2013 DOE Bioenergy Technology Office (BETO) Project Peer Review

Development of New Gasification Processes for Biomass Residues: Gasification Kinetics at Pressurized Conditions

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Technology Area Review: Gasification

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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 to 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.

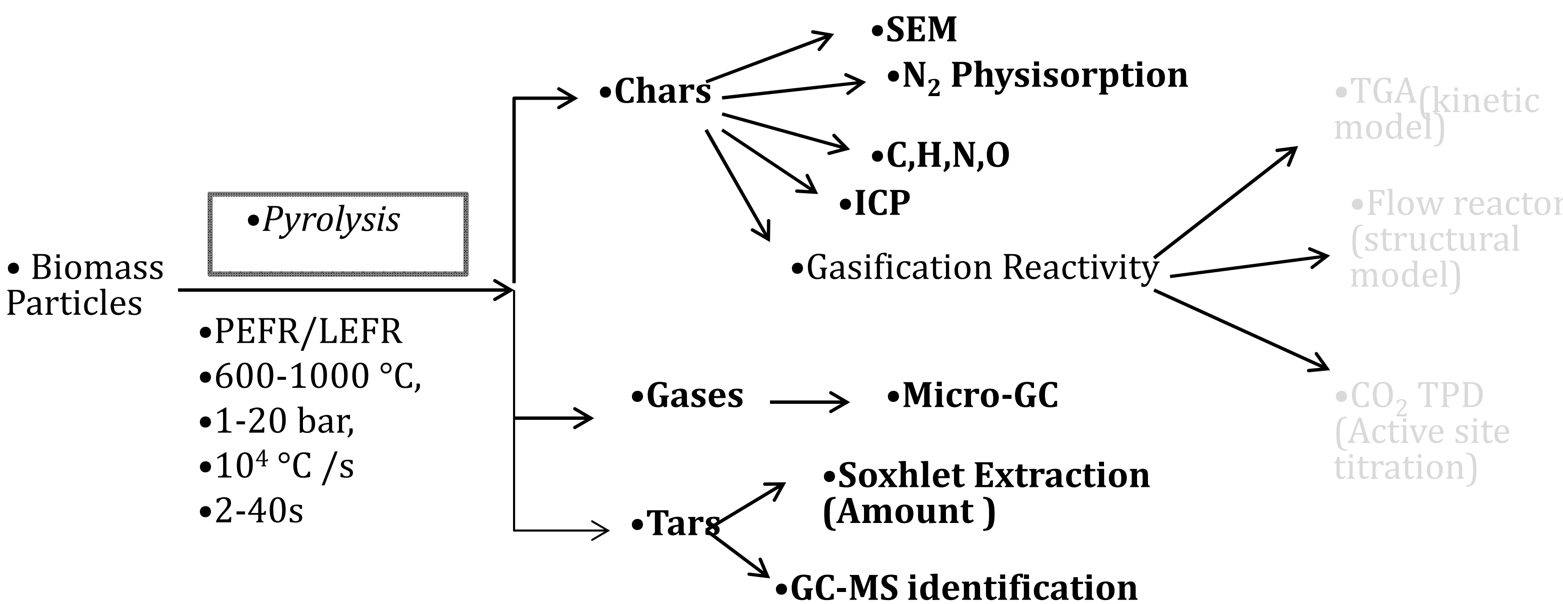
- Georgia Tech student carries out PTGA studies at the NREL under the supervision of co-PI, and weekly reports are submitted. Conference calls between the two co-PIs at regular interval are used to make sure that adequate progress is being made towards the above milestones. In addition, co-PI site visits 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 (10^3-10^4 °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

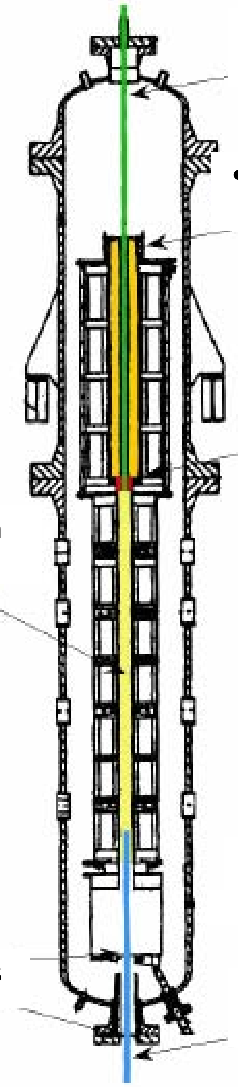


Experimental Approach

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

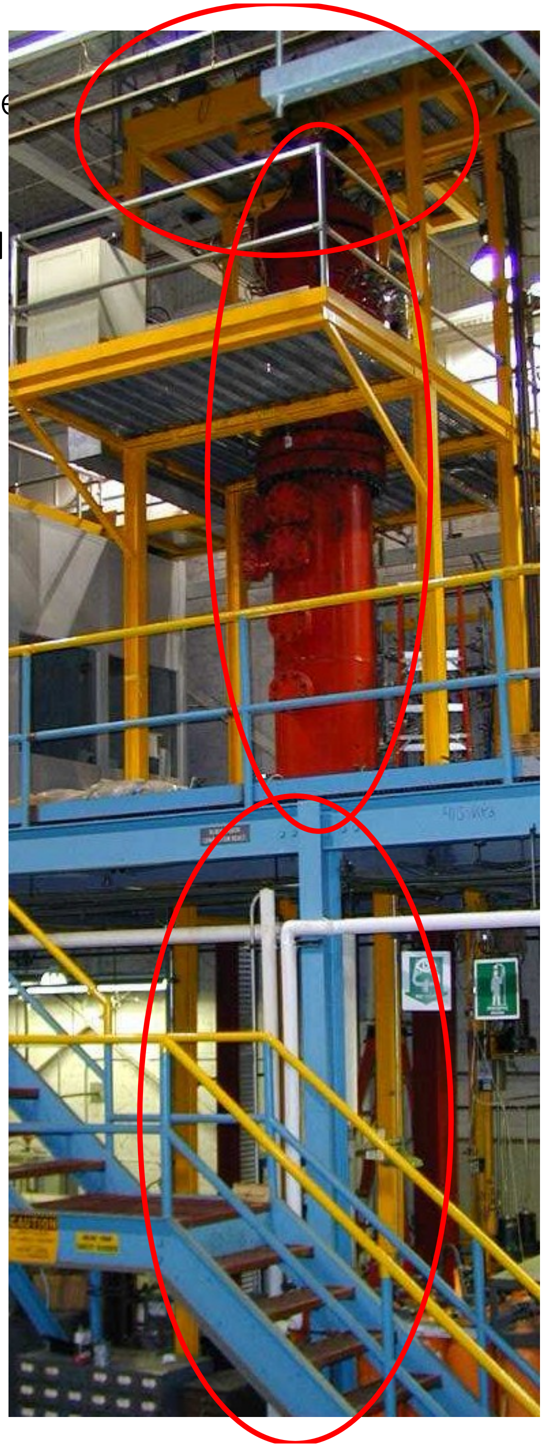
- Complementary reactor types:
  - Laminar Entrained flow reactor (LEFR/PEFR)
  - Thermogravimetric Analyzers (TGA/PTGA)

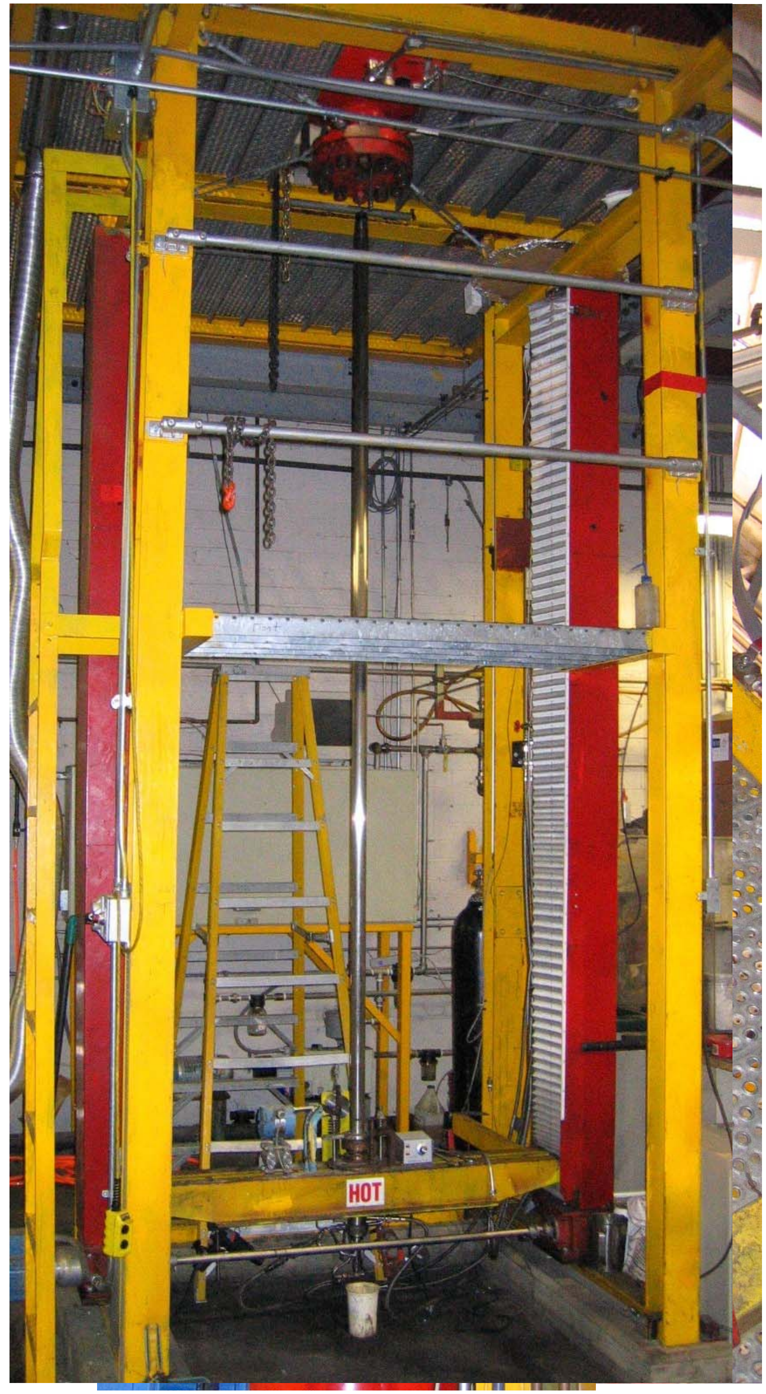
Operating Parameter	PEFR	LEFR	PTGA†	TGA
T (°C) Limits	1500	1500	1100	1500
P (atm) Limits	80	1	100	1
Heating rate	10^4 °C/s	10^4 °C/s	10 °C/min	50 °C/min
Residence Time	Up to 40 s	Up to 4s	Up to Hours	Up to Hours



