Goals and Objectives

Project Goals

1. To obtain experimental data on the rates of carbon gasification and hydrocarbons and tar formation during pressurized gasification of biomass

2. To develop kinetic models that describe the carbon gasification rates

Addresses the following MYPP barrier

- **Gasification of biomass**: developing an understanding of gasification options and their chemistries for materials including wood, energy crops, sorted municipal solid waste, agricultural residues high in minerals and lignin, and high-moisture organic residues

Addresses the following pathways

- Agricultural residues
- Energy crops
- Forest resources
Project Overview
Background/Context

- Gasification offers the benefit that agricultural residues, forest waste and all parts of plants (including cellulose and lignin) can be utilized.

- The data on formation of tars and hydrocarbons and the rate of biomass gasification at high pressures are needed for gasifier design.

- Gasification involves two series processes – pyrolysis (devolatilization) and char gasification. Char gasification activity is affected by the pyrolysis conditions (heating rate, temperature, and pressure), ash content and composition, and gasification conditions.

- The challenge is to develop experimental protocols that would allow collecting experimental data at conditions that mimic the heating rate, temperature, pressure, and residence time likely in a commercial gasifier.
Approach

- The approach involves using two complementary reactors - Pressurized Entrained Flow Reactor (PEFR) and Pressurized Thermogravimetric Analyzer (PTGA).

- PEFR utilizes short contact times and high heating rates that closely mimic commercial gasifier conditions. This allows generation of a representative char in terms of its morphology, surface area and gasification activity.

- PTGA is used to measure char gasification rates under controlled environment, while monitoring for transport effects.

- PTGA provides useful detailed information on the evolution of gaseous species during pyrolysis, leading to improved understanding of the role of biomass constituents.

- Mathematical models that incorporate kinetics and transport effects are developed and validated in the PEFR gasification experiments.
Approach… contd.

- A set of five milestones guide the overall progress: (i) effect of pyrolysis conditions on char morphology and activity (PEFR), (ii) kinetics of char gasification (PTGA), (iii) mathematical models to predict gasification under transport limited conditions, (iv) model validation (PEFR), and (v) effect of pyrolysis conditions on formation of tars and hydrocarbons.

- Georgia Tech student carries out PTGA studies at the NREL under the supervision of co-PI, and weekly reports are submitted. Conference calls between the two co-PIs at regular interval are used to make sure that adequate progress is being made towards the above milestones. In addition, co-PI site visits are used for detailed review and discussion.

- The team at Georgia Tech meets every week to review the goals and the next steps.
Approach

• Previous research has focused on slow pyrolysis (heating rate: 0.1-100 °C/s)
• At high heating rates (10³-10⁴ °C/s), effect of T or P alone has been studied

✓ Need to study effects of both T and P at high-heating rates to understand pyrolysis chemistry in industrial reactors
✓ Characterization of pyrolysis products is important
Experimental Approach

• Three types of biomass:
  • Loblolly Pine
  • Switchgrass
  • Cornstover

• Complementary reactor types:
  • Laminar Entrained flow reactor (LEFR/PEFR)
  • Thermogravimetric Analyzers (TGA/PTGA)

<table>
<thead>
<tr>
<th>Operating Parameter</th>
<th>PEFR (°C/Min)</th>
<th>LEFR (°C)</th>
<th>PTGA† (°C)</th>
<th>TGA (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C) Limits</td>
<td>1500</td>
<td>1500</td>
<td>1100</td>
<td>1500</td>
</tr>
<tr>
<td>P (atm) Limits</td>
<td>80</td>
<td>1</td>
<td>100</td>
<td>1</td>
</tr>
<tr>
<td>Heating rate</td>
<td>$10^4$ °C/s</td>
<td>$10^4$ °C/s</td>
<td>10 °C/min</td>
<td>50 °C/min</td>
</tr>
<tr>
<td>Residence Time</td>
<td>Up to 40 s</td>
<td>Up to 4 s</td>
<td>Up to Hours</td>
<td>Up to Hours</td>
</tr>
</tbody>
</table>

† Located at NREL
• Pressurized
• Entrained
• Flow
• Reactor
PTGA-MS-FTIR

- Pressurized TGA: 100 bar, 1100°C
- Equipped with FTIR and MS for evolved gas analysis
## Biomass Samples

