Microwave-Assisted Syngas Cleanup: Catalytic Reforming of Gasifier Tar Using a Low-Cost Iron Catalyst

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Disclaimer

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Outline

- **Introduction**
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  - Microwave Chemistry
  - Importance of Tar Reduction and Syngas Cleanup
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- **Results**
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  - Performance
  - Energy Efficiency Analysis
  - Reaction Pathway
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- **Conclusions**

Introduction

Background of the Process - Gasification

- Convert carbon-containing solid fuel to syngas for power generation and for value-added chemicals (F-T synthesis, etc.)
- Reliable way to upcycle waste with emission control

Coal/Biomass/Plastics

Chemicals

Electricity

Fuels

- Challenges
  - Bulky
  - Energy intensive

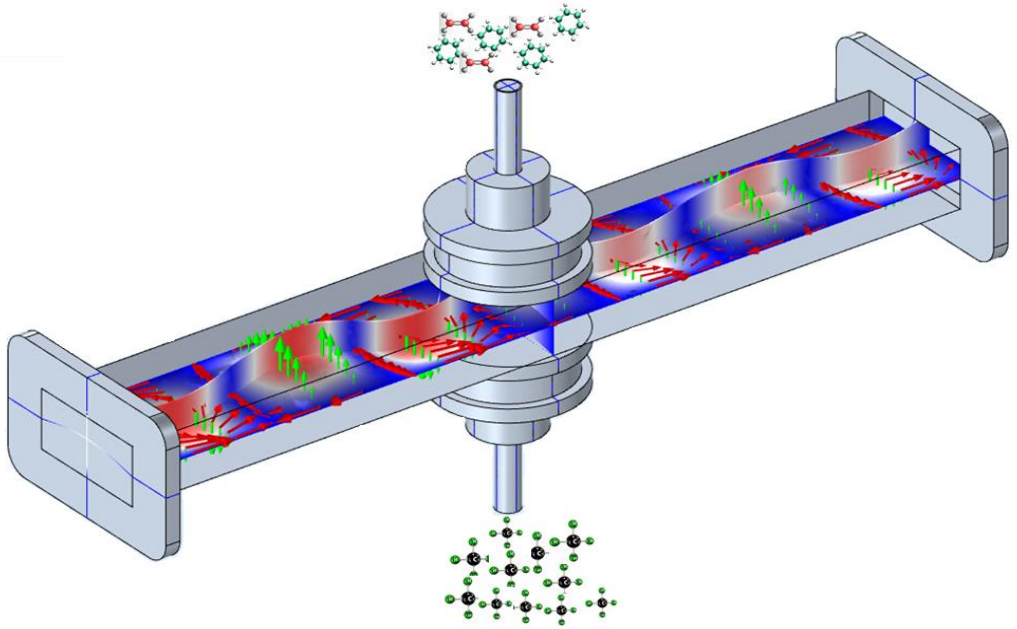
https://www.cbpengineering.com/wp-content/uploads/2013/02/Coal-gasification-plant.jpg

Introduction

Microwave Chemistry

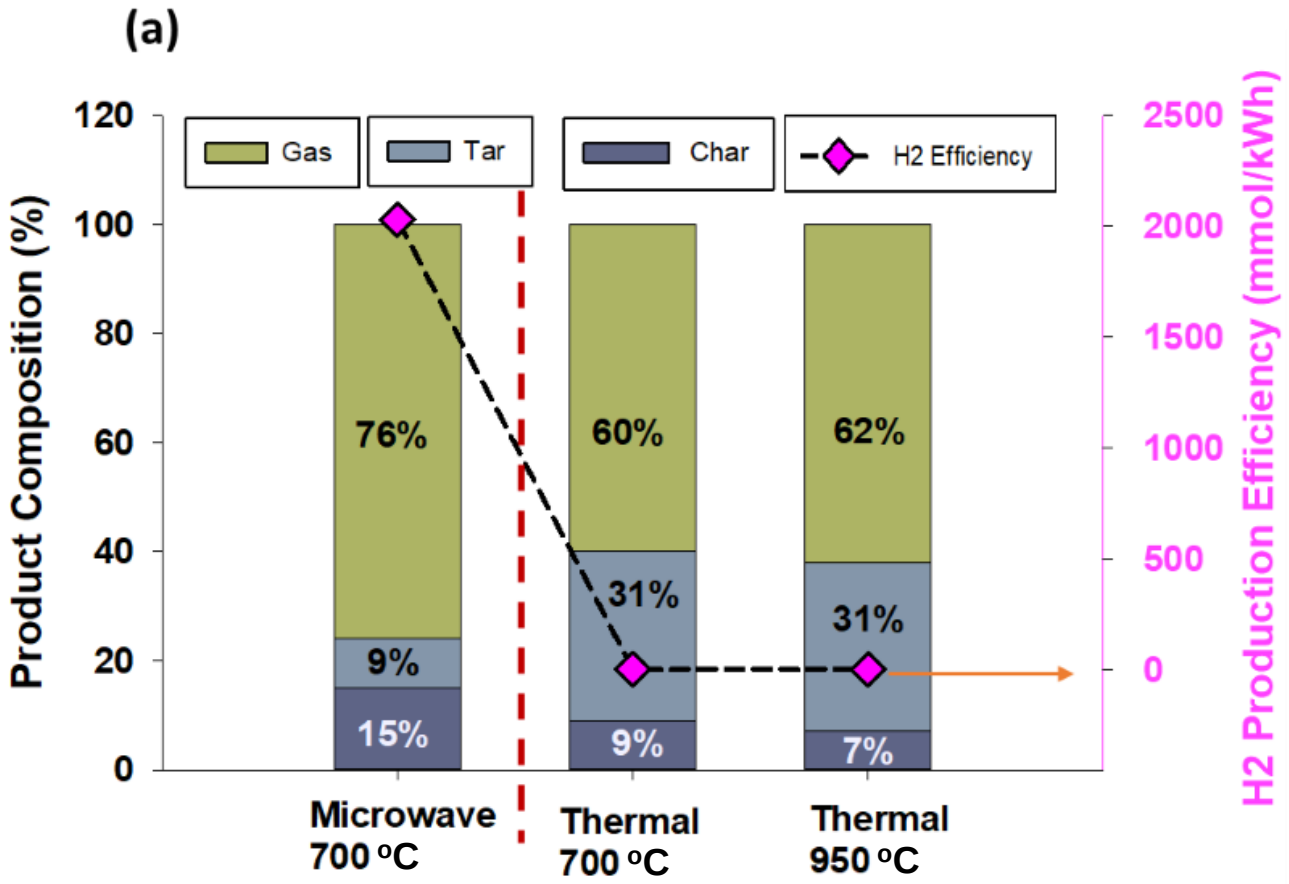
- Microwave: A type of electromagnetic wave with a frequency between 300 MHz to 300 GHz

- Microwave Chemistry: Usage of MW in a chemical reaction system, either as a heating source or not
  - Compact, modular design
  - Scale-up or down flexibility
  - Selective volume-based heating
  - Rapid startup/shutdown
  - Enhanced reaction rates: electrification