•† Located at NREL

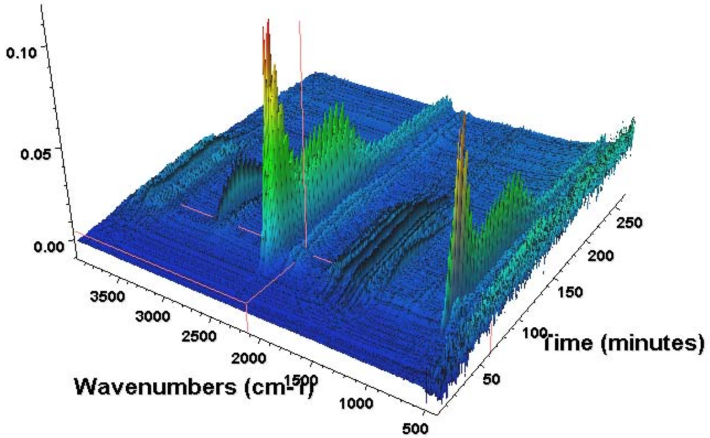
- Pressurize
- Entrained
- Flow
- Reactor

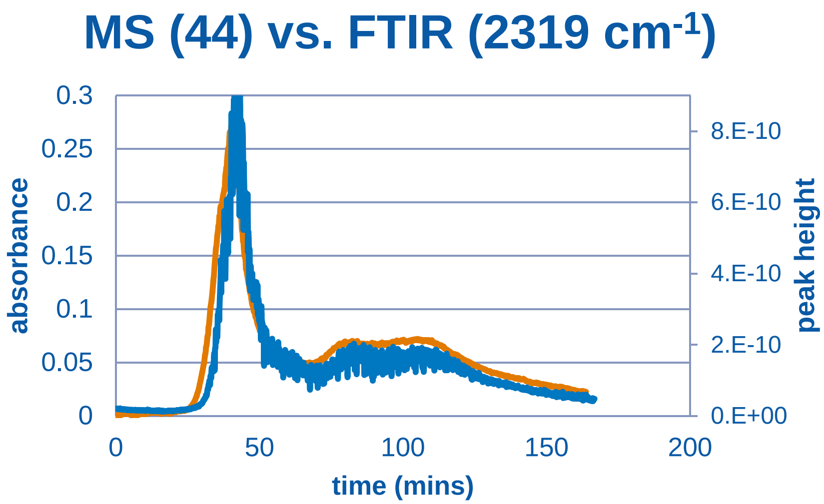


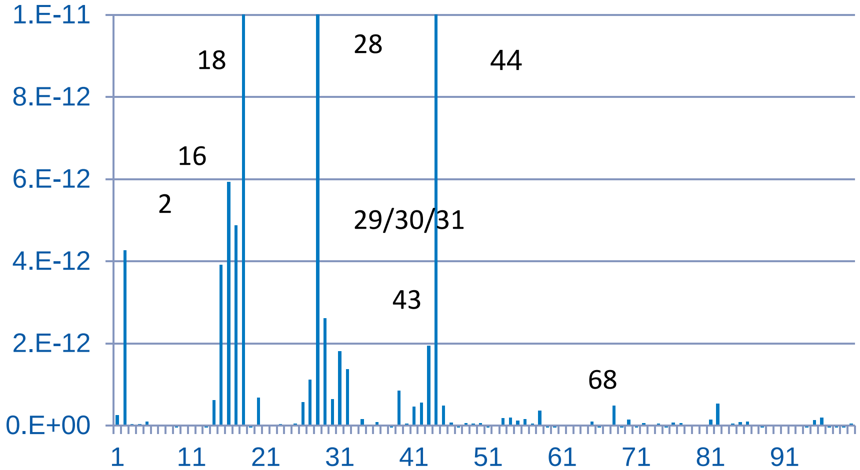


PTGA-MS-FTIR

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





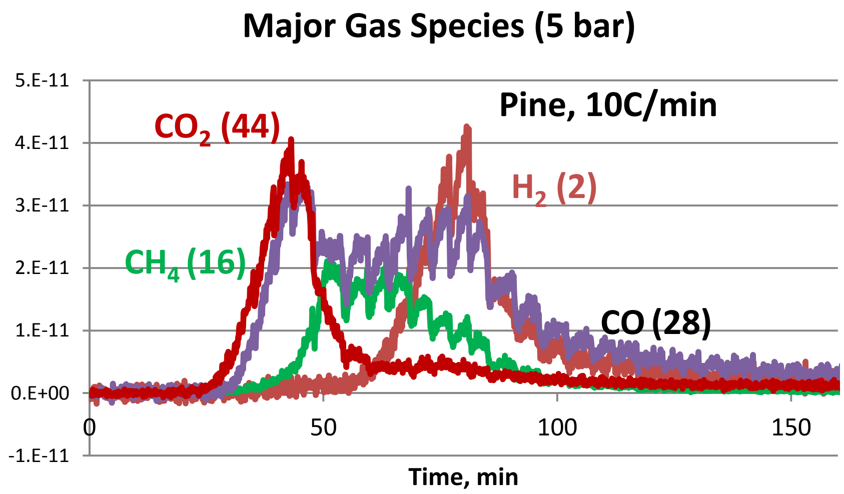


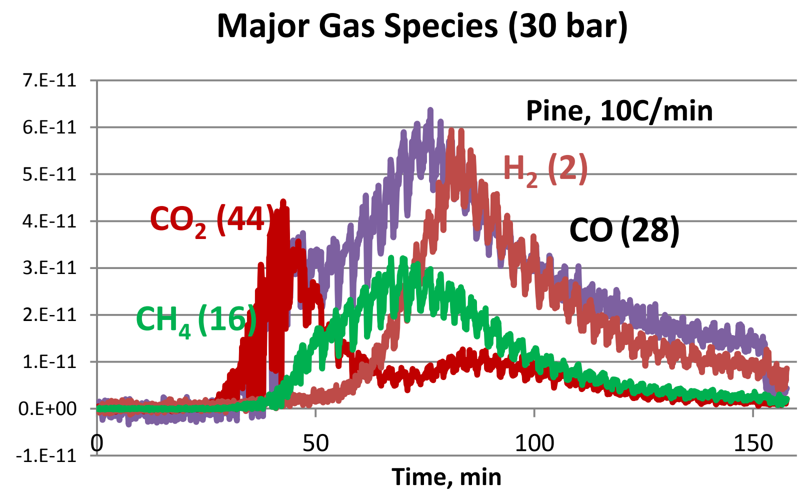
Biomass Samples

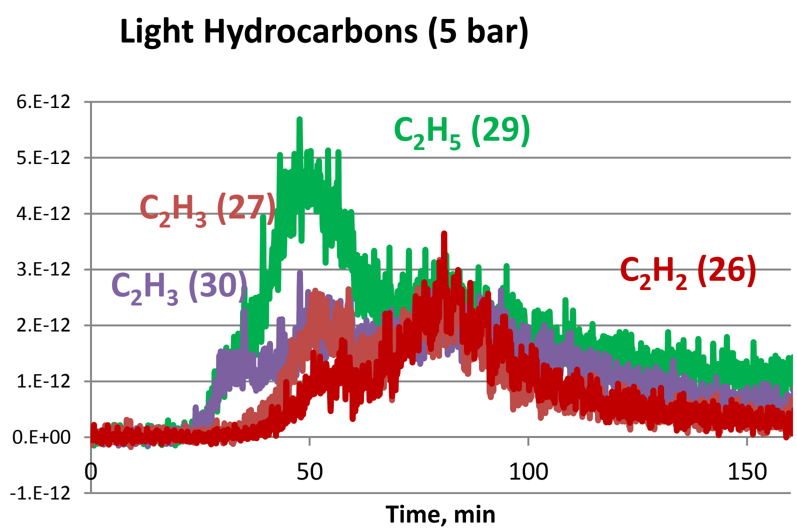
Element	Loblolly Pine	Switchgrass	Cornstover
C	52.4%	48.3%	43.7%
H	6.3%	6.1%	5.9%
N	0.07%	0.36%	0.59%
O	40.9%	44.7%	45.3%
Ash	0.3%	2.2%	6.1%
Volatile Matter	79.1%	77.6%	74.4%
Fixed Carbon	12.8%	12.4%	12.6%

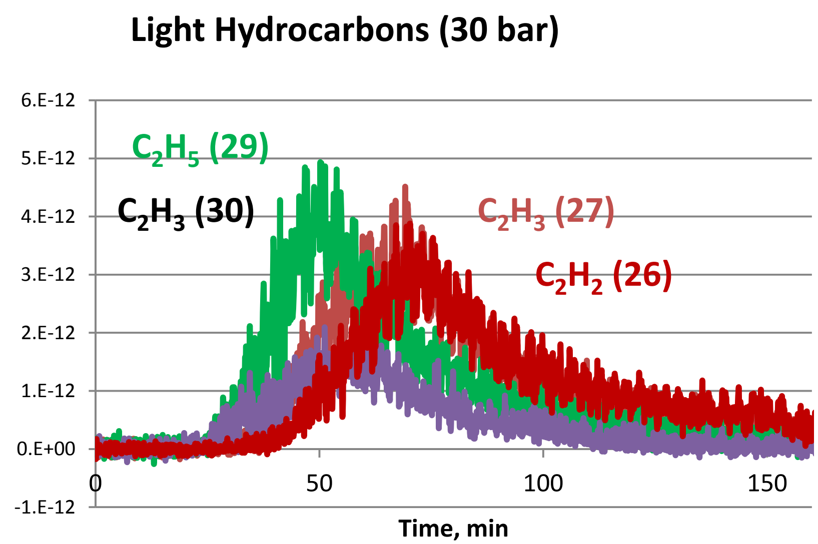
Technical Accomplishments/Progress/Results

