DOE Bioenergy Technologies Office (BETO) Project
2015 Peer Review

NC A&T Renewable Energy Center

-Production of High-Quality Syngas via Biomass Gasification for Catalytic Synthesis of Liquid Fuels

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Technology Area Review: Biomass Gasification

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Goal Statement

The major goal of this project is to study an integrated biomass gasification and hot syngas cleaning process to produce high-quality syngas from woody biomass and agricultural residues and study an efficient Fisher-Tropsch process to convert biomass-derived syngas into liquid fuels.

Quad Chart Overview

Timeline

- Project start date: 01/01/2012
- Project end date: 09/30/2015
- Percent complete: 75%

Budget

	Total costs FY10-FY12	FY13	FY14	Total planned funding
DOE Funded	219 K	235 K	145 K	151K
Project cost share	0 K	61 K	110 K	16.5K

Barriers

- Barriers addressed
  - Tt-C. Gasification of Wood, Biorefinery Residue Streams and Low Sugar Content Biomass
  - Tt.-F. Syngas Cleanup and Conditioning
  - It-E. Engineering Modeling Tools

Partners

- N/A

Project Overview

Significance:

Biomass gasification in a fluidized bed gasifier involves complicated physicochemical and structural evolution of biomass particles, and reactive gas-particle behavior. Several impurities in syngas can severely interfere with the catalytic Fisher-Tropsch (F-T) synthesis of liquid fuels from the syngas.

Objectives:

- Uncover biomass gasification chemistry by investigating the physicochemical and structural changes and gasification kinetics
- Develop computational tools to predict and analyze fluidized bed gasification of biomass
- Study hot biomass-derived syngas cleaning technology
- Study the catalytic Fisher-Tropsch synthetic process for the conversion of biomass derived syngas into liquid fuels

1 – Approach (Technical)

Study 1: Experimental determination of the physicochemical and structural evolution of biomass particles during pyrolysis and gasification

Study 2: Model biomass gasification kinetics and interactions between bed material and solid biomass particles, and incorporate them into the CFD model under the ANSYS Fluent simulation platform via User Defined Functions (UDF)

Study 3: Develop a new generation of advanced Reduced-Order Models (ROMs) for multiphase reactive flows.

Study 4: Study the hydrodynamics and mixing characteristics of selected biomass materials in a laboratory bubbling fluidized bed column to improve the design and operations of a bubbling fluidized bed gasifier

Study 5: Investigation of monometallic and bimetallic nickel-based catalysts for the catalytic reforming of tar in hot syngas.

Study 6: Development bi-functional catalysts for Fischer-Tropsch synthesis of liquid fuel from syngas with CO_2 and optimization of process conditions

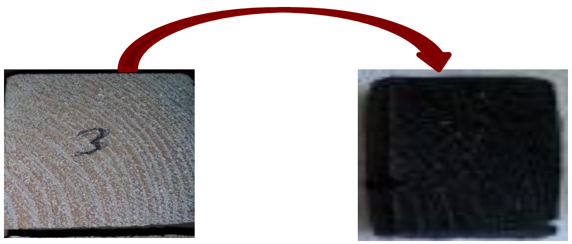
1 – Approach (Management)

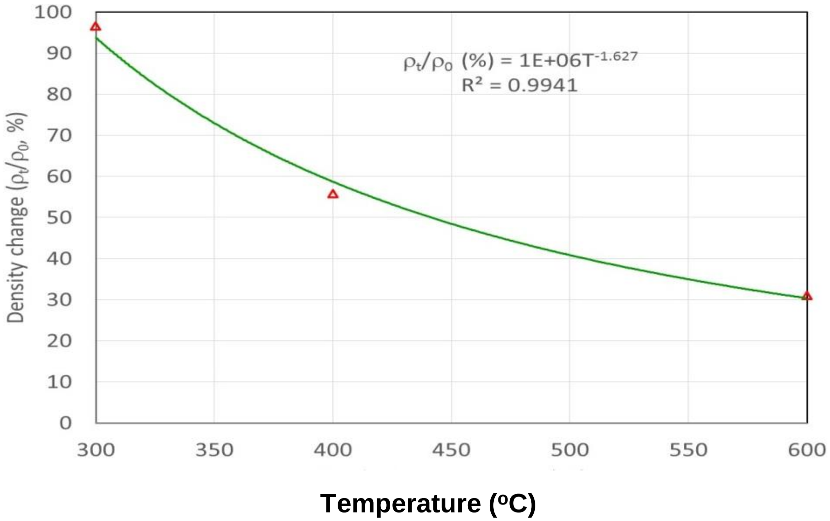
Research topic	Personnel	Expected degree	Major
Gasification chemistry	John Eshun	Ph.D.	Energy and Environmental systems
Process modeling (CFD model)	Samuel Agyemang	Ph.D.	Computational Science and Engineering
Process modeling (Reduced order model)	Anton Pylypenko	Postdoc	Engineering Mechanics and Mathematics
Gasifier design and operation	Hyacinth Okoli	M.S.	Chemical Engineering
Syngas cleaning	Talal Ahmed	Ph.D.	NanoEngineering
Fisher-Tropsch	Mohammad Rafati	Ph.D.	Energy and Environmental Systems

