Sub Topic: Chemical Kinetics

2024 Spring Technical Meeting of the Western States Section of The Combustion Institute
March 4 – 5, 2024
University of Utah, Salt Lake City, Utah

Gasification of Coal/Plastic Mixtures: Fundamental Studies in a Laminar Entrained-Flow Reactor

*Afeez Kareem, Kevin J. Whitty**

Department of Chemical Engineering, University of Utah
50 Central Campus Dr, Room 3290, Salt Lake City, Utah 84112 USA
**Corresponding Author Email: kevin.whitty@utah.edu*

Introduction

Plastic co-gasification with other feedstocks has been the subject of numerous studies to enhance syngas energy density and facilitate the management of waste plastics. Pinto et al (2002) was one of the first to propose the co-gasification of plastic. The study, which co-gasified plastic with biomass in a fluidized bed gasifier (FBG) with steam as the gasifying agent, demonstrated an increased gas yield, exceptionally high H_2, elevated energy conversion, and reduced tar formation when PE plastic constituted up to 60% of the blended mixture. Subsequently, several studies on plastic co-gasification have been carried out, which include various plastics co-gasification with pinewood pellets by Bura (2013), PE and garden waste gasification by Fazil (2022), and plastic waste, coal, and wood co-gasification by Zaccariello (2023). All these studies were done in FBG, and the key takeaways include increased gas yield, improved carbon conversion, reduced syngas tar content, and enhanced CO and H_2 formation.

While literature reports various instances of plastic co-gasification with biomass/coal in fluidized bed gasifiers, research in coal and plastic gasification in entrained flow gasifier (EFG) is limited. Entrained flow gasification is of great interest considering its elevated temperature, flexibility of feedstocks fed, high efficiency, low cost of operation, low carbon emissions, and large-scale commercial applicability. EFG operates with liquid or slurries containing small solid particles, high pressure (3-8 MPa), and typically uses pure oxygen to partially oxidize the feedstock. Compared to other gasification types, it maximizes the carbon conversion rate, lowers methane content (enabling detachment of H_2 from hydrocarbon molecules), promotes atomization of slurries to increase the heat transfer rate, and typically runs in a slagging mode, i.e., at high temperature where the ash becomes molten.

There is interest in co-gasification of granulated plastics and pulverized coal in a pressurized, oxygen-blown, entrained-flow system. It is unclear how the introduction of plastics will affect coal conversion and the associated production of CO and CO_2. Relative to coal, plastics have a much higher volatile content (essentially 100%), and the volatiles are released at lower temperatures. With the addition of volatiles in the oxygen-rich portion of the burner, there is a question of whether oxygen that would otherwise be available for coal burnout will be consumed by the plastics volatiles (competitive oxidation).

To answer the research question, the University of Utah has lab-scale facilities to help understand the fundamentals of co-gasification, including a high-temperature laminar entrained-flow reactor and thermogravimetric analyzers, as well as analytical equipment including gas analyzers, an analyzer for total carbon and sulfur, and scanning electron microscopes. In this co-gasification study, the addition of plastic enhances CO/CO_2, and residence time and particle size were found to have a significant effect on the carbon conversion and CO/CO_2 ratio.

2. Experimental

2.1 LEFR Reactor System

The experimental setup for this study, as illustrated in Figure 1, features a specialized Laminar Entrained Flow Reactor (LEFR) designed as an entrained flow gasifier (EFG). The LEFR configuration comprises several crucial components. It includes a high-temperature furnace (Carbolite, single zone, with a maximum operating temperature of 1600 °C and a heated length of 610 mm), a solid fuel feeder driven by a syringe pump from Harvard apparatus, an injection probe equipped with gas and cooling water ports, a collection probe, gas supply, and a cooling water circulator. The downstream of the system consists of integrating essential elements such as a cyclone (for char collection), a filter for syngas particulate matter removal, and a vacuum pump for gas product ejection and pressure balance maintenance. Within the high-temperature furnace, two coaxial ceramic tubes are vertically installed. The inner tube functions as the reactor zone, while the outer tube is a protective sheath. The outer tube and the inner tube have dimensions of 89 mm o.d. × 75 mm i.d. × 1500 mm long and 87.4 mm o.d. × 76.7 mm i.d. × 1371.6 mm long, respectively, and are securely held in place by sealing flanges. These flanges also feature four gas ports through which preheated nitrogen gas is introduced, creating a reduced environment within the reactor zone. At the top of the coaxial tubes, a ceramic honeycomb serves as a flow straightener, ensuring a laminar flow of the preheated nitrogen and preventing heat loss to the surroundings. A moderate pressure drop from the flow straightener generates uniform and laminar flow, enabling entrained particles to travel along the reactor tube's centerline, ensuring identical reaction conditions. To facilitate particle entrainment and a consistent fuel flow, the solid fuel feeder incorporates a small electric rotor vibrator and a gas port. The syringe pump, aided by a pusher block, maintains a steady fuel flow from the feeder into the reactor. The injection probe is water-cooled to prevent solid fuel pyrolysis before entry into the reactor, and the collection probe is water-cooled to prevent its melting in the reduction zone. Further quenching with nitrogen gas occurs to prevent char oxidation after exiting the reactor. Mass flow controllers (MFC) play a pivotal role in regulating gas flow rates, and they are connected to an OPTO interface, allowing the visual monitoring