Cleaning biomass-generated syngas: is biochar a cheaper alternative to expensive catalysts?

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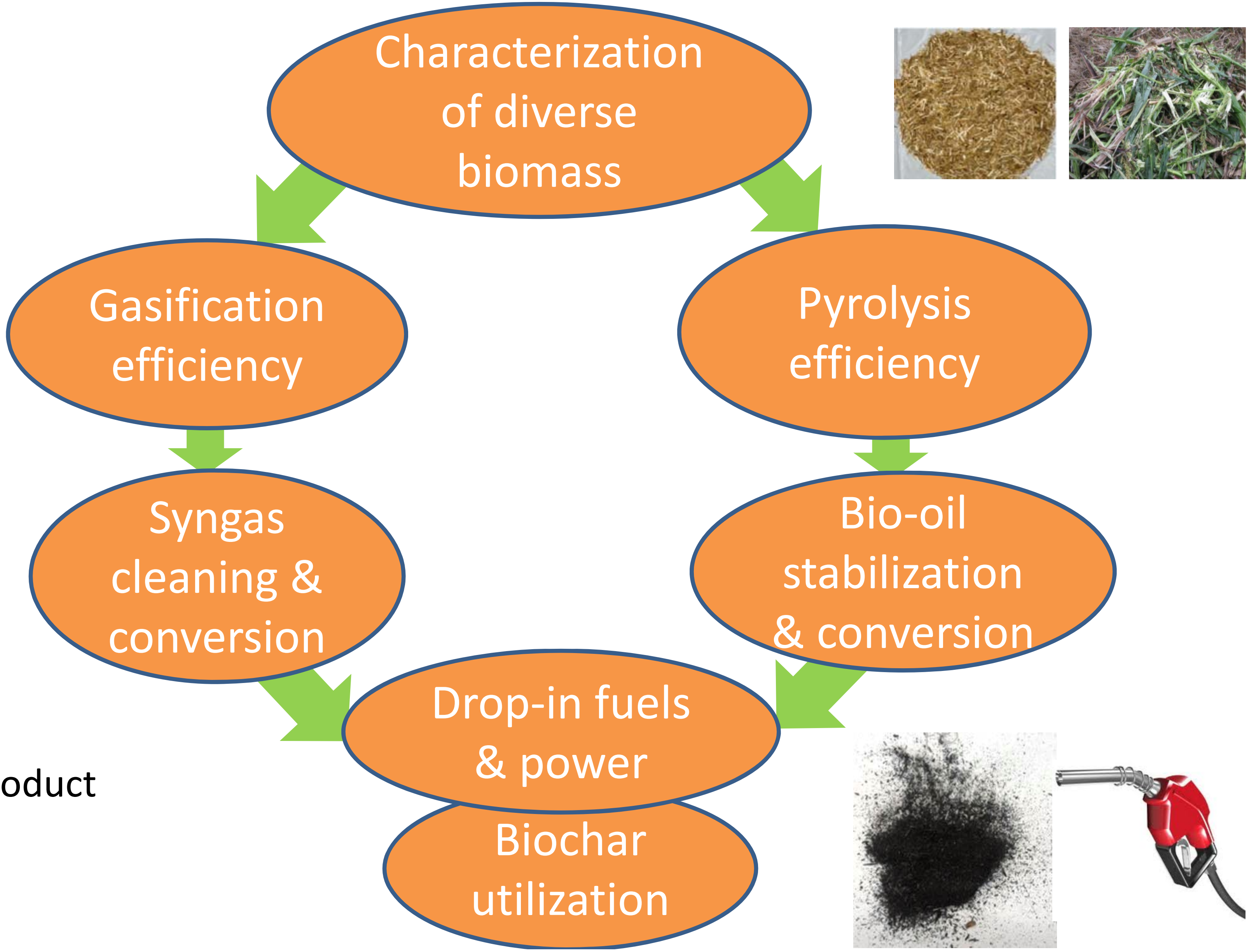
Biofuels through Thermochemical Conversions



Biomass Feedstocks

Characterization of diverse biomass

Conversions

Gasification efficiency

Pyrolysis efficiency

Intermediate products

Syngas cleaning & conversion

Bio-oil stabilization & conversion

Product/byproduct Utilization

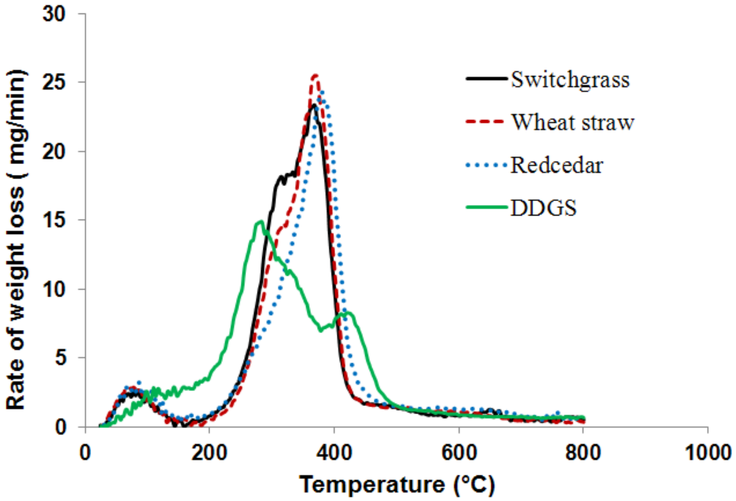
Drop-in fuels & power

Biochar utilization

Current Activities

- Biomass Characterization
  - All biomass are not created equal.
  - Effects of biomass properties on products must be investigated to utilize diverse feedstocks.