Effect of Pressure on Gas Species Evolution



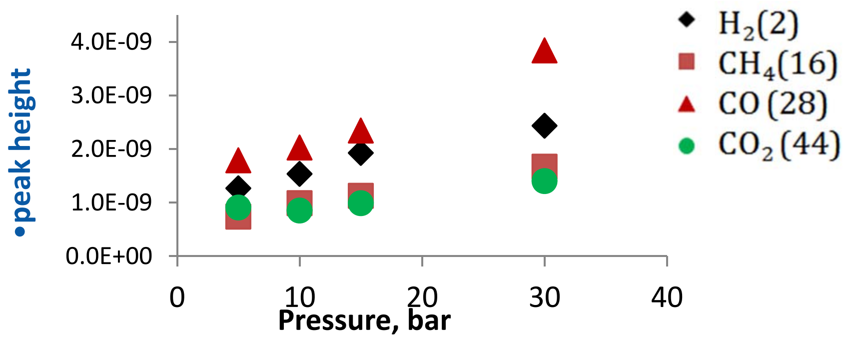


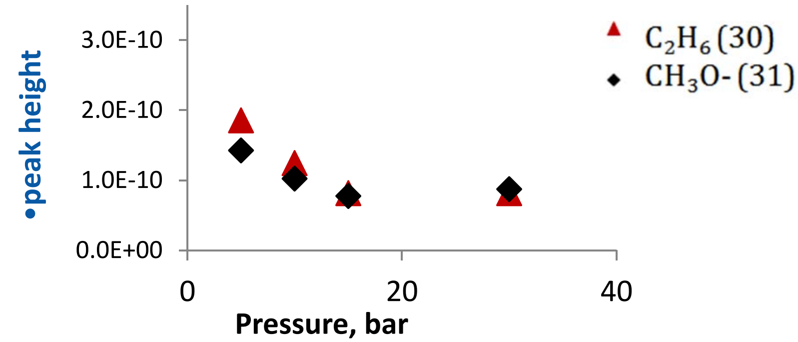


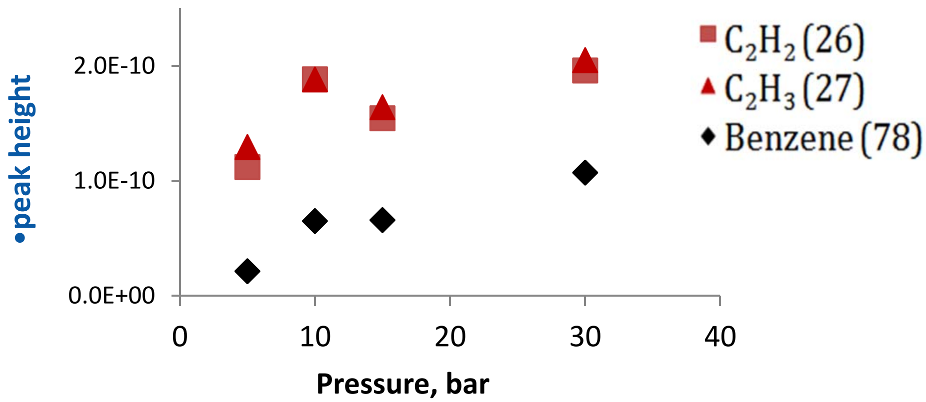


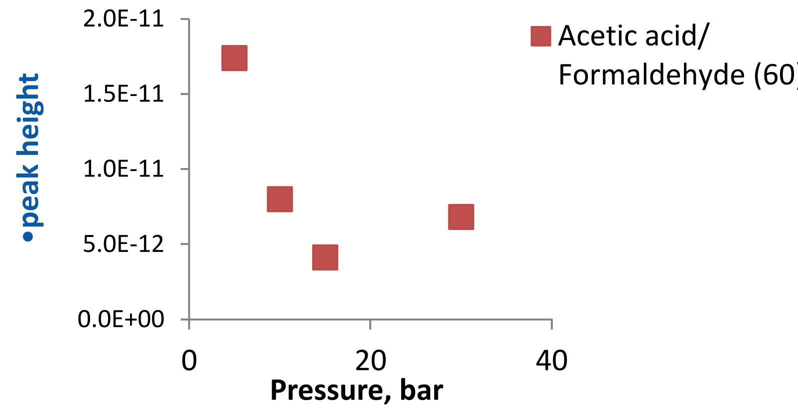
Technical Accomplishments/Progress/Results

Effect of Pressure on Gases (PTGA)









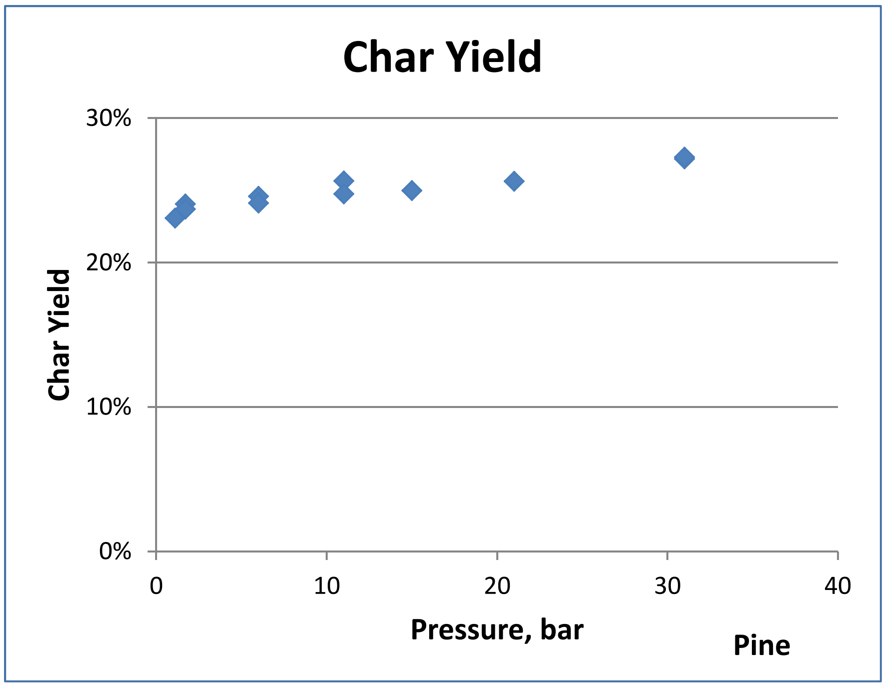
- Major light gases and C_2H_4, C_6H_6 increases with pressure
- Oxygenates and hydrocarbon fragments decrease with pressure

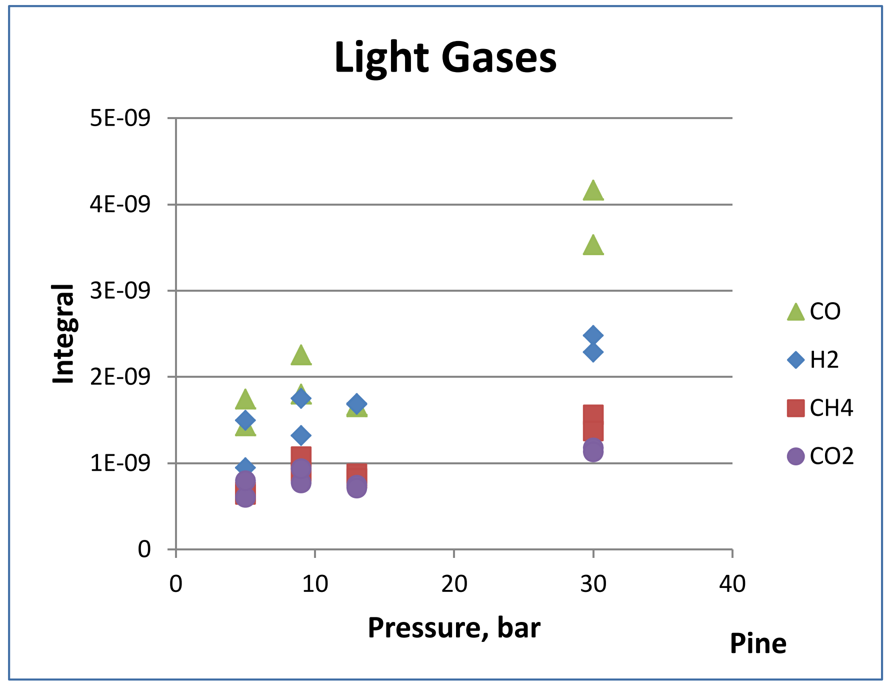
✓ Evolution of gases with time can be monitored in PTGA
✓ Thermal-degradation mechanism can be better understood

•†Performed by NREL

Technical Accomplishments/Progress/Results

Char yield and light gas species increase as pressure is increased





Technical Accomplishments/Progress/Results

Gases-switchgrass Pyrolysis

Gas from PEFR → Tedlar Bags → micro-GC analysis

Temperature °C	**600**			**800**			**1000**				
RT	**40s**			**40s**			**1.7s**	**5s**	**40s**		
Pressure bar	**5**	**10**	**15**	**5**	**10**	**15**	**5**	**5**	**5**	**10**	**15**
Carbon Monoxide	44.79	39.52	39.44	41.21	41.41	37.43	46.10	45.49	61.03	70.76	65.29
Carbon dioxide	16.58	17.17	17.68	16.93	15.26	17.7	12.69	13.03	12.07	5.29	5.89
Hydrogen	9.73	17.23	17.4	24.52	31.32	29.07	19.65	18.71	21.9	22.42	25.98
Methane	20.94	21.69	21.72	16.6	11.71	15.63	14.27	17.65	4.75	1.52	2.84
Ethane	1.4	0.38	0.1				0.57	0.49			
Ethylene	5.65	3.78	3.43	0.52	0.26	0.16	5.17	3.98	0.1	0.03	
Acetylene	0.09	0.13	0.2	0.22	0.04		0.67	0.36	0.15		
Propane	0.03						0.01	0.00			
Propylene	0.65	0.06					0.61	0.21			
Butane											
1-Butene							0.03				
1,3- Butadiene	0.14	0.04	0.03				0.23	0.08			

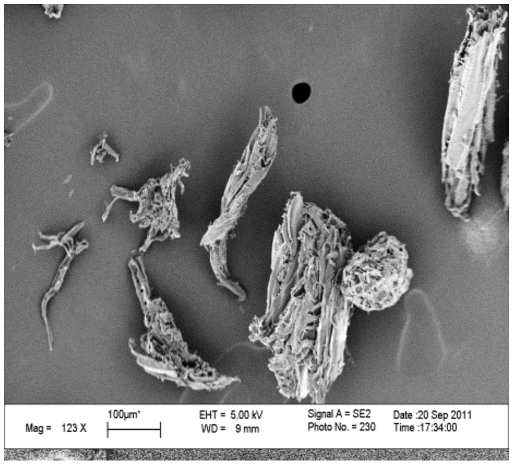
- Steam reforming, tar cracking, water-gas shift equilibrium, gasification reactions influence the gas compositions at various T, P, RT

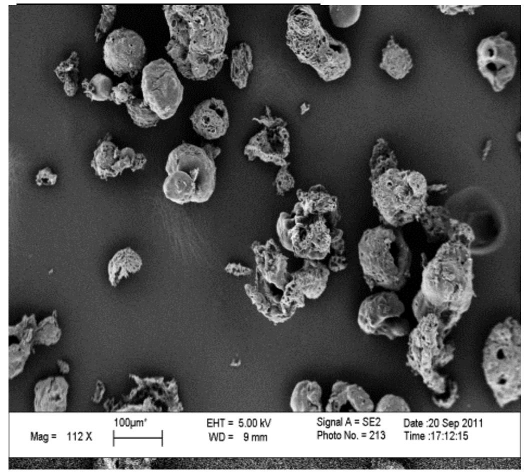
Georgia Tech

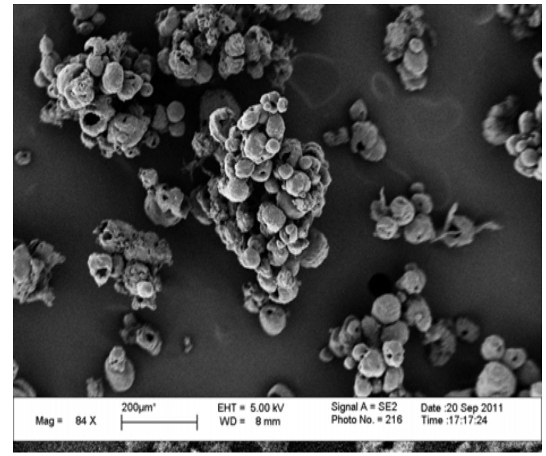
Technical Accomplishments/Progress/Results

Pine Chars

•Effect of Temp.





