Effect of Pressure and Heating Rates on Biomass Pyrolysis and Gasification

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Workshop on Lignocellulosic Biofuels Using Thermochemical Conversion

Strategies for production of fuels from lignocellulosic biomass

Georgia Tech

Feedstock	Process	Intermediate	Upgrading	Products
Cellulosic Biomass	*Gasification*	SynGas ($CO + H_2$)	*Fischer-Tropsch* *Methanol, Water-Gas Shift*	Alkanes, Methanol Liquid Fuels Hydrogen
	Hydrolysis	Aqueous sugar	*Fermentation, Dehydration* *Aqueous-Phase Processing*	Ethanol Aromatic Hydrocarbons Liquid Alkanes or Hydrogen
		Lignin	*Lignin Upgrading*	Liquid Fuels
	Pyrolysis or Liq.	Bio-oils	*Zeolite Upgrading* *Hydrodeoxygenation*	Liquid Fuels

Photo credit:
U.S. Department of Energy,
Energy Efficiency & Renewable
Energy Network (EREN)

Huber et al., *Catal. Today* **2006**, *111*, 119.

Characteristics of Gasification

- Pyrolysis and Char gasification proceed sequentially
- Pyrolysis pressure and temperature affect char reactivity
- Char reactivity depends on temperature, gas composition, porosity, ash contents, and transport effects
- Langmuir-Hinshelwood kinetic models suggested in the literature for biomass/char gasification
- High pressure gasification has particular significance

Sutton et al., Fuel Processing Technology, 73 (2001) 155-73

Di Blasi,, Progress in Energy & Combustion Science 35 (2009) 121-140

Cetin, Gupta, and Moghtaderi, Fuel, 84 (2005) 1328-1334

Impact of Pressure on Gasification

- Carbon gasification rate slow step in conversion of biomass to syngas ($CO + H_2$)

  $C + H_2O \rightarrow CO + H_2$

  $C + CO_2 \rightarrow 2\ CO$

  - Rate catalyzed by alkali metals
  - Langmuir-Hinshelwood type kinetics
  - CO and H_2 inhibit gasification
- Devolatilization impacts amount of carbon to be gasified and gas composition, including tar and hydrocarbon formation

Alkali Catalyzed Carbon Gasification

* + CO_2 <-> *(CO_2)
*(CO_2) <-> *(O) + CO
* + H_2O <-> *(O) + H_2
*(O) + C → * + C(O)
C(O) → CO

$$-r = \frac{k}{1 + \frac{P_{CO}}{aP_{CO_2}} + bP_{CO}}$$

$$-r = \frac{k'}{1 + \frac{P_{H_2}}{a' P_{H_2O}}}$$

$$-r_C = \frac{k_1 p_{H_2O} + k_2 p_{CO_2}}{1 + ap_{CO_2} + bp_{H_2} + cp_{CO}}$$

Need to Obtain Rate Data Including Impacts of All Relevant Species

Biomass Gasification Background

- Biomass gasification is a combination of 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 most likely mimic the heating rate, temperature, pressure, residence time, and transport effects likely to be encountered in a commercial gasifier.

Goals/Objectives

- Quantitative understanding of the gasification and pyrolysis along with an improved understanding of the catalytic effect of inorganics present in biomass

- Role of particle morphology in mass transport effects as well as the char reactivity

- Identifying process conditions where synergistic effects of biomass-coal blending are observed. This will include effect of particle size, residence time and proximity of the two feed types

- Building mathematical models based on science and engineering principles that would predict the biomass gasification rate at a given pressure, temperature and feed composition.

- Quantify the effect of pressure and temperature on the formation of tars and light hydrocarbons.

Methods

- Experiments in two complementary reactors:
- Pressurized entrained-flow reactor (PEFR) at Georgia Tech
- Pressurized thermogravimetric apparatus (PTGA) at NREL
  - Differences in heating rate, reaction time
  - Mass/heat transfer limitations

- Three biomass types:
  - Loblolly pine
  - Switch grass
  - Corn stover

PEFR Vs. PTGA

REACTOR	PEFR	PTGA
Pressure	Up to 80 bar	Up to 100 bar
Temperature	Up to 1500 C	Up to 1200 C
Mode	Co-current flow	Semi-Batch
Sample size	~1 g/min	10-100 mg
Heating Rate	~10,000 C/s	~10 C/min
Residence time	Up to 10 s	Up to hours
Kinetic Control Limit	>1000°C	~800°C
Gas analysis	FTIR, GC	MS, FTIR

Elemental Composition of Biomass Feed

Element	Loblolly Pine	Switchgrass	Cornstover
C	52.4%	48.3%	43.7%
H	6.3%	6.1%	5.9%
N	0.07%	0.36%	0.59%
O	40.9%	44.7%	45.3%
Ash	0.3%	2.2%	6.1%
Volatile Matter	79.1%	77.6%	74.4%
Fixed Carbon	12.8%	12.4%	12.6%

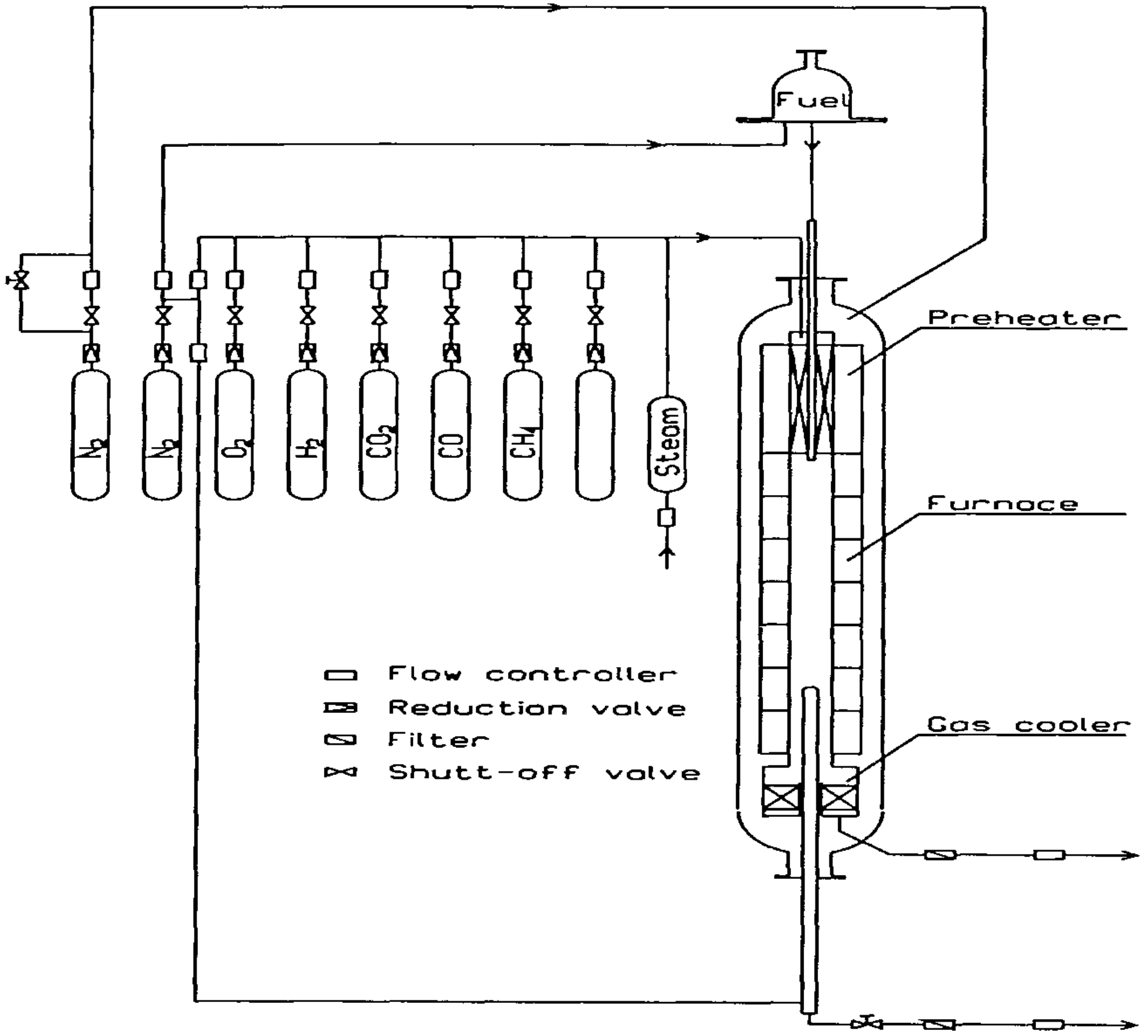
Elemental Analysis of Feed Biomass (ICP)

Element	Loblolly Pine	Switchgrass	Cornstover
Ca	490	1790	1900
Fe	38	20	437
K	358	4980	8675
Mg	203	1540	1325