Biomass thermal degradation



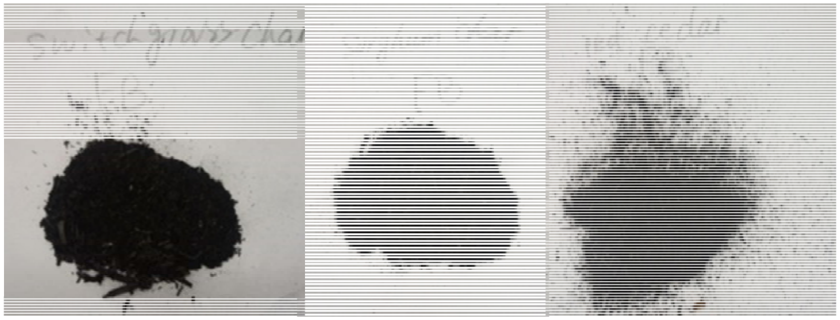
- Gasification
  - Improved reactor design is needed to use low-density biomass.
  - Optimization of operating conditions is needed through
    - Fluidization
    - Steam addition
    - Modeling of reaction kinetics

Current Activities

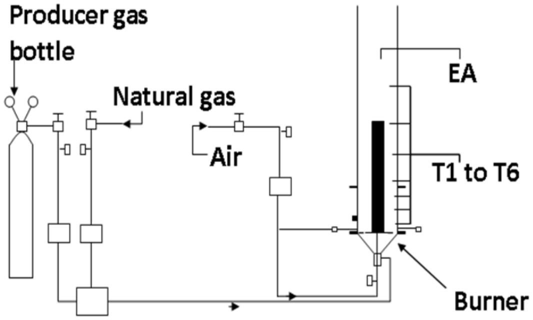
- Syngas Conditioning
  - Biochar-based catalysts and oil-based wet scrubbing system has potential to drastically reduce cost of syngas cleaning.

Catalyst	Toluene removal efficiency (%)
Biochar	86.69[c] ± 3.59
Activated carbon	91.60[b] ± 1.29
Acidic surface activated carbon	97.56[a] ± 0.99

- Biochar Production and Utilization
  - Biochar properties are influenced of biomass and gasification conditions.
  - To find high-value utilization of biochar, its properties must be investigated.



- Biopower
  - Syngas co-firing with natural gas can reduce carbon and other emissions associated with natural gas.



Syngas Contaminants

NH_3	H_2S	PM	Alkalis	Tars
• Poison catalysts • Precursors for NOx and photochemical smog • Promote corrosion	• Poison methanol production catalysts • Tar cracking catalysts sensitivity	• Valve functioning • Clog fuel lines • Foul equipment surfaces	• Deposition of vapors • Fouling, Slagging and corrosivity • Deactivate catalysts	• Handling & Disposal problems • Plugging & Fouling • Dehydration to form char & coke
•Dolomite or Ni/Fe based Catalyst •Mixed metal oxide catalysts •Scrubbers	•Wet Scrubbers •Adsorption on metal oxides	• Cyclonic or barrier filters • ESP	• Product condensation • ESP	• Wet ESP • Ni/Dolomite/ Biochar type catalysts • Thermal treatment

Biochar

- Biochar
  - is derived from carbon containing materials through thermochemical processes
  - Contains carbon and minerals
- What is the use of biochar?
  - Soil amendment
  - Activated carbon
  - Carbon-based materials
  - **Carbon-based catalysts**

Biochar Production & Utilization

- How is it produced?
  - Slow pyrolysis
  - Fast pyrolysis
  - Gasification

- Why gasification-based biochar is used here?
  - Properties of biochar through gasification is not well-known.
  - Need to find high-value applications of byproduct char.

Biochar vs. commercial catalysts for cracking toluene (model tar)