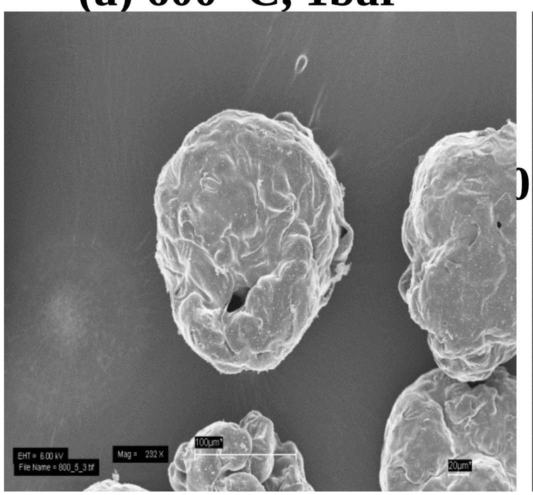


(a) 600 °C, 1bar

°C, 1 bar

°C, 1 bar

•Effect of Pressure



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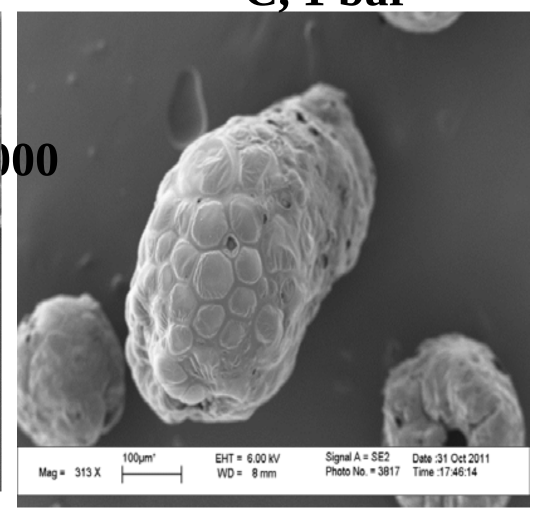


(a) 800 °C, 5 bar

°C, 10 bar

°C, 15 bar

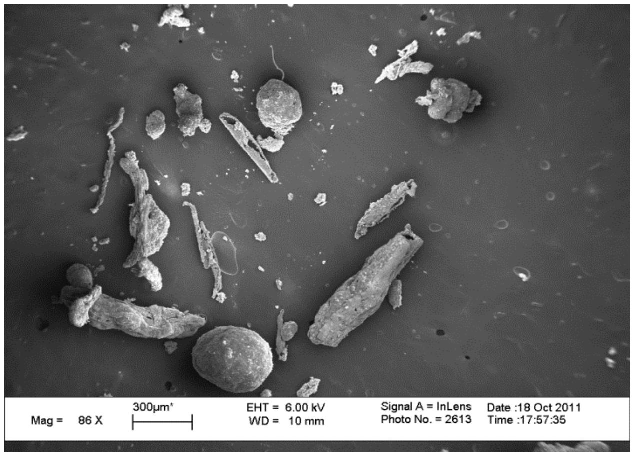
(b) 800

(c) 800

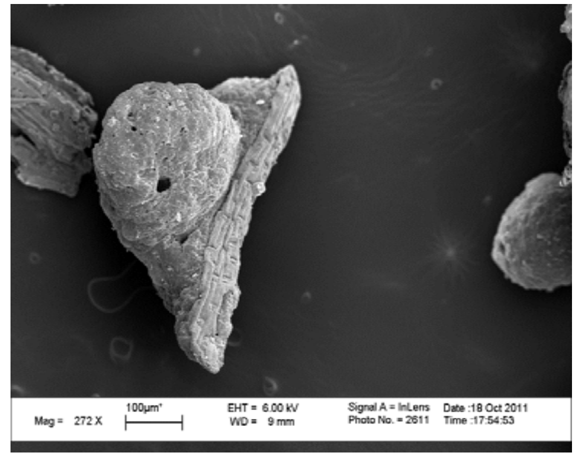
Technical Accomplishments/Progress/Results

Switchgrass Chars

Incomplete melting of char



(a) 1000 °C, 15 bar

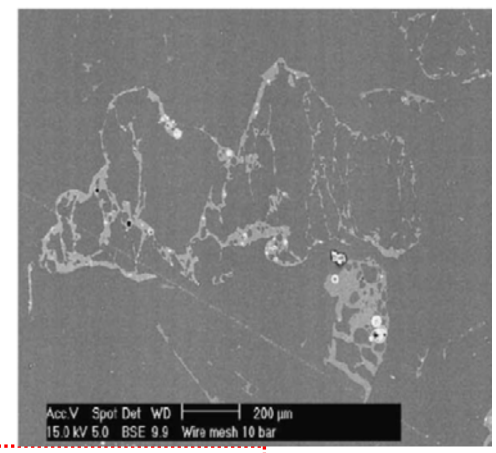


(b) 1000 ° C, 10 bar

•BET Surface Areas

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

•Formation of cavities at high pressures

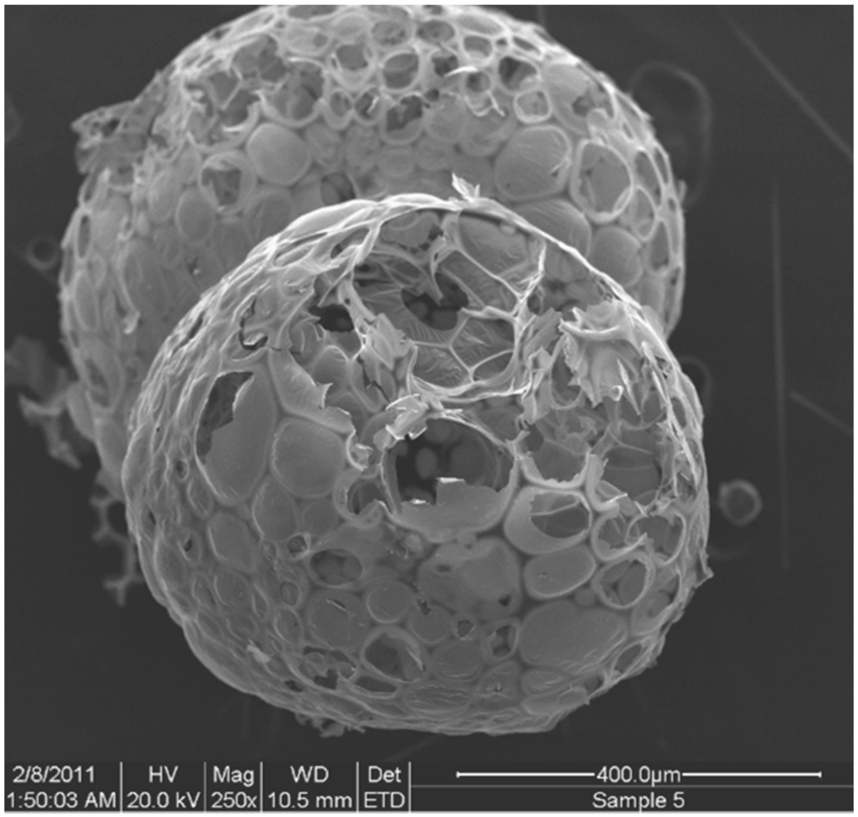


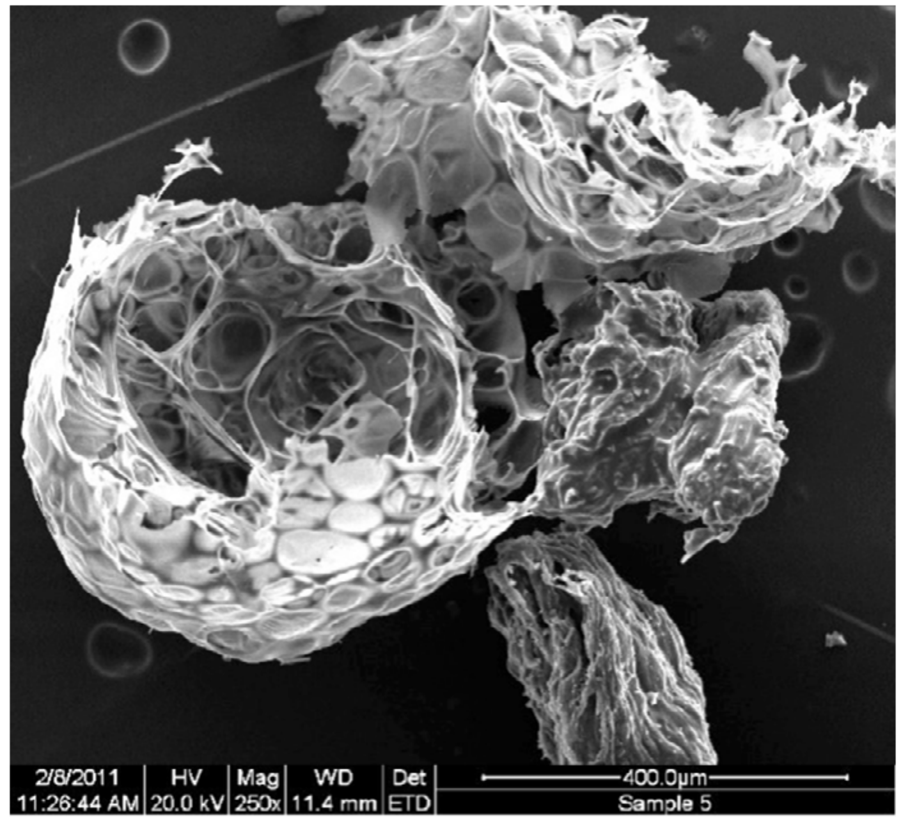
- ✓ Evaluate Surface Areas, pore volumes of all chars
- ✓ ICP, CHON analysis for total char yield