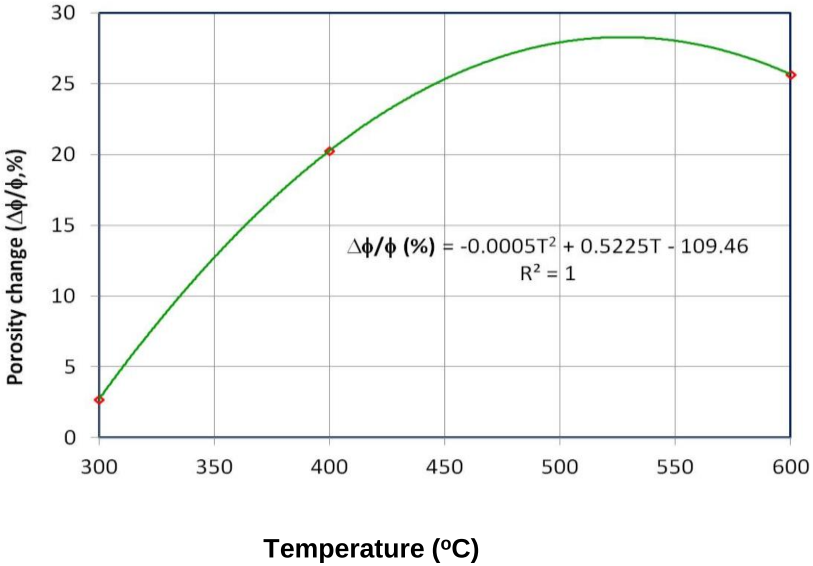
2 - Technical Accomplishments/ Progress/Results

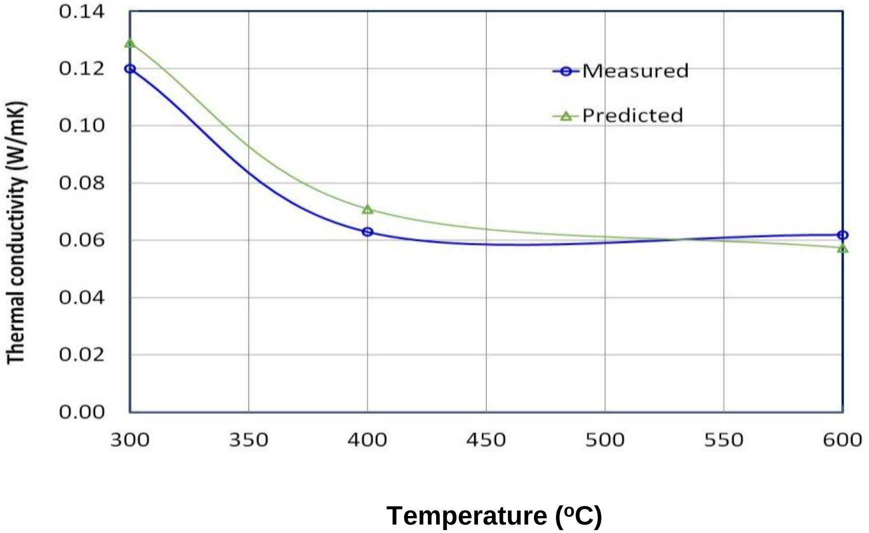
(1) Biomass Gasification Chemistry (a)

Physicochemical and structural evolution of biomass particles during pyrolysis and gasification





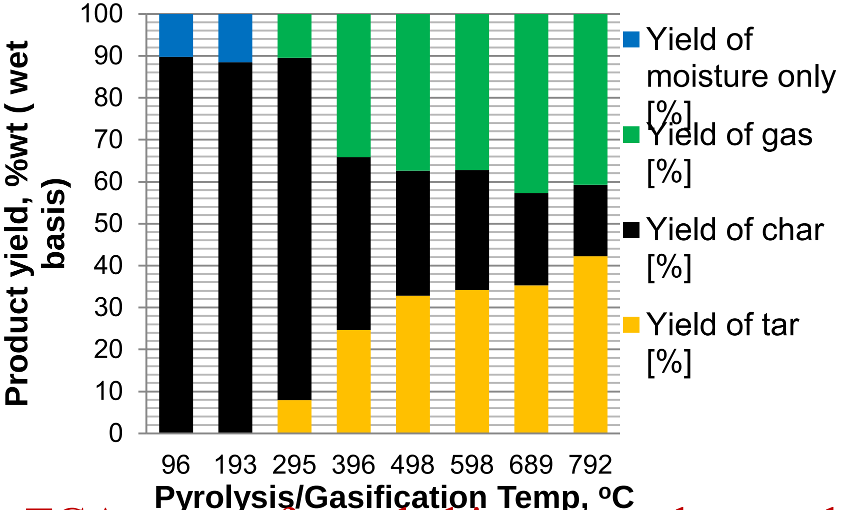




2 - Technical Accomplishments/ Progress/Results

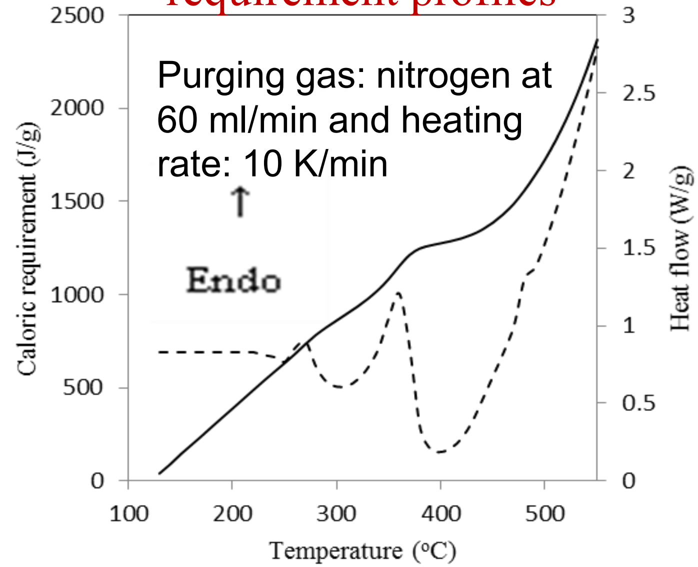
(1) Biomass gasification chemistry (b)