Approach

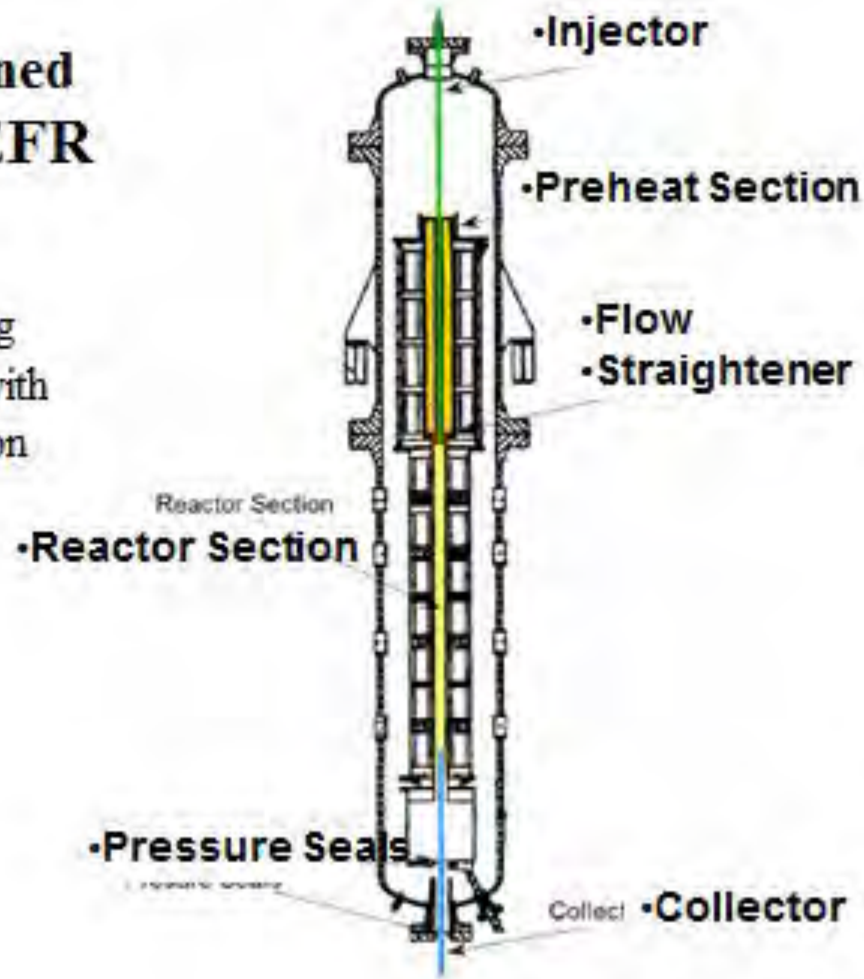
- Investigate high temperature pyrolysis of biomass - effect of pressure and temperature on char morphology and reactivity towards gasification
- Gasification kinetics of chars generated from pyrolysis (individual chars, blend pyrolysis chars, and blending of chars generated individually)
- Catalytic effect of inorganics (ash) on char gasification
- Transport effects and mathematical models

Pressurized Entrained Flow Reactor



Pressurized Entrained Flow Reactor - PEFR

- Rapid heating and cooling
- Differential conditions with respect to gas composition



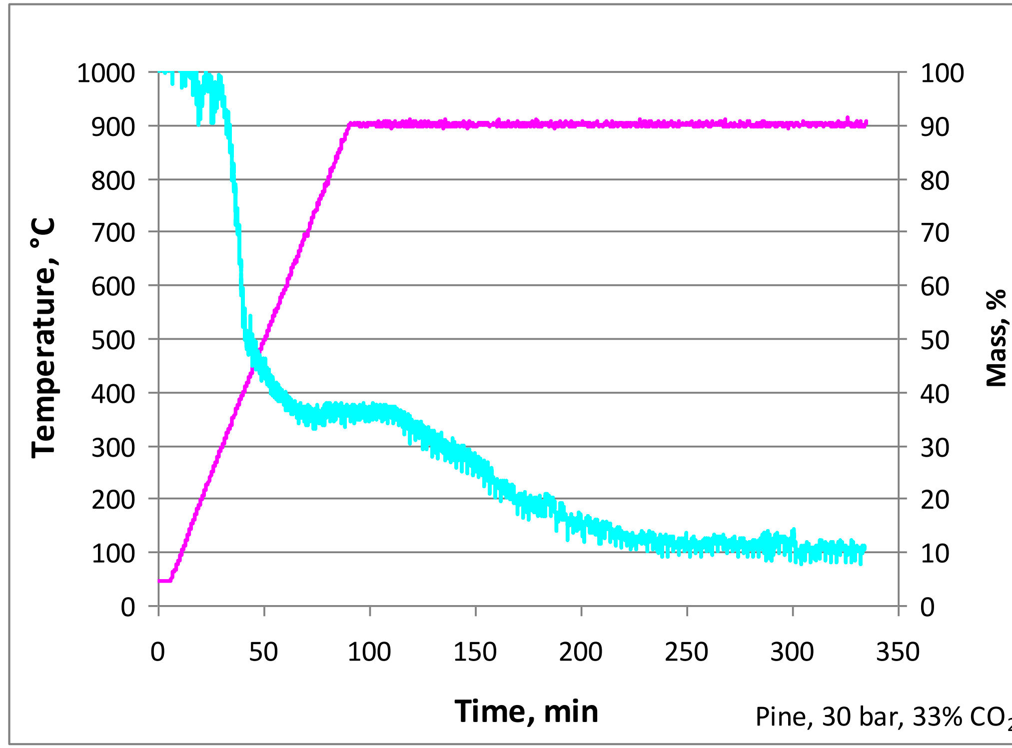
P ressurized

E ntrained

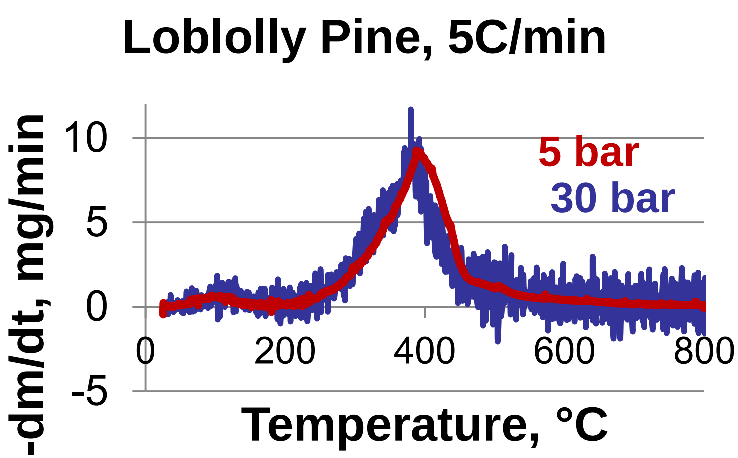
F low

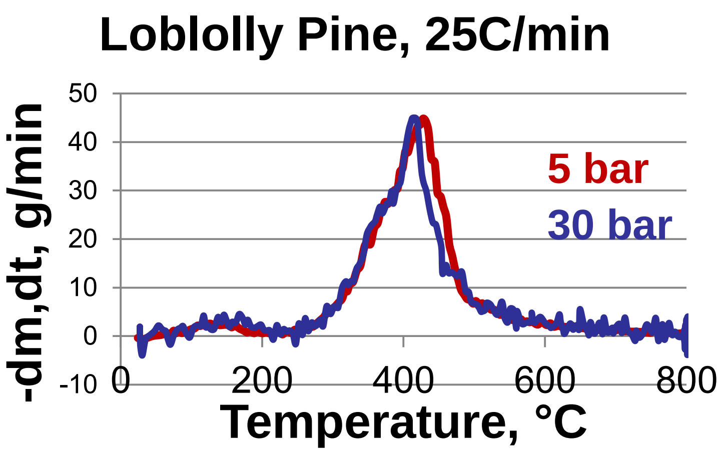
R eactor

Pressurized Thermobalance (PTGA)