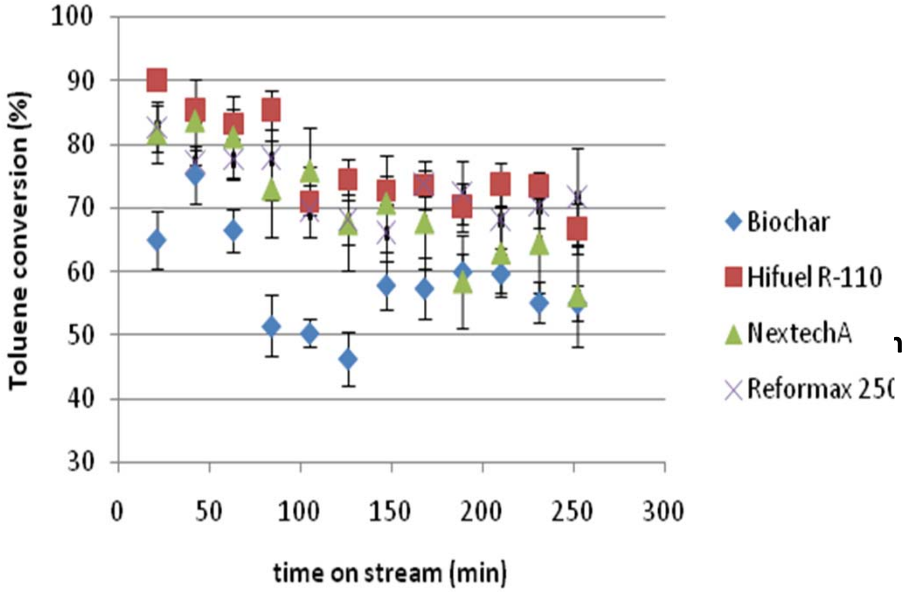


Fig: Performance of all catalysts at 700°C

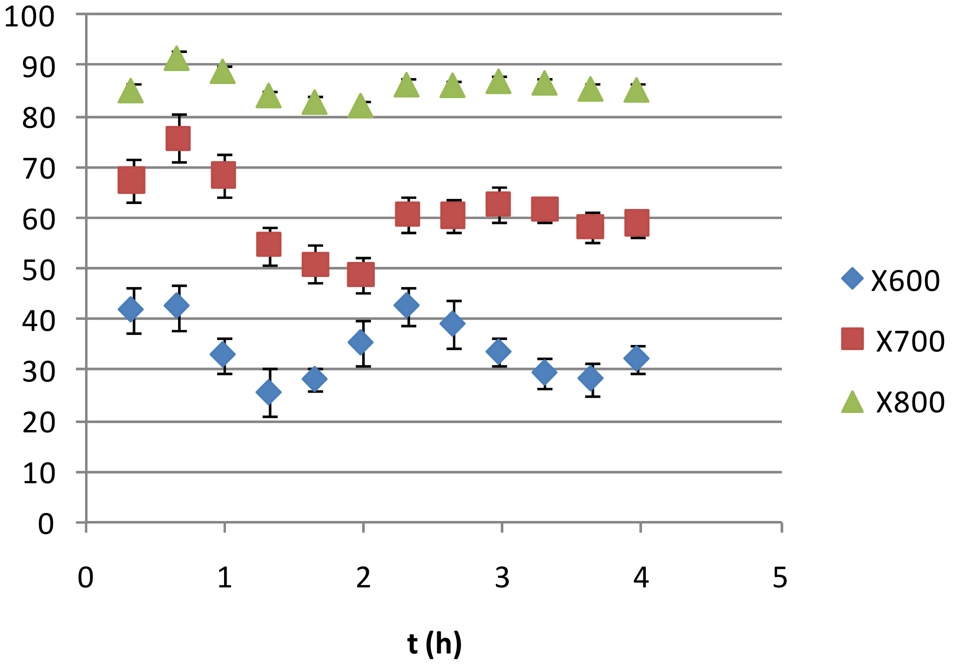
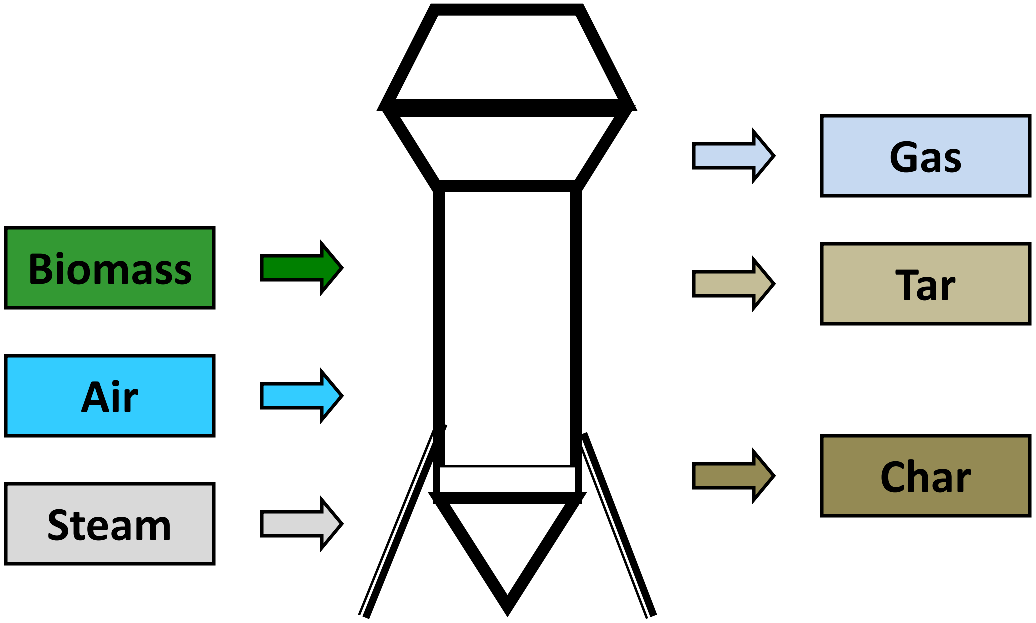


Fig: Performance of char at 600, 700 and 800°C

Biochar through Gasification

Switchgrass

Forage Sorghum



Biomass

Air

Steam

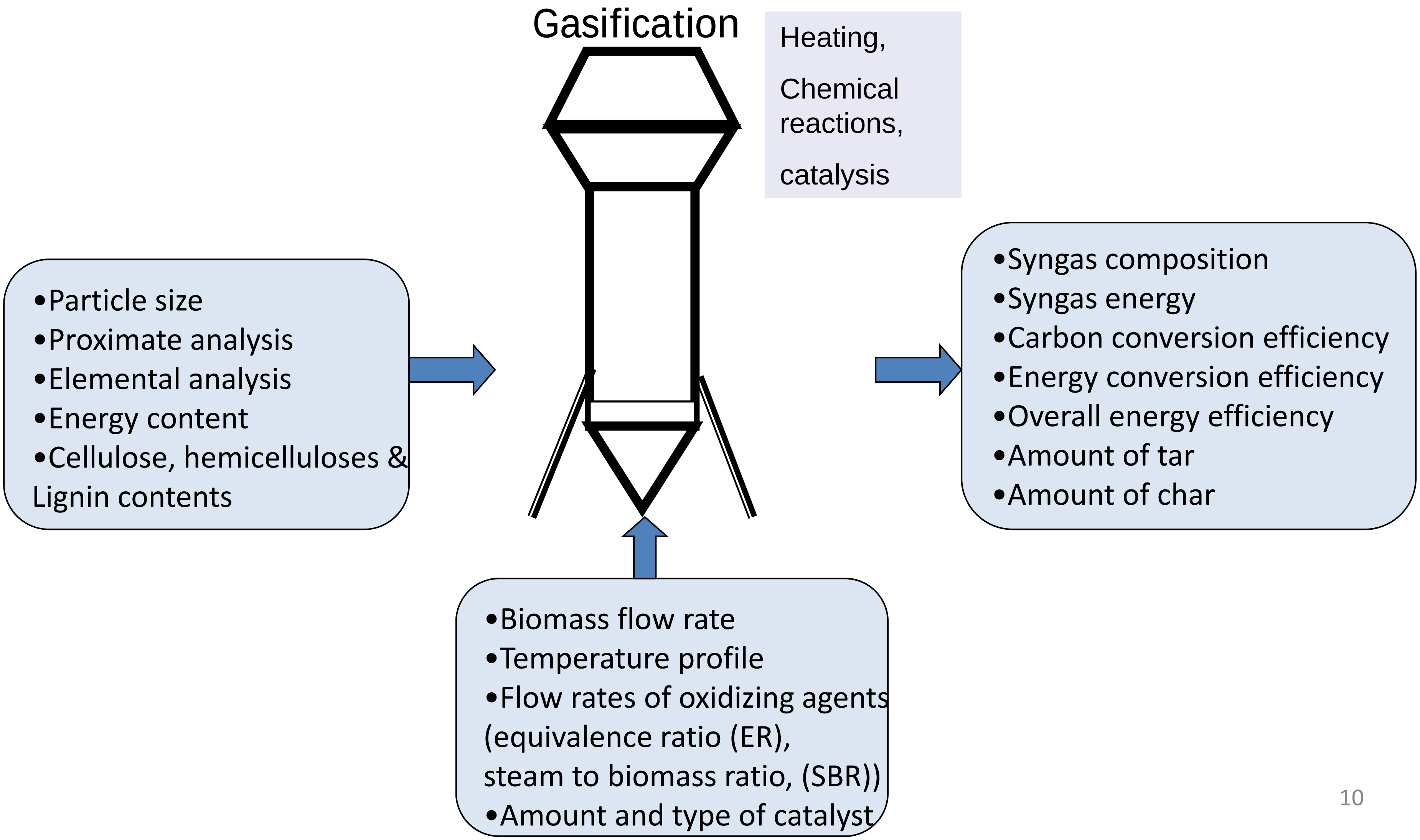
Gas

Tar

Char

- Required: high temperature & oxidizing agent
- biomass + air + H_2O C (char)+ CH_4+ CO + H_2 + CO_2 + N_2 + H_2O (unreacted steam) + ash + tar