Yields of products from pyrolysis/ CO_2 gasification of woody biomass in a 100 ml tubular reactor

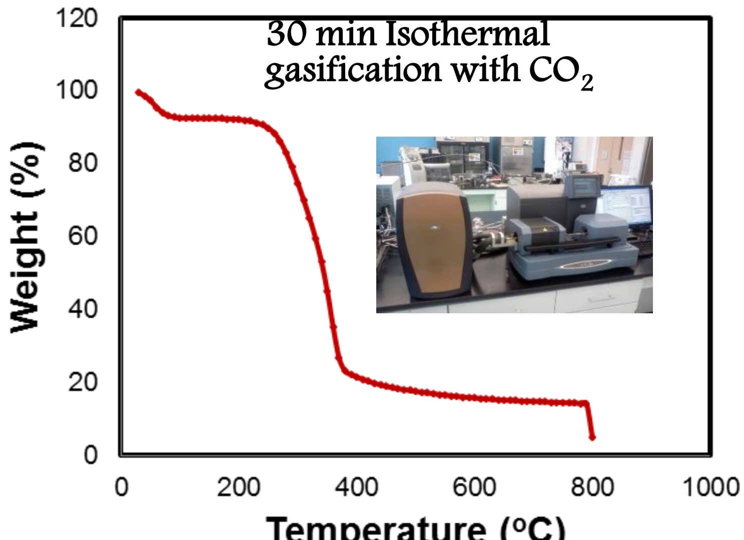


Heating rate: 50°C/min, Cooling time:<2 min, N_2: 2.5 l/min and CO_2 2.5 l/min

Heat flow and caloric requirement profiles



TGA curve of woody biomass under pyrolysis and subsequent CO_2 gasification at 800°C



Pyrolytic reaction constants

	Temp range (°C)	Heating rate (K/min)	A (s^{-1})	E_a (kJ/mol)
Wood	210-410	20	8.53×10^5	77.42
	210-410	40	2.16×10^6	79.87
	210-410	60	5.08×10^7	94.15

For pyrolyzing wood, the maximum weight loss rate was 19%/min which occurred at 380°C and the residual weight at 500°C was 20.2%. The activation energy at 40 K/min was 79.87 kJ/mol. It required 1727 J/g heat to pyrolyze wood at 500°C

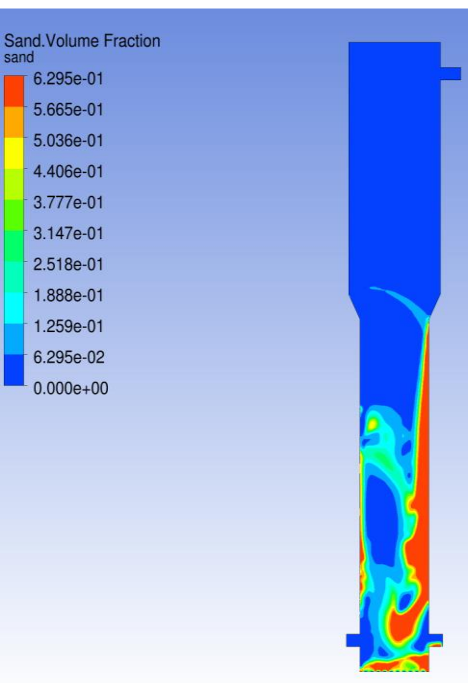
2 - Technical Accomplishments/ Progress/Results

(2) Biomass gasification process modeling (a)

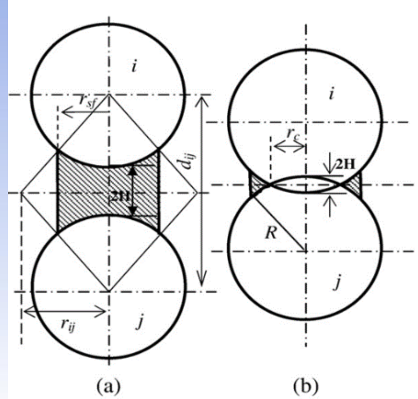
Main focuses:

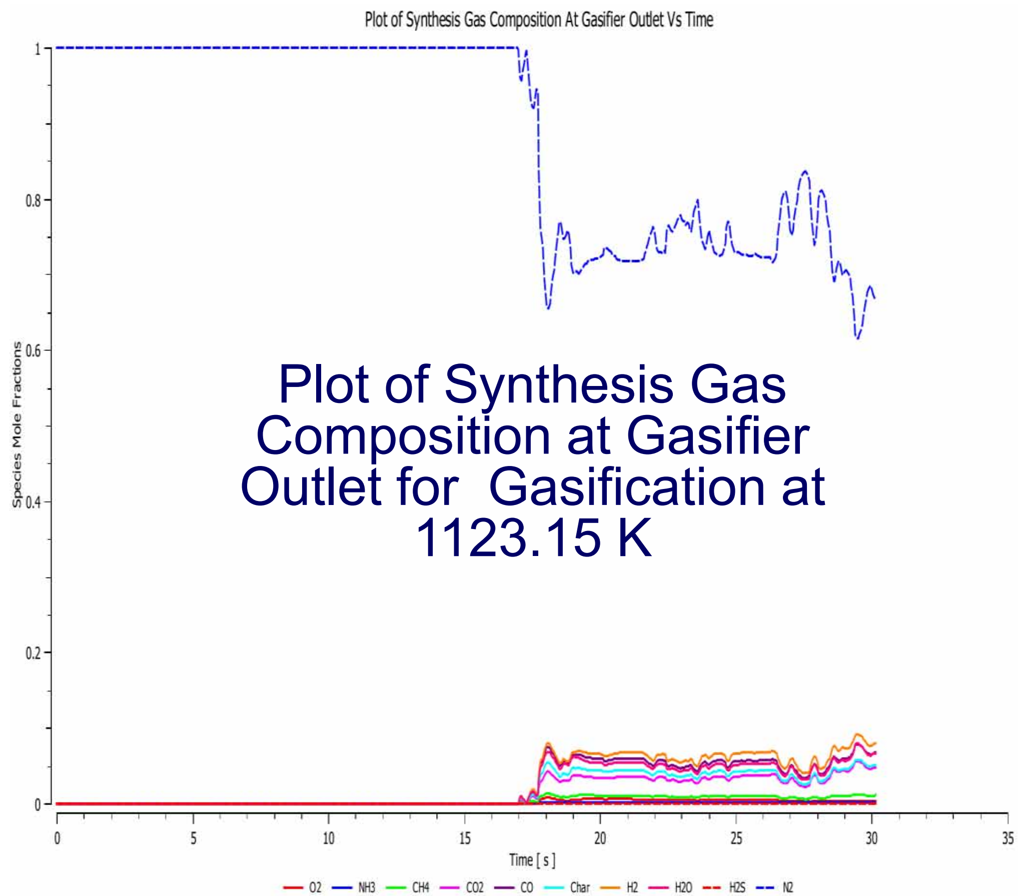
- Model biomass gasification kinetics and incorporate them into the CFD model under the ANSYS Fluent simulation platform via User Defined Functions (UDF)
- Model interactions between bed materials and solid biomass particles and incorporate them into the CFD model via UDFs

Distribution of sand volume fraction:



Particle-Particle Heat Transfer Coefficient:





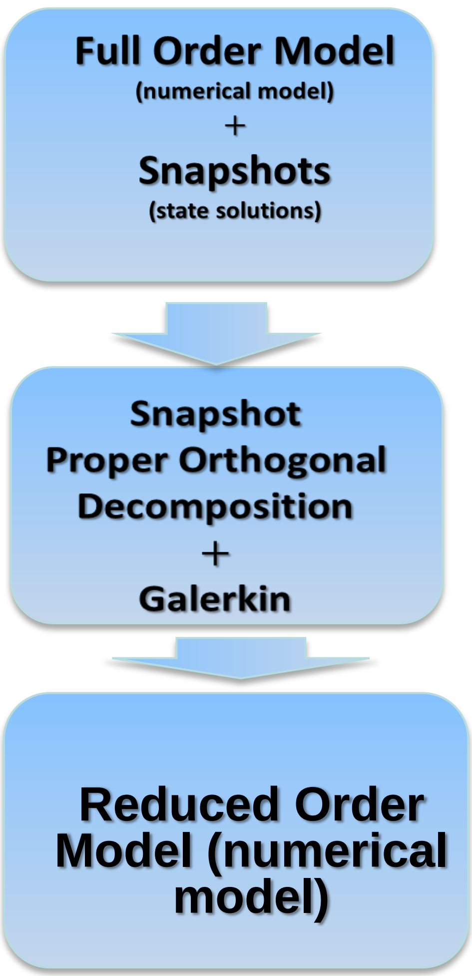
Plot of Synthesis Gas Composition at Gasifier Outlet for Gasification at 1123.15 K

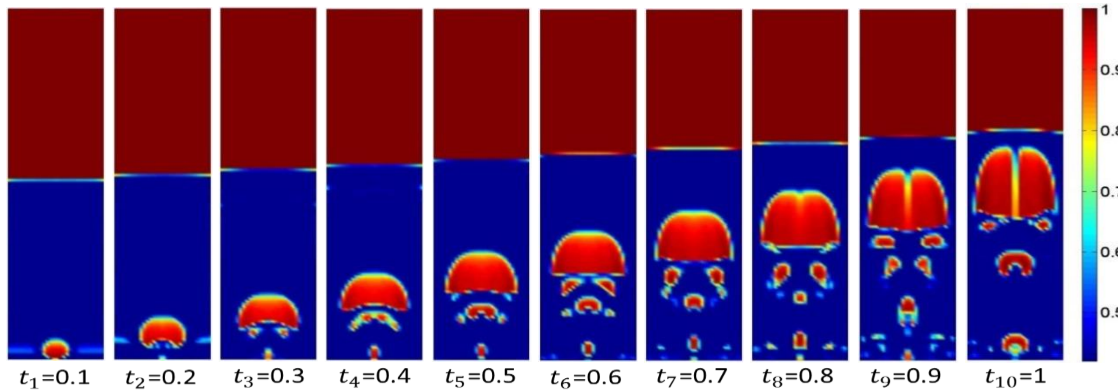
2 - Technical Accomplishments/ Progress/Results