•Cetin et al. Fuel (2004), 83, 2139

Technical Accomplishments/Progress/Results

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

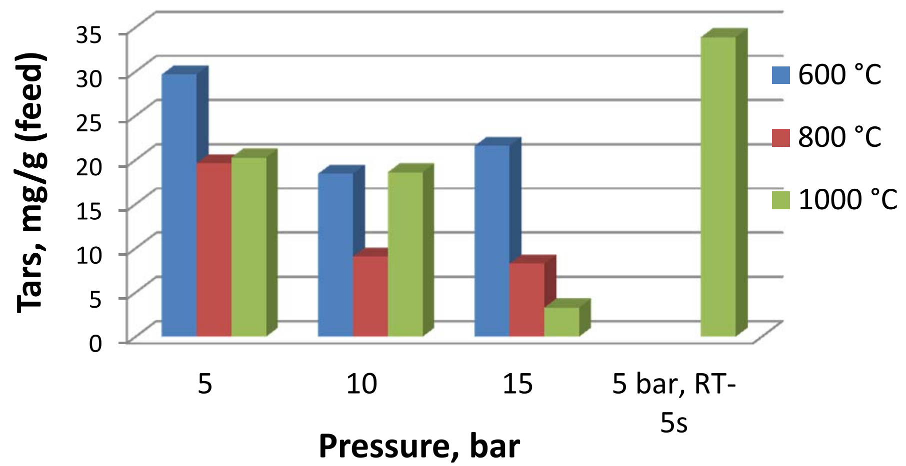




Technical Accomplishments/Progress/Results

Tars

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

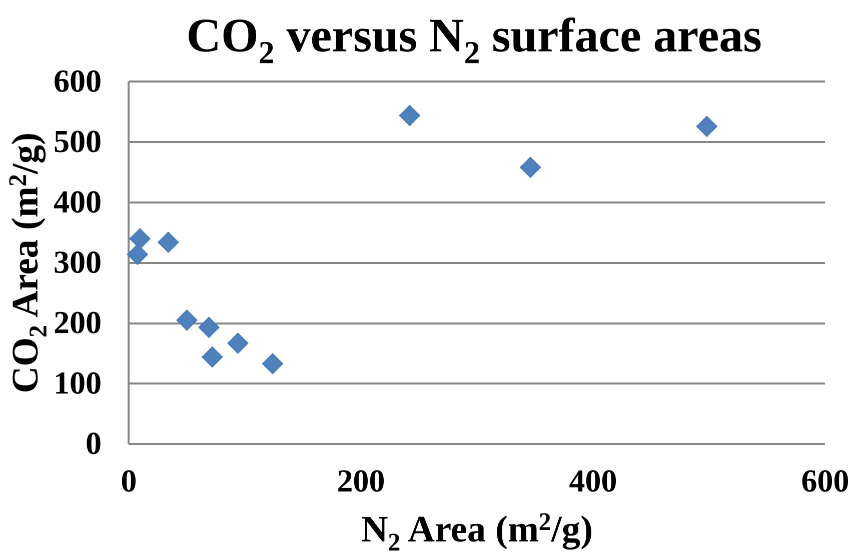


- **Primary:** *o,m,p* Dihydroxybenzes → Short Residence times only
- **Secondary:** Dibenzofuran, Biphenyl → Only at 600 °C and 800 °C
- **Tertiary** : Fluorene, Anthracene, Phenanthrene Napthalene → At all conditions

✓Extraction followed by GC-MS
✓Tars measured represent lower limit

Technical Accomplishments/Progress/Results

Effect of pyrolysis T and P on char surface area (Pine)



T (°C) /P (bar)	600	800	1000
5	526	314	144
10	340	133	205
15	458	193	167
20	544	334	
Pine	142		

- CO_2 adsorption measures higher surface areas compared to N_2 physisorption. CO_2 adsorption takes into account the sub-nano pore volume which N_2 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

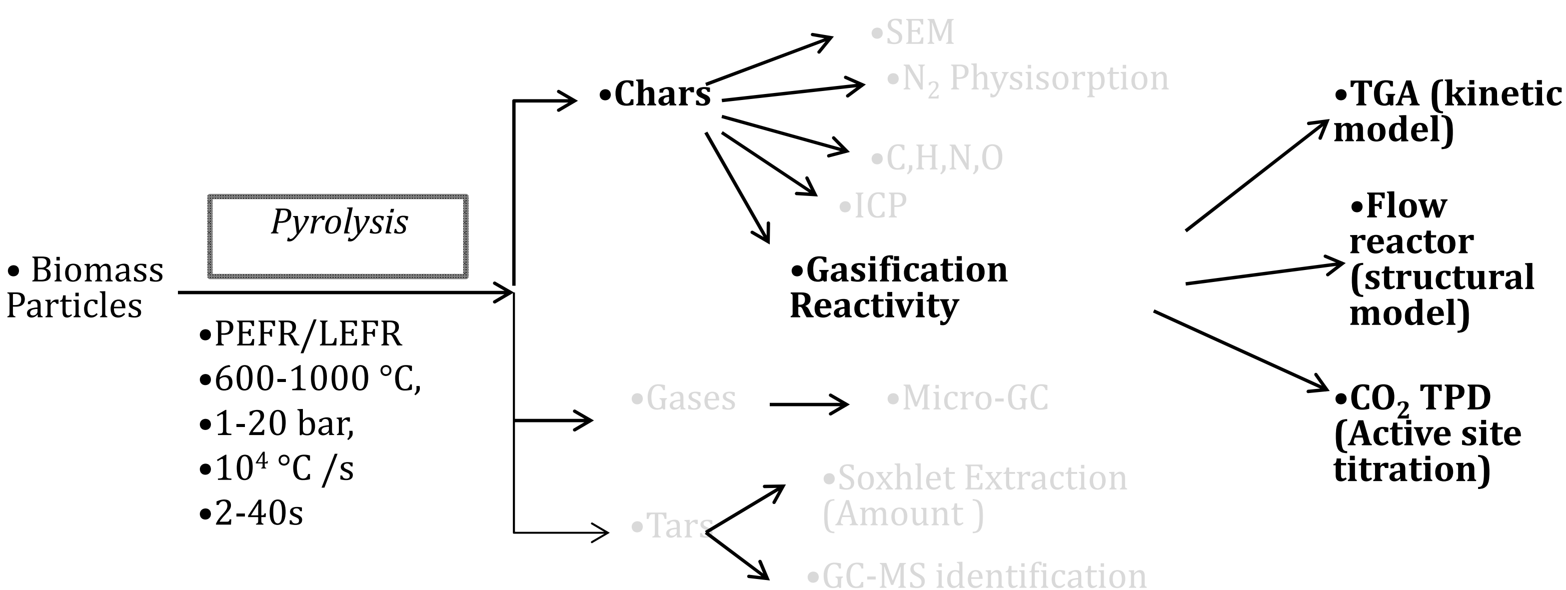
Technical Accomplishments/Progress/Results

Char Gasification Activity

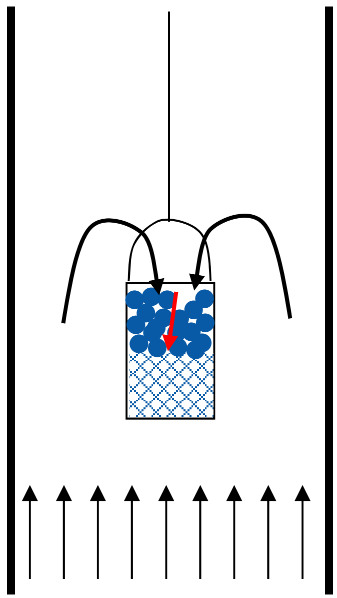
- $R = r_c\,(T, P, C_t) * r_s\,(X)$

- 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

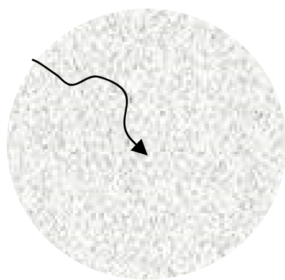
Generalized model is required: for any type of feedstock, with varied pyrolysis history



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

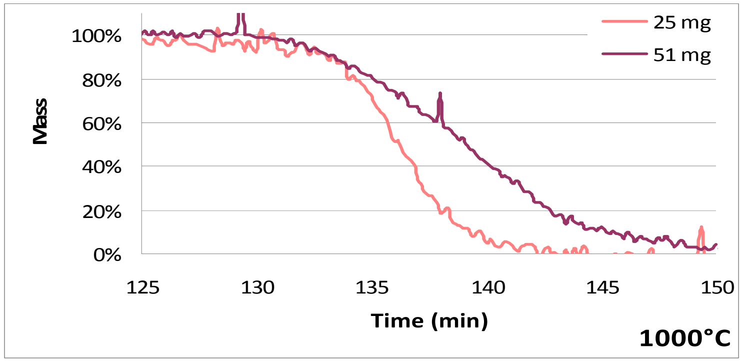


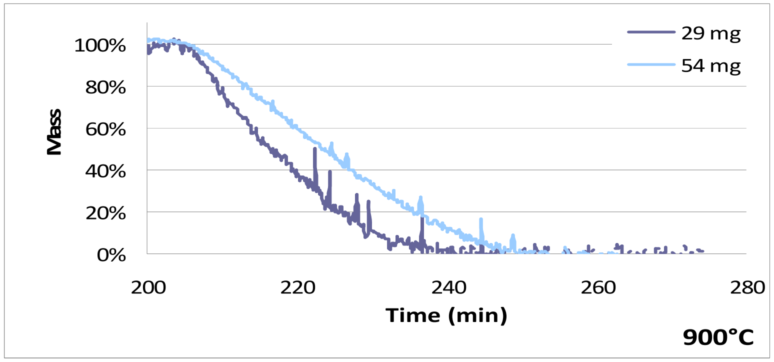
- Tests for impact by changing
  - gas flow rate
  - sample size
  - particle size