Introduction

Microwave-Assisted Gasifier for Co-Gasification of Biomass and Mixed Plastics



- Tar Formation
  - Lower tar percentage in the microwave gasifier, but still at 9 wt.%.
  - Negatively affect gasification efficiency
  - Causes clogging
- Tar Reduction methods:
  - Carrying out the gasification in the microwave reactor
  - Using catalyst during gasification
  - Applying after-process cleanup

A. Abedin, X. Bai, et al., 2023 Energy Conversion and Management, vol. 280, 116774, ISSN 0196-8904

Objectives

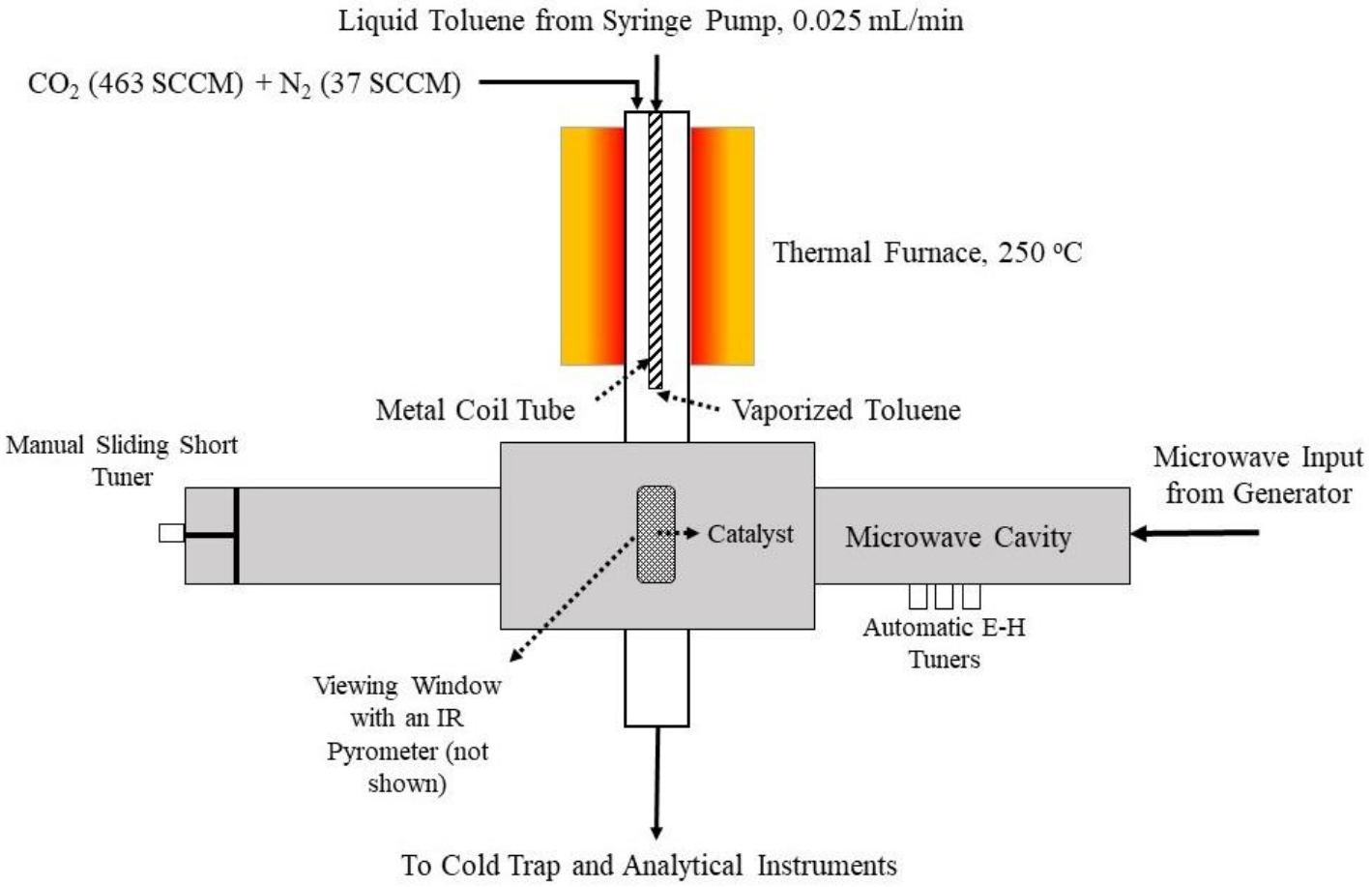
Tar Reforming with MW

- Enables low-tar solid fuel gasification
  - Microwave enhances in-situ tar conversion at mild temperature, which can lower the tar content in the outlet
- Acts as after-process syngas cleanup
  - Compact, modular design makes this process versatile to connect to other reactors
- Utilizes CO_2 for the production of value-added chemicals

Reactor Setup

Microwave-Assisted Reformer

- Catalyst: 10 wt.% Fe-Al_2O_3
  - Ball-milled mixture of magnetite and alumina, reduced at 700 °C under 20 vol% H_2 for 2 hours
  - SiC-TiC pellets were used as bed filler, heat transfer enhancer, and microwave absorber
- Temperatures: 400-700 °C (with 200-350 W of MW power input)