(2) Biomass gasification process modeling (a)

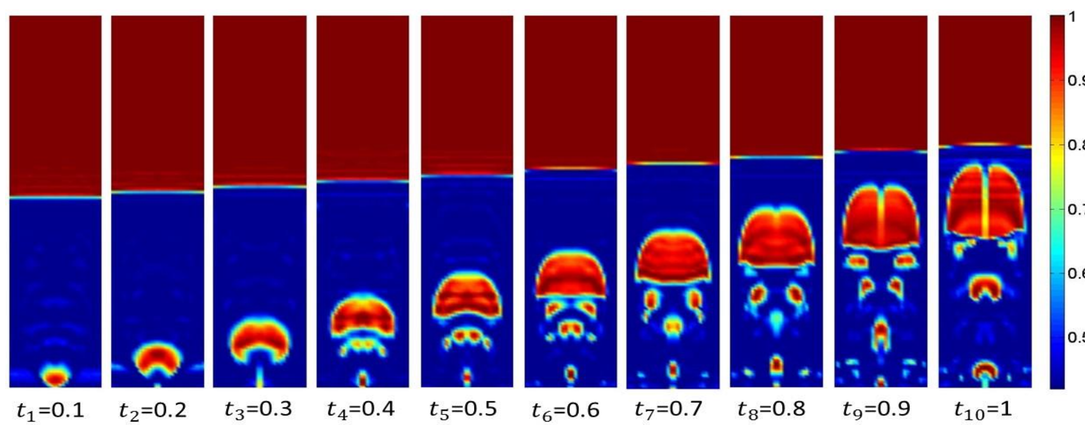
Reduced order models based on Proper Orthogonal Decomposition (POD) technique

Comparison of flow patterns obtained by MFIX full model simulation and POD reconstruction reveals qualitatively good agreement





Original void fraction snapshots distribution



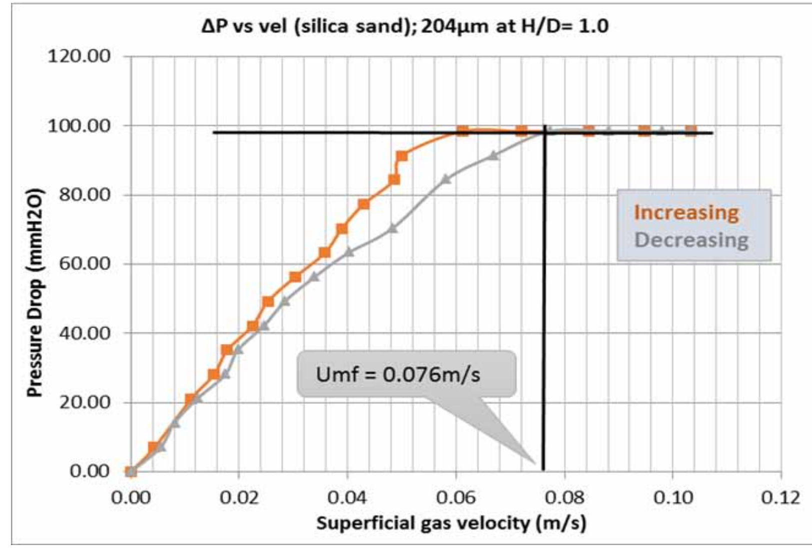
POD-based reconstruction of original snapshots

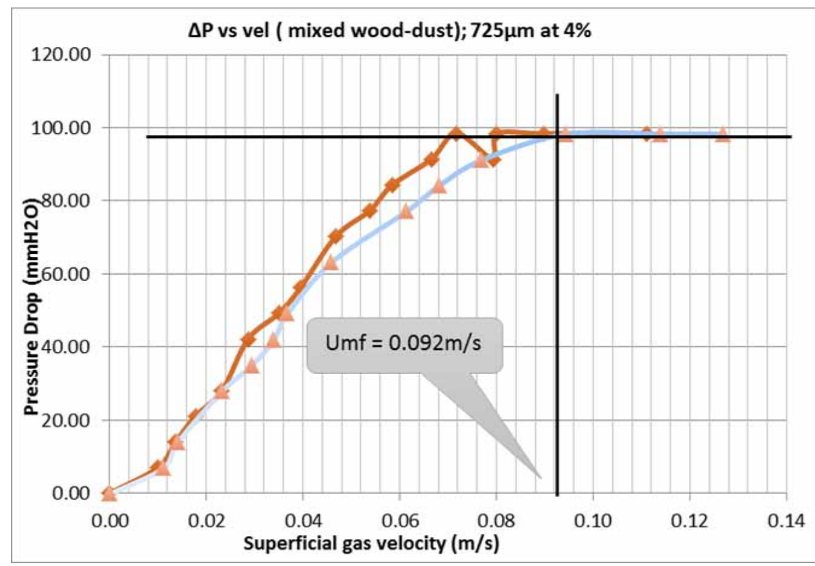
2 - Technical Accomplishments/ Progress/Results

(3) Biomass gasification process experimentation

Cold flow hydrodynamics

Set some operating parameters for gasifier





1. Sand Particle size
2. Biomass particle size
3. Lower fluidization velocity
4. Weight percentage of biomass in the fluidized bed

Design Parameters

u_{mf}(m/s)	u_f(m/s)	u_t(m/s)
0.092	**0.508**	**0.916**
$\dot{m}_{Air}$(Kg/hr.)	$\dot{m}_{Fuel}$ (Kg/hr.)	ER
6.74	**4.4**	**0.28**
Bed diameter (m)	Bed Height	Reactor Area
0.102	**0.102**	**0.008172**

By applying appropriate design equation, the operating fluidization velocity was calculated to be 0.508 m/s with Biomass mass flow rate of 4.4 kg/h.