<table>
<thead>
<tr>
<th>Element</th>
<th>Loblolly Pine</th>
<th>Switchgrass</th>
<th>Cornstover</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>52.4%</td>
<td>48.3%</td>
<td>43.7%</td>
</tr>
<tr>
<td>H</td>
<td>6.3%</td>
<td>6.1%</td>
<td>5.9%</td>
</tr>
<tr>
<td>N</td>
<td>0.07%</td>
<td>0.36%</td>
<td>0.59%</td>
</tr>
<tr>
<td>O</td>
<td>40.9%</td>
<td>44.7%</td>
<td>45.3%</td>
</tr>
<tr>
<td>Ash</td>
<td>0.3%</td>
<td>2.2%</td>
<td>6.1%</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>79.1%</td>
<td>77.6%</td>
<td>74.4%</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>12.8%</td>
<td>12.4%</td>
<td>12.6%</td>
</tr>
</tbody>
</table>
Technical Accomplishments/Progress/Results
Effect of Pressure on Gas Species Evolution

Major Gas Species (5 bar)
- CO₂ (44)
- H₂ (2)
- CH₄ (16)
- CO (28)

Major Gas Species (30 bar)
- CO₂ (44)
- H₂ (2)
- CO (28)
- CH₄ (16)

Light Hydrocarbons (5 bar)
- C₂H₅ (29)
- C₂H₃ (27)
- C₂H₂ (26)

Light Hydrocarbons (30 bar)
- C₂H₅ (29)
- C₂H₃ (30)
- C₂H₂ (26)
Technical Accomplishments/Progress/Results

Effect of Pressure on Gases (PTGA)

- Major light gases and C₂H₄, C₆H₆ increases with pressure
- Oxygenates and hydrocarbon fragments decrease with pressure

- Evolution of gases with time can be monitored in PTGA
- Thermal-degradation mechanism can be better understood

†Performed by NREL
Technical Accomplishments/Progress/Results

Char yield and light gas species increase as pressure is increased

![Char Yield Graph](image1)

![Light Gases Graph](image2)
Technical Accomplishments/Progress/Results
Gases-switchgrass Pyrolysis

Gas from PEFR $\rightarrow$ Tedlar Bags $\rightarrow$ micro-GC analysis

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40s</td>
<td>40s</td>
<td>1.7s</td>
</tr>
<tr>
<td>Pressure bar</td>
<td>5</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>44.79</td>
<td>39.52</td>
<td>39.44</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>16.58</td>
<td>17.17</td>
<td>17.68</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>9.73</td>
<td>17.23</td>
<td>17.4</td>
</tr>
<tr>
<td>Methane</td>
<td>20.94</td>
<td>21.69</td>
<td>21.72</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.4</td>
<td>0.38</td>
<td>0.1</td>
</tr>
<tr>
<td>Ethylene</td>
<td>5.65</td>
<td>3.78</td>
<td>3.43</td>
</tr>
<tr>
<td>Acetylene</td>
<td>0.09</td>
<td>0.13</td>
<td>0.2</td>
</tr>
<tr>
<td>Propane</td>
<td>0.03</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Propylene</td>
<td>0.65</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Butene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.14</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

- Steam reforming, tar cracking, water-gas shift equilibrium, gasification reactions influence the gas compositions at various T, P, RT
Technical Accomplishments/Progress/Results

Pine Chars

• Effect of Temp.

(a) 600 °C, 1 bar

(b) 800 °C, 5 bar

(c) 800 °C, 10 bar

• Effect of Pressure

(a) 800 °C, 1 bar

(b) 800 °C, 10 bar

(c) 800 °C, 15 bar
Technical Accomplishments/Progress/Results
Switchgrass Chars

Incomplete melting of char

- BET Surface Areas

<table>
<thead>
<tr>
<th>m²/g</th>
<th>600°C</th>
<th>800°C</th>
<th>1000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 bar</td>
<td>1.8</td>
<td>2.9</td>
<td>75</td>
</tr>
<tr>
<td>5 bar</td>
<td>3.0</td>
<td>187</td>
<td>321</td>
</tr>
<tr>
<td>10 bar</td>
<td>3.3</td>
<td>175</td>
<td>278</td>
</tr>
<tr>
<td>15 bar</td>
<td>5.2</td>
<td>108</td>
<td>198</td>
</tr>
</tbody>
</table>

- Formation of cavities at high pressures

- Evaluate Surface Areas, pore volumes of all chars
- ICP, CHON analysis for total char yield

*Cetin et al. Fuel (2004), 83, 2139*
Technical Accomplishments/Progress/Results

Gas-Filled Pockets Formed at High Pressures Pine Char Formed at 15 bars
Technical Accomplishments/Progress/Results