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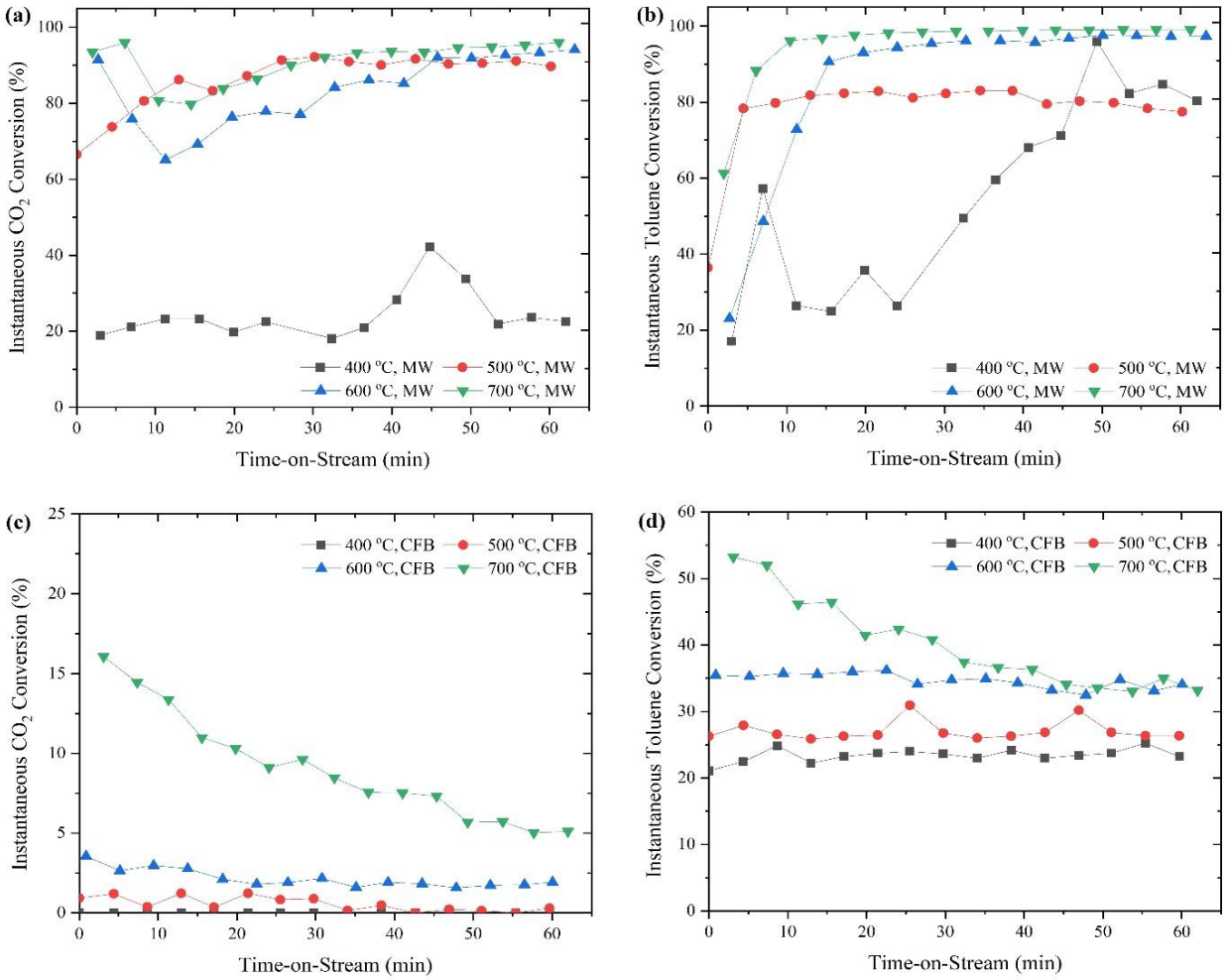
Results: Effect of Temperature

CO_2 and Toluene Conversions



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MW: Microwave

CFB: Conventional fixed-bed

In MW:

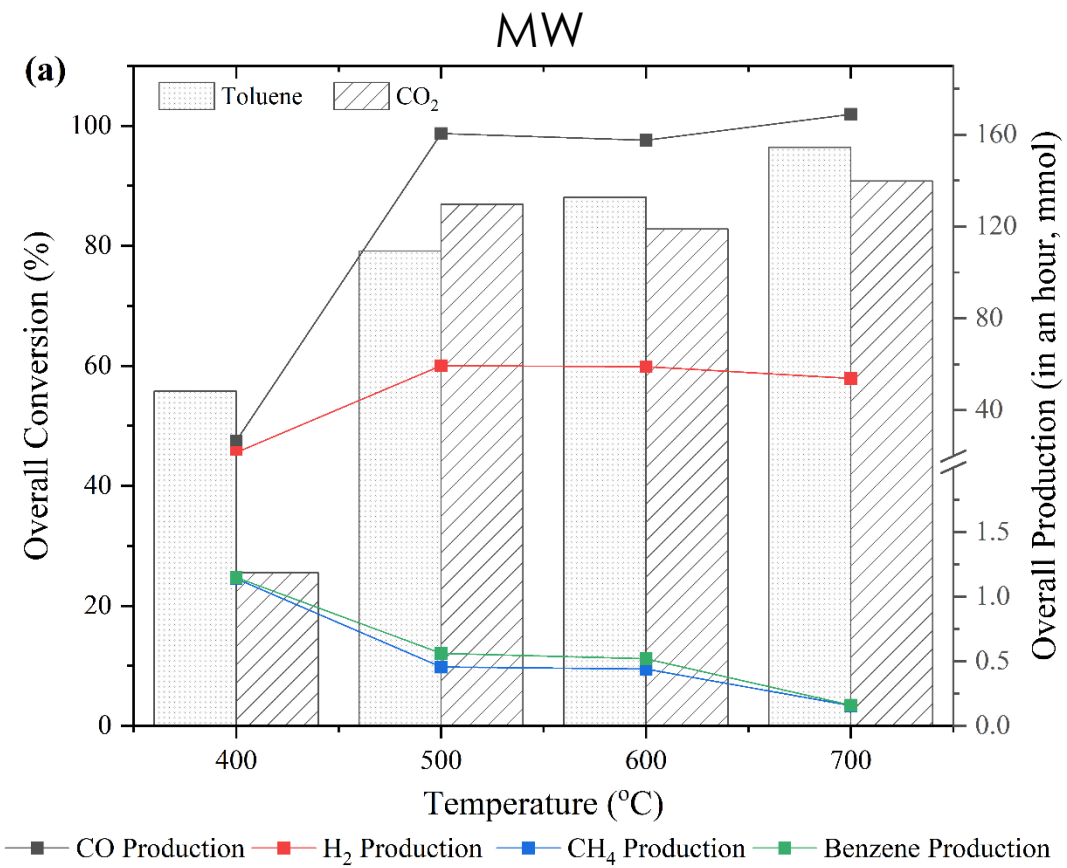
- CO_2 conversion was stable and slightly increased
- Toluene conversion was low at the beginning, then increased

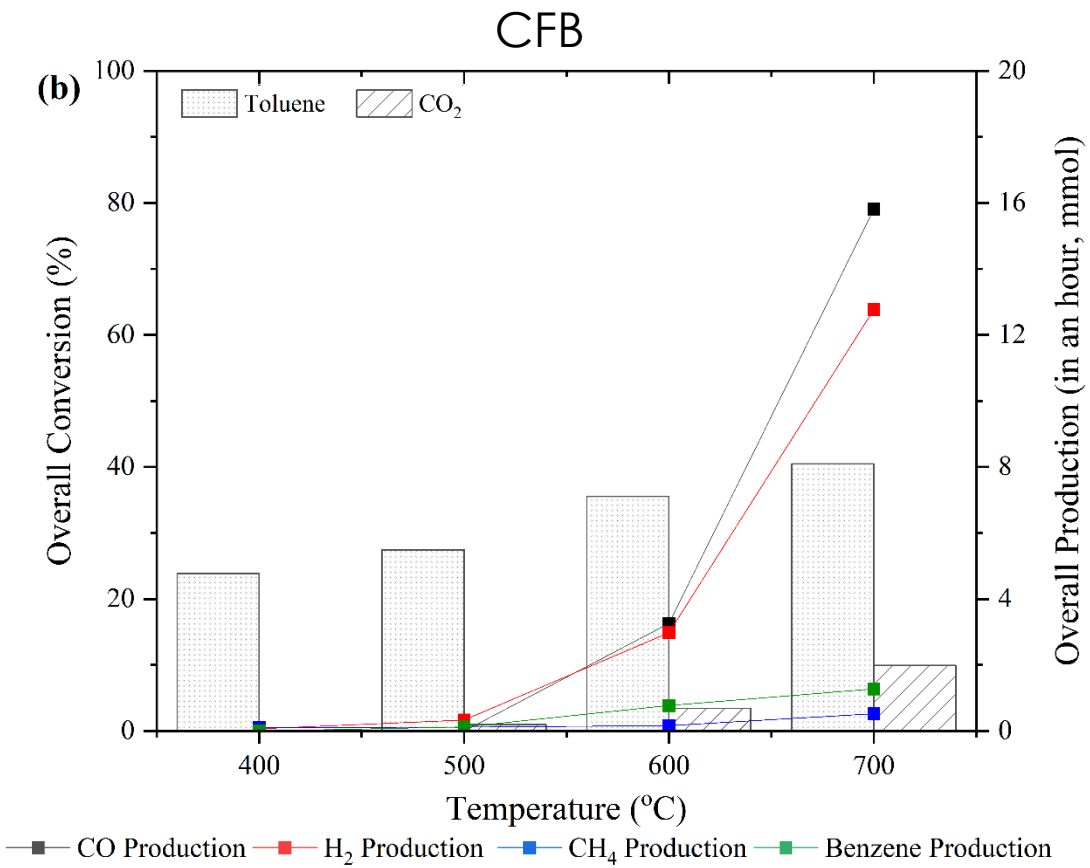
In CFB:

- CO_2 conversion was higher at the beginning, then decreased
- Toluene conversion was higher at the beginning (700 °C); consistent for the rest of the temperatures

Results: Effect of Temperature

Overall Comparison





MW: Microwave
CFB: Conventional fixed-bed

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Results: Energy Efficiency Analysis

Energy Consumption Comparison

Heating Mode (Method – Temperature)	P_T (kWh)	H_2 Energy Efficiency (mmol/kWh)	CO Energy Efficiency (mmol/kWh)
Microwave – 400 °C	0.1105	195.2	240.7
Microwave – 500 °C	0.1016	585.5	1559
Microwave – 600 °C	0.1880	311.2	838.4
Microwave – 700 °C	0.2616	204.2	645.4
Conventional – 600 °C	0.3776	7.822	8.636
Conventional – 700 °C	0.4987	24.56	31.68

Power absorbed by material for tar reforming (P_{fwd})

Power delivered to material ($P_{in} = P_{fwd} + P_{ref}$)

Energy to power MW (P_T)

- Absorption efficiency (η_{ab})
  - Ratio of forwarded power (P_{fwd}) and power input (P_{in}).
  - For a general lab-scale mono-mode system, >95% based on the lab record.
- Electricity-to-generator efficiency (η_e)
  - Ranges from 80%-90%, with a typical value of 85% [1].

$$\eta_{ab} = \frac{P_{fwd}}{P_{in}} = \frac{P_{in} - P_{ref}}{P_{in}}$$

$$P_T = \frac{P_{in}}{\eta_e} \quad \text{where } \eta_e = 0.85$$

[1] A. Santhoshkumar, R. Anand, 5 - Microwave-assisted fast pyrolysis of hazardous waste engine oil into green fuels, in: K. Azad (Ed.) Advances in Eco-Fuels for a Sustainable Environment, Woodhead Publishing, 2019, pp. 119-155.

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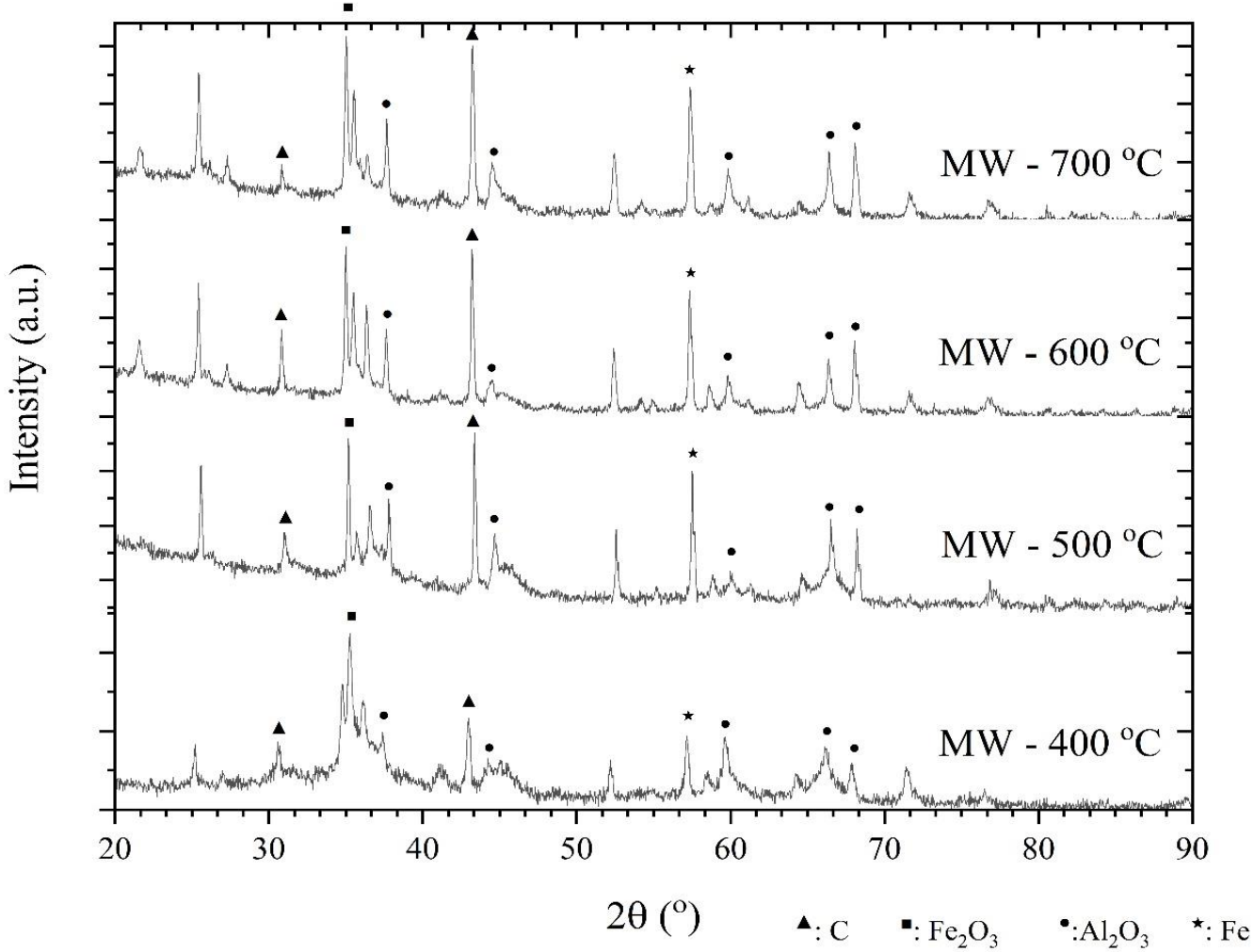
Results: Characterizations