2 - Technical Accomplishments/ Progress/Results

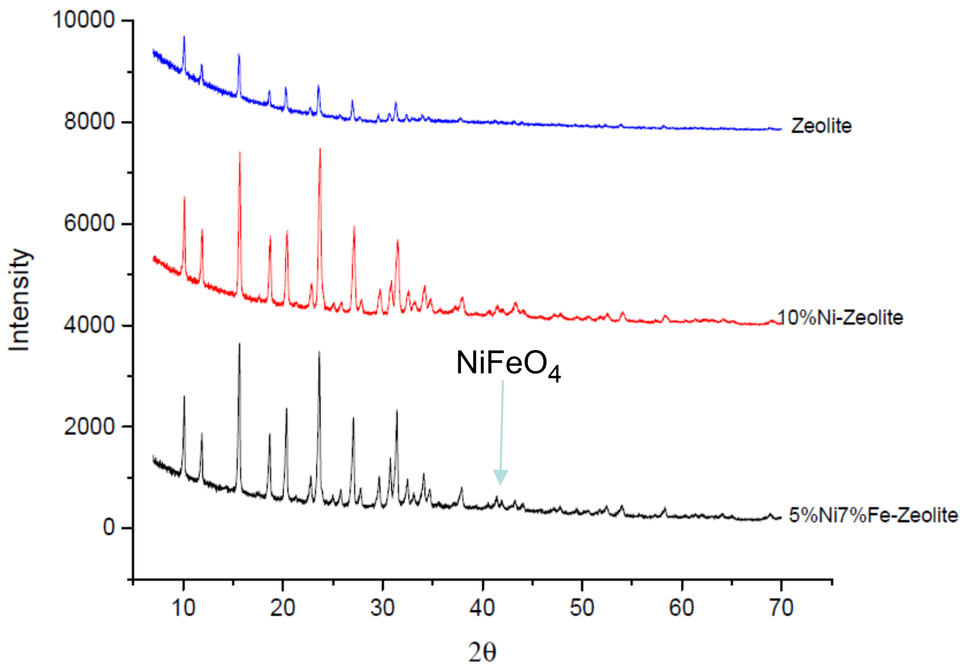
-(4) Hot syngas cleaning: monometallic and bimetallic nickel-based catalysts for the catalytic reforming of tar in hot syngas

BET surface area of catalysts

Catalyst	Surface Area (m^2/g)
3% Ni-Zeolite Y	520
5 % Ni- Zeolite Y	475
10 % Ni – Zeolite Y	400
15 % Ni - Alumina	192.3

Catalyst	Surface Area (m^2/g)
3% Ni-5%Fe-ZeoliteY	400
5% Ni-7%Fe-ZeoliteY	340
7% Ni-9%Fe-ZeoliteY	315

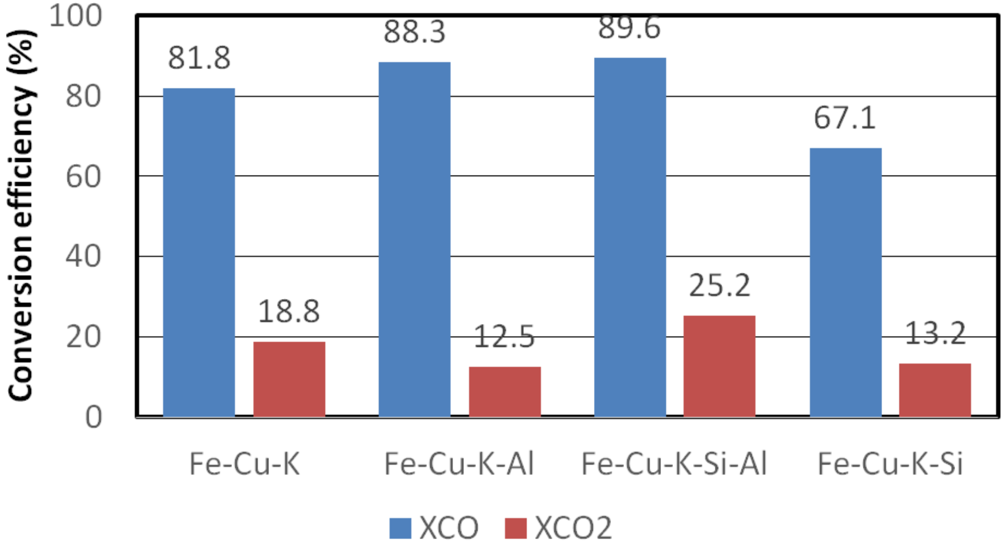
XRD pattern of monometallic and bimetallic nickel-based catalysts



The high surface area of the catalysts can enhance their adsorption capability. The strong metallic interaction as indicated by XRD shows that the addition of iron to nickel as a promoter could increase the nickel resistance to coke formation at a high temperature and thus increase the catalytic cracking efficiency at a high temperature.