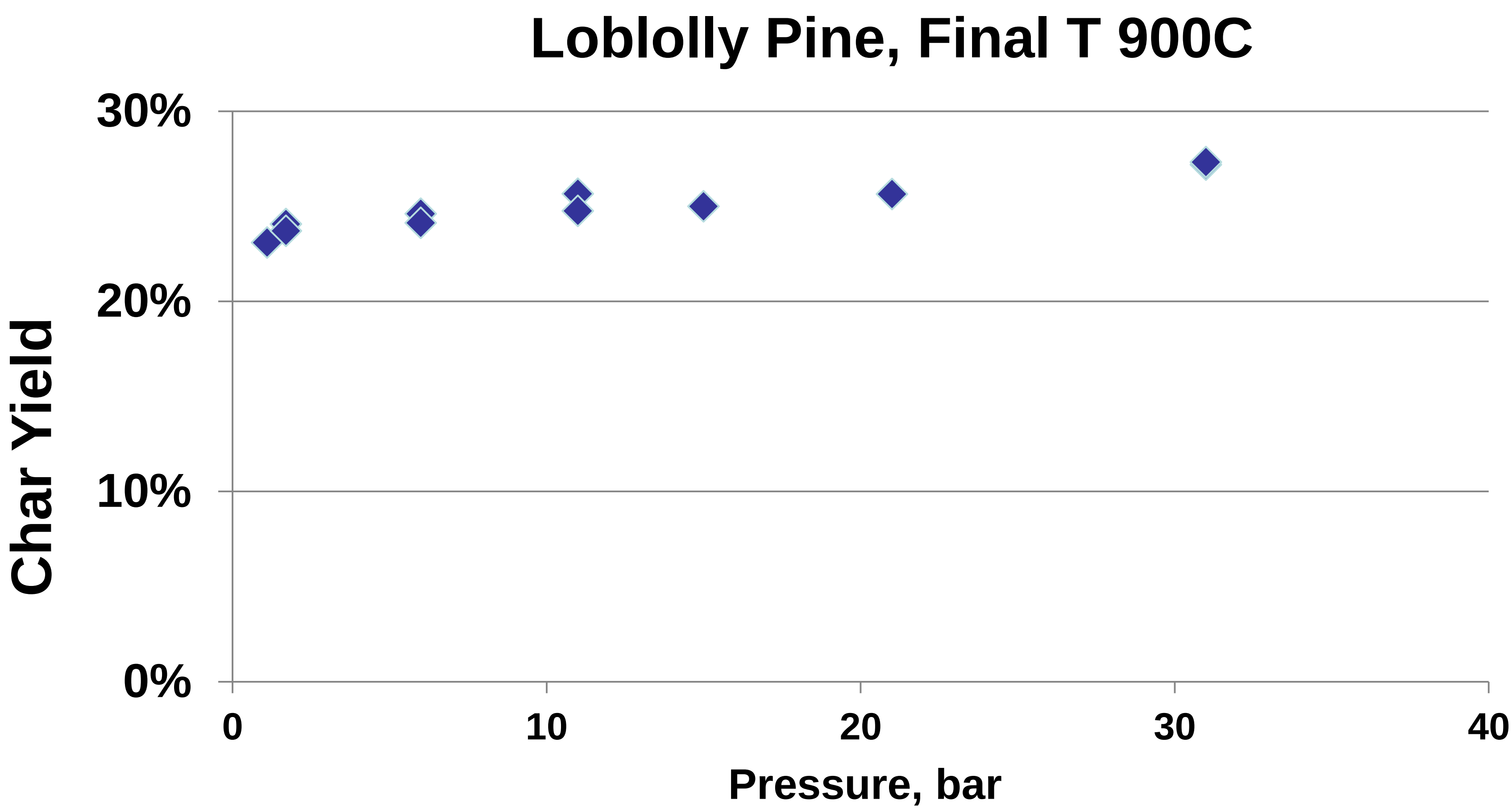


Effect of Pressure and Heating Rate on Loss of Mass in PTGA Pyrolysis

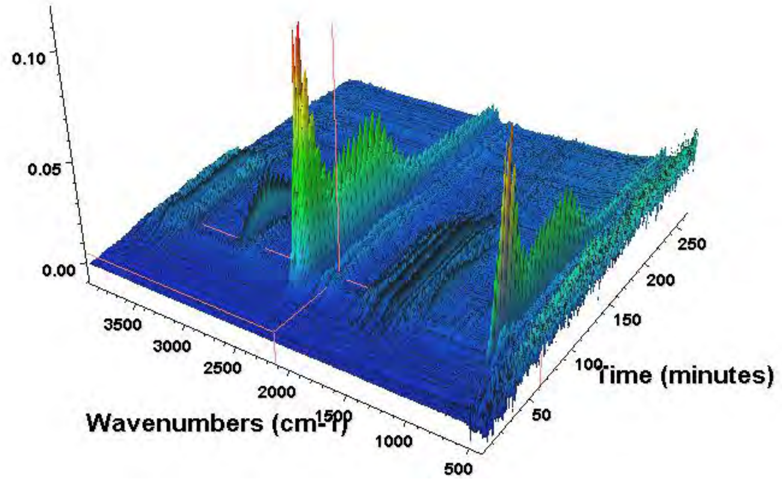


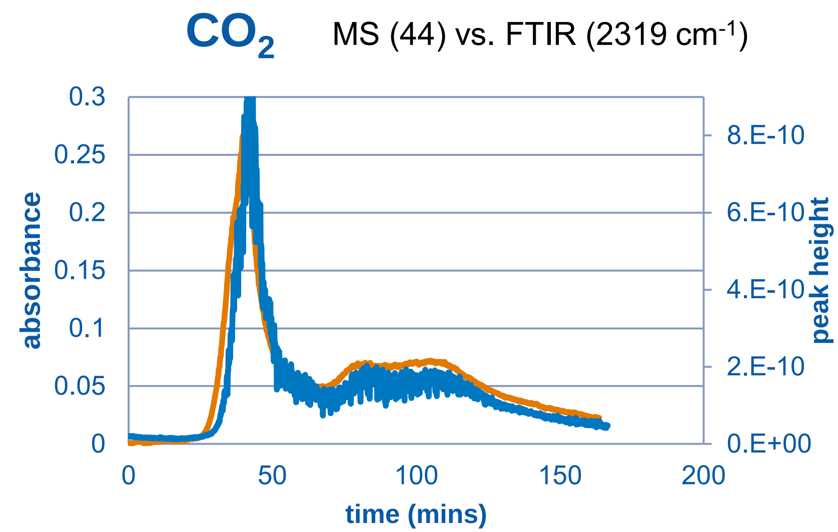


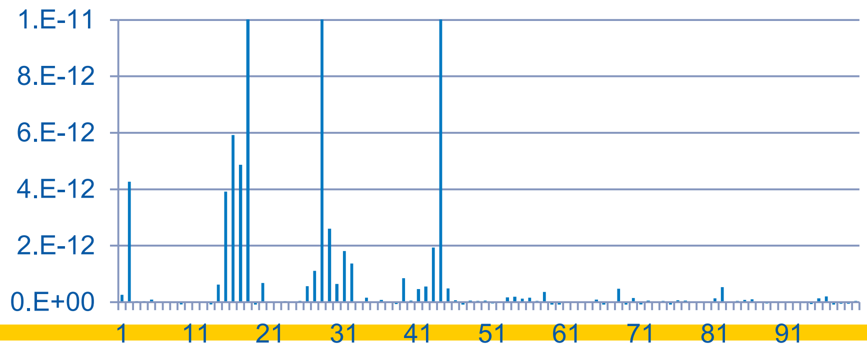
Effect of Pressure on Residual Char



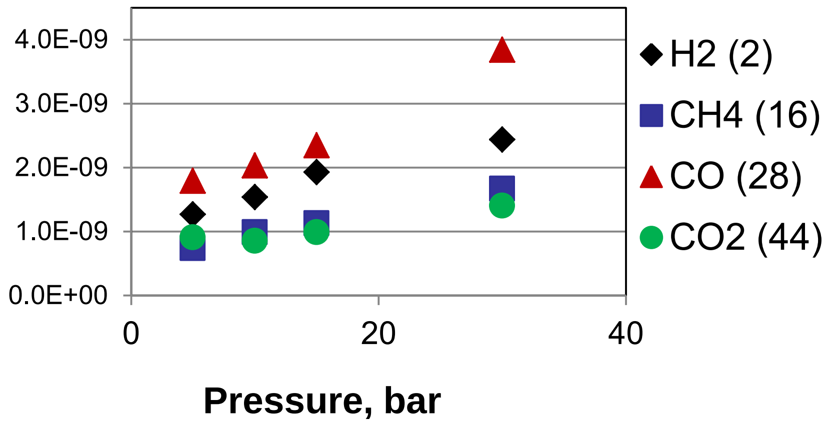
FTIR vs. Mass Spectrometer in PTGA

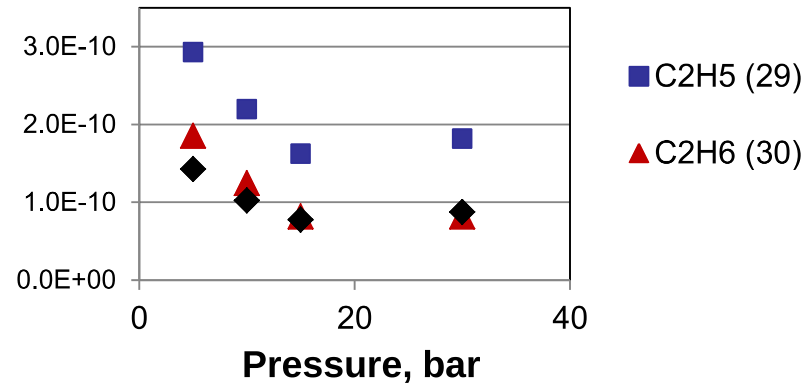


