ENERGY FROM BIOMASS AND WASTE:
IMPACT OF METAL SPECIES

*RAPSODEE Centre UMR CNRS 5302, Ecole des Mines Albi, France
**City College - The City University of New York, USA
*** Gaz Technology Institute - Des Plaines, Illinois, USA
OUTLINE

ENERGY FROM BIOMASS AND WASTE: IMPACT OF METAL SPECIES

1. Introduction to pyro-gasification of biomass and waste
2. Structure of pyro-gasification chars containing inorganics
3. Role of Inorganics (Metals)
   3.1. Role of Transition Metals
   3.2. Role of Alkali and Alkaline Earth Metals (AAEM)
4. Conclusions an Future works
1. Introduction to pyro-gasification of biomass and waste

Pyro-gasification for Energy/Materials Recovery from Waste and Biomass

- Energy recovery from waste/biomass results in reduction of volume of waste, low (or zero) net CO₂ emissions, and presents a distributed energy source

Pyro-gasification Process

- Pyro-gasification reactor
  - Solid Fuel (biomass, waste, RDF)
  - Gas (air, N₂, H₂O, CO₂)
- Reactor temperature: ~350-900°C
- Gas products (CO, CO₂, H₂, CH₄, and C₃’s) (syngas = CO + H₂)
- Tar (condensable organics)
- Catalyst
- Ash or char
- Energy Recovery
  - Fuel Cells
  - Gas turbines
  - Fuels and chemicals
  - To landfill
1. Introduction to pyro-gasification of biomass and waste

Reaction scheme for biomass and waste pyro-gasification

Gasifying agent: H₂O, CO₂ or O₂

Biomass or Waste

Drying

Pyrolysis

Char-M*: char with metal agglomerate at the surface

Tar

Char-M*

Gas
H₂, CH₄, CO, CO₂...

Gasification + side reactions

Tar
(Toluene,..)

Char/Ash

Gas

Gas cleaning

Char-M*: char with metal agglomerate at the surface
1. Introduction to pyro-gasification of biomass and waste

Challenges

✓ The cost of biomass processing must be decreased by designing new technologies and catalytic systems

✓ The decomposition of tar in Syngas

✓ Technological Challenges (Corrosion, fouling, …)
1. Introduction to pyro-gasification of biomass and waste

Main and side-reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
<th>Energy Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + H₂O → CO + H₂</td>
<td>*Steam gasification</td>
<td>+ 131 MJ/kmol</td>
</tr>
<tr>
<td>CO + H₂O ↔ CO₂ + H₂</td>
<td>* Water-gas shift (WGS)</td>
<td>- 41 MJ/kmol</td>
</tr>
<tr>
<td>C + CO₂ → 2CO</td>
<td>Boudouard</td>
<td>+ 172 MJ/kmol</td>
</tr>
<tr>
<td>C + O₂ → CO₂</td>
<td>Combustion</td>
<td>- 394 MJ/kmol</td>
</tr>
</tbody>
</table>

Examples of syngas end-uses and their approximate H₂/CO ratio requirements

<table>
<thead>
<tr>
<th>Syngas end-use</th>
<th>H₂/CO ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid oxide fuel cells (SOFC)</td>
<td>4.0 – 6.0</td>
</tr>
<tr>
<td>Gas turbine combustion</td>
<td>2.5 – 4.0</td>
</tr>
<tr>
<td>Fischer Tropsch (diesel fuels)</td>
<td>1.5 – 3.0</td>
</tr>
<tr>
<td>Fischer Tropsch – Fe and Co – based catalyst process</td>
<td>0.5 – 1.5</td>
</tr>
</tbody>
</table>
OUTLINE

ENERGY FROM BIOMASS AND WASTE: IMPACT OF METAL SPECIES

1. Introduction to pyro-gasification of biomass and waste

2. Structure of pyro-gasification char containing inorganics

3. Role of Inorganics (Metals)
   3.1. Role of Transition Metals
   3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

4. Conclusion an Future works
2. Structure of pyro-gasification char containing inorganics

Catalysts or inhibitors for pyro-gasification? Impact of syngas rate, reaction light off?