Gasification process - factors



Gasification

Heating,

Chemical reactions,

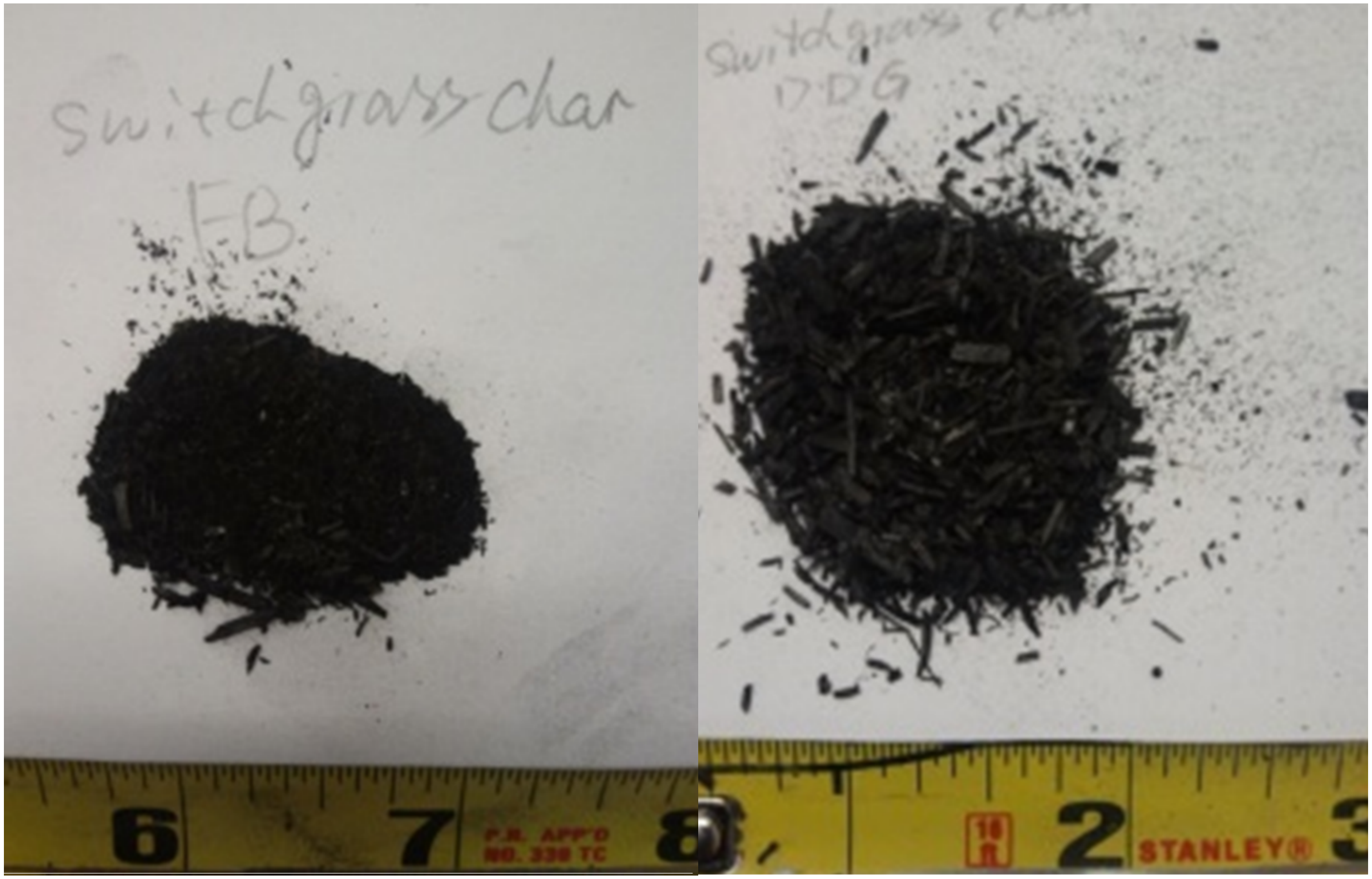
catalysis

- Particle size
- Proximate analysis
- Elemental analysis
- Energy content
- Cellulose, hemicelluloses & Lignin contents

- Biomass flow rate
- Temperature profile
- Flow rates of oxidizing agents (equivalence ratio (ER), steam to biomass ratio, (SBR))
- Amount and type of catalyst

- Syngas composition
- Syngas energy
- Carbon conversion efficiency
- Energy conversion efficiency
- Overall energy efficiency
- Amount of tar
- Amount of char