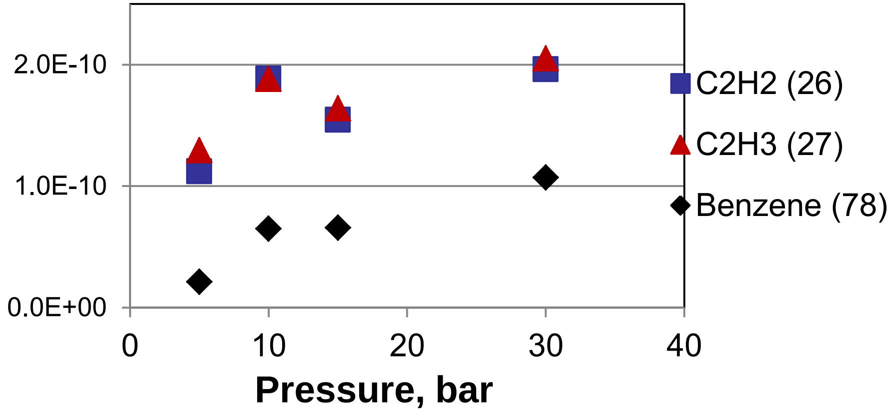


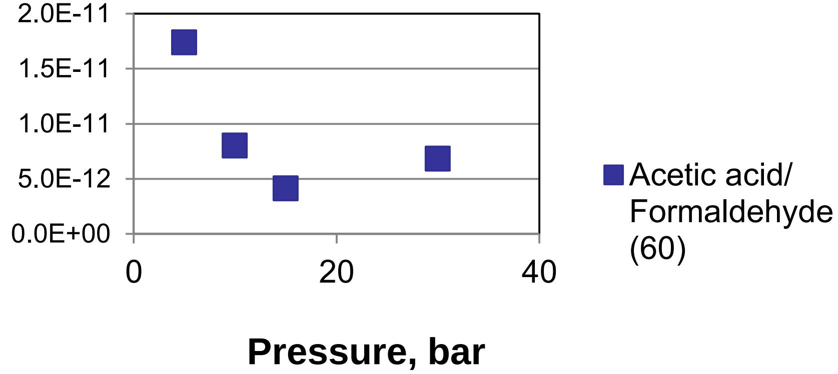


Effect of Pressure on Gas Species Evolution









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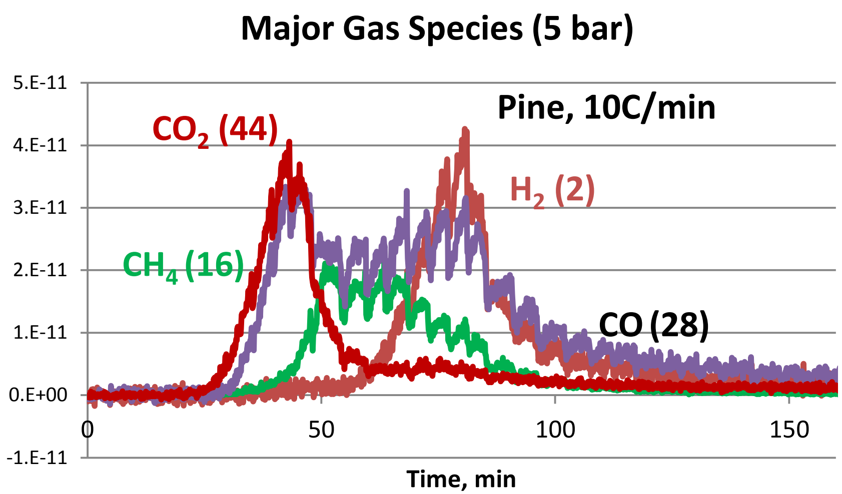
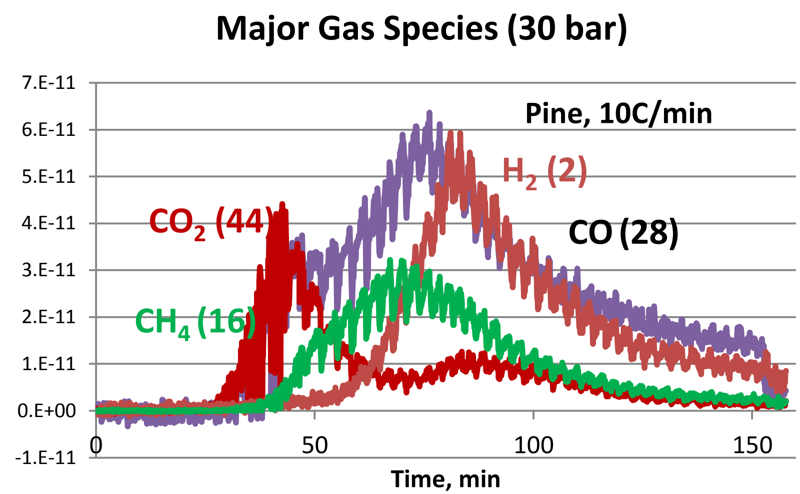
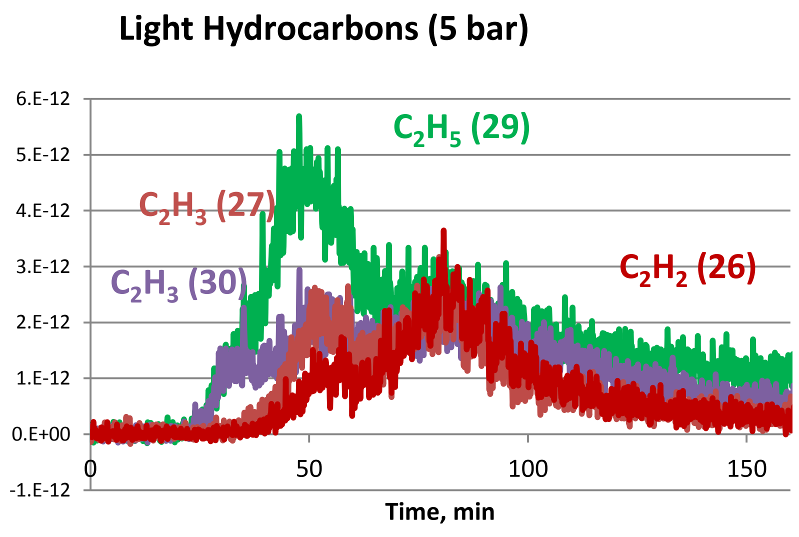
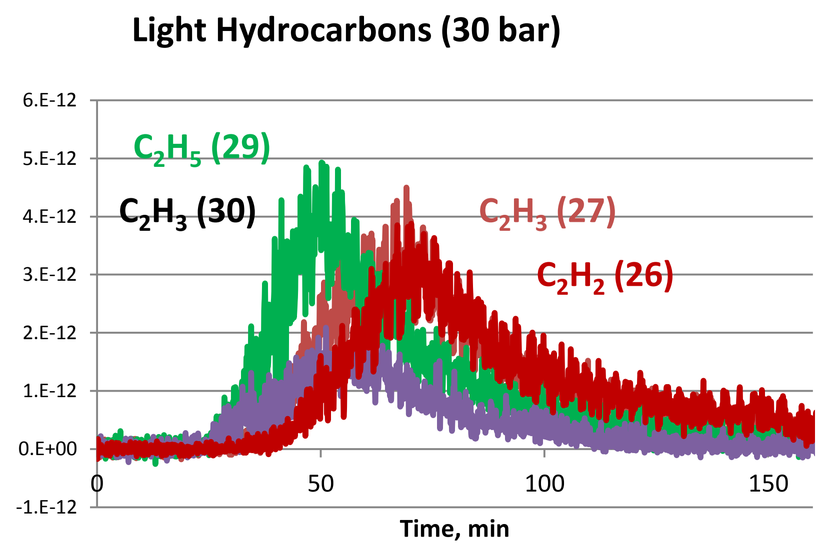
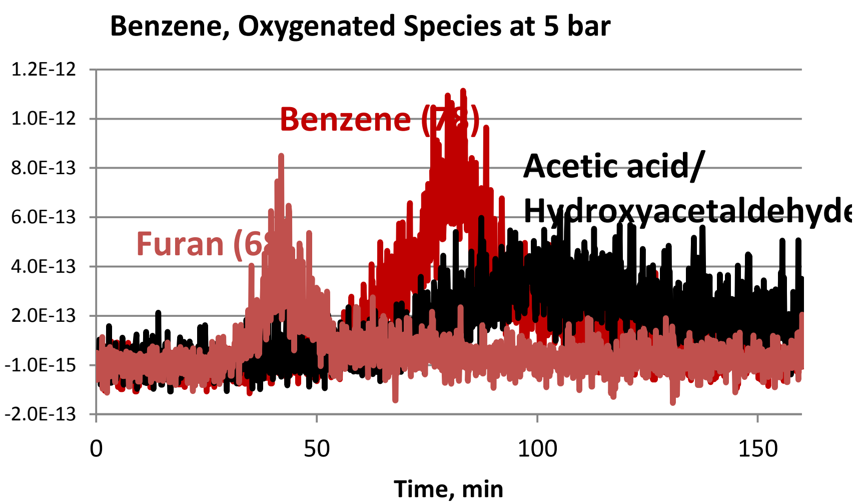


