.agritechproducers.com">http://www.agritechproducers.com</a></td>
</tr>
<tr>
<td>Auger torrefaction</td>
<td>Agri-Tech Producers</td>
<td><a href="http://www.agritechproducers.com">http://www.agritechproducers.com</a></td>
</tr>
<tr>
<td></td>
<td>International Tech Corporation</td>
<td><a href="http://www.internationaltechcorp.org/IT-info.htm">http://www.internationaltechcorp.org/IT-info.htm</a></td>
</tr>
<tr>
<td></td>
<td>eGenesis CR-2 pyrolysis unit</td>
<td><a href="http://www.egenindustries.com">http://www.egenindustries.com</a></td>
</tr>
<tr>
<td></td>
<td>Whitfield Bio-char LLC</td>
<td></td>
</tr>
</tbody>
</table>

## SLOW PYROLYSIS

- **Auger Pyrolysis**
- **Auger torrefaction**
- **BiogreenR**
- **Agri-Tech Producers**
- **International Tech Corporation**
- **eGenesis CR-2 pyrolysis unit**
- **Whitfield Bio-char LLC**
Frequency of type of organization leading bio-char projects (IBI survey)

- Research Institution: 45%
- Commercial Group: 19%
- Individual or Family: 12%
- Other/Youth Group/Government: 11%
- NGO: 8%
- Community Group: 5%

SLOW PYROLYSIS

SLOW PYROLYSIS is well suited for producing bio-char and heat/electricity from the Agricultural Wastes with high contents of alkalines.

Main Hurdles:

- The deployment of environmentally friendly slow pyrolysis technologies able to produce heat and bio-char (Technological constraints)
- Higher value products from bio-char have to be developed
- Lack of consumer awareness
- Access to financing
- Not possible to predict yield gains (lack of performance certification)
SLOW PYROLYSIS (RESEARCH)

- Carboxylic groups form rapidly, then Lactone Groups
- Oxidation Slows after first 10-20 minutes
- CEC increases strongly with oxidation
**Fast Pyrolysis**

Fast pyrolysis is a process in which very small biomass particles (less than 2 mm diameter) are heated at 450 – 600 °C in the absence of air/oxygen to produce high bio-oil yield (60-75 mass%).

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Liquid</th>
<th>Char</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>High heating rates, small particles, short</td>
<td>60-75 %</td>
<td>12-20 %</td>
<td>13-20 %</td>
</tr>
<tr>
<td>residence time of vapors</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FAST PYROLYSIS

Model of Biomass Economy Based on Pyrolysis and Rural Refineries

- Biomass
- Mobile Pyrolysis Unit
  - Crude Bio-oil
  - Bio-char
- Stationary Pyrolysis Unit
  - Bio-char
  - Crude Bio-oil
  - Bio-char
- Mobile Pyrolysis Unit
  - Rural Bio-oil refinery
  - Bio-char
  - Stabilized Bio-oil
    - (Potentially: 46,120 barrels/day)
    - (11.4 % of current consumption)
- Bio-plastics, lipids, ethanol, chemicals...

Petroleum or Oil Seed Refinery

Green Gasoline, Green Diesel and Jet Fuel

Potential Production
(11.4 % of Current WA Oil Consumption)

- 6,140 t/day of stabilized bio-oil

Petroleum Refineries
1. Tacoma (Oil US): 4,600 t crude oil/day
2. Anacortes (Tesoro): 14,400 t crude oil/day
3. Anacortes (Shell): 19,000 t crude oil/day
4. Ferndale (Conoco): 14,000 t crude oil/day
5. Cherry Point (BP): 30,000 t crude oil/day

Rural Bio-oil Refineries
- 300 t crude bio-oil/day
- 1,200 t crude bio-oil/day
- 2,400 t crude bio-oil/day

Potential Production of Stabilized Bio-oil: 6,140 t/day (46,120 barrels/day)
Potential per-capita of Stabilized Bio-oil: 6.9 barrels per day/1000 people
Current WA per-capita consumption: 60.4 barrels per day/1000 people
World per capita consumption: 31.7 barrels per day/1000 people

Assumptions: (1) Yield of crude bio-oil: 60 mass % of the biomass processed (2) Yield of stabilized bio-oils: 50 mass % of the crude bio-oil obtained
Fast Pyrolysis Reactors

The sand used to achieve high heating rates contaminates the bio-char and is the source of several technological problems.

