Microwave-Assisted Catalytic Conversion of Tar Using Iron Catalyst Doped with Ni/La/Ce

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NATIONAL ENERGY TECHNOLOGY LABORATORY

Authors and Contact Information

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Outline

- **Introduction**
  - Tar and its classification
  - Tar analysis from different plastics
  - Microwave Chemistry
- **Reactor Setup**
- **Results**
  - Conventional Reactor vs. Microwave Reactor
  - Performance
  - Reaction Mechanism
- **Conclusions**

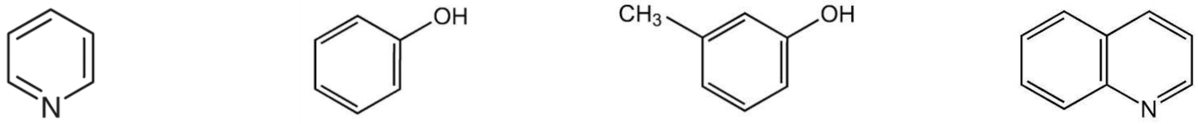
Background: Tars

Horvat, A., 2016. (Doctoral dissertation, University of Limerick).

- Blockage
- Corrosion in downstream filters, fuel lines, engine nozzle, and turbines
- Bad odor
- Poison catalyst
- Decrease in conversion efficiency

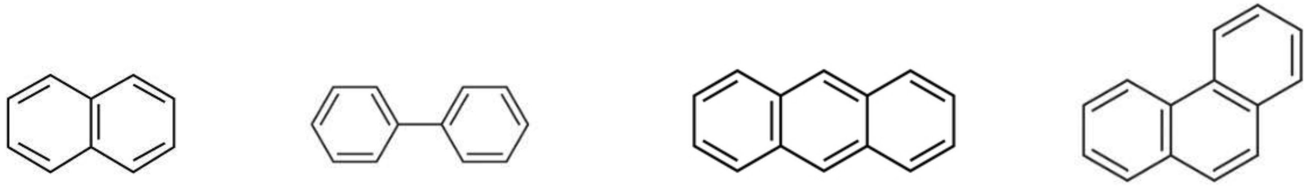
Biomass Tar Classification

- Class 1: GC undetectable
- Class 2: Heterocyclic aromatics

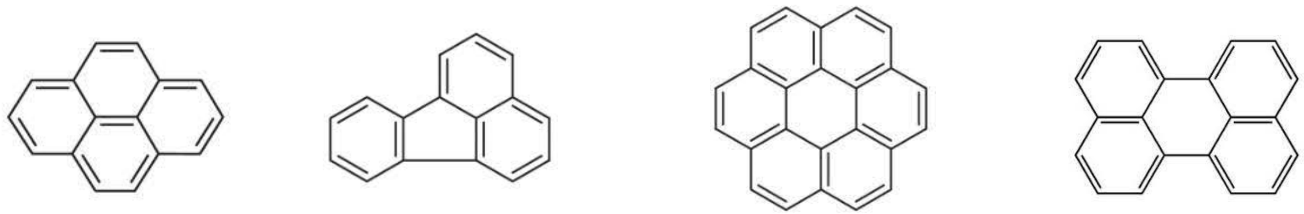


- Class 3: Light Aromatic

- Class 4: Light PAH compounds

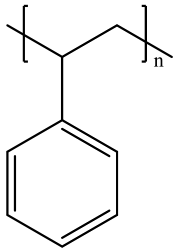


- Class 5: Heavy PAH compounds

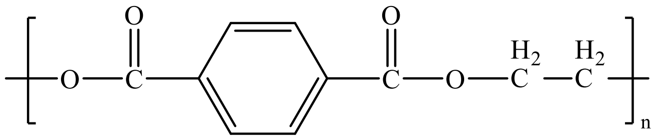


Renewable and Sustainable Energy Reviews, **2016**, 58, 450-461

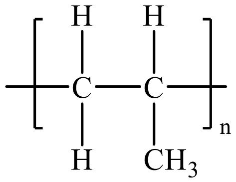
Tar from Different Plastics



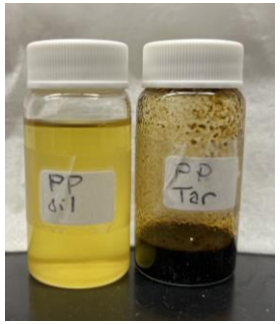
Polystyrene (PS)

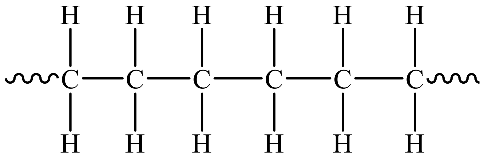


Polyethylene terephthalate (PET)

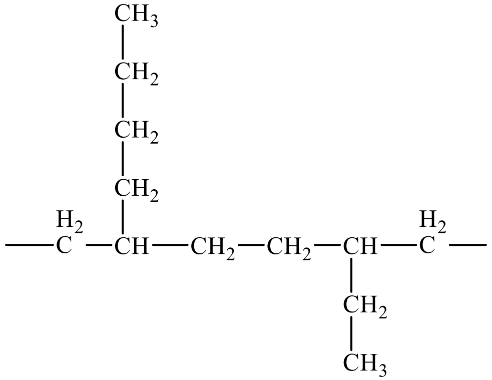


Polypropylene (PP)

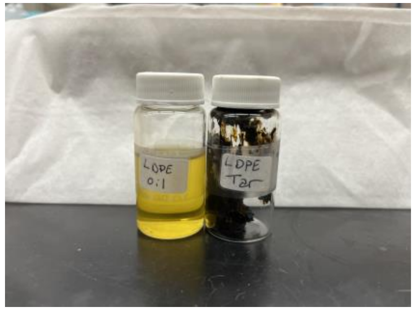




High density polyethylene (HDPE)