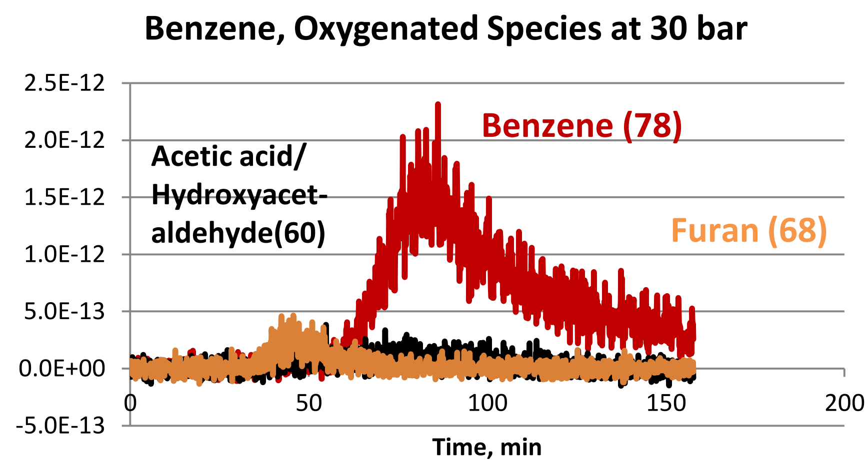


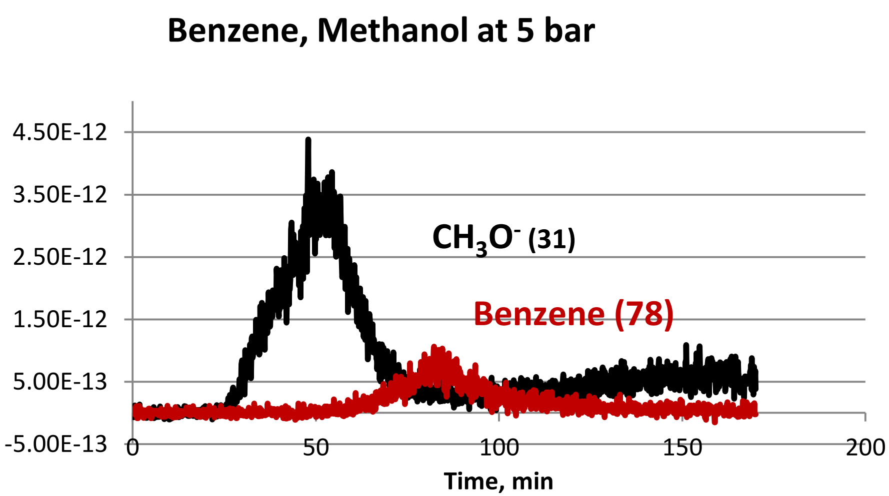


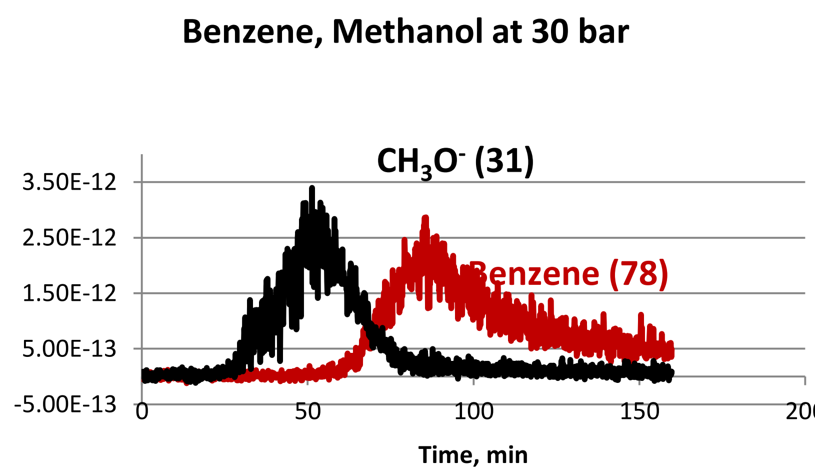


Effect of Pressure on Minor Gaseous Products



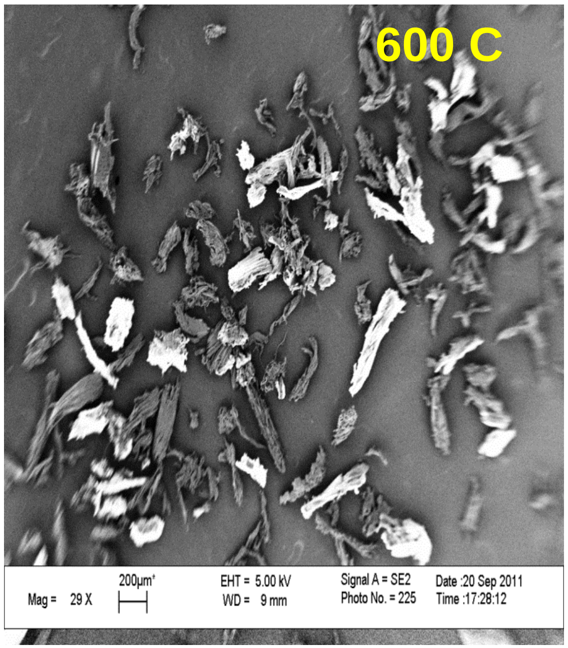


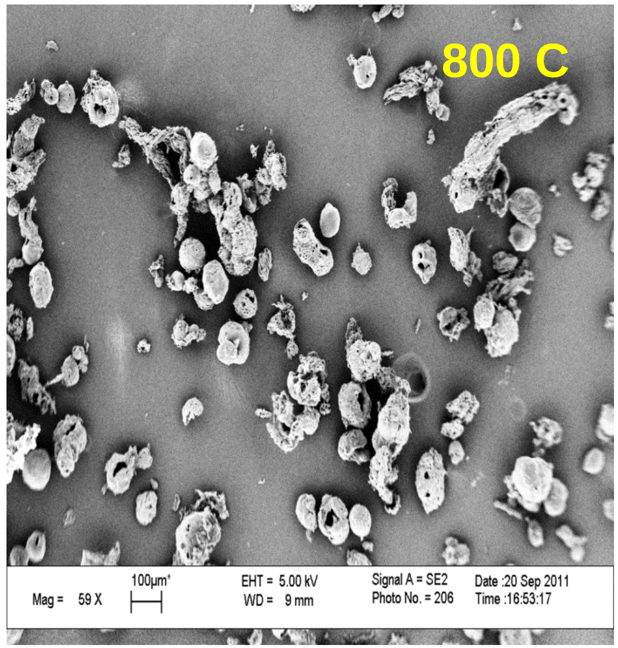


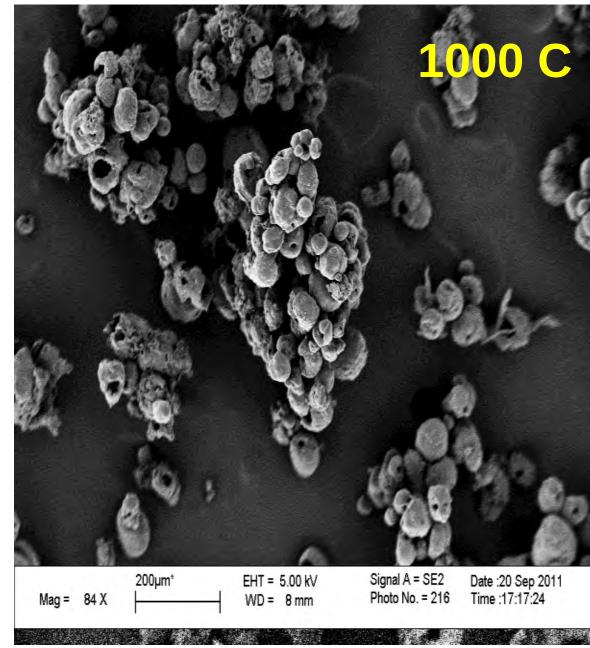


Morphology Studies

Effect of Temperature at Constant pressure

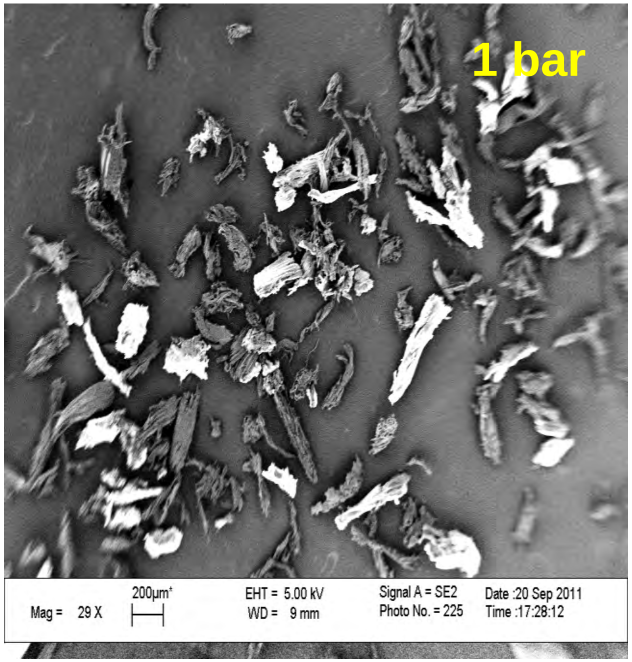


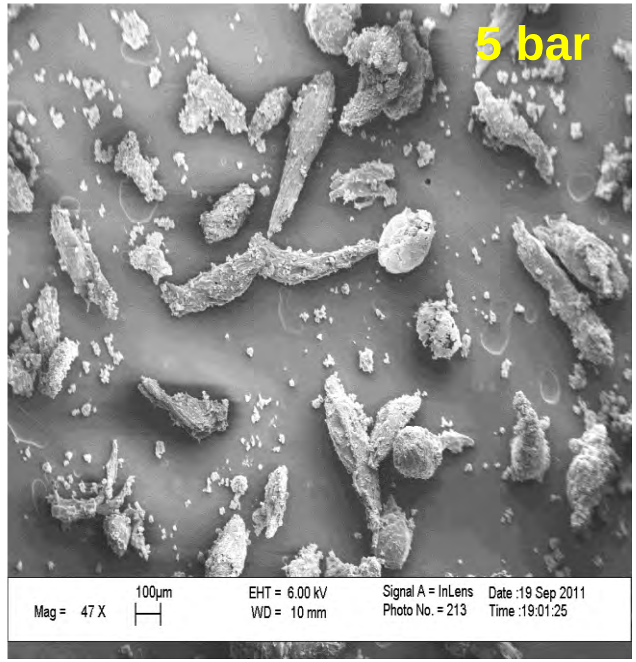


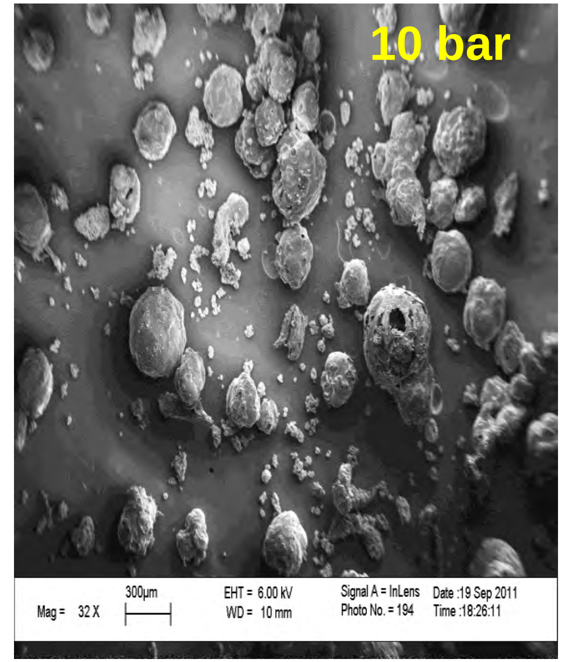


Char generated in LEFR

Effect on Pressure at constant temperature

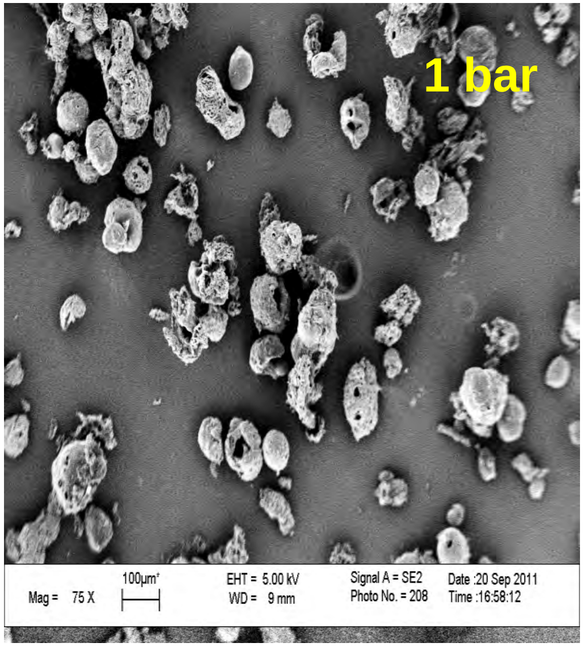


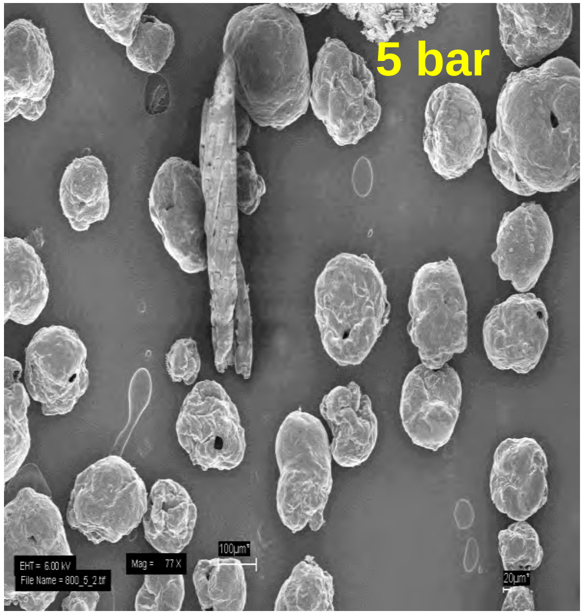


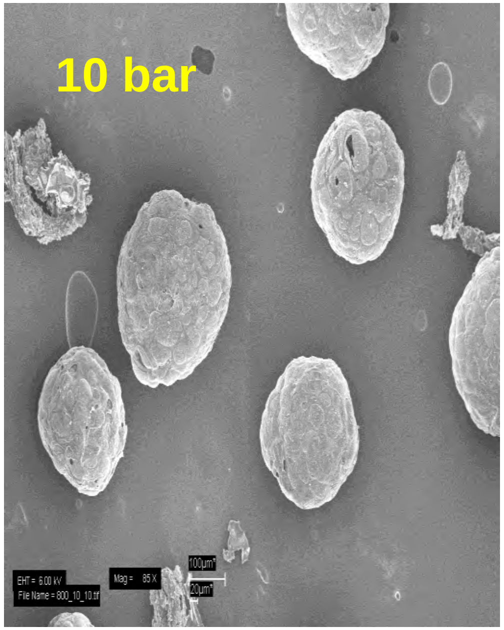


600 C

Effect on Pressure at constant temperature