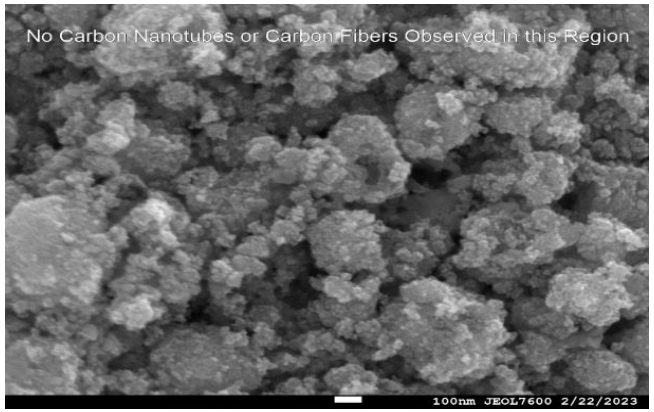
X-Ray Diffraction



Results: Characterizations

Surface Area and Microscopic Imaging

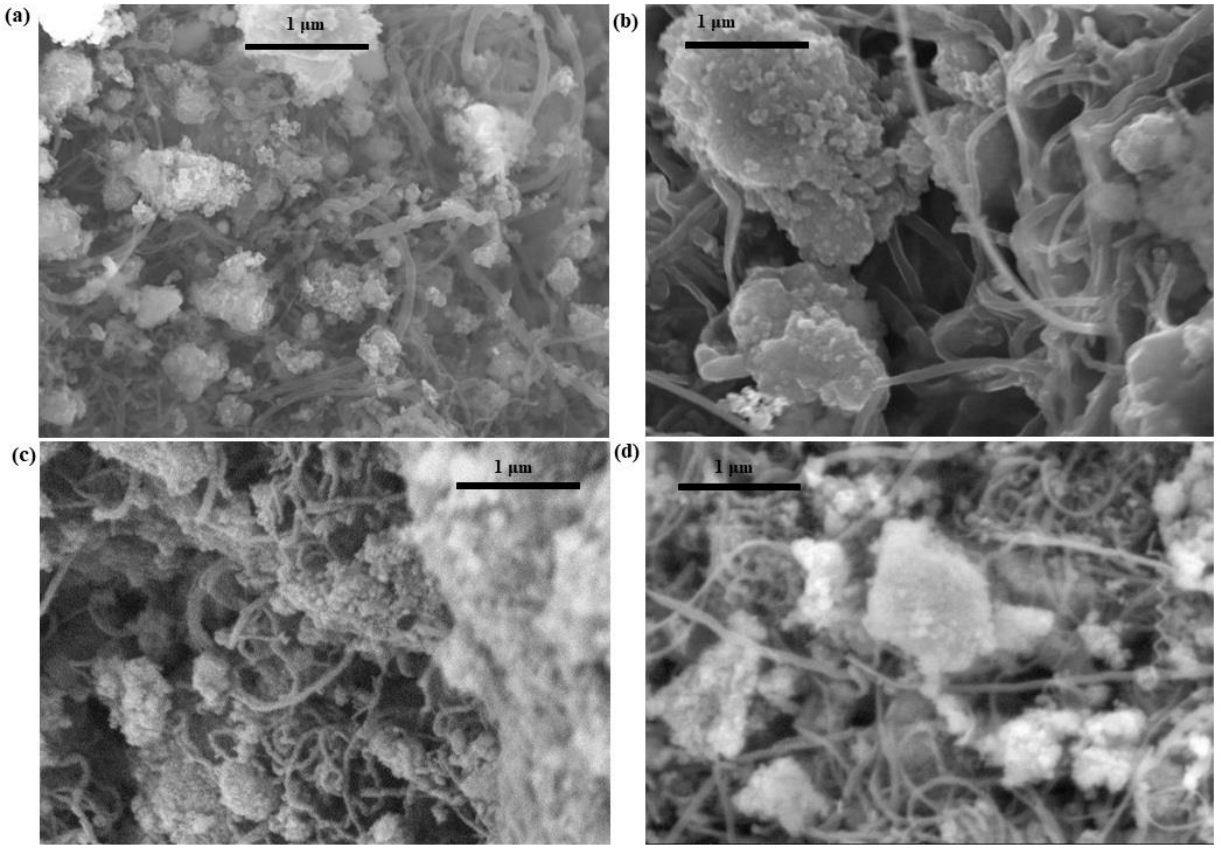
Sample Name	Heating Mode (Method – Temperature)	BET Surface Area (m^2/g)
Al_2O_3 Fresh	N/A	128.0 [39]
10 wt.% Fe/Al_2O_3	N/A	110.0
MW-400 °C 10wt.% Fe/Al_2O_3	Microwave – 400 °C	42.2
MW-500 °C 10wt.% Fe/Al_2O_3	Microwave – 500 °C	36.0
MW-600 °C 10 wt.% Fe/Al_2O_3	Microwave – 600 °C	31.8
MW-700 °C 10wt.% Fe/Al_2O_3	Microwave – 700 °C	27.9
CFB-400 °C 10wt.% Fe/Al_2O_3	Conventional – 400 °C	103.6
CFB-500 °C 10wt.% Fe/Al_2O_3	Conventional – 500 °C	100.1
CFB-600 °C 10 wt.% Fe/Al_2O_3	Conventional – 600 °C	79.7
CFB-700 °C 10wt.% Fe/Al_2O_3	Conventional – 700 °C	52.4