Low density polyethylene (LDPE)

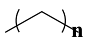


GC-MS Analysis of Plastic Tar

High density polyethylene (HDPE)

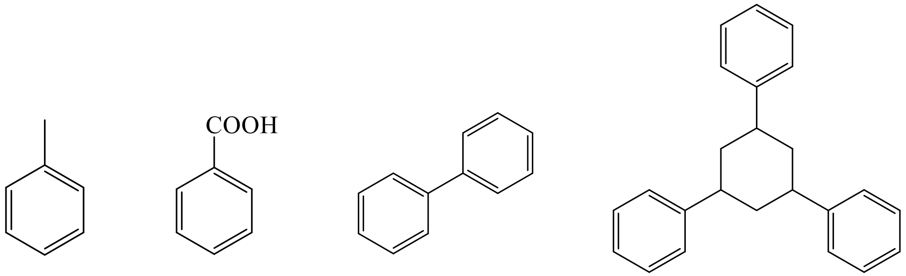
Low density polyethylene (LDPE)

Polypropylene (PP)

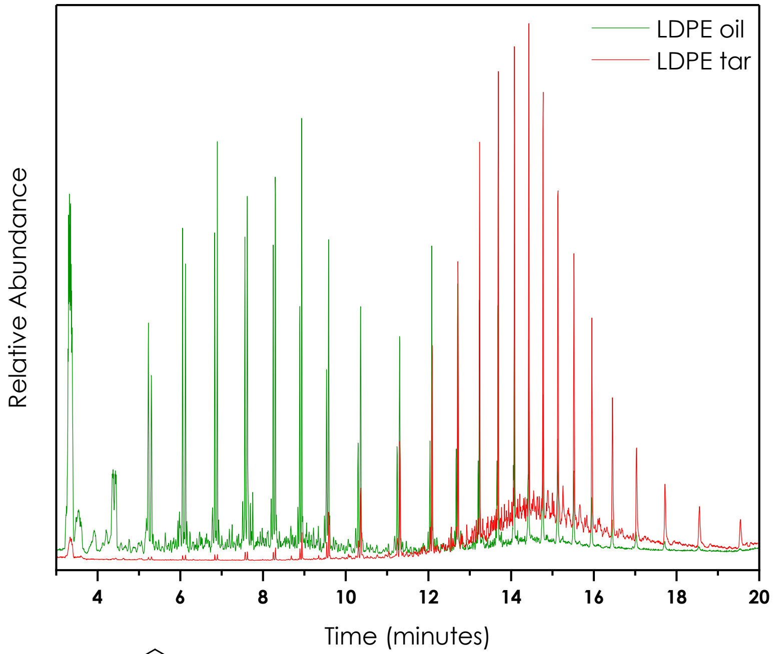


n= 8 to 36

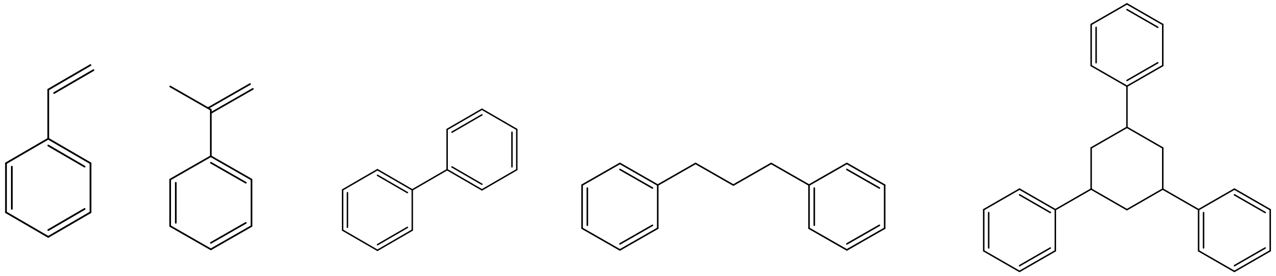
Polyethylene terephthalate (PET)



GC-MS spectra of LDPE tar and Oil

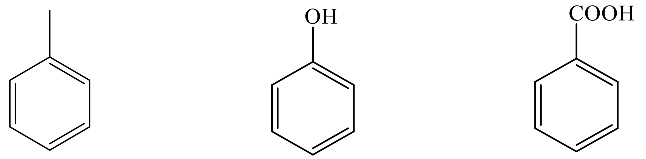


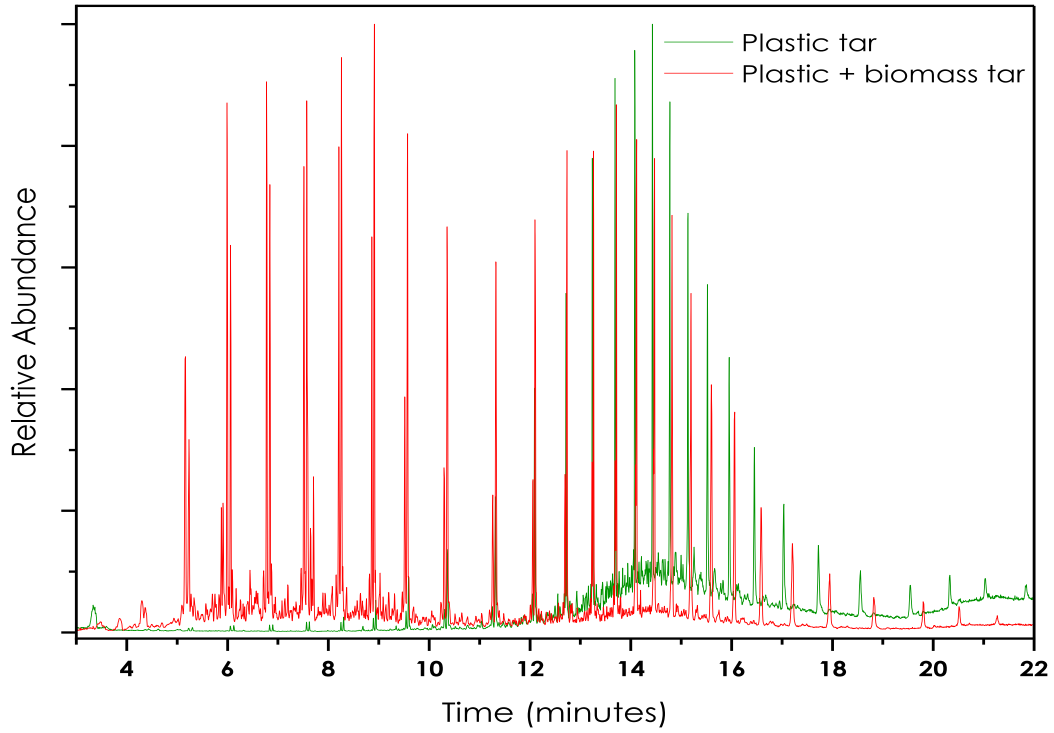
Polystyrene (PS)