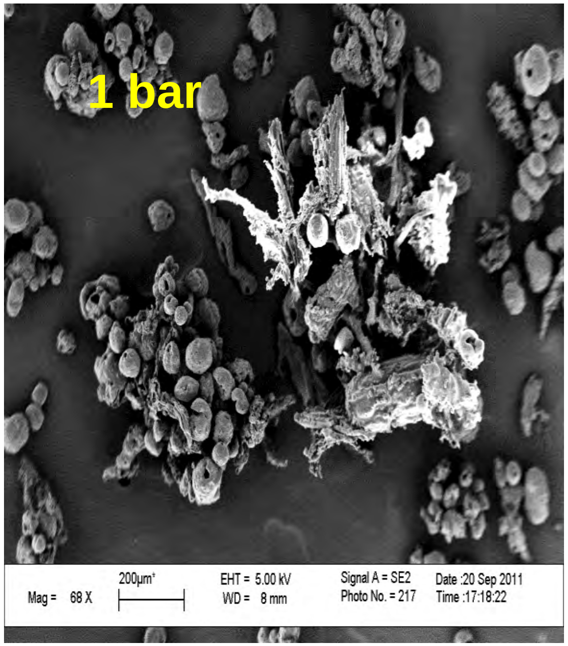


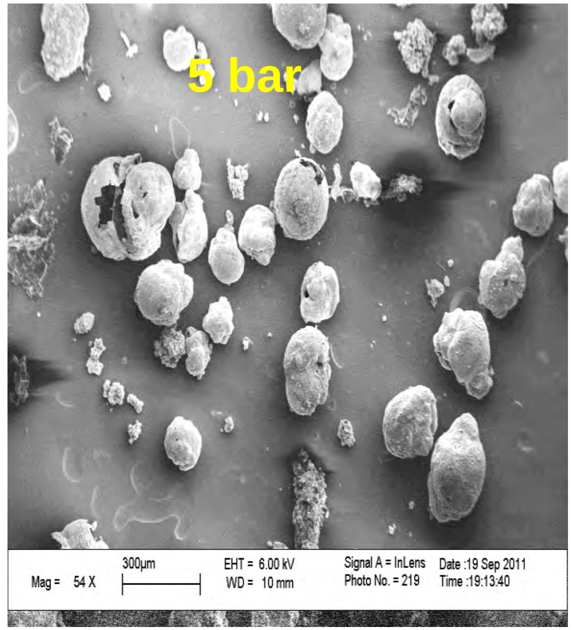


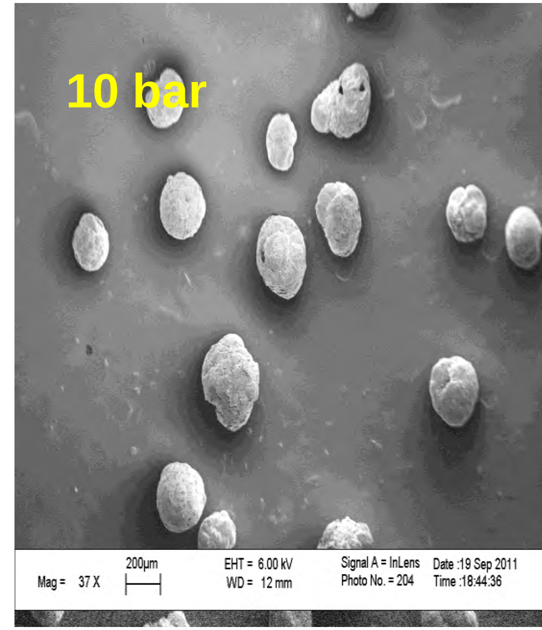


800 C

Effect on Pressure at constant temperature

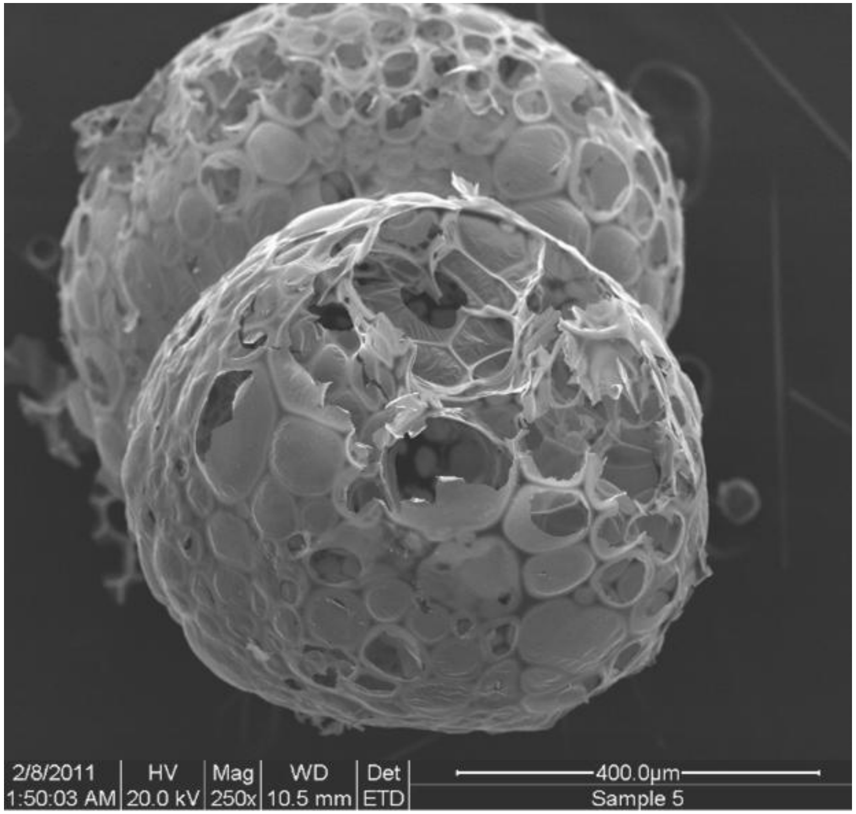


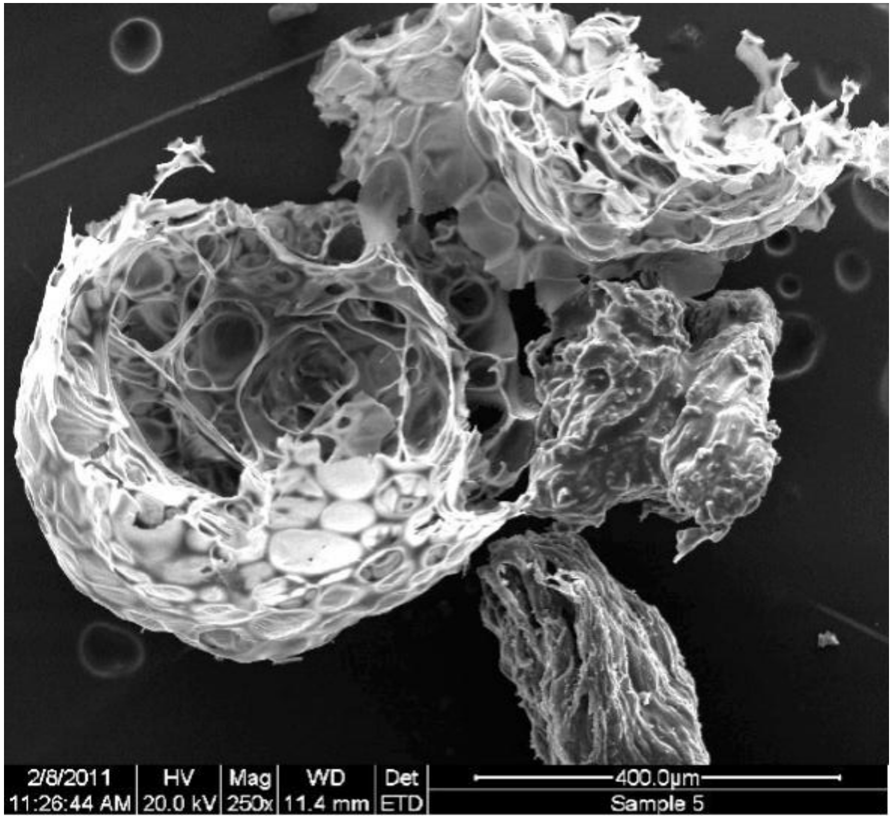




1000 C

Gas-Filled Pockets Formed at High Pressures
Pine Char Formed at 15 bars and 1000 C





Gas Composition during Pyrolysis

Species	Gas Composition (mole%) at 5 bars		
	600 ^oC	800 ^oC	1000 ^oC
CO	45.2	41.2	61.0
CO_2	16.7	16.9	12.1
H_2	8.9	24.5	21.9
CH_4	21.1	16.6	4.75
C_2H_6	1.42		
C_2H_4	5.70	0.52	0.10
C_2H_2	0.09	0.22	0.15
C_3H_8	0.03		
C_3H_6	0.66		
C_4H_{10}			
C_4H_8			
C_4H_6	0.14		

Gas Composition during Pyrolysis

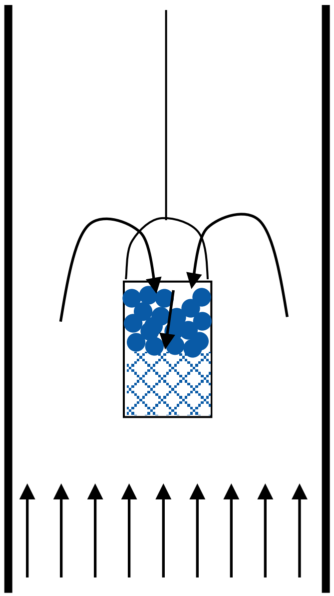