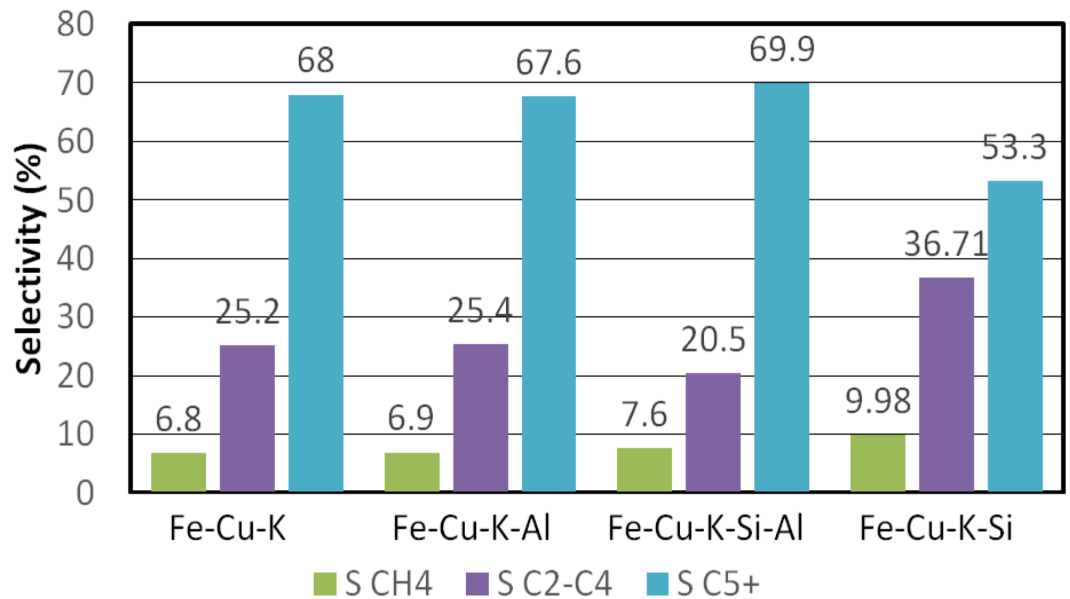
2 - Technical Accomplishments/ Progress/Results

-(5) Fischer-Tropsch Synthesis of liquid fuels from syngas



Reaction condition: 54%H_2/10%CO/29%CO_2/7% N_2, 300°C, 20 bar, and 30 ml/min/g-catalyst for 72h on stream

Doubly-promoted catalysts (Fe-Cu-K-Si-Al) using Si and Al has higher activity for the conversion of CO and CO_2 than non-promoted catalyst (Fe-Cu-K) and the catalyst promoted by either Al or Si probably due to higher dispersion of active phases and better contact between Fe and K.



3 - Relevance

- M6.11. Demonstrate and validate cost-effective biomass gasification of wood, forest residues and other process residues; and synthesis gas clean up in a forest resources mill environment

- M6.13. Demonstrate and validate production of non-ethanol fuels from syngas in a forest resources mill environment

4 - Critical Success Factors

(1) Biomass chemistry:

- ❖ Temperature-dependent physicochemical and structural properties of biomass
- ❖ Structured biomass gasification kinetic models

(2) Biomass process modeling:

- ❖ Computational tools for predicting fluidized bed gasification of biomass with different design and operating parameters
- ❖ Accuracy of the predications and computational time

(3) Process experimentation:

- ❖ Operating parameters
- ❖ Syngas yield and quality

(4) Hot syngas cleaning:

- ❖ Catalyst resistance to coke formation at a high temperature
- ❖ Catalytic cracking efficiency at a high temperature

(5) Fisher-Tropsch synthesis:

- ❖ Conversion efficiency and selectivity of F-T synthesis of liquid fuels from syngas with different $H_2/(2CO + 3CO_2)$ ratios and CO and CO_2 compositions
- ❖ CO_2 utilization, and carbon, hydrogen, and energy conversion efficiencies of a combined biomass gasification and F-T synthesis process

5. Future Work

-Research activities (a)

Biomass chemistry:

❖BET and XRD analysis of biomass and char particles as part of the investigation of the structural evolution of biomass particles during pyrolysis and gasification

❖Establishment of structured biomass gasification kinetic models to describe biomass char gasification

Biomass process modeling:

❖CFD simulation of biomass using steam and CO_2 as gasifying agents of externally heated fluidized bed gasification

❖ Development of reduced-order models for multiphase reactive flows

❖ Analysis of the effects of bed-height and material densities on gas-solid fluidized bed hydrodynamics, and the effects of particle size distribution and particle shape on the yield and composition of syngas during fluidized bed gasification of biomass using a 3D MFIX model

5. Future Work

-Research activities (b)

Process experimentation:

- To investigate the effect of temperature and pressure on the bed hydrodynamics using a laboratory scaled fluid-bed column.

Hot syngas cleaning:

- Investigate the monometallic and bimetallic catalysts in a fixed bed reactor (FBR) to study their catalytic activity and selectivity under different operating conditions.
- Optimize the process and develop a kinetic model for syngas cleaning.