GC-MS Analysis of Plastic and Biomass Tar

- Tar from plastic(LDPE) had mostly saturated hydrocarbons
- Tar from plastic(LDPE) and biomass (corn stover) mixture had mostly satured hydrocarbons and few aromatics





Toluene as Tar model Compound

Tar Mitigation Techniques

Physical methods

- Cyclone separators
- Cooling/Wet scrubbing
- Granular Filters
- Electrostatic precipitation
- Oil Gas scrubbing

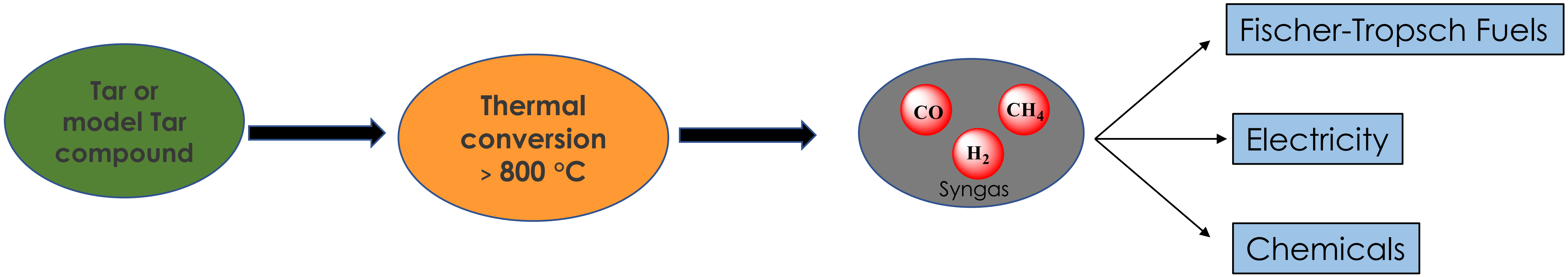
Thermal decomposition

- Tar is heated to high temperature/addition of air or oxygen
- heavy aromatics cracked down to lighter once

Catalytic conversion

- Use milder conditions
- Operates at same temperature as exit product gas temperature
- Trap particulate matter

Thermal Conversation of Tar to Syngas



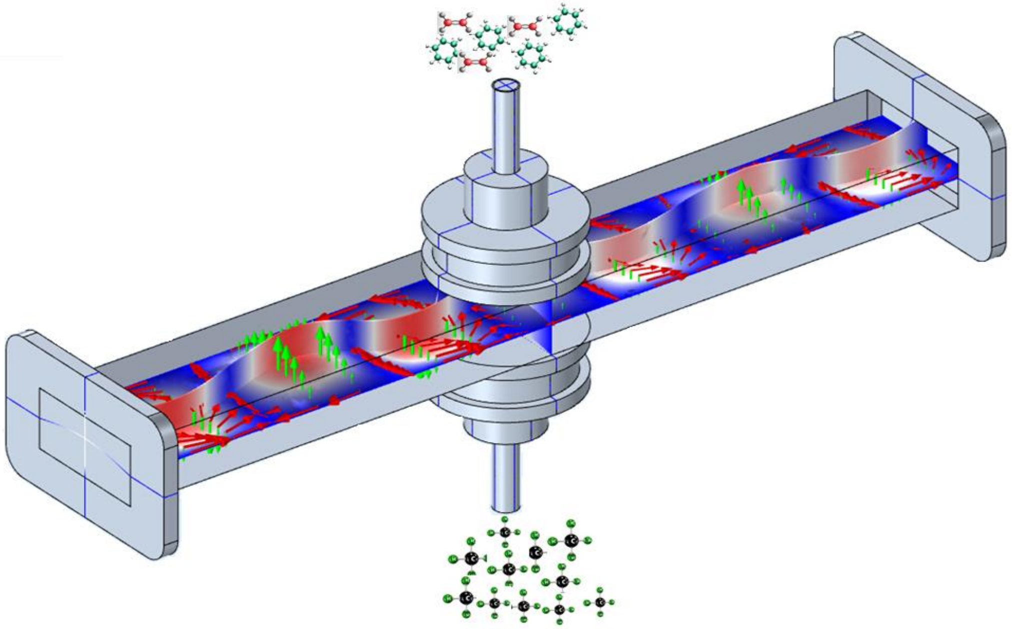
Challenges:

- Bulky
- High cost of heating
- Long preparation time
- Energy intensive

Microwave-Assisted Tar Reforming

Advantage of microwaves in chemical reactions as a heating source:

- Compact, modular design
- Enhanced reaction rates
- Increased energy efficiency
- Rapid start/stop operation
- Selective volume-based heating