The rate of the gasification process is affected by the process conditions, and is catalysed/inhibited by a number of different species:

**Inorganics: Metals:**

- Alkali (M?): Li, Na, K
- Alkaline Earth (Often M²⁺): Mg, Ca, Be, Ba, Sr
- Transition: Ni, Pb, Zn, …
2. Structure of pyro-gasification char containing inorganics

Catalysts or inhibitors for pyro-gasification?

Small aromatic structural units, with the oxygen present mostly within heterocyclic and phenolic groups. The structural units are cross-linked by ether and olefinic linkages.

Metals:
- Alkali: Li, Na, K
- Alkaline Earth: Mg, Ca, Be, Ba, Sr
- Transition: Ni, Pb, Zn, ...

Structure of Char-M vs temperatures towards graphitic structures

Exposition of Carbon atoms

2. Structure of pyro-gasification char containing inorganics

Why is char a good catalyst?

- Char-M often considered a ‘low value’ product
- Opportunity to “valorize” Char-M

**Catalytic metals**

Char-M contains metals and minerals used as catalysts in many common processes

- Fe, Ni, Mg, Mn, Ca, Al, Na, K measured in Char-M

**Surface area & catalytic sites**

High porosity increases available catalyst sites

- Char-M contains micro-pores (d<2nm)

ESEM images

Char-M after heating to 900°C

Char-M from gasification with steam

Char-M after heating to 900°C
1. Introduction to pyro-gasification of biomass and waste
2. Structure of pyro-gasification char containing inorganics

3. Role of Metals
   3.1. Role of Transition Metals
   3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

4. Conclusion and Future works
## 3.1. Role of Transition Metals

### Composition in metals for various biomass and waste

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Wheat Straw*</th>
<th>Beech Wood*</th>
<th>Demol Timber</th>
<th>Phyto Remed</th>
<th>Sewage Sludge</th>
<th>Chicken Litter</th>
<th>Paper Sludge</th>
<th>Recov Fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal (mg kg⁻¹ dry basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>0.18</td>
<td>3.5</td>
<td>550</td>
<td>22</td>
<td>(10)</td>
<td>-</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>0.2</td>
<td>1.0</td>
<td>8</td>
<td>-</td>
<td>38</td>
<td>-</td>
<td>&lt;0.4</td>
<td>350</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9-12</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>3.0</td>
<td>2.5</td>
<td>1060</td>
<td>107</td>
<td>91</td>
<td>112</td>
<td>110</td>
<td>100</td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
<td>43</td>
<td>1080</td>
<td>70</td>
<td>330</td>
<td>71</td>
<td>310</td>
<td>450</td>
</tr>
<tr>
<td>Hg</td>
<td>0.06</td>
<td>0.12</td>
<td>10</td>
<td>8</td>
<td>2.7</td>
<td>-</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
<td>(73)</td>
<td>(2500)</td>
<td>-</td>
<td>950</td>
<td>596</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27</td>
<td>39</td>
<td>&lt;10</td>
<td>-</td>
<td>480</td>
</tr>
<tr>
<td>Pb</td>
<td>6</td>
<td>33</td>
<td>6300</td>
<td>55</td>
<td>159</td>
<td>-</td>
<td>160</td>
<td>480</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
<td>(15)</td>
<td>-</td>
<td>-</td>
<td>1318</td>
<td>209</td>
<td>470</td>
<td>170</td>
</tr>
</tbody>
</table>

3.1. Role of Transition Metals

Pyrolysis (N₂) of poplar wood contaminated with Ni, Cd, Zn

- Metals increase and accelerate the wood weight loss from 70 to 370°C and inhibit it from 370 to 900°C in a presence of N₂.
- 850°C: wood contaminated by Cd has the same weight loss as raw wood
  ⇔ Cd evaporation and not inhibitive effect from this point.
- No catalytic effect of Ni is observed in a presence of N₂
3.1. Role of Transition Metals

Gasification (CO₂) of poplar wood contaminated with Ni, Cd, Zn

- Zn inhibits gasification reactions more than Cd
- Cd and Zn are inhibitors of gasification reactions
- Ni catalyses gasification reactions
3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