Effects of Gasifier Design



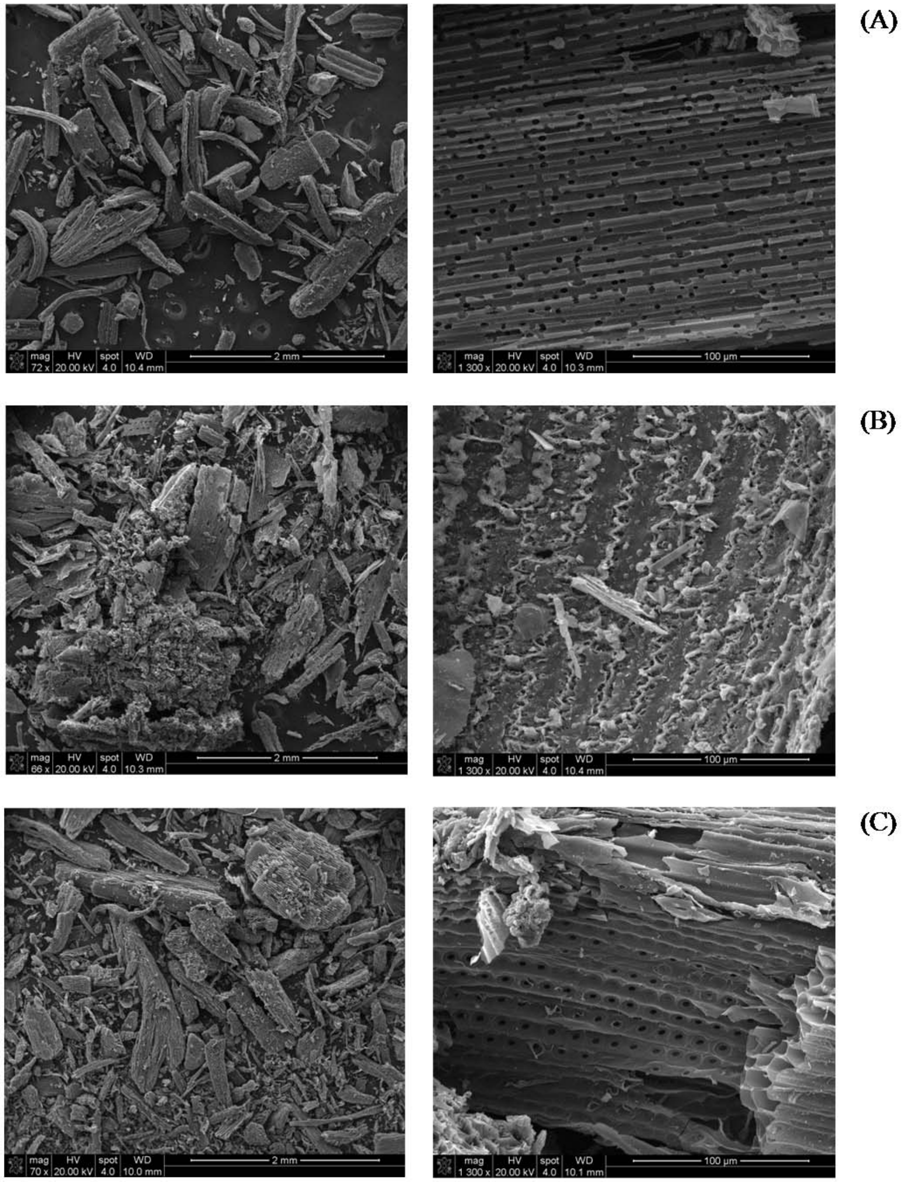
- Downdraft gasifier showed larger biochar (potentially unconverted).

SEM of biochar

Switchgrass

Sorghum

Red Cedar



Objectives

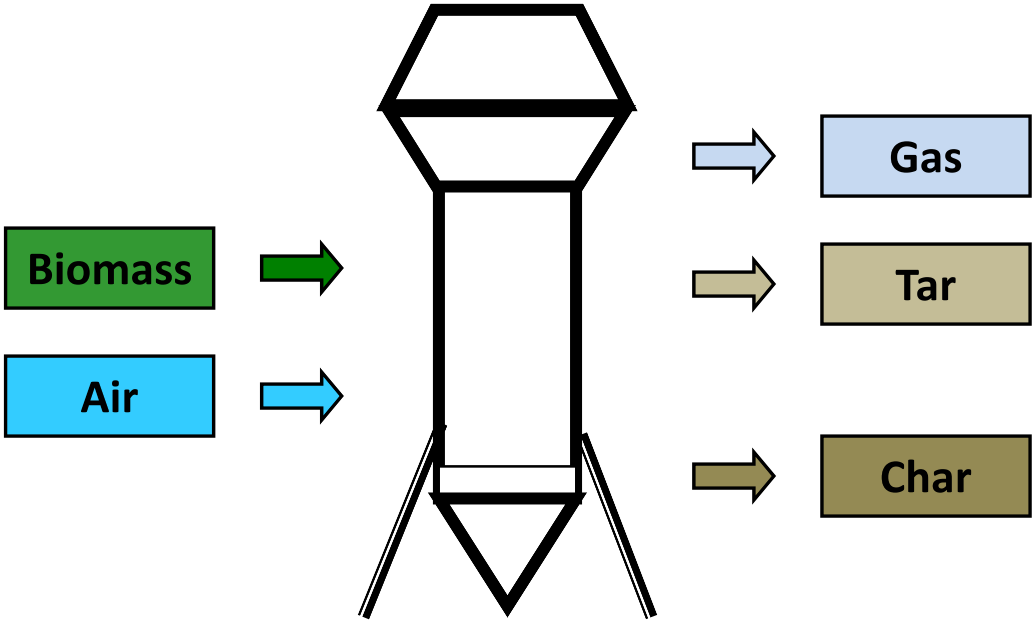
- The objectives of this study were to:
  1. synthesize carbon-based catalysts (biochar, activated carbon, and acidic surface activated carbon), and

  2. evaluate the effectiveness of the three novel catalysts to remove tars, ammonia, and H_2S from syngas in a fixed-bed reactor.