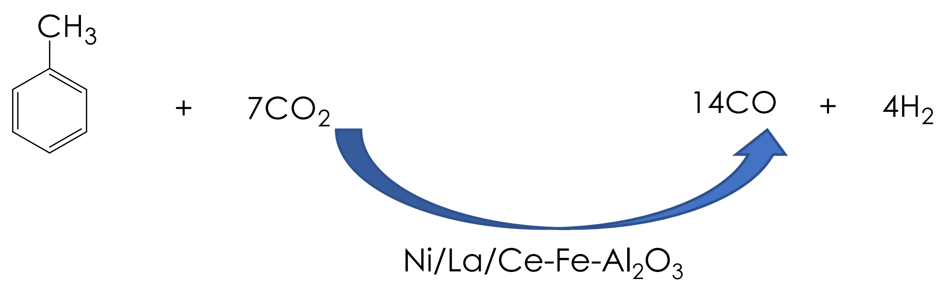
https://netl.doe.gov/sites/default/files/rdfactsheet/R-D215_4.pdf

Objectives

CO_2 Dry Reforming of Toluene Using Microwaves

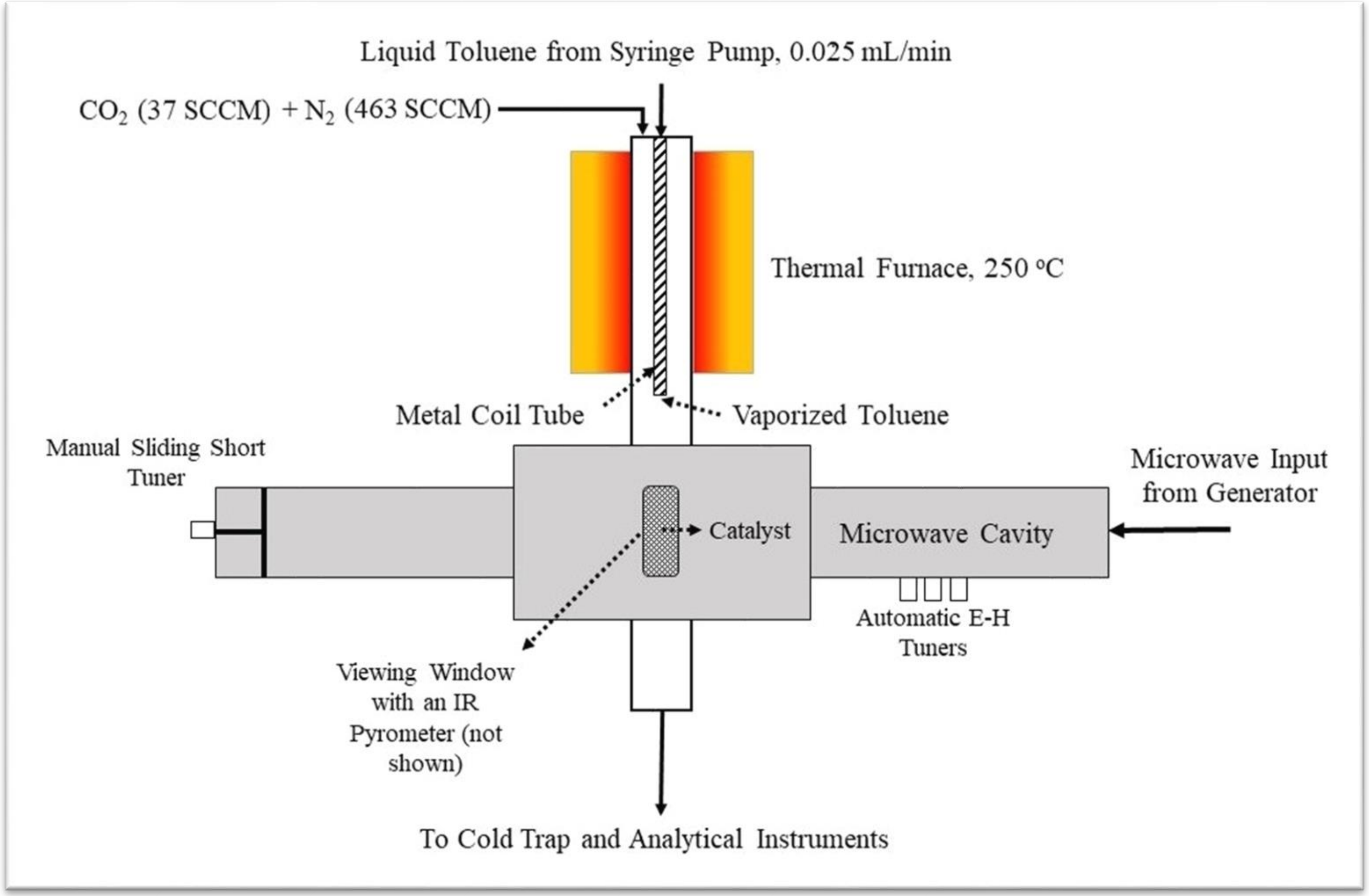
- Enables low-tar solid fuel gasification
- Acts as after-process syngas cleanup
- Utilizes CO_2 for the production of value-added chemicals