Current technologies use high volumes of carrier gas and sand as heat carriers. High yields of oil (60-75 wt. %)

Are the designs that have been scaled up reliable enough or will they be replaced by new ones when bio-oil refineries are deployed?
EFFECT OF VAPORS RESIDENCE TIME INSIDE THE PYROLYSIS REACTOR (University of Twente)
EFFECT OF PARTICLE SIZE (C-Z Li, Monash University)

SEM Pictures of 1 mm beech wood particles

SEM Pictures of beech wood particles smaller than 80 micron

(1) Use of Intermediate Pyrolysis reactors without sand
(2) Two Step Pyrolysis to reduce grinding energy
(3) Two Step Condensation Systems to Separate C1-C4 molecules and water from bio-oil

Collaboration with Twente University (Netherlands) and Curtin University (Australia)
Performance of Auger Pyrolysis Reactor

FAST PYROLYSIS
Effect of Pyrolysis Temperature

Graphs showing the yield of liquid, solid, gas, and water as a function of temperature for different reactors (Auger, Fluidized Bed, Fixed-Bed) and feedstocks (Pine, Mallee, Beech).
1. High hydrogen consumption making the process cost-prohibitive to get 3 $/gallon of bio-fuel

2. No high value by-products are produced to make the plant economics viable

3. The fuel produced from the hydrotreatment of bio-oil is rich in aromatics and naphthalene but has low content of paraffins and iso-paraffins. This limits its application as a jet fuel.

Source of Figure: http://www1.eere.energy.gov/biomass/pdfs/pyrolysis_report_summary.pdf
### FAST PYROLYSIS

#### Chemicals that can be obtained from bio-oils

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic Acid</td>
<td>World Production: 7 million tons/year, potential price: 0.6 $/kg</td>
<td>Patel et al. 2006, Rasrendra et al. 2010</td>
</tr>
<tr>
<td>Aldehydes and ketones</td>
<td>Separation of aldehydes and ketones have been investigated by bio-coup</td>
<td>Vitasari et al. 2010, Resasco et al 2010</td>
</tr>
<tr>
<td>Alkylaromatics</td>
<td>Conversion using zeolites</td>
<td></td>
</tr>
<tr>
<td>Antioxidants</td>
<td>Antioxidant properties of lignin derived compounds</td>
<td>Garcia-Perez et al 2010</td>
</tr>
<tr>
<td>Asphalt paving substitution</td>
<td>Production of asphalt emulsions</td>
<td></td>
</tr>
<tr>
<td>Bio-carbon electrodes</td>
<td>Production of electrodes, calcinations at 1000 °C and graphitization at 2700 °C.</td>
<td>Mullaney et al. 2002, Cautinho et al. 2000</td>
</tr>
<tr>
<td>Coal dust suppression</td>
<td>The current product used to coat coal piles is a plasticizer that is bio-degradable and does not contaminate ground water</td>
<td>Mullaney et al 2002</td>
</tr>
<tr>
<td>Fertilizer</td>
<td>Amides, imines and mannich reaction products, are produced from the reaction of bio-oil functional groups (carbonyl, carboxyl, hydroxyl, phenolic and methoxyl) with ammonia, urea, and other amino compounds and can function as slow release organic fertilizers</td>
<td>Radlein et al. 2005</td>
</tr>
<tr>
<td>Food additives</td>
<td>Commercialized by Red Arrow Products and RTI. A new method for the separation of glycoaldehyde from pyrolysis oil via physical extraction has been reported by researchers from the Eindhoven University of Technology</td>
<td>Mohan et al. 2006, Czernik and Bridgwater 2004, Vitasari et al 2010</td>
</tr>
<tr>
<td>Glucose</td>
<td>Can be obtained by hydrolyzing hydrolyzable sugars (levoglucosan, cellobiosan)</td>
<td>Lian et al. 2010, Patel et al. 2006</td>
</tr>
<tr>
<td>S-hydroxymethyl furfural (HMF)</td>
<td>Attractive building block for further derivatization</td>
<td>Patel et al. 2006</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>By using demineralized cellulose, high yields of levoglucosan (up to 46 wt. %) and levoglucosenone (up to 24 wt. %) can be generated</td>
<td>Radlein et al (1999), Czernik and Bridgwater 2004</td>
</tr>
<tr>
<td>Methanol</td>
<td>Can be produced from the distillation of pyroligneous water</td>
<td>Emrich 1985</td>
</tr>
<tr>
<td>Pesticides</td>
<td>Significant activity against two bacteria and the Colorado potato beetle were shown using bio-oil derived from dried coffee grounds.</td>
<td>Bedmutha et al. 2011, Booker et al. 2010</td>
</tr>
<tr>
<td>Impermiabilizer</td>
<td>Black residue of tar distillation commercialized to impermiabilize ships.</td>
<td>Emrich 1985</td>
</tr>
<tr>
<td>Road de-icer</td>
<td>Calcium salts of carboxylic acids</td>
<td>Czernik and Bridgwater 2004</td>
</tr>
<tr>
<td>Surfactants</td>
<td>More than 10 commercial grades are used for ore flotation</td>
<td>Emrich 1985</td>
</tr>
<tr>
<td>Wood preservatives</td>
<td>Bio-oils can act as insecticides and fungicides due to some of the terpenoid and phenolic compounds present</td>
<td>Czernik and Bridgwater 2004, Mohan et al. 2008</td>
</tr>
</tbody>
</table>
Conversion of acetic acid contained in the aqueous phase collected in the second condenser into lipids
Hybrid Refining Technologies