Biochar through Gasification

Switchgrass

Forage Sorghum



Biomass

Air

Gas

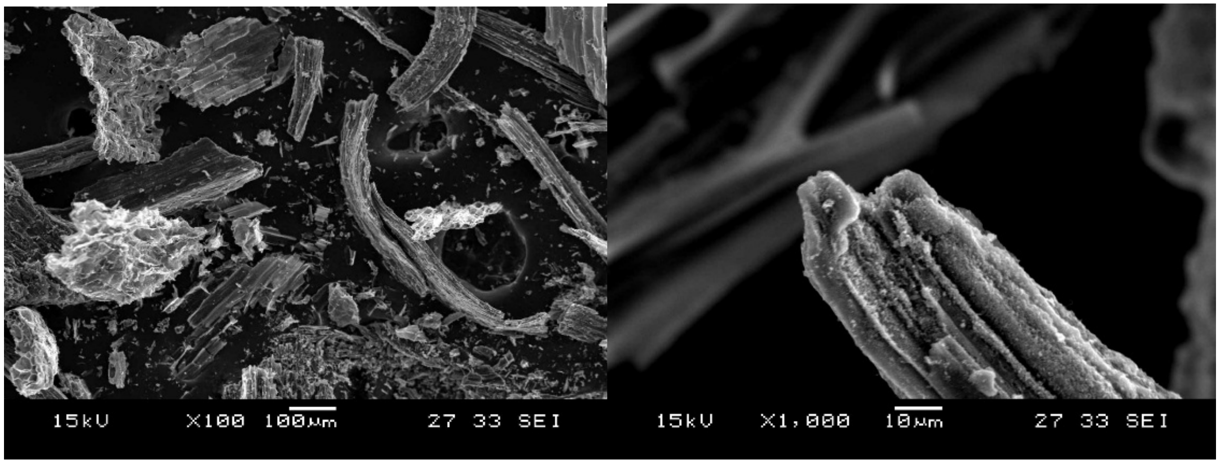
Tar

Char

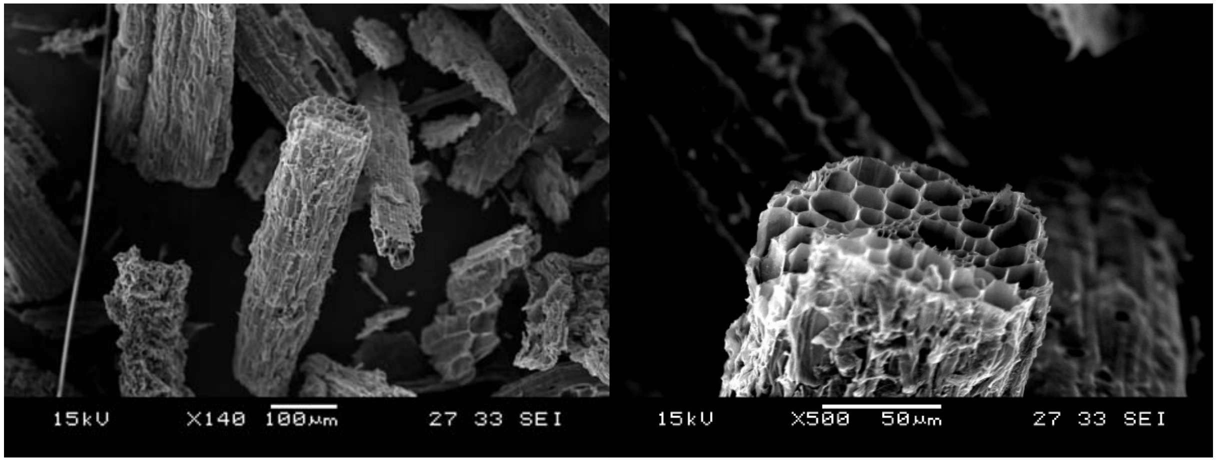
- biomass + air + H_2O ⇨ C (char)+ CH_4+ CO + H_2 + CO_2 + N_2 + H_2O (unreacted steam) + ash + tar