Toluene Dry Reforming

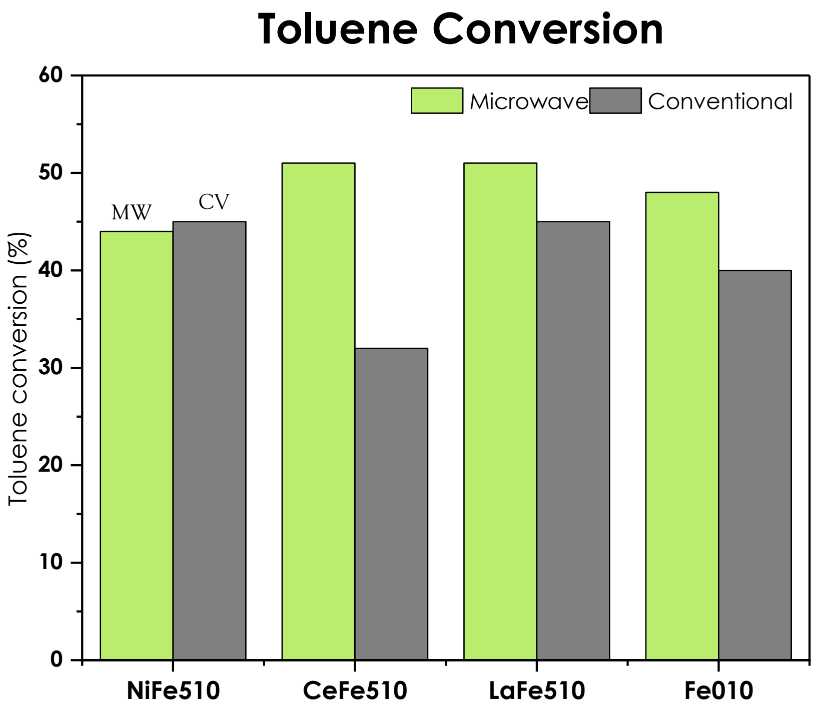


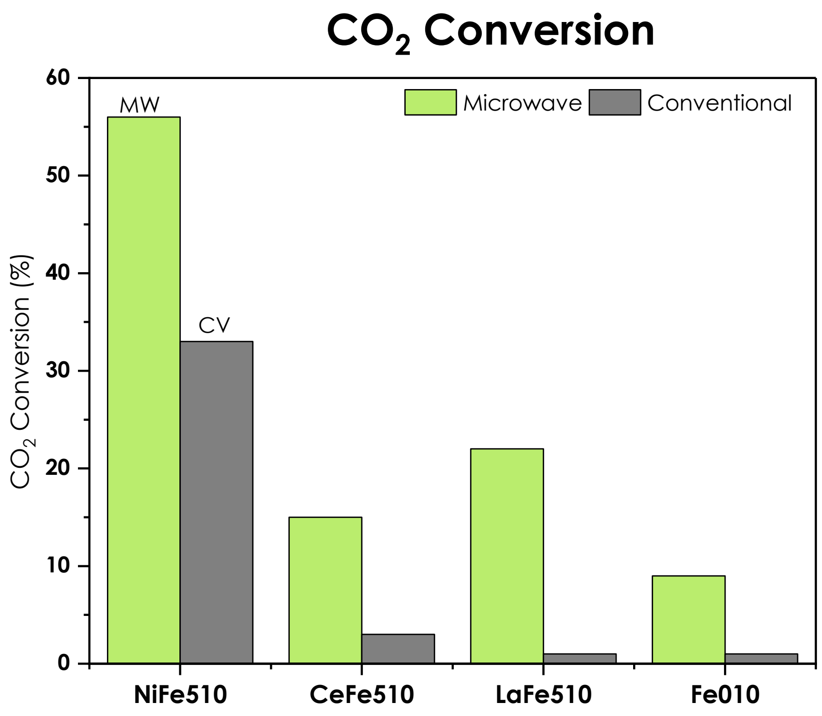
Microwave Reactor Setup

- Catalyst: 10 wt.% Fe and 5wt% of (Ni/La/Ce over Al_2O_3)
- Microwave absorber: SiC
- Temperatures: 500 °C
- MW power: 200-350 W



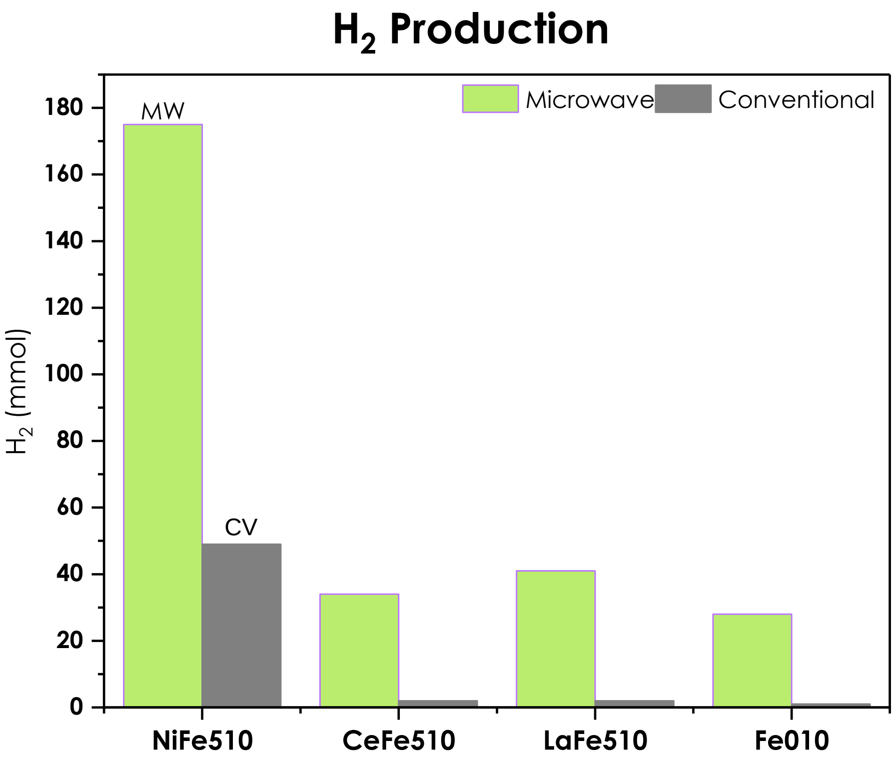
Effect of Catalyst on Toluene and CO_2 Conversion