Catalytic effect of alkali carbonates (M: Li, Na, K): Mechanisms

✓ CO₂ gasification (Bourdouart)

\[
\begin{align*}
M_2CO_3 + 2 C & \rightarrow 2 M + 3 CO \\
2 M + CO_2 & \rightarrow M_2O + CO \\
or M_2O + CO_2 & \rightarrow M_2CO_3 \\
C + CO_2 & \rightarrow 2 CO
\end{align*}
\]

✓ Steam gasification:

\[
\begin{align*}
M_2CO_3 + 2 C & \rightarrow 2 M + 3 CO \\
2 M + 2 H_2O & \rightarrow 2 MOH + H_2 \\
2 MOH + CO & \rightarrow M_2CO_3 + H_2 \\
2 C + 2 H_2O & \rightarrow 2 CO + 2 H_2
\end{align*}
\]

CO loop

Steam-to-carbon ratio: 0.8 to 1.5

✓ Syngas (CO+H₂)
✓ H₂
✓ CO

McKee DW.. Carbon 1982; 20: 59-66
3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

- Gasification of 14 biomass samples (including sawdust, bark, agricultural waste,...) Experimental conditions: 50kPa, 850°C
  Reactivity towards steam of 14 biomass chars with respect to the AAEM content
  Group I: [K]+[Na] > [Ca];
  Group II: [Ca] > [K]+[Na];
  Group III: high [SiO₂]

- Conversion of fir char with different catalysts under 100% CO₂ at 10°C/min temperature ramp
  Huang Yet al.; Biotechnology Advances 2009; 27: 568–572
3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

Catalytic performances: Catalyst testing for CH₄ cracking

Reaction: CH₄ (or Toluene) → C + H₂ (+intermediate hydrocarbons < C₆)
- CH₄ cracking is a reaction with few products
  → easier to compare performance of chars
- Experiments done in a thermo gravimetric analyzer (TGA)
  → enables continuous measurement of reaction via carbon deposition (mass gain)

Comparison to commercial catalysts

<table>
<thead>
<tr>
<th>Light off temperature (°C)</th>
<th>Char-M</th>
<th>Pt/Al₂O₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction extent (% mass gain)</td>
<td>20</td>
<td>11</td>
<td>6</td>
</tr>
</tbody>
</table>

Char catalyst lights off at a lower temperature than commercial metal catalyst

OUTLINE

ENERGY FROM BIOMASS AND WASTE: IMPACT OF METAL SPECIES

1. Introduction to pyro-gasification of biomass and waste
2. Structure of pyro-gasification char containing inorganics
3. Role of Metals
   3.1. Role of Transition Metals
   3.2. Role of Alkali and Alkaline Earth Metals (AAEM)

4. Conclusion an Future works
CONCLUSIONS and FUTURE WORKS

✓ Energy recovery from waste/biomass results in reduction of volume of waste, low (or zero) net CO$_2$ emissions, and presents a distributed energy source

✓ The rate of the gasification process is affected by the process conditions, and is catalysed/inhibited by a number of different species: Inorganics, Metals:
  - Alkali: Li, Na, K
  - Alkaline Earth: Mg, Ca, Be, Ba, Sr
  - Transition: Ni, Pb, Zn, …

✓ Li, K, Na, Ca, Ni inherent in biomass and waste are the most effective catalysts. Particular emphasis on Group I (Na, K, Ca)

Prospects:

✓ Initial metal (AAEM) characterization is a key issue
✓ Modeling of reaction rate and behavior
✓ Make these processes cost-competitive in today's market
RECENT PAPERS FROM OUR GROUP IN THE FIELD

1. Ducousso M., Weiss-Hortala., Castaldi M., Nzihou M., Reactivity enhancement of gasification biochars for catalytic applications. *Fuel, Accepted June 2015*


Call for abstracts:
**WasteEng2016** Conference and Summer School, May 23-26, 2016, Albi - FRANCE

July 31, 2015: Deadline for abstracts submission

http://www.wasteeng2016.org/

Organized by:

Summer school: (Credits: CEU, PDH)
Thank You!