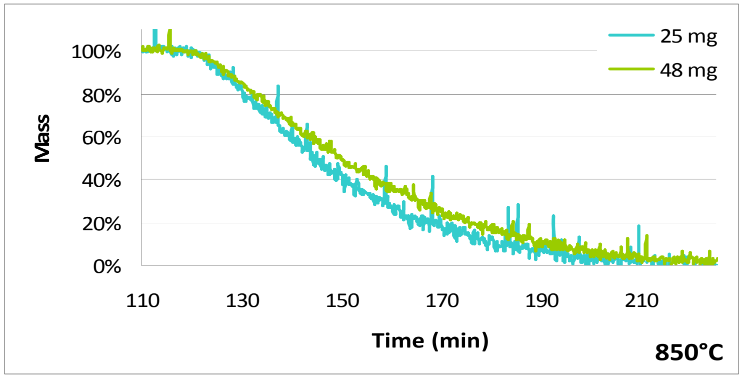
Technical Accomplishments/Progress/Results

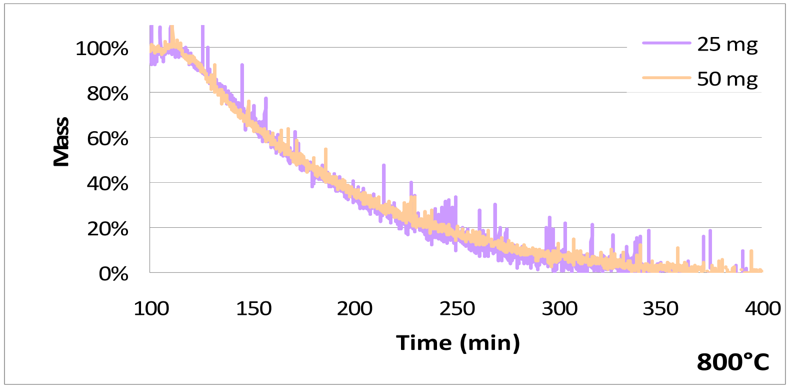
External Transport in PTGA

- Varying char sample sizes in PTGA
- Gasified at different temperatures
- Kinetic regime < 800 °C





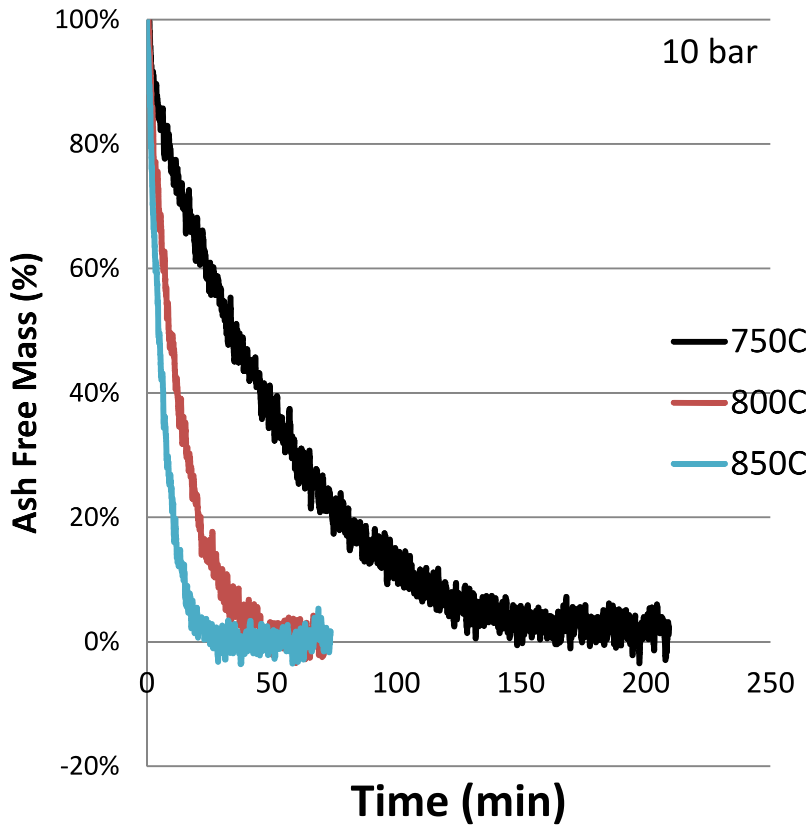




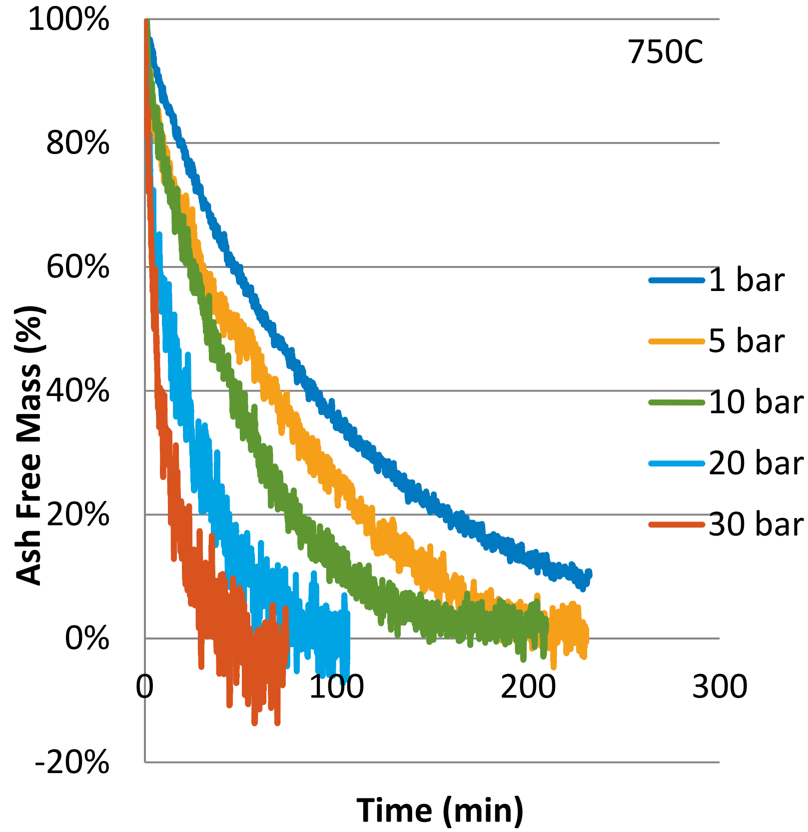
Technical Accomplishments/Progress/Results

Impact of Gasification Conditions

Gasification Temperature



Gasification Pressure



Switchgrass char prepared at 5 bar/1000°C

Technical Accomplishments/Progress/Results
Analysis of Data

Gasification curves fit with different particle models

- Uniform Conversion Model
  - Reaction rate uniform throughout particle
  - Rate proportional to amount of ungasified carbon

  $-dm_t/dt=k(m_t-m_{ash})$ $X=(m_o-m_t)/(m_o-m_{ash})$

  $-\ln(1-X) = kt$

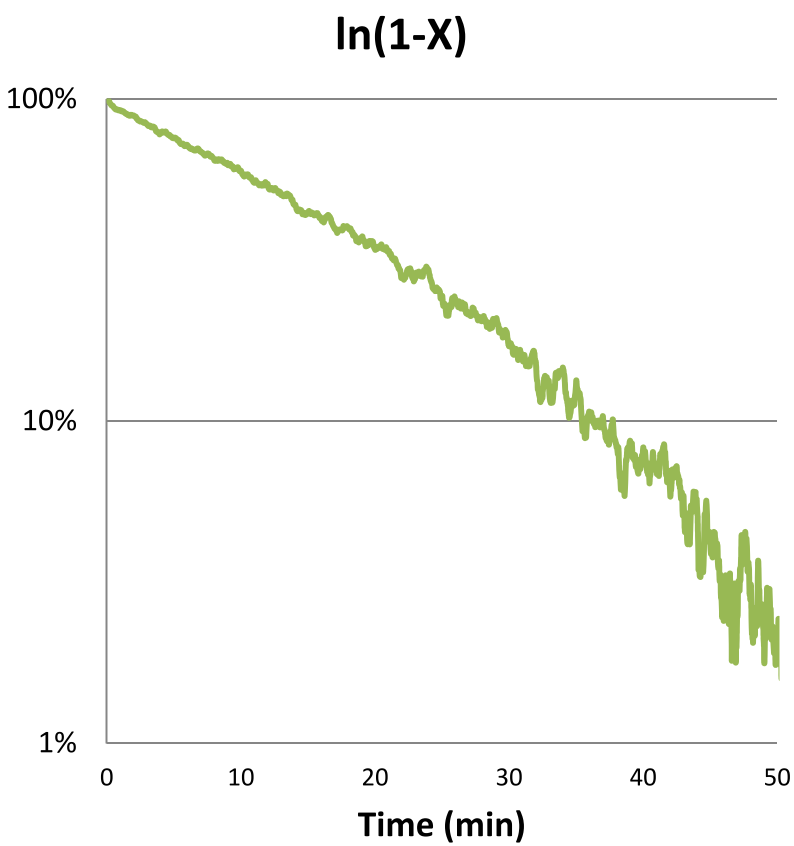
- Grain Model
  - Particle consists of grains which each react according to shrinking core model
  - Rate proportional to surface area of grains

