Pyrolysis Characteristics of Thai Lignite and Biomass Blends: An In Depth Experimental Investigation

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Introduction

World Coal Deposit And Reserve

Well distributed
Movable coal reserve 164 years

Effective & Clean use of coal/low rank coal (Lignite)

World Energy Security in this 21 century

Source: www.accuracyingenesis.com/coal.html
Thailand: Energy Situation

Primary Energy Supply

- Lignite: 16%
- Natural Gas: 56%
- Hydro: 9%
- Oil: 14%

Energy Demand

- Industry: 39%
- Transportation: 34%
- Commerce: 16%
- etc.: 11%

Energy Demand in Industry

- Coal/Lignite: 25%
- Electricity: 20%
- Petroleum: 22%
- RE: 23%
- etc.: 10%

High dependency on Coal/Lignite

Source: http://www.dede.go.th
Thailand: Agricultural Country

Agricultural Residues
Biomass Resources

- Corncob
- Ricehusk
- Rice straw
- Corn cob
Co-processing of Lignite and Biomass

Conversion Process
- Pyrolysis
- Gasification
- Liquefaction
- Combustion
- Etc.

- Reducing Lignite consumption
- CO$_2$, SO$_2$, NOx reduction
- Energy Source Stabilization
- Self sufficiency in Thailand

Power
Fuel
Chemicals
Objectives

To understand the fundamental pyrolysis characteristics of lignite and biomass while paying a special attention to the synergetic effects during Co-pyrolysis in order to support the development of effective conversion processes.
Methodology

As Received (local available)
Lignite and Corncob (biomass)

(1) Grindning
(2) Sieving 200mesh (d<74μm)
(3) Drying 70°C, at vacuum
(4) Blending

TG-MS
Weight Change
Gas formation rates
Heating rate: 10°C/min
He flow: 50ml/min
Sample: 15mg

Fixed Bed Reactor
Production Behaviors
Heating rate: 10°C/min
He flow: 50ml/min
Sample: 500mg

Solid
Liquid
Gas

GC/MS
GC-TCD
Experimental Set-up of Fixed bed reactor

[Diagram of experimental setup with labeled components such as temperature controller, mass flow meter, helium cylinder, sample, quartz wool, stainless mesh, gas bag, condenser, and ice water.]
## Results

### Table: Ultimate and Proximate Analyses

<table>
<thead>
<tr>
<th>Samples</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O(diff)</th>
<th>Volatile matter</th>
<th>Fixed carbon</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignite</td>
<td>58.7</td>
<td>5.0</td>
<td>2.0</td>
<td>0.9</td>
<td>33.4</td>
<td>49.1</td>
<td>32.6</td>
<td>18.3</td>
</tr>
<tr>
<td>Corncob</td>
<td>45.5</td>
<td>6.2</td>
<td>1.3</td>
<td>0.0</td>
<td>47.0</td>
<td>82.2</td>
<td>16.9</td>
<td>0.9</td>
</tr>
<tr>
<td>(90, 10)</td>
<td>57.2</td>
<td>5.1</td>
<td>1.8</td>
<td>0.6</td>
<td>35.3</td>
<td>50.9</td>
<td>32.5</td>
<td>16.6</td>
</tr>
<tr>
<td>(50, 50)</td>
<td>53.9</td>
<td>5.1</td>
<td>1.5</td>
<td>0.5</td>
<td>39.0</td>
<td>54.4</td>
<td>30.2</td>
<td>15.4</td>
</tr>
<tr>
<td>(10, 90)</td>
<td>49.2</td>
<td>5.4</td>
<td>1.0</td>
<td>0.3</td>
<td>44.1</td>
<td>66.2</td>
<td>24.4</td>
<td>9.4</td>
</tr>
</tbody>
</table>
**Results:** Pyrolysis Behaviors of lignite and corncob blend

Monotonic changes with blending ratios

- Minimum secondary cracking
- Short residence time

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**MS**

Vacuum

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Vacuum gases Sample(15mg)

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$Y_{calc} = x_1 Y_1 + x_2 Y_2$

slight weight loss discrepancy

Synergies?
Experimental Set-up of Fixed bed reactor

- Lignite
- Corncob

Pyrolysis Temperature
300, 350, 400, 500, 600°C
Pyrolysis behaviors in Fixed bed

Production Behavior: single layer

Solid

- Lignite
- Corncob
- (50, 50)
- Calc.

Liquid

- Lignite
- Corncob
- (50, 50)
- Calc.

Gas

- Lignite
- Corncob
- (50, 50)
- Calc.

Gas production Behaviors

CH₄

- Lignite
- Corncob
- (50, 50)
- Calc.

CO

- Lignite
- Corncob
- (50, 50)
- Calc.

CO₂

- Lignite
- Corncob
- (50, 50)
- Calc.
Hypothesis

Co-pyrolysis in well blended condition

- Solid yield decreased by 500°C
- Liquid yield increased by 400°C
- Gas yield increased at 400°C
- CH₄ yield increased at 400°C

Synergies between volatiles?? or Volatile and particle??

Secondary Cracking

Retention time
- Lignite: 1.5s
- Corncob: 3s
- Blend: 2.2s

Secondary cracking

D: depth
- Corncob
- Lignite

D: ½ inch

Corncob volatile

Lignite volatile

Temperature controller

1/2 inch in 1. D.
Stainless

Sample (500 mg)

Quartz wool

Stainless mesh

Condenser

small vessel (10ml)

Ice water

Mass flow meter

Electro furnace

Helium cylinder

Gas bag (5 l)

Cotton absorbent

50 ml/r

Corncob volatile

Lignite volatile

Retention time

Lignite: 1.5s
Corncob: 3s
Blend: 2.2s
Sample arrangement

Sample Fixing (Co-pyrolysis)

Double layers (separated arrangement)

Corncob (250 mg)
Quartz wool
Lignite (250 mg)

Gas flow

Single layer

To investigate the synergetic effects between corncob volatile and lignite char
Comparison of production behavior between single and double layer

- **Solid**: Decreased

- **Liquid**: Increased

**CH₄**

**CO**

**CO₂**

**Comparison**

- **Solid Layer**: Decreased
- **Double Layers**: Increased
Below 350°C, corncob volatile was thought to affect the early stage of lignite pyrolysis process giving rise to the higher liquid yields, compared to the calculated values.

From 350°C to 500°C, secondary cracking of lignite volatiles resulted in significantly higher CH₄ yield at around 400°C compared to the calculated values.

This thermal cracking is thought to partly be enhanced by the interaction with corncob volatiles accelerating the pyrolysis reactions at lower temperatures, and longer residence time for lignite volatile in the blend compared to pure lignite.

Other mechanisms such as synergies among adjacent particles could also be expected during co-pyrolysis of lignite/corncob
Acknowledgements

Thank you very much for your attentions
(3) Lignite/Corncob Tar

~No Particular Changes in Tar Composition

Summative Behavior with The tar of lignite and corncob
Liquids Composition Analysis
GC-MS; Elite-5MS column
Methanol soluble portion

(1) Lignite Tar
Phenolic Materials
Hydrocarbon (Olefin:C10-C14)

Secondary Tar Cracking

CH₄ Production

300 °C
~No Hydrocarbon

400 °C
Many Hydrocarbons

600 °C
~No Hydrocarbon

Secondary Tar Cracking

CH₄ Production
(2) Biomass Tar

Oxygenated materials;
Acetic acid, Furan, Alkyl phenol, Alkyl methyl phenol

~No Hydrocarbon