Tars

• Weight of filter
• Amount
• Soxhlet Extraction
• Identification by GC-MS

• Primary: o,m,p Dihydroxybenzes ➔ Short Residence times only
• Secondary: Dibenzo(ghi)perylene, Biphenyl ➔ Only at 600 °C and 800 °C
• Tertiary: Fluorene, Anthracene, Phenanthrene, Napthalene ➔ At all conditions

✓ Extraction followed by GC-MS
✓ Tars measured represent lower limit
CO₂ adsorption measures higher surface areas compared to N₂ physisorption. CO₂ adsorption takes into account the sub-nano pore volume which N₂ physisorption fails to measure accurately.

Overall the surface area of chars decreases as the pyrolysis temperature and increases.

With increase in pyrolysis pressure the surface area decreases from 5-15 bar, and increases from 15-20 bar.
Technical Accomplishments/Progress/Results
Char Gasification Activity

• $R = r_c (T, P, C_i) \times r_s (X)$
  • Langmuir-Hinshelwood kinetics best suited for $r_c$
  • Structural Models use adjustable fitting parameters
  • Catalytic effects need to be incorporated
  • Studies involve char generated by slow pyrolysis
  • Heat and Mass transport effects not considered

Generalized model is required: for any type of feedstock, with varied pyrolysis history

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**Pyrolysis**

- Biomass Particles
  - PEFR/LEFR
  - 600-1000 °C,
  - 1-20 bar,
  - $10^4 \, ^\circ C / s$
  - 2-40s

- **Chars**
  - SEM
  - N$_2$ Physisorption
  - C,H,N,O
  - ICP

- **Gasification Reactivity**
  - Micro-GC
  - Soxhlet Extraction (Amount )
  - GC-MS identification

- **Gases**

- **Tars**

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**TGA (kinetic model)**

- Flow reactor (structural model)

- **CO$_2$ TPD (Active site titration)**
Mass Transfer Limitations in Thermobalances

• Mass transfer:
  • from bulk gas to surface of sample holder
  • from surface of sample to bottom of sample
  • from surface of particle to center of particle

• Tests for impact by changing
  • gas flow rate
  • sample size
  • particle size
Technical Accomplishments/Progress/Results

External Transport in PTGA

• Varying char sample sizes in PTGA
• Gasified at different temperatures
• Kinetic regime < 800 °C
Technical Accomplishments/Progress/Results

Impact of Gasification Conditions

Gasification Temperature

- 750°C
- 800°C
- 850°C

Ash Free Mass (%)

Time (min)

Gasification Pressure

- 1 bar
- 5 bar
- 10 bar
- 20 bar
- 30 bar

Ash Free Mass (%)

Time (min)

Switchgrass char prepared at 5 bar/1000°C
Gasification curves fit with different particle models

- **Uniform Conversion Model**
  - Reaction rate uniform throughout particle
  - Rate proportional to amount of ungasified carbon
    \[-\frac{dm_t}{dt} = k(m_t - m_{ash})\]
    \[X = \frac{m_o - m_t}{m_o - m_{ash}}\]
    \[-\ln(1-X) = kt\]

- **Grain Model**
  - Particle consists of grains which each react according to shrinking core model
  - Rate proportional to surface area of grains
    \[-\frac{dm_t}{dt} = k (m_t - m_{ash})^{2/3}\]
    \[3[1-(1-X)^{1/3}] = kt\]
Technical Accomplishments/Progress/Results

Uniform Conversion Model

\[ \ln(1-X) \]

Time (min)

100%
10%
1%

0 10 20 30 40 50

Grainy Pellet Model

\[ 1-(1-X)^{(1/3)} \]

Time (min)

1.0
0.8
0.6
0.4
0.2
0.0

0 10 20 30 40 50

Switchgrass char prepared at 5 bar/1000°C, gasified at 5 bar/800°C
Technical Accomplishments/Progress/Results

Arrhenius Plot

- Uniform Conversion: $E_a = 241$ kJ/mol
- Grain model: $E_a = 240$ kJ/mol

Nth order reaction rate

- Uniform conversion: $n = 0.79$, $R^2 = 0.9743$
- Grain model: $n = 0.77$, $R^2 = 0.9738$

Switchgrass char prepared at 5 bar/1000°C
Technical Accomplishments/Progress/Results