Strategy for up-grading bio-oil (Brown 2010).

FAST PYROLYSIS
Old wood distillation industry’s bio-refinery concept (Klar and Rule 1925).
FAST PYROLYSIS

Simplified scheme which uses bio-oil/biochar slurries to produce Fischer-Tropsch (FT) syngas (Henrich et al. 2009).
Bio-refinery Concept based on Bio-oil Esterification (Radlein 2005). This concept is being studied by the group of Professor Chun-Zhu Li at Curtin University (Australia).
CONCLUSIONS

• **Two types of Pyrolysis Technologies can be developed (1)** Slow Pyrolysis units to produce bio-char and heat (electricity, mostly from Agricultural wastes) **(2) More selective** fast pyrolysis to produce bio-char and bio-oil. Bio-oil has to be further processed in a rural refinery to obtain stabilized **bio-oil compatible with existing petroleum refineries** and **high value chemicals**.

• Using **bio-char as a soil amendment** is one of the most promising methods for carbon sequestration. Implementing this method could provide a large market for the bio-char produced. However, **in order for this to be economically viable high value bio-chars with enhanced agronomical functions must be developed**.

• The development of **high value products** from **bio-oil** is critical for the survival, development and economic viability of the fast pyrolysis technologies identified.

• A balanced investment in the creation of new knowledge (**science**) in the design, testing and scale up of **new technologies** for pyrolysis reactors, bio-oil refineries, and **the development of new products** (from bio-oils and bio-char) which address the needs of the **market** are all critical for the deployment of a biomass economy based on pyrolysis technologies.
Acknowledgement

We would like to thank the funding agencies supporting my Research Program:

WASHINGTON STATE UNIVERSITY AGRICULTURAL RESEARCH CENTER
WASHINGTON STATE DEPARTMENT OF ECOLOGY
WASHINGTON STATE DEPARTMENT OF AGRICULTURE
SUN GRANT INITIATIVE, U.S. DEPARTMENT OF TRANSPORTATION, USDA
U.S. NATIONAL SCIENCE FOUNDATION
U.S. DEPARTMENT OF ENERGY
QUESTIONS?