CFB-700 °C

MW-400 °C

MW-500 °C



MW-600 °C

MW-700 °C

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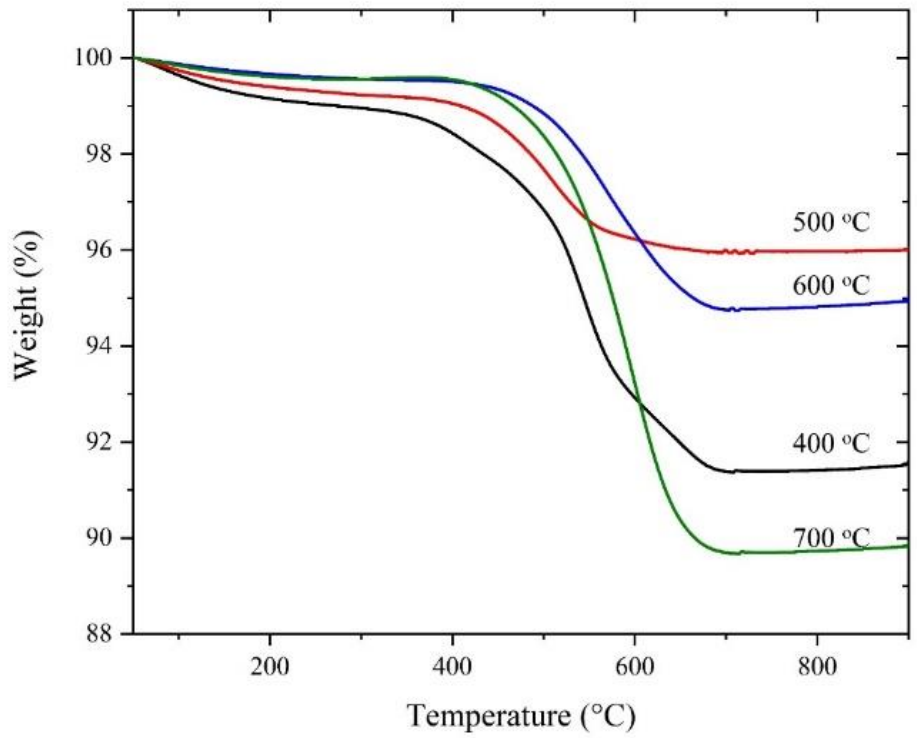
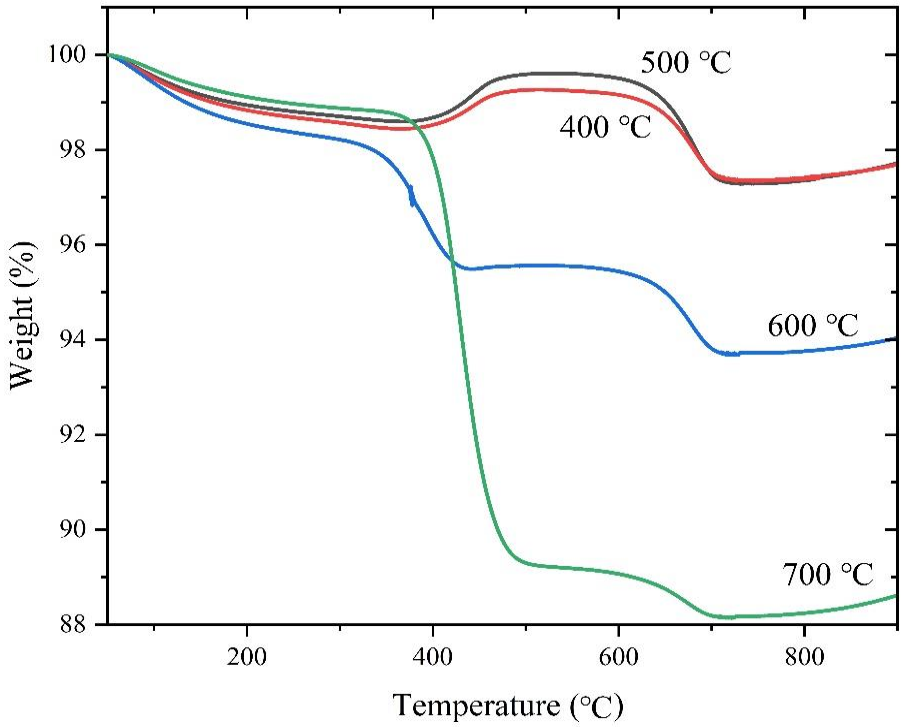
Results: Characterizations

Carbon Deposition Analysis

MW



CFB



MW: Microwave
CFB: Conventional fixed-bed

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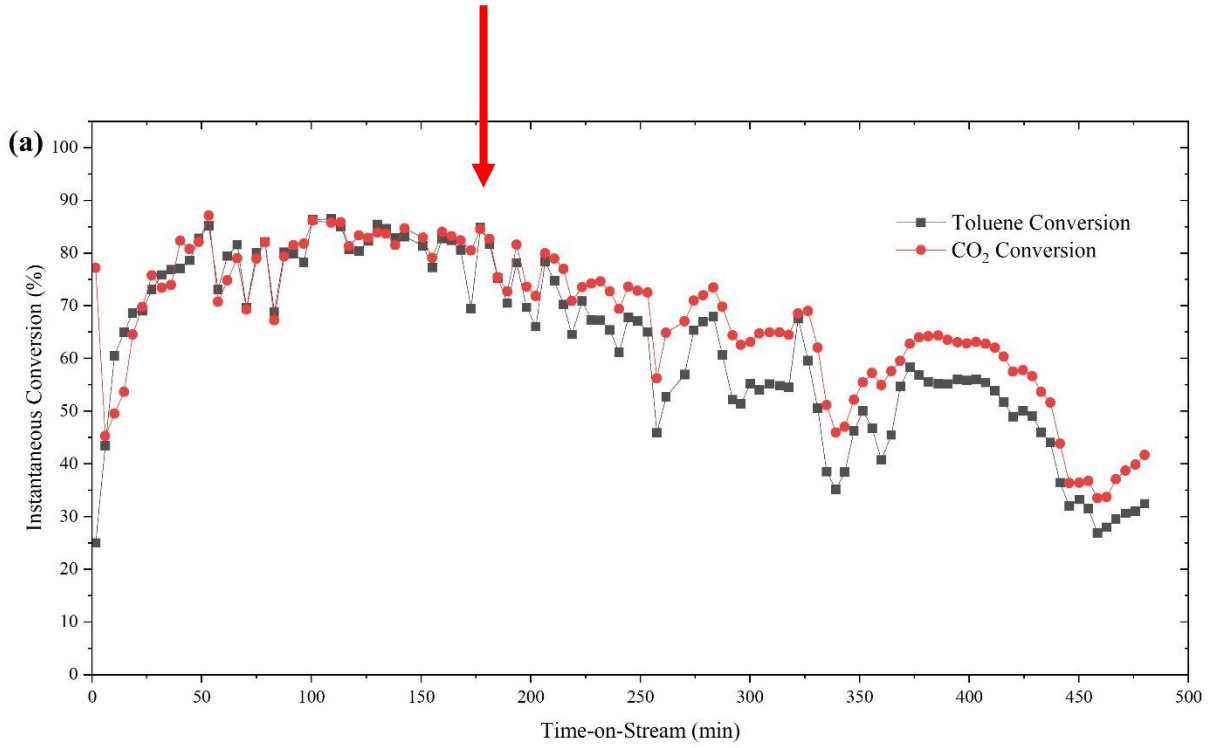
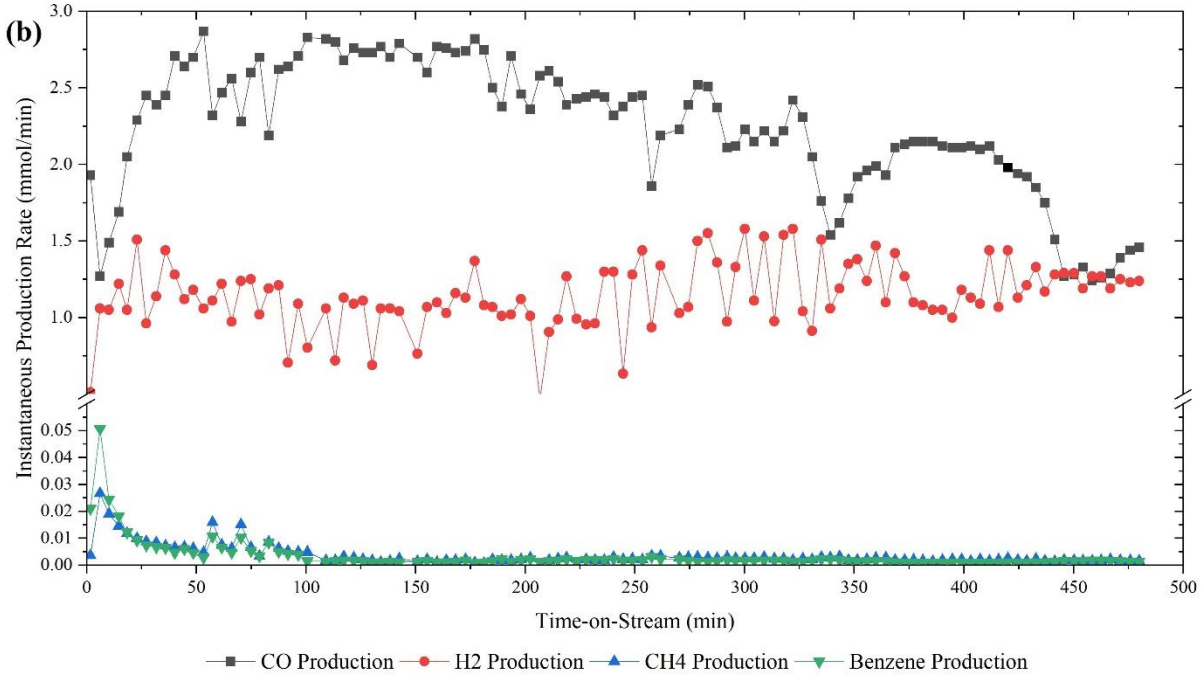
Results: Stability Test