Species	Gas Composition (mole%) at 15 bars		
	600 ^{o}C	800 ^{o}C	1000 ^{o}C
CO	39.4	37.5	65.3
CO_2	17.7	17.7	5.9
H_2	17.4	29.0	26.0
CH_4	21.7	15.6	2.84
C_2H_6	0.1		
C_2H_4	3.40		
C_2H_2	0.20	0.16	
C_3H_8			
C_3H_6			
C_4H_{10}			
C_4H_8			
C_4H_6	0.03		

BET Surface Area of Switchgrass Chars generated in PEFR

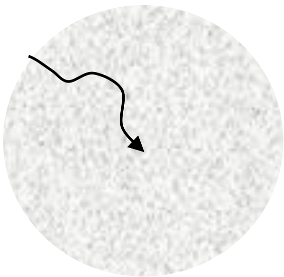
Reference: Switchgrass feed BET area 0.8 m^2/gm

	600 ^oC m^2/gm	800 ^oC m^2/gm	1000 ^oC m^2/gm
1 bar	1.8	2.9	75
5 bars	3.0	187	321
10 bars	3.3	175	278
15 bars	5.2	108	198

Mass Transfer Limitations in Thermobalances



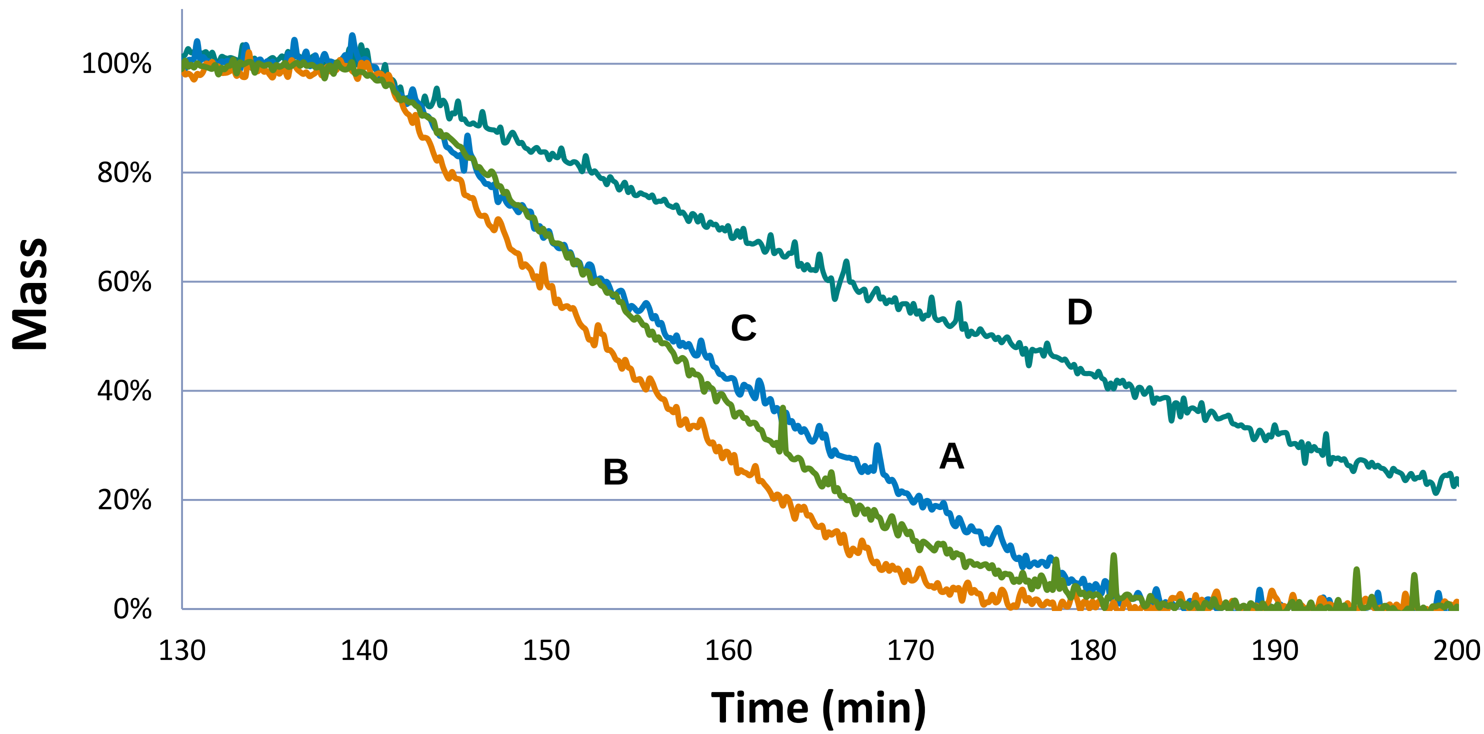
Mass transfer:
- from bulk gas to surface of sample holder
- from surface of sample to bottom of sample
-from surface of particle to center of particle