Catalyst Synthesis

Biochar



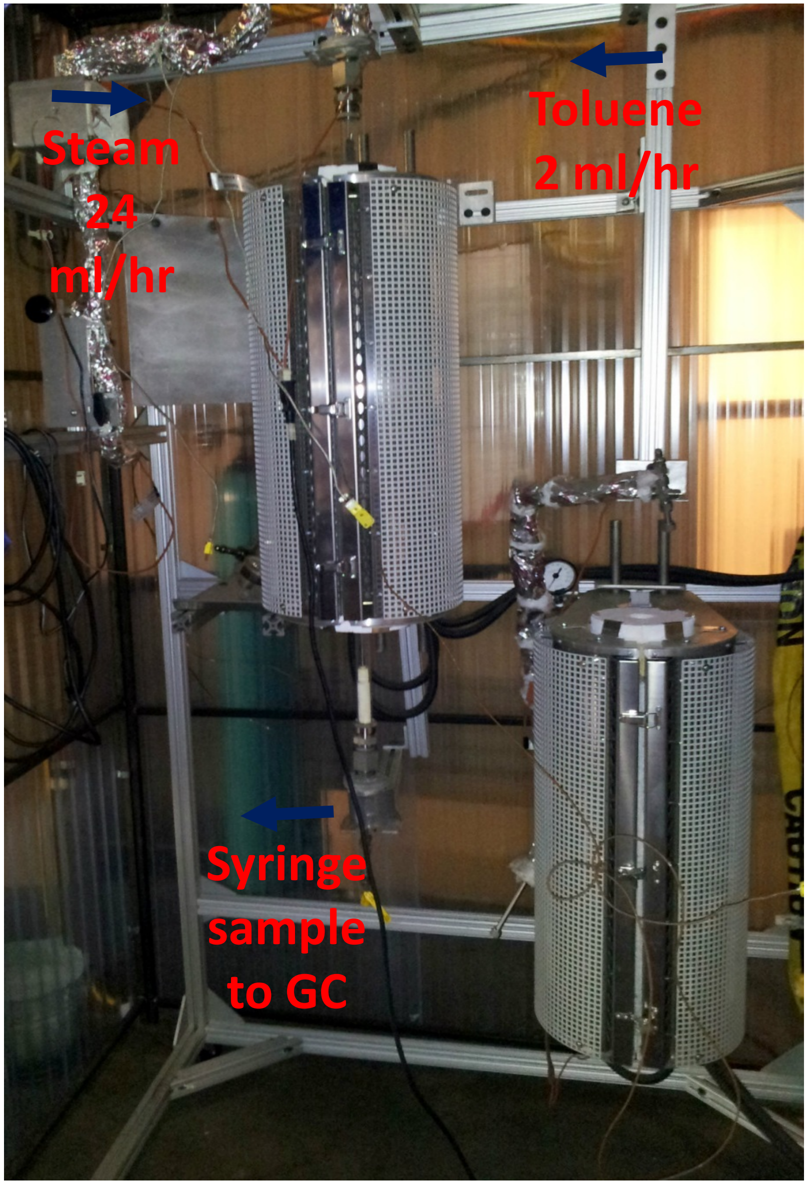
Activated Carbon

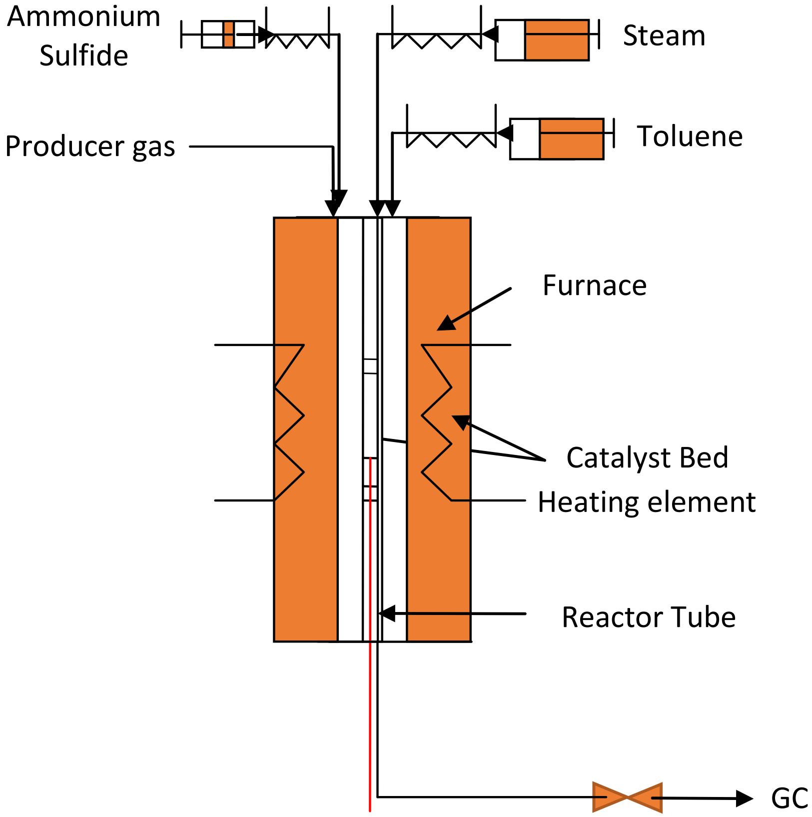


Acidic Surface Activated Carbon

Dilute ascorbic acid coating

Fixed-bed reactor





Surface area (m^2/g)

Method	Biochar		Activated carbon		Acidic surface activated carbon	
	Fresh	Used	Fresh	Used	Fresh	Used
Multipoint BET	16.73[e]	6.244[f]	703.3[a]	695.5[a]	697.1[a]	634.0[b]

Pore volume (cc/g)

Pore Volume Method	Biochar		Activated carbon		Acidic surface activated carbon	
	Fresh	Used	Fresh	Used	Fresh	Used
Total Pore Volume for pores with Radius less than 13.4 A° at P/P_0 = 0.31475	0.009[f]	0.003[g]	0.393[b]	0.401[a]	0.401[a]	0.352[c]

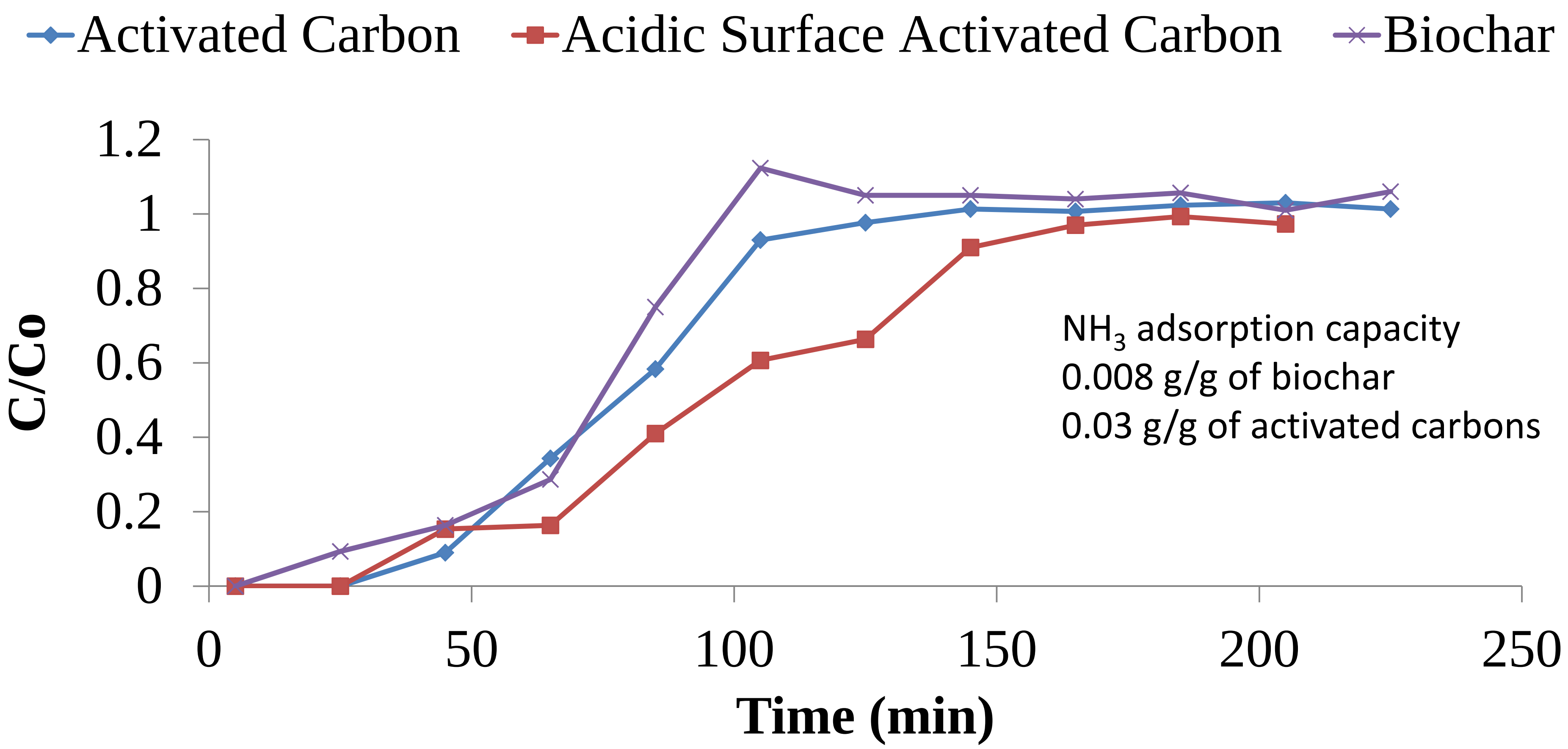
Mean toluene conversion for carbon-based catalysts