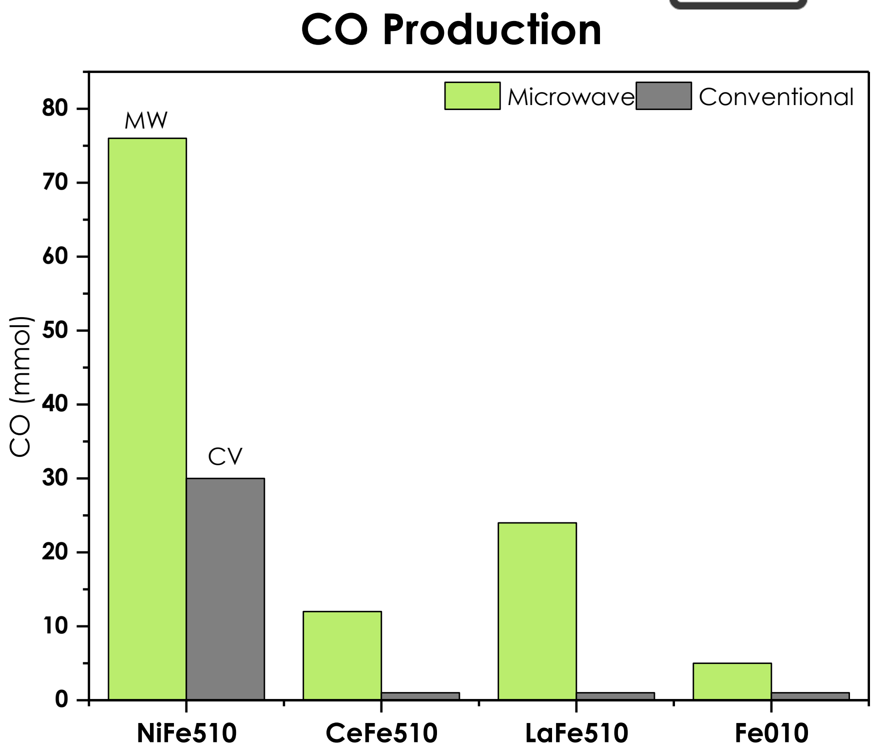




- Toluene conversion rates were similar both under microwave and conventional conditions
- CO_2 conversion rates were higher for MW reactions

Effect of Catalyst on Syngas Production

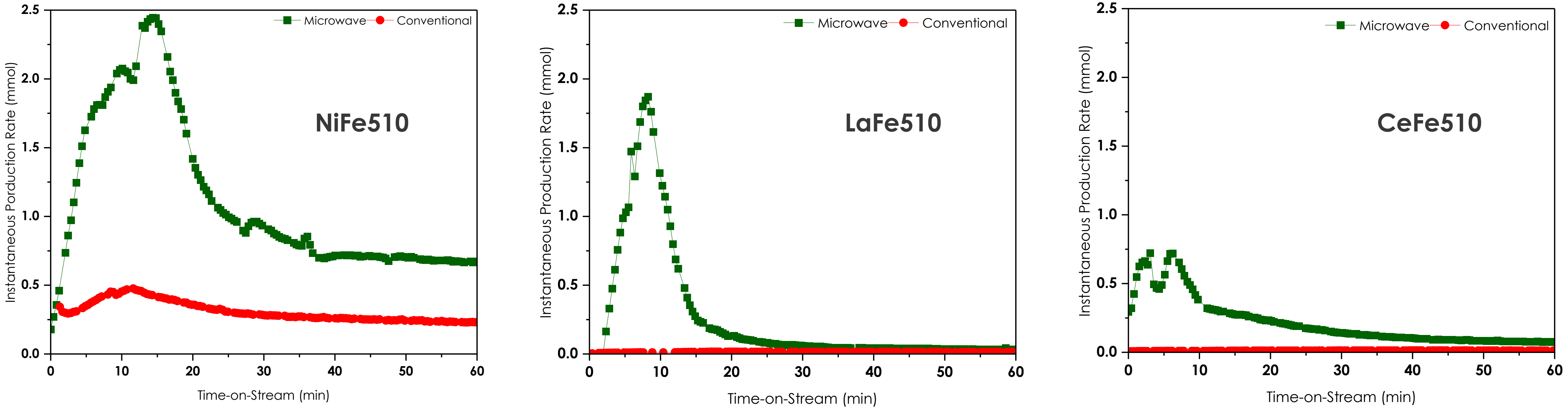




- Nickel doped catalyst produced higher syngas
- MW reactions produced higher gases compared to thermal reactions

Time on Stream Data for H_2 Production-Catalytic Stability

Instantaneous H_2 Production Rate

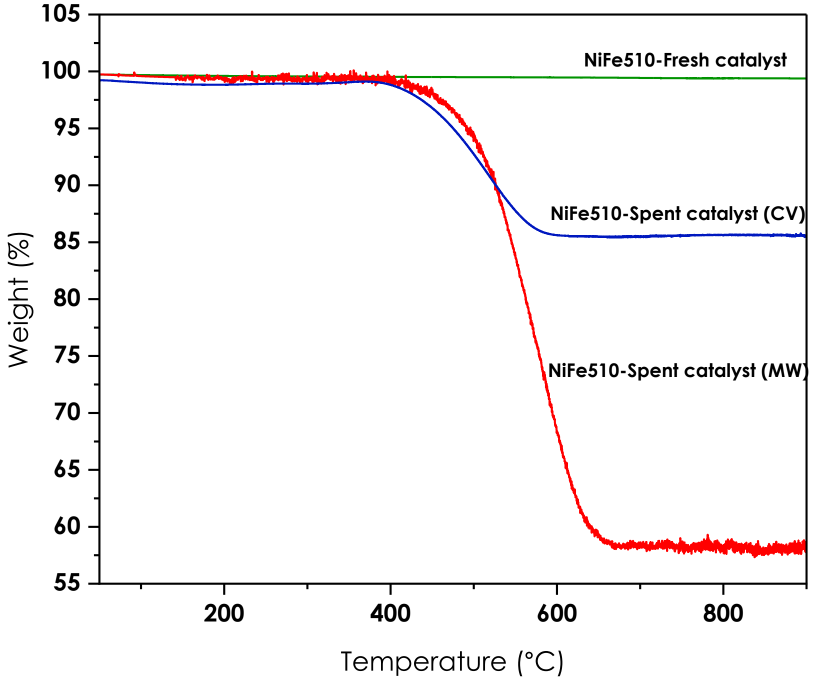


- In Microwave, H_2 conversion was higher at the beginning
- In Conventional, H_2 conversion rate was lower at the beginning and stayed consistent

