Influence of Pyrolysis Conditions on Gasification of Biomass Chars Formed in an Entrained-Flow Reactor

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Biomass Utilization Pathways

Biomass

Hydrolysis

Aqueous sugars

Lignin

Pyrolysis or Liquefaction

Bio-oils

Gasification

Syngas (CO + H₂)

Fischer-Tropsch synthesis

Alkanes

Methanol synthesis

Methanol

Water-gas shift

Hydrogen
Benefits of High Pressure Gasification

- Syngas needs to be pressurized for its downstream applications.
- Pressurized gasification can help reduce costs of the overall process.
### Experimental Approach

**Pyrolysis**

- Loblolly Pine

- Temperature: ~10³ °C/s
- Temperature: 600–1000 °C
- Pressure: 5–20 bar
- Time: 4–30 s

**Char**

- Analytical techniques:
  - SEM
  - XRD
  - Ultimate Analysis
  - ICP

**Gasification**

- Products: \( \text{CO}_2, \text{H}_2\text{O} \)
- Temperature: ~25 °C/min
- Temperature: 800 °C
- Pressure: 1 bar

Additional resources:

- [Pellet Stoves](http://www.pelletstoves.ie/page26.php)
How Does Temperature Affect Reactivity?

Effect of Temperature
at 5 bar

Initial Reactivity (1/min)

600 °C
800 °C
1000 °C
Effect of Temperature

600 °C  800 °C  1000 °C
Effect of Temperature

- **600 °C**
- **800 °C**
- **1000 °C**

- Lowest surface area
- Least H/C
- Lowest ash wt. %
- Most graphite-like
- Least reactive
How Does Pressure Affect Reactivity?

Effect of Pressure at 800 °C

Initial Reactivity (1/min)

- 5 bar
- 10 bar
- 15 bar
- 20 bar

Graph showing the effect of pressure on reactivity with different pressures: 5 bar, 10 bar, 15 bar, and 20 bar.
Effect of Pressure

5 bar

10 bar

15 bar

20 bar
Effect of Pressure

Low pressure

Intermediate pressure

High pressure

Least microporous
Most graphitic
Least H/C
Least Reactive
Catalytic Effect of Inorganics

![Graph showing the effect of inorganics on reactivity](image)

- Avicel char + $K_2CO_3$
- Avicel char +CaO
- Avicel char

Initial Reactivity (1/min) vs. M/C Atomic Ratio
Conclusions

• Pyrolysis operating conditions lead to drastic differences in char morphology and reactivity
  – Finding an optimum range of these operating condition is key for gasifier design
  – High temperature leads to very low reactivity. Intermediate pressure chars are least reactive.

• Surface area, inorganic content in char, and the chemical character of carbon in char together determine the char gasification reactivity.
  – Studying these parameter in isolation is not feasible and all of the parameters need to be considered for each char
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Tars

Increase in Residence Time

Glycoldehyde dimer

4-Methyl-5H-furan-2-one

Dibenzofuran

Pyrene

Fluorenone

Primary → Secondary → Tertiary
Product Gas Composition

Gas composition at 800 °C, 10 bar

- CO: 51%
- CO\(_2\): 16%
- H\(_2\): 20%
- CH\(_4\): 13%
- C\(_2\)-C\(_4\): 0.1%

C\(_2\)-C\(_4\) Hydrocarbon variation with T and P

[Graph showing hydrocarbon variation with temperature and pressure]
H/C Ratio in Char

![Graph showing the relationship between initial reactivity (1/minute) and H/C atomic ratio at different temperatures: 600 °C (blue), 800 °C (red), and 1000 °C (green). The graph includes a dashed line with an R² value of 0.61.](image-url)
Effect of Pressure
Surface area and Graphitization
Increase in pyrolysis temperature, forms char with bigger cavities and increasingly graphitic
Effect of Residence Time

4 s

15 s

28 s
Effect of Residence Time
Graphitization of Char

- Crystallinity of cellulose in wood gets destroyed and graphite like char is formed.
Effect of Residence Time
Surface Area of Char

- Longer residence time char has a more open structure with low surface area
Effect of Residence Time
Gasification Reactivity

- Longer residence times form less reactive chars