Catalyst	**Toluene Conversion (%)**			
	Toluene with N_2		Toluene with syngas	
	700°C	**800°C**	**700 °C**	**800°C**
Biochar	78.65 ± 12.05	81.01 ± 11.83	69.18 ± 11.89	78.83 ± 4.74
Activated Carbon	86.28 ± 7.7	91.69 ± 4.9	82.08 ± 7.73	88.55 ± 6.62
Acidic Surface Activated Carbon	80.78 ± 7.7	92.09 ± 8.4	79.13 ± 7.78	88.14 ± 7.89

Outlet gas concentration in syngas

Gas (% v/v)	Syngas	Biochar		Activated Carbon		Acidic Surface Activated Carbon	
		700 °C	800 °C	700 °C	800 °C	700 °C	800 °C
CO	19.3	15.64	17.55	19.7	19.9	19.6	19.29
CO_2	16.8	17.65	16.04	15.75	15.60	16.62	17.02
H_2	5.1	4.77	3.11	4.19	8.30	4.85	9.11
CH_4	7.5	6.29	6.65	5.52	5.57	6.78	6.25

Ammonia

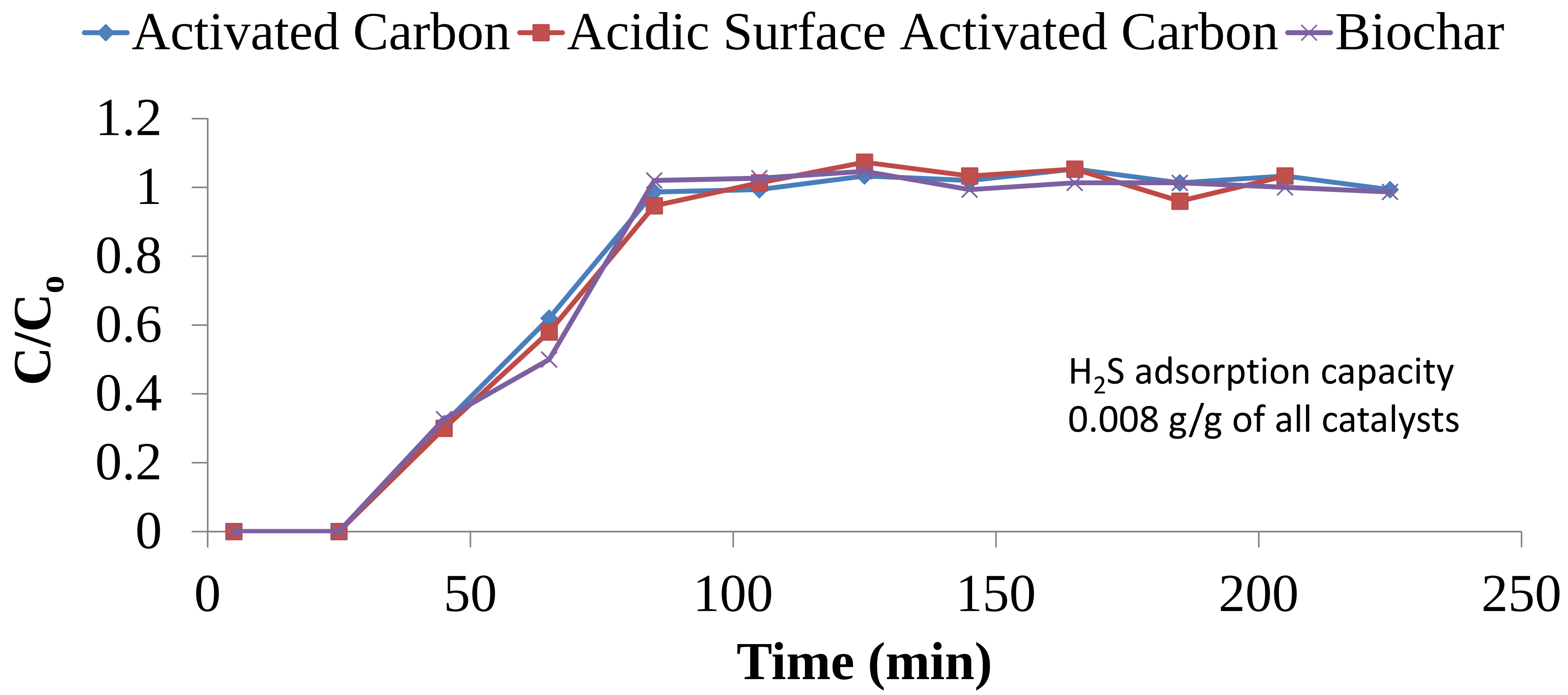


NH_3 adsorption capacity
0.008 g/g of biochar
0.03 g/g of activated carbons

Figure: Breakthrough curve for ammonia

C/C_0: ratio of final outlet ammonia concentration (ppm) to inlet ammonia concentration (ppm)

H_2S



H_2S adsorption capacity
0.008 g/g of all catalysts

Figure: Breakthrough curve for H_2S

C/C_0: ratio of final outlet ammonia concentration (ppm) to inlet ammonia concentration (ppm)

Toluene removal efficiency (%) in presence of syngas with NH_3 and H_2S.

Catalyst	**Toluene removal efficiency (%)**	
	without NH_3 and H_2S	with NH_3 and H_2S
Biochar	78.83 ± 4.74	86.69[c] ± 3.59
Activated carbon	88.55 ± 6.62	91.60[b] ± 1.29
Acidic surface activated carbon	88.14 ± 7.89	97.56[a] ± 0.99

Conclusions

- Surface area of activated carbon (>900 m^2/g) was significantly higher than that of its precursor biochar (~15 m^2/g).

- Biochar, activated carbon and acidic surface activated carbon showed toluene removal efficiencies of approximately 78, 89, and 88 %, respectively in the presence of syngas at 800 °C.

- NH_3 adsorption capacities were 0.008 g NH_3/g catalyst for biochar and 0.03 g NH_3/g catalyst for activated carbon and acidic surface activated carbon.

- H_2S adsorption capacities were 0.008 g H_2S/g catalyst for all biochar-based catalysts.

- The toluene removal efficiencies in the presence of NH_4 and H_2S in the syngas.

Research Team and Sponsors

PIs:

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