Langmuir-Hinshelwood Kinetics

\[ r_c = \frac{k_1 C_t P^{\alpha} \text{CO}_2 + k'_1 C_t P^{\beta} \text{H}_2 \text{O}}{1 + k_2 P_{\text{CO}} + k_3 P_{\text{H}_2 \text{O}} + k_4 P_{\text{CO}_2} + k_5 P_{\text{H}_2} + k_6 P_{\text{CH}_4}} \]

\[ r_c = \frac{k_1 P_{\text{CO}_2}}{1 + k_4 P_{\text{CO}_2}} (m_t - m_{ash}) = k (m_t - m_{ash}) \]

\[ \frac{1}{k} = \frac{1}{k_1 P_{\text{CO}_2}} + \frac{k_4}{k_1} \]

- Switchgrass char prepared at 5 bar/1000°C, gasified at 750°C
Technical Accomplishments/Progress/Results

Comparison of avicel char with negligible ash content with different size fractions of pine char demonstrates that avicel char can be used to establish a baseline behavior for reactivity studies.
Technical Accomplishments/Progress/Results

Avicel Char + Inorganics

<table>
<thead>
<tr>
<th>Condition</th>
<th>Initial Reactivity (1/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avicel+K2CO3</td>
<td>0.16</td>
</tr>
<tr>
<td>Avicel+5%K2CO3</td>
<td>0.14</td>
</tr>
<tr>
<td>Avicel+MgO</td>
<td>0.12</td>
</tr>
<tr>
<td>Avicel+Cao</td>
<td>0.10</td>
</tr>
<tr>
<td>Avicel+Al2O3</td>
<td>0.08</td>
</tr>
<tr>
<td>Avicel Crushed</td>
<td>0.04</td>
</tr>
</tbody>
</table>
The “initial reactivity (5-10% conversion)” of char decreases with increase in pyrolysis temperature.

It decreases with increase in pyrolysis pressure. This result is consistent with PTGA results.

Gasification performed at 800 C, 100% CO2.
Technical Accomplishments/Progress/Results

Cornstover Gasification in PEFR – higher pressures lead to increased carbon remaining as residue char

<table>
<thead>
<tr>
<th>Residence Time</th>
<th>Percent carbon remaining in the char Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure 5 bars</td>
</tr>
<tr>
<td>3 sec</td>
<td>21.5%</td>
</tr>
<tr>
<td>6 sec</td>
<td>20.3%</td>
</tr>
<tr>
<td>10 sec</td>
<td>13.2%</td>
</tr>
</tbody>
</table>

Gasification Conditions: 10% CO$_2$, 2% H$_2$O, 0.3% H$_2$, 1.72% CO, 86% N$_2$

$900 \, ^{\circ}$C  particle size 106-180 $\mu$m
Project Relevance

• The goals of this project are consistent with the platform goals and objectives of the Biomass Program Multi-Year Program Plan (optimize gasifier design and syngas production). There are no reliable data on the kinetics of high pressure gasification and tars and hydrocarbon formation.

• The project results would provide critical data and information needed for developing optimum gasifier configurations, while improving energy efficiency by minimizing hydrocarbon and tar formation.

• The three biomass candidates represent forest resource (pine), energy crops (switchgrass), and agricultural residue (corn stover), respectively. The protocols being developed should be extendable to other biomass species with different ash composition.
Critical Success Factors

• Success Factors
  – Kinetic data/models
  – Ability to obtain high carbon conversion at high pressures
  – Ability to minimize tar and hydrocarbon formation by changing pressure and/or gas composition
  – Ability to quantitatively measure tar and hydrocarbons
  – Ability to develop quantitative approach that relates char gasification activity to the gasifier conditions (pressure and temperature)
  – Validation of mathematical model incorporating kinetics and transport effects in PEFR
Future Work
Langmuir-Hinshelwood Kinetics

- 100% CO₂
- 5% H₂O
- 20% CO₂, 5% H₂O
- +75% N₂
- +1% CO, 74% N₂

L-H kinetics with inhibitory effects have never been studied on such chars

Only a specific char will be studied using this method
Future Work
Structural Model: Catalytic effects

• Impregnating avicel (cellulose) chars will metals like K, Ca, Si
• Performing steps a-c on impregnated chars
• Correlating \( R (X) = f \left[ \text{Reactive CO (X), TSA (X), } \varepsilon(X) \right] \) for biomass chars, cellulose char and impregnated chars

- Can reactivity be expressed as a simple function of char active surface area?
- Is \( \text{CO}_2 \) TPD a good test for determining char reactivity?
- Is this approach applicable to char from any type of biomass (wood/agricultural residues/cellulose)?