Fisher-Tropsch synthesis:

- Study the effect of addition of WGS-active transition metals on FTS activity and selectivity of iron-based FT catalysts in hydrogenation of CO_2 and CO/CO_2 mixture
- Improve the design of combined biomass gasification and FTS process to increase CO_2 utilization, and carbon, hydrogen, and energy conversion efficiencies though ASPEN Plus process modeling software

Summary

Major research outcomes:

- Gasification chemistry and kinetic models
- Advanced CFD and reduced-order models as a tool for the design and operation of a fluidized bed gasifier
- Novel hot syngas cleaning technology
- Fisher-Tropsch catalysts and process analysis
- Three manuscripts which are ready for submission for publication

Major educational outcomes:

- 1 postdoc
- 4 Ph.D and 1 M.S. students
- 2 undergraduate students

Facilities and Equipment

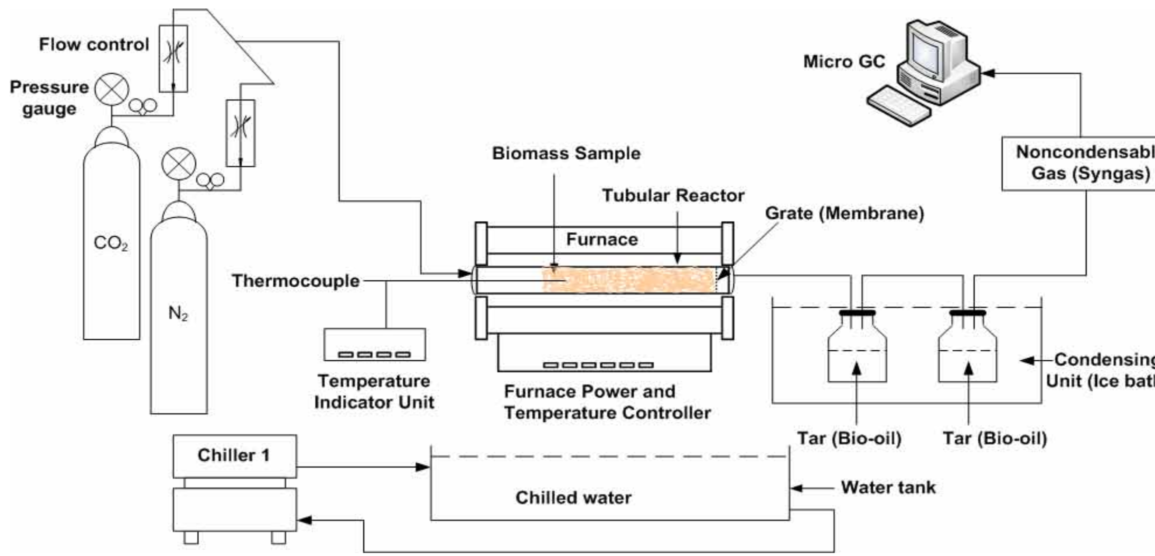
-Biomass gasification chemistry

TGA-DSC-MS for measuring thermal degradation characteristics, heat flow and evolving gas profile

Frontier Micro-Py-GC-MS for testing fast pyrolysis and identifying and quantifying chemicals and biofuels

CHONS elemental analyzer

Schematics of a 10-ml and 1 L tubular reactor-GC unit used to prepare samples for the measurement of physical, chemical and thermal properties during pyrolysis/gasification

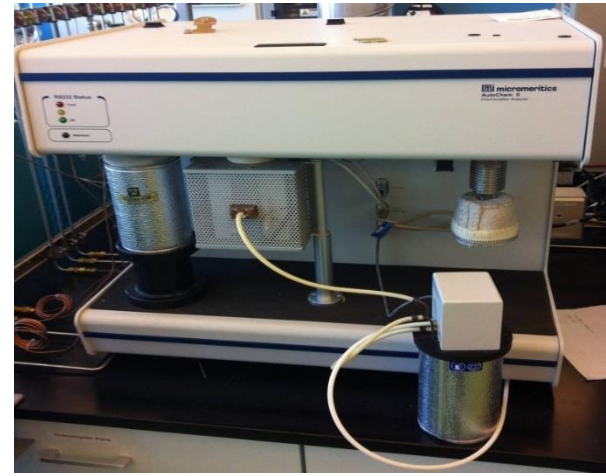


Facilities and Equipment

-Catalyst preparation, characterization and testing

CSRT reactor for preparation of catalysts through co-precipitation

ASAP 2020 BET analyzer for measuring surface area, pore volume and size distribution



Autochem 2920 Chemisorption unit

The autoclave engineer's BTRS-JR plug flow reactor unit and four mass flow controllers for testing FT synthesis

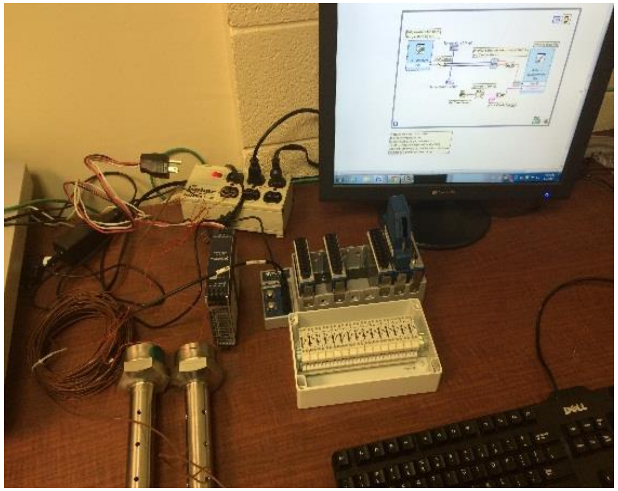
A 10 ml plug flow reactor for testing catalytic tar cracking process

Facilities and Equipment

-Fluidized bed gasification process and simulation

Cold flow hydrodynamics testing unit

Lab-scale fluidized bed gasifier



LabVIEW data acquisition system for monitoring and controlling gasification processes

Micro-GC for syngas analysis