  $-dm_t/dt = k\,(m_t-m_{ash})^{2/3}$

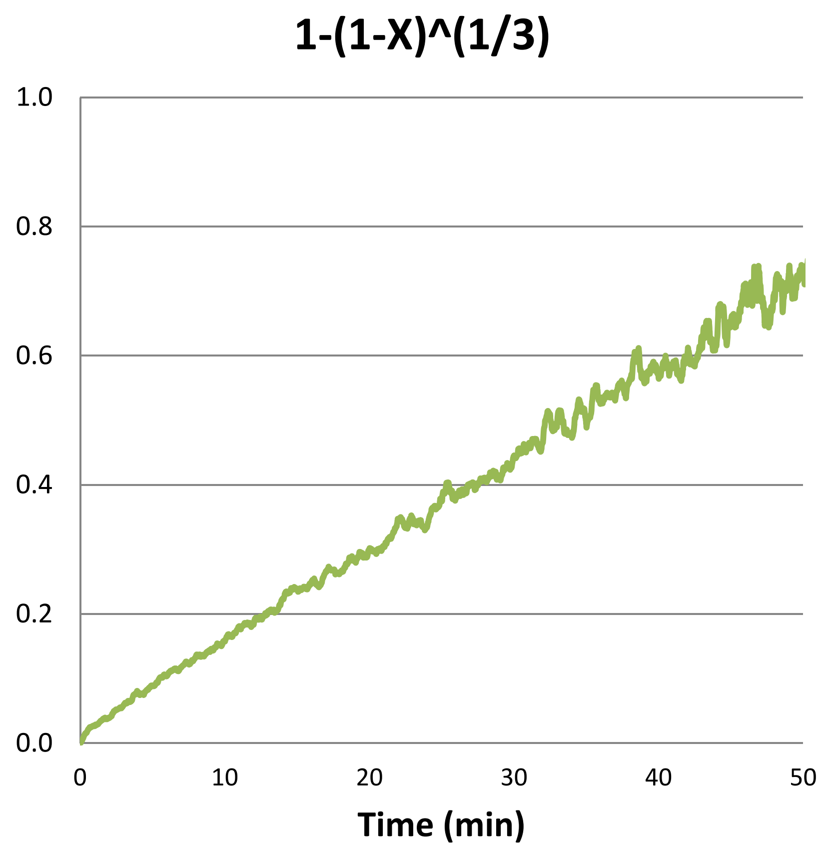
  $3[1-(1-X)^{1/3}] = kt$

Technical Accomplishments/Progress/Results

Uniform Conversion Model



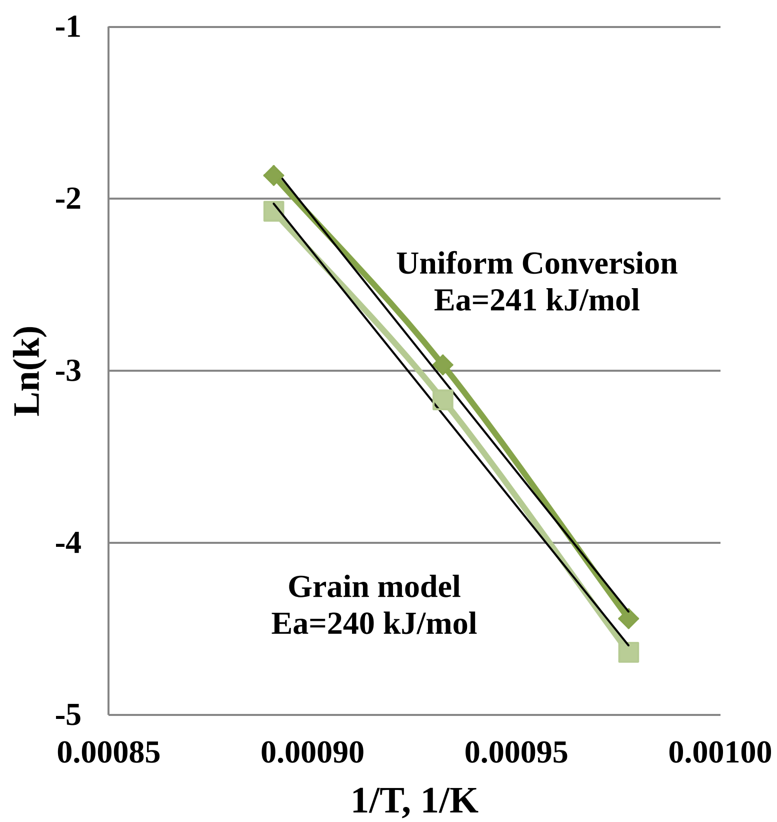
Grainy Pellet Model



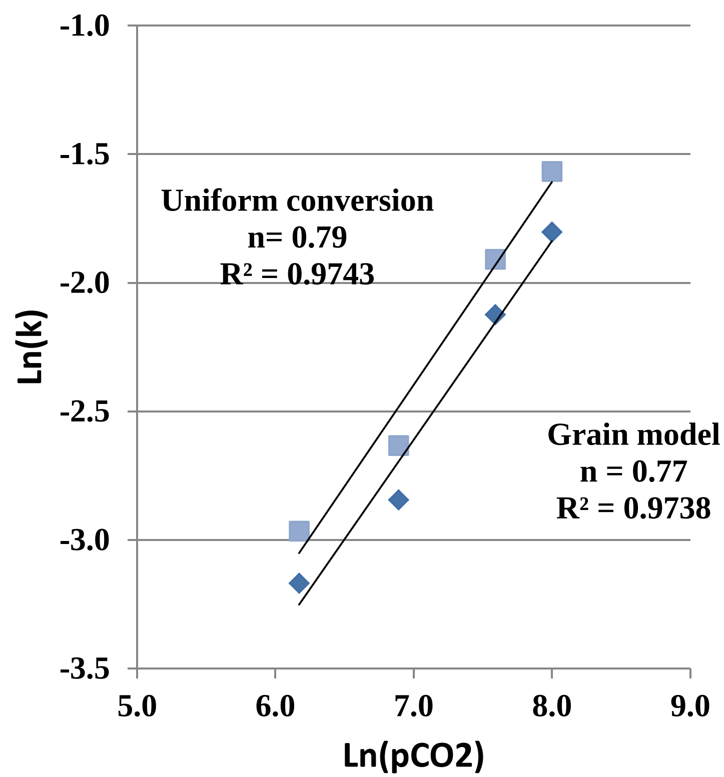
Switchgrass char prepared at 5 bar/1000°C, gasified at 5 bar/800C

Technical Accomplishments/Progress/Results

Arrhenius Plot



Nth order reaction rate



Switchgrass char prepared at 5 bar/1000°C

Technical Accomplishments/Progress/Results

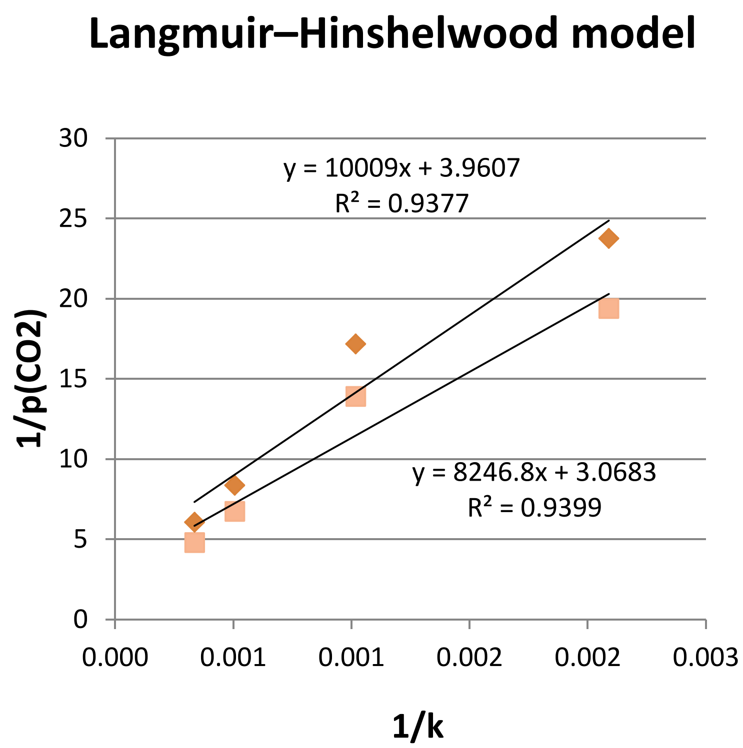
Langmuir-Hinshelwood Kinetics

$$r_c = \frac{k_1 C_t P^{\alpha}{}_{CO_2} + k_1' C_t P^{\beta}{}_{H_2O}}{1 + k_2 P_{CO} + k_3 P_{H_2O} + k_4 P_{CO_2} + k_5 P_{H_2} + k_6 P_{CH_4}}$$

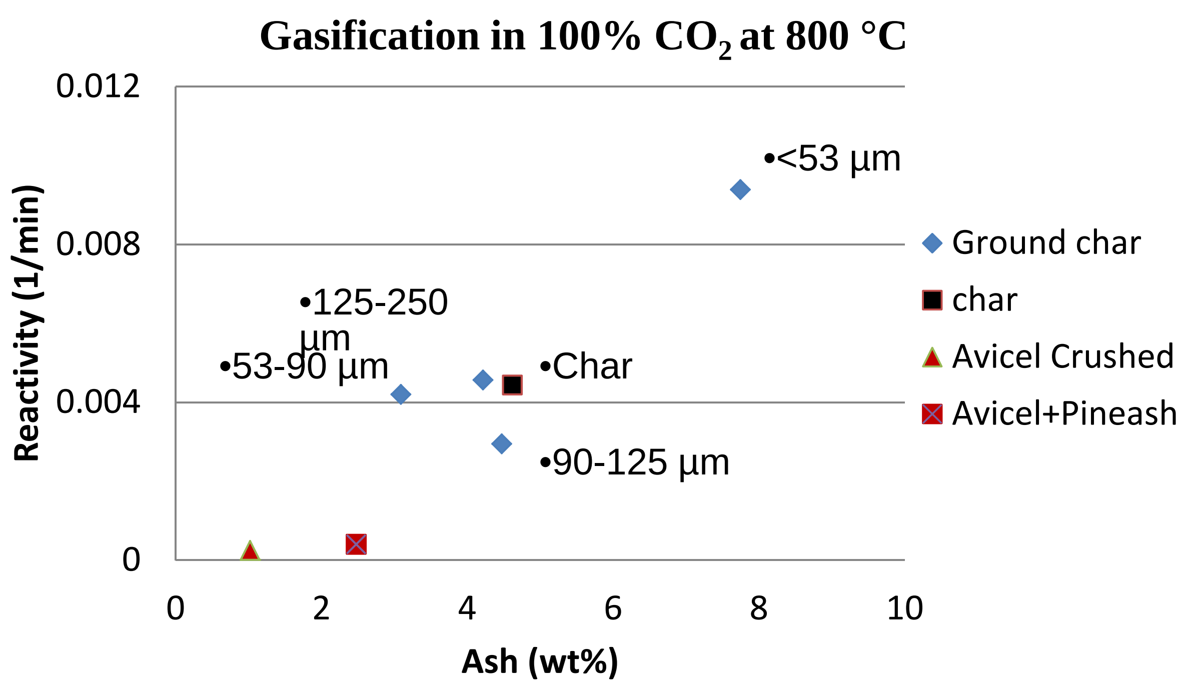
$$r_c = \frac{k_1 p_{CO2}}{1 + k_4 p_{CO2}} (m_t - m_{ash}) = k(m_t - m_{ash})$$