Impact of Heating Rate

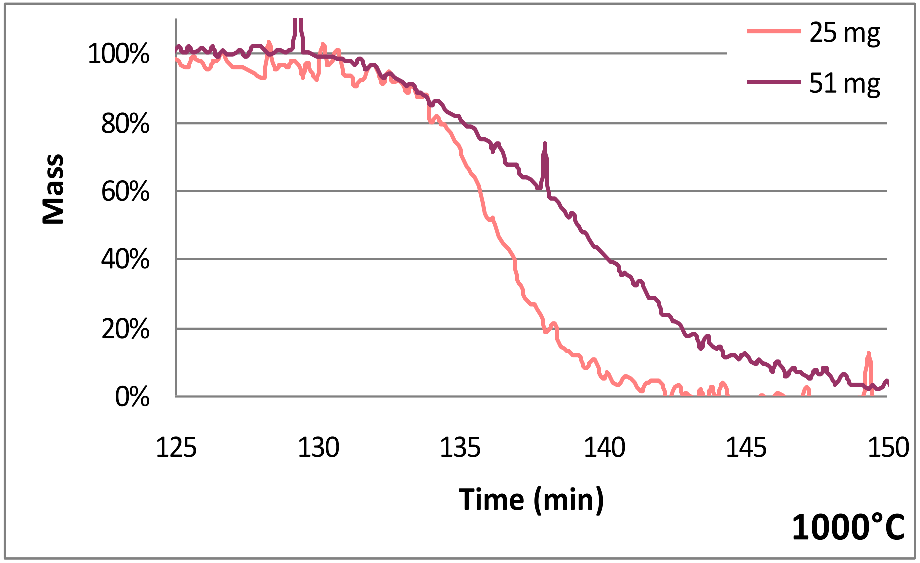
Chars prepared in PEFR (high heating rate) and PTGA (low heating rate) gasified in PTGA

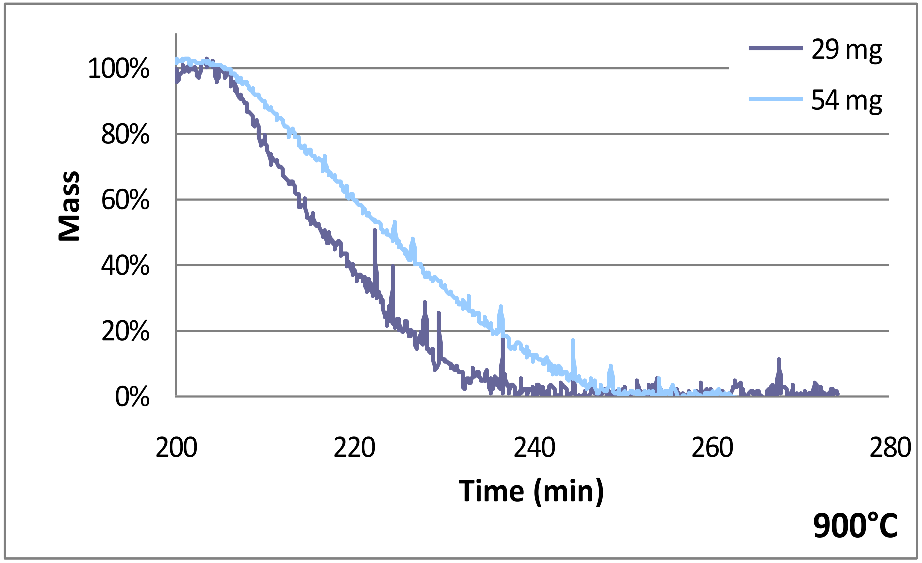
A	PEFR	600C	5 bar
B	PEFR	1000C	5 bar
C	PEFR	600C	15 bar
D	PTGA	900C	5 bar

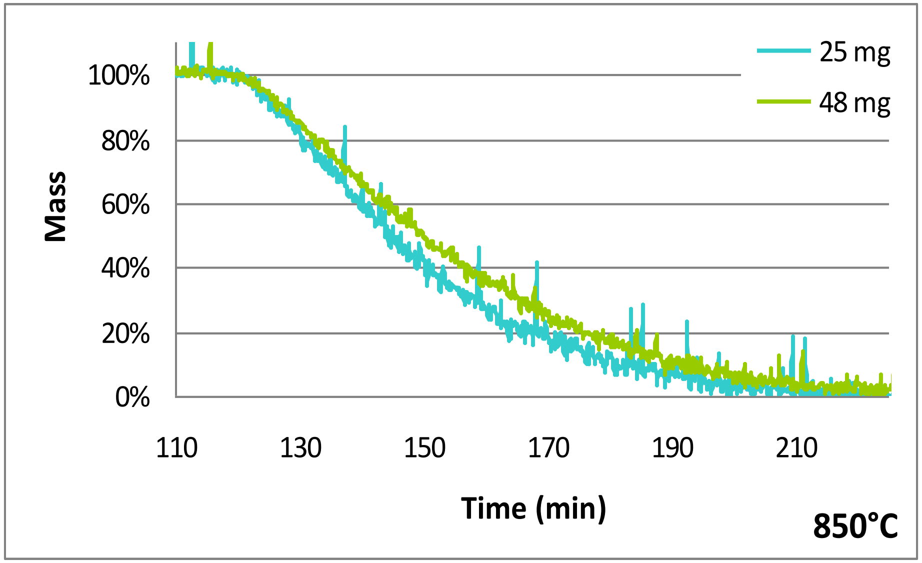


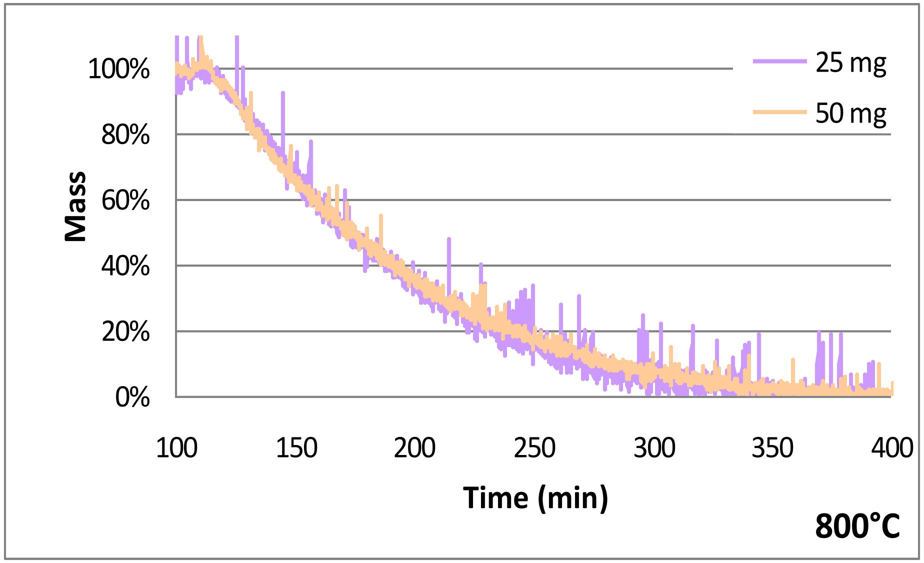
900C, 5 bar, CO_2

Testing for Mass Transfer Limitations









Loblolly Pine Gasification in PEFR

Residence Time	Percent carbon remaining in the char Residue	
	Pressure 5 bars	Pressure 15 bars
3 sec	50.4 %	52.9 %
6 sec	40.0 %	
10 sec	24.5 %	32.0 %

Gasification Conditions: 10% CO_2, 2% H_2O, 0.3% H_2, 1.72% CO, 86% N_2

900 ^oC particle size 180-250 µm

Cornstover Gasification in PEFR

Residence Time	Percent carbon remaining in the char Residue	
	Pressure 5 bars	Pressure 15 bars
3 sec	21.5%	29.7%
6 sec	20.3%	24.0%
10 sec	13.2%	18.6%

Gasification Conditions: 10% CO_2, 2% H_2O, 0.3% H_2, 1.72% CO, 86% N_2

900 ^oC particle size 106-180 µm

Conclusions

Pyrolysis pressure and temperature greatly affect char yield and char morphology.

High heating rates in PEFR produce char that mimick commercial gasifier operation.

PEFR can provide useful kinetic information on biomass conversion, but it will have limitations due to the need to run integral operation.

PTGA operation is similar to a semi-batch reactor, which makes it possible to build the kinetic model. Caution is needed to ensure that results are not masked by the transport effects.

Both PTGA and PEFR have limitations if used alone. However, when combined together, the two are complementary and would provide a basis for building a reliable mathematical model.

Future Work

- Characterization of Chars – ICP EA, Nitrogen physisorption, SEM, NMR (?), FTIR , C,H,N,O Analysis – carbon balance

- Effect of pyrolysis conditions on the formation of tars and light hydrocarbons- tar characterization

- Kinetics of char gasification (L-H models)

- Catalytic role of recycled ash and inorganic species in char gasification

- Mathematical modeling (transport effects)

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