Catalytic Pyrolysis

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Catalytic Fast Pyrolysis for fuel production

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Some concerns I had

• Limited knowledge of chemistry
  • Which reactions are catalyzed?, which ones do we want to catalyze?

• Ill defined goal
  • Stabilization of oil (?)
  • Oxygen removal (yield often neglected)
  • Production of specific compounds – aromatics (yield and separation neglected)
  • My goal = fuel precursor

• Catalysts de-activation
  • Coke, interaction with K, Cl, Ca, S, etc..

• High reactivity of pyrolysis products

• Solid catalyst - solid biomass?
  • Catalysis of what? Vapors, Gases, Aerosols?
Agenda

Results of different feeds using different catalyst (synthetic & ashes in feed) in different reactors showing that ......

Firstly I present experimental results without synthetic catalyst which are of interest for the interpretation of results obtained with catalyst
Equipment: pyrolysis

- 50 mg biomass
- Fast heating (5000 °C/s) by hot screen
- Rate of products leaving the reaction zone controlled by pressure (5 Pa – 1 bar)
- Very fast quenching (< 20 ms)

- 1 kg/h feed
- Fluidized bed
- (also) fast heating (10,000 °C/s)
- 0.5 – 1 bar
- Staged condensation
- 1-2 s residence time of hot vapors
Equipment: fluidized bed for catalytic pyrolysis

IN-SITU FLUIDIZED BED (ISFB)
Equipment: downer for catalytic pyrolysis

**EX-SITU downer (ESD)**

- Biomass
- Fluidized bed pyrolyser (500 °C)
- ESP condenser (25 °C)
- Cyclone
- Filter
- Liquid products
- Spent catalyst
- Catalyst
- Screw conveyor
- Downer (500 °C)
- Intensive cooler (-5 °C)
- Aqueous condensate
- Permanent gases
- N₂

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Feeds and catalysts

- Pine
- Straw
- Hay
- Bagasse
- Avicel cellulose
- Cotton
- Lignins

- ZSM-5
- Na$_2$O on Al$_2$O$_3$
- Ashes, K$_2$CO$_3$

All results at 500 – 530 °C, unless stated otherwise
My model of catalytic pyrolysis

- **Processes at particle level**
  - Mass and Heat transport
  - Pyrolysis reactions
  - Catalysis by AAEMs
  - Char is a catalyst

- **Processes in vapor phase**
  - Homogeneous reactions

- **Processes on / in catalysts**

Can be studied in Screen-Heater
Influence of AAEMs on yields of lumped product
feed = cellulose

AAEMs = natural catalyst (they accumulate on the catalyst)
Influence negative ion

Potassium concentration 1000 mg kg\(^{-1}\)

C\(_{\text{glucose}}\) / C\(_{\text{cellulose}}\) (kg kg\(^{-1}\))

SH @ 500 Pa
Influence of AAEMs on sugar chemistry

Hardly sugars in contact with catalyst
Production of sugars – effect of pressure

![Graph showing the relationship between pressure (Pa) and production of sugars (YAS) and fraction of DP1 (fDP1) for acid leached bagasse.](image)

- **YAS**: Experiment (solid square) vs. Model I (solid line)
- **fDP1**: Experiment (red circle) vs. Model I (dashed line)

Key:
- 5 Pa
- Acid leached bagasse

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**Equation**: $Y_{AS} = f_{DP1}$

**Explanation**: The graph illustrates the experimental data (squares) compared to the model predictions (lines) for the production of sugars ($Y_{AS}$) and the fraction of DP1 ($f_{DP1}$) under varying pressures for acid leached bagasse. The model seems to fit the data reasonably well, especially at lower pressures.
Pyrolysis of Lignin

- Processed/extracted lignins
  - Solvolysis
  - Pyrolytic

- Milled wood lignin
  (closest to native)

- Similar C, H, O

- 600 –3600 Da (weight averaged)

- 0 – 35% β-O-4

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<th>Code</th>
<th>C</th>
<th>H</th>
<th>O *</th>
<th>N</th>
<th>H/C</th>
<th>&lt;Mw&gt; **</th>
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* Oxygen content by difference: (100 − C − H − N); ** <Mw> is calculated from UV detector response; – Not measured
Molecular weight distribution

Light Lignin

Heavy Lignin

SH
MW of oil vs. MW of Lignin

‘Lignin’ on contact with catalyst is of rather small MW
Bond balance

<table>
<thead>
<tr>
<th>Oxygen Bonds</th>
<th>Milled wood lignin</th>
<th>Oil at 500 Pa</th>
<th>Oil at 1 bar</th>
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</thead>
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<tr>
<td>β-aryl ether</td>
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‘Lignin’ that is in contact with the catalyst hardly contains C-O-C bonds, instead it is C-C bonded
Intermediate conclusion

The catalyst is in contact with:

- Light decay products of sugars (highly oxygenated)
- Re-polymerized C-C bonded Lignin of ~ 500 Da
- Most likely aerosols
Interpretation of catalytic fast pyrolysis experiments

Pyrolysis oil

Water addition (FP)

Naturally (CFP)

Phase separation

Aqueous phase organics (APO)
O = 50 wt%
MW = 100 Da
Mainly sugar based

Oil phase organics (OPO)
O = 35 wt%
MW = 600 Da
Mainly lignin based
Our first results with ZSM-5

< 20 wt% oil yield
Oxygen content of 20 wt%

CFP and CVUP
Cracking: MWD of oils

![Graph showing MWD of oils for Thermal, Zeolite, and Na ex-situ processes.](image-url)
Coke, water & gas yields

(ESD & ISD)
Yield and Oxygen % of the aqueous phase organics

Aqueous phase organics (APO) \( \rightarrow \) coke + water + gas

No de-oxyxygenation of APO

(ESD & ISD)
Yield and Oxygen % of the oil phase organics

![Graphs showing carbon yield and oxygen content for different catalyst/biomass combinations.](ESD & ISD)
Conversion of sugars over regenerated ZSM-5
ZSM-5 + ashes
Catalytic pyrolysis
Take home messages

• Different reactor, different feedstocks, different contacting modes: never more that 20C% yield and lowest O content was 15% (10)

• The whole sugar fraction (2/3 of initial thermal oil) is lost to coke, water and gas.

• Only solution: new catalysis converting the sugar fraction into fuel.
... It is not easy being green...