8-hour Continuous Run (500 °C)





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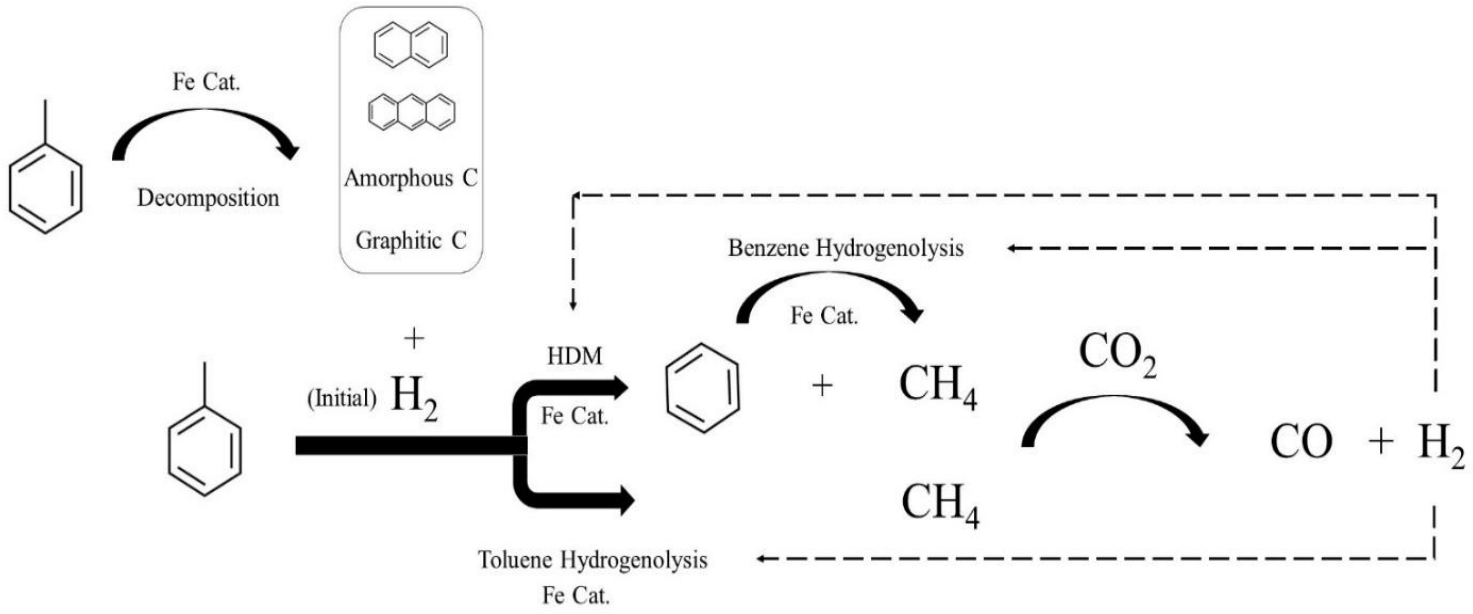
Discussion: Reaction Pathway



- Dehydrogenation/decomposition
  - Initial hydrogen formation
- Initial toluene hydrodemethylation (HDM)
  - Requires hydrogen to initiate
- Aromatics hydrogenolysis

- Methane dry reforming
  - Syngas production
- Boudouard reaction

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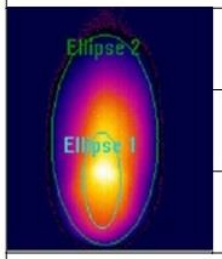
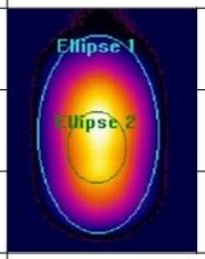
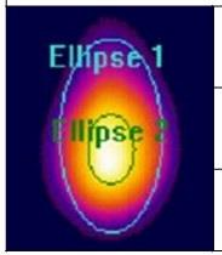
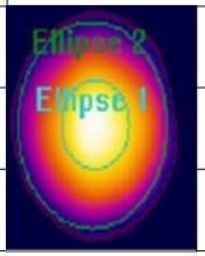
Discussion: Microwave-Material Interaction

- "Hot-spots"
  - ~100-290 °C higher than the bulk, depending on the material
  - 78-124 °C temperature difference in this case

MW 400			MW 500		
	Mean Outer Ellipse (°C)	455.2		Mean Outer Ellipse (°C)	506.8
	Mean Inner Ellipse (°C)	502.8		Mean Inner Ellipse (°C)	560.2
	Max Temperature (°C)	524.0		Max Temperature (°C)	578.4
MW 600			MW 700		
	Mean Outer Ellipse (°C)	644.5		Mean Outer Ellipse (°C)	693.1
	Mean Inner Ellipse (°C)	681.5		Mean Inner Ellipse (°C)	760.5
	Max Temperature (°C)	690.6		Max Temperature (°C)	779.1

- Synergy between electromagnetic field and "Hot-spots"
  - Toluene hydrodemethylation
  - Aromatics hydrogenolysis
  - π-electron polarization of the benzene ring

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Conclusion

- By using a low-cost Fe-Al_2O_3 catalyst with state-of-the-art microwave reactor design, dry reforming of toluene, as a model compound of tar, can be achieved with:
  - >80% of CO_2 and toluene conversions at 500 °C
  - 3 hours continuous operation without significant deactivation, 8 hours maximum lifespan
  - Co-production of crystallized carbon species
- Reactions involved in the process include:
  - Toluene hydrodemethylation (initial)
  - Aromatics hydrogenolysis
  - Boudouard reaction
  - Methane dry reforming
- Microwave irradiation not only provides selective heating, but also initiates electron polarization which triggers certain reactions under mild conditions