$$\frac{1}{k} = \frac{1}{k_1 p_{CO2}} + \frac{k_4}{k_1}$$

- **Switchgrass char prepared at 5 bar/1000°C, gasified at 750°C**

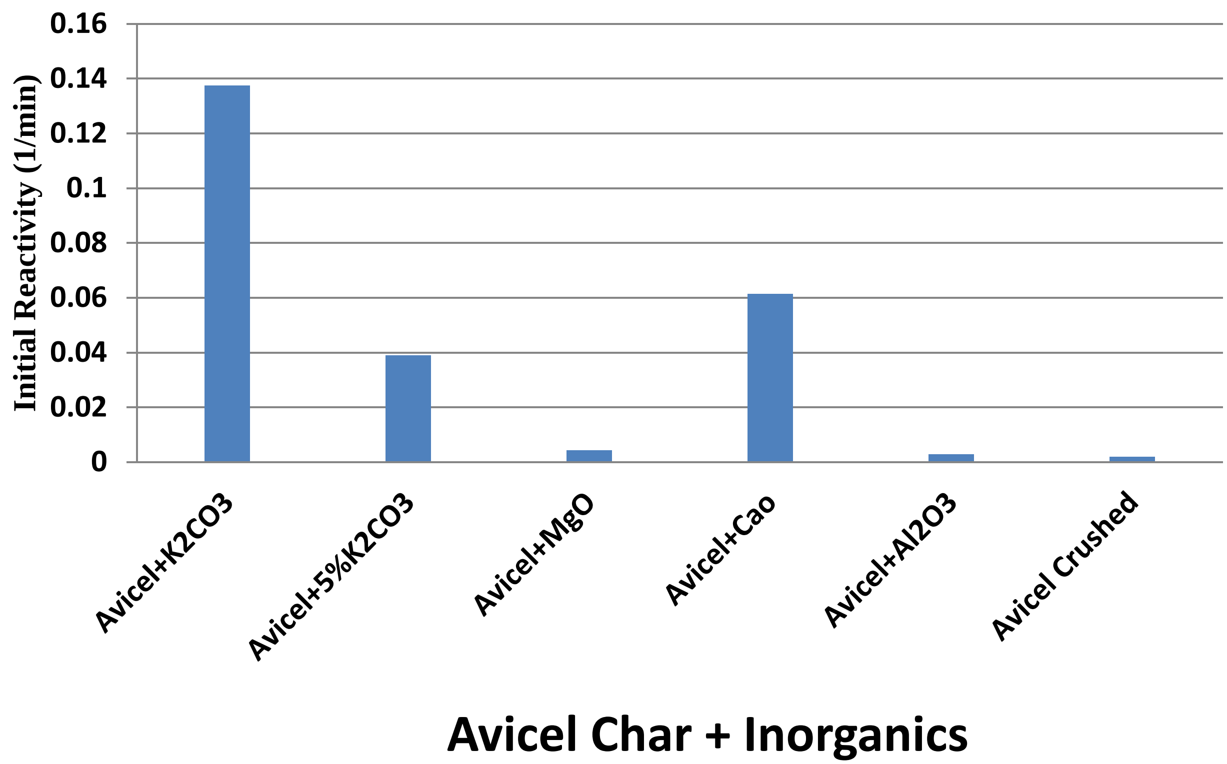


Technical Accomplishments/Progress/Results

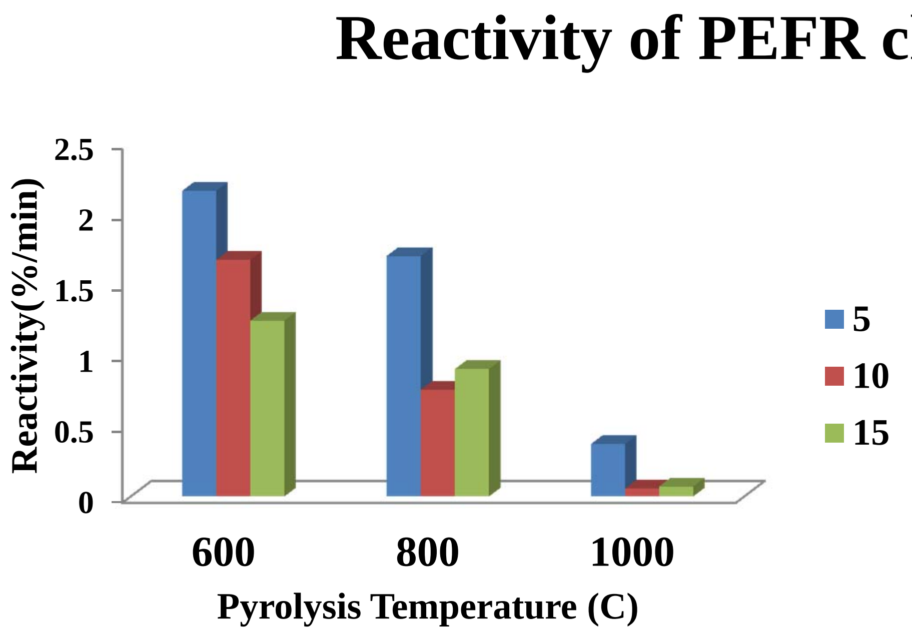


- Comparison of avicel char with negligible ash content with different size fractions of pine char demonstrates that avicel char can be used to establish a baseline behavior for reactivity studies.

Technical Accomplishments/Progress/Results



Technical Accomplishments/Progress/Results



- 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% CO_2

Technical Accomplishments/Progress/Results

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

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

Project Relevance

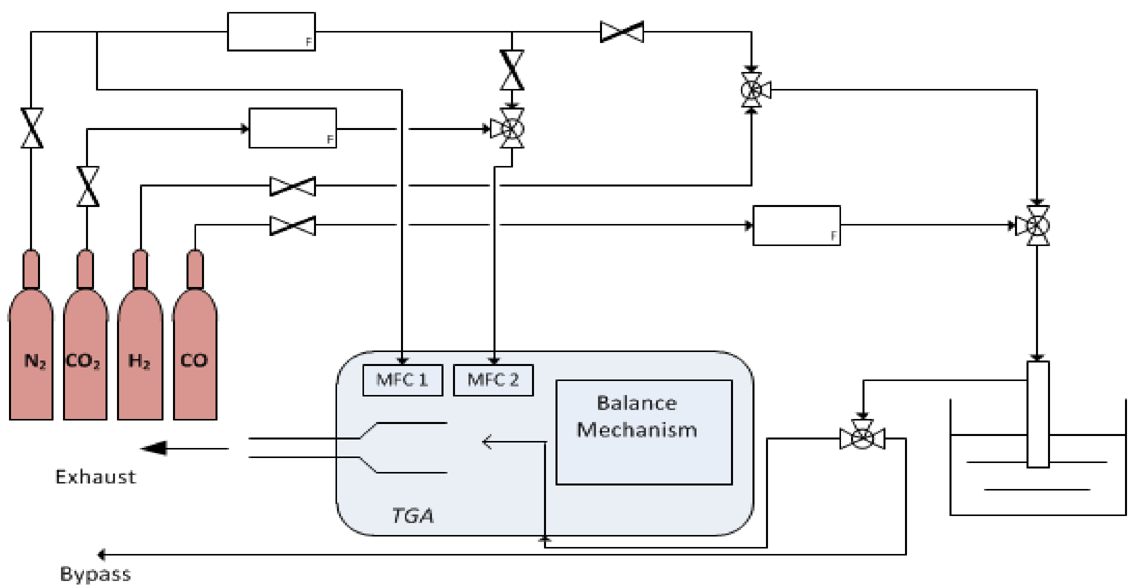
- The goals of this project are consistent with the platform goals and objectives of the Biomass Program Multi-Year Program Plan (optimize gasifier design and syngas production). There are no reliable data on the kinetics of high pressure gasification and tars and hydrocarbon formation.
- The project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

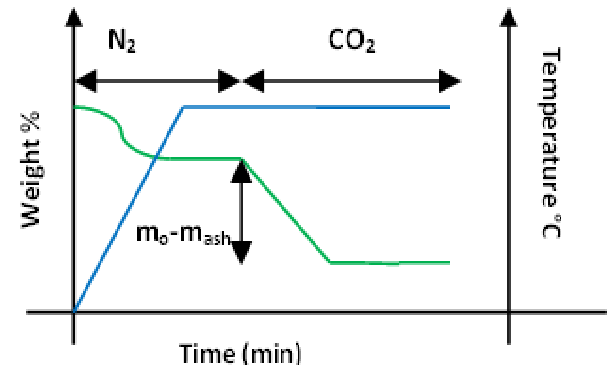
Critical Success Factors

- **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





$$R = \frac{-1}{m_0 - m_{ash}} \frac{dm_t}{dt}; \; X = \frac{m_0 - m_t}{m_0 - m_{ash}}$$

$$r_c = \frac{k_1 \cancel{C_t} P^{\alpha}{}_{CO_2} + k_1' \cancel{C_t} P^{\beta}{}_{H_2O}}{1 + \cancel{k_2 P_{CO}} + \cancel{k_3 P_{H_2O}} + \cancel{k_4 P_{CO_2}} + \cancel{k_5 P_{H_2}} + \cancel{k_6 P_{CH_4}}}$$

- 100 % CO_2
- 5 % H_2O
- 20 % CO_2, 5 % H_2O
- \+ 75 % N_2
- or + 1 % CO, 74 % N_2

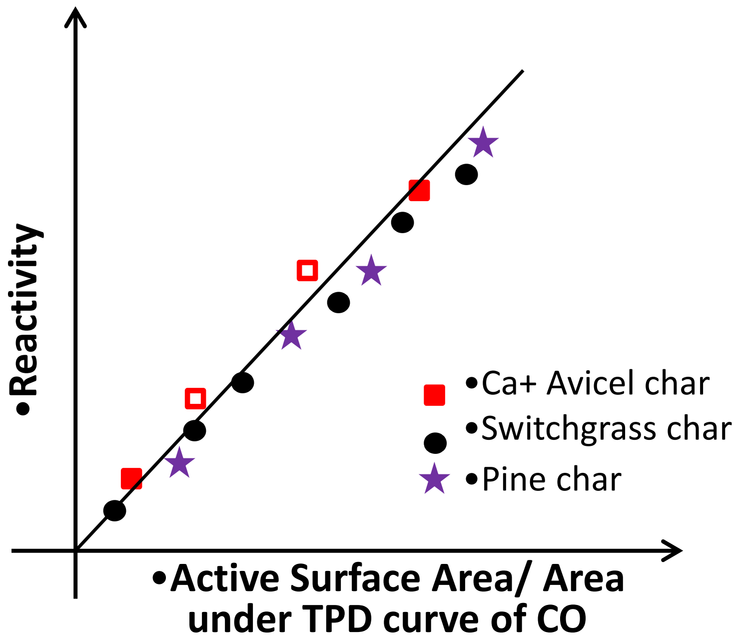
✓ L-H kinetics with inhibitory effects have never been studied on such chars

✓ 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 [Reactive CO (X), TSA (X), ε(X)] for biomass chars, cellulose char and impregnated chars



•Can reactivity be expressed as a simple function of char active surface area?

•Is 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)?