Catalyst Characterization

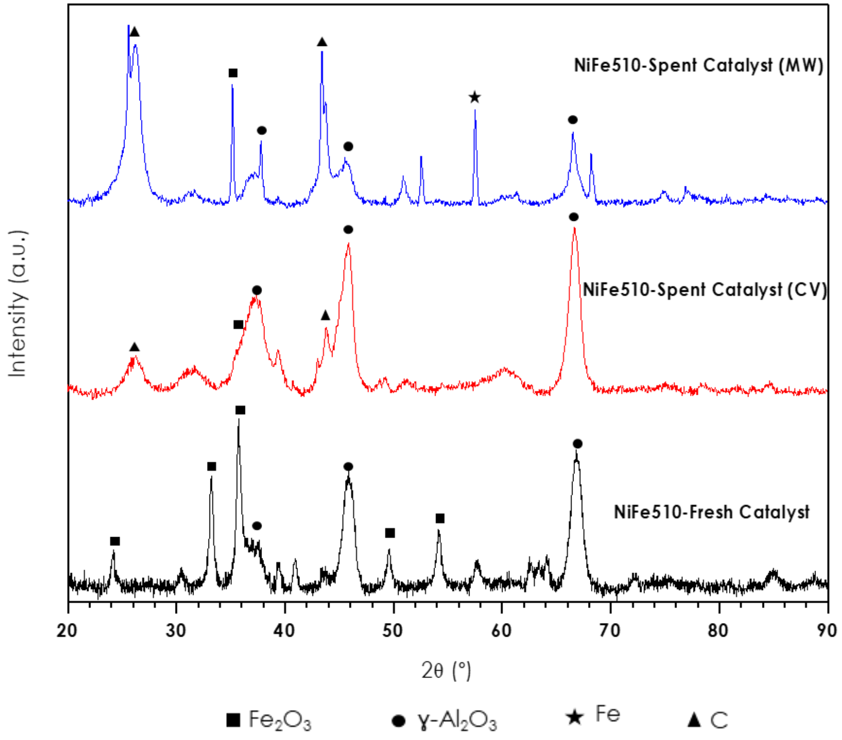
MW= Microwave; CV=Conventional

TGA Analysis



- Weight loss between 400-650 °C
- Weight loss was higher for Microwave reaction
- Carbon was accumulating at higher temperature - catalyst deactivation

XRD Analysis



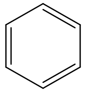
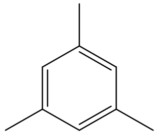
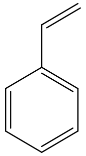
Microwave reaction promoted both amorphous and graphitic carbon formation

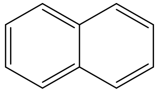
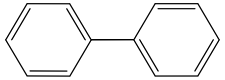
Results: Energy Efficiency Analysis

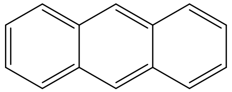
Energy Consumption Comparison

Catalyst/Heating mode At 500 °C	H_2 Energy efficiency (mmol/kWh)	CO Energy efficiency (mmol/kWh)
NiFe510-Microwave	844	367
NiFe510-Conventional		
CeFe510-Microwave	465	166
CeFe510-Conventional		
LaFe510-Microwave	518	299
LaFe510-Conventional		