Acknowledgments

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Microwave Gasification Team

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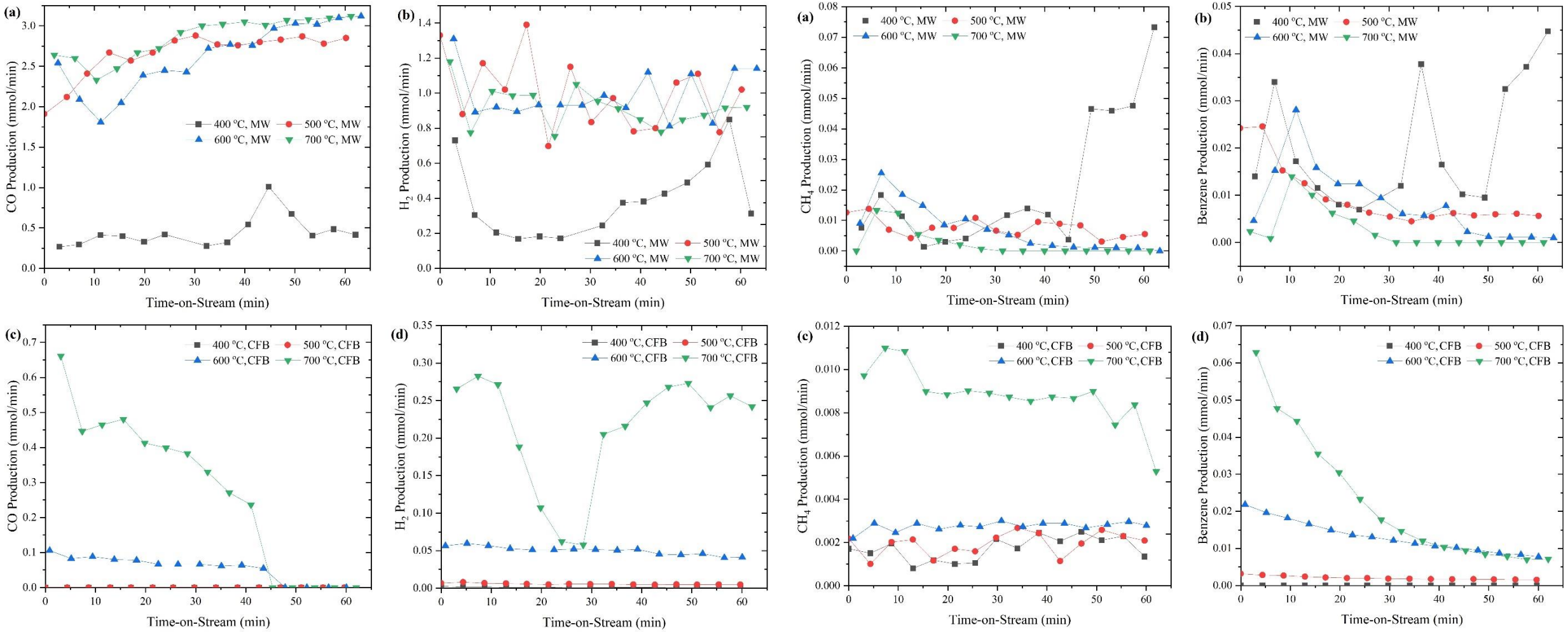
Results: Effect of Temperature

Product Distribution



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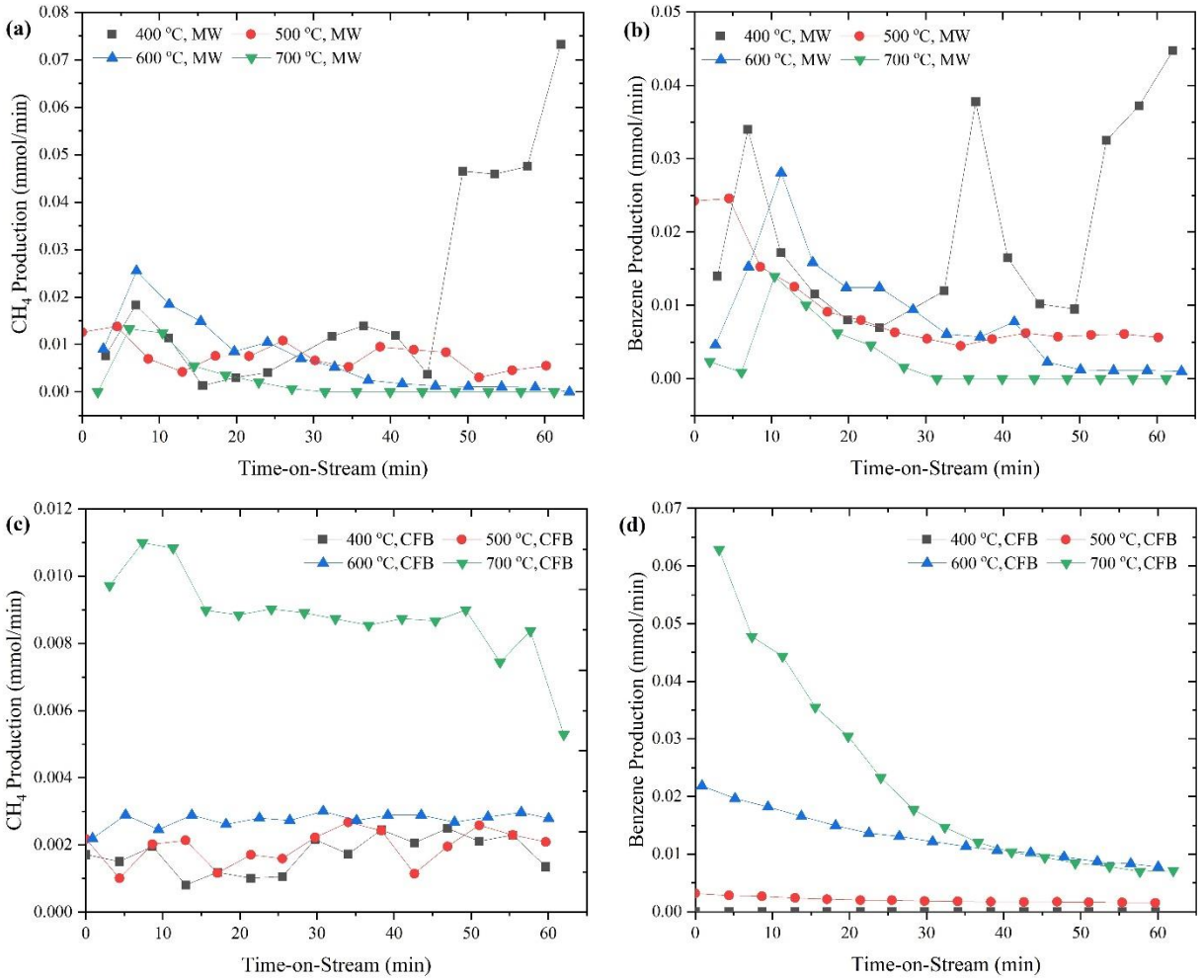

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