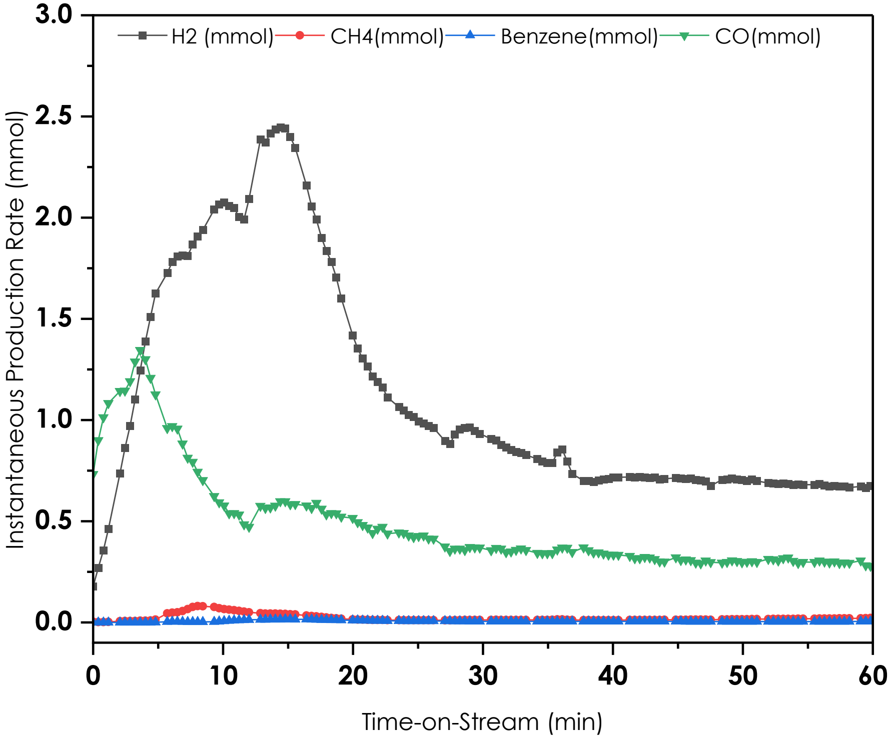
GC-MS Data of Condensates

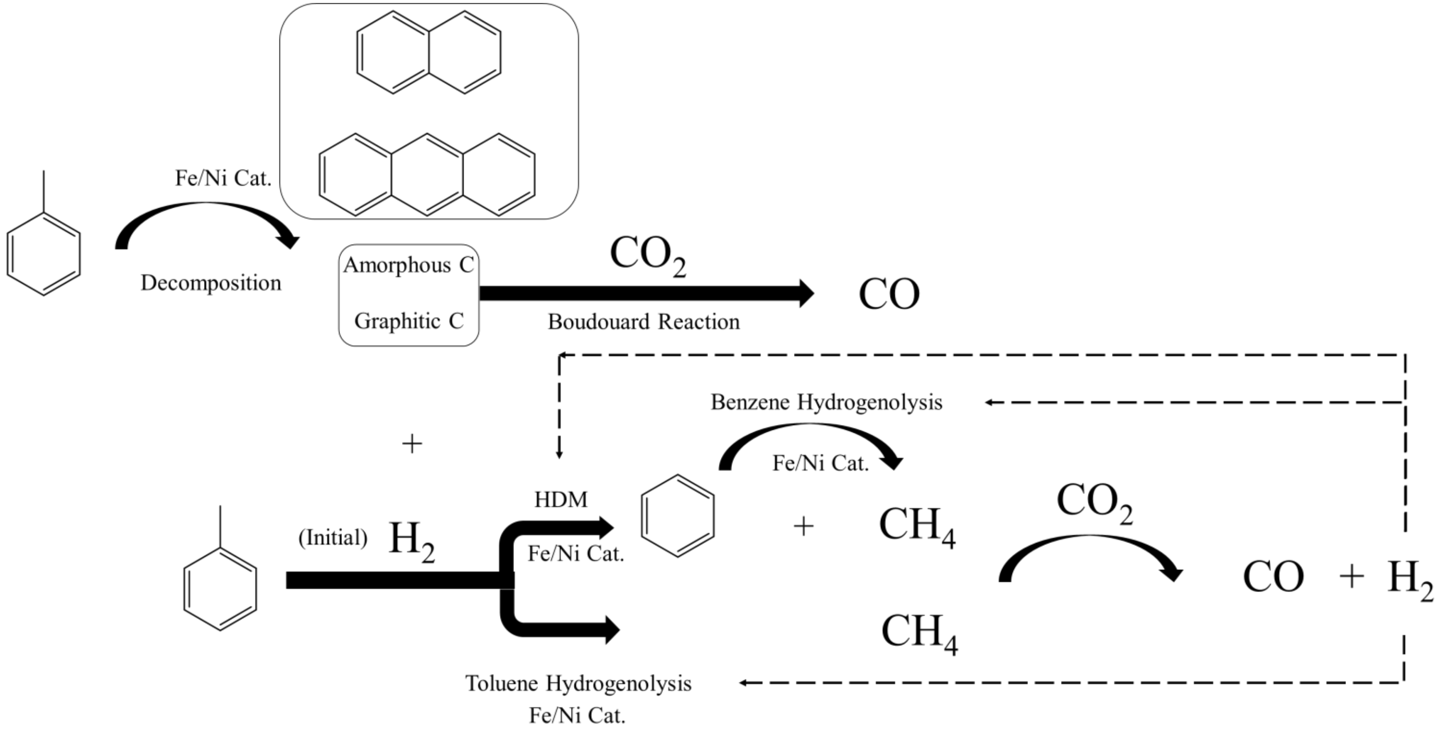
- Formation of one-ring aromatics   

- Formation of two-ring aromatics  

- Formation of three-ring aromatics 

Proposed Reaction Mechanism



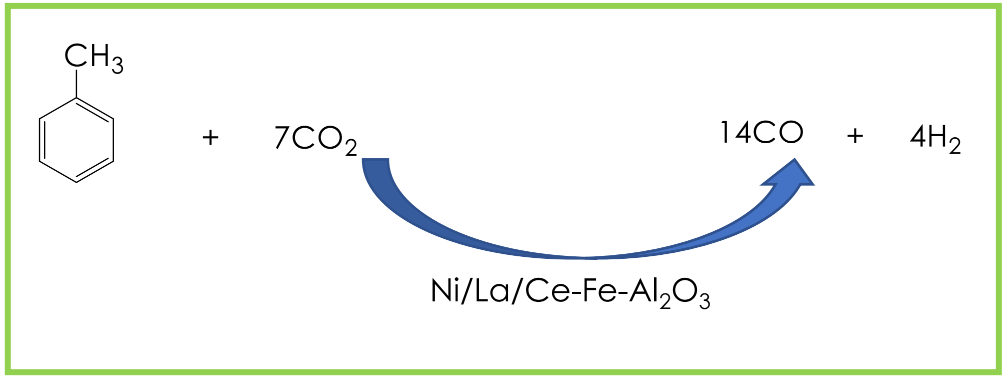


HDM = Hydrodemethylation

Fuel, 2024, 370, 131843; Chem Eng J 2022; 433:134445; J Phys Chem C 2013;117:26871–80.

Conclusion

➢ Low-cost Fe-Al_2O_3 catalyst with a promoters Ni/Ce/La is a promising catalyst for microwave-assisted CO_2 dry reforming of Toluene.



➢ The CO_2 dry reforming of Toluene can proceeds through hydrodemethylation, aromatics hydrogenolysis, Boudouard reaction and 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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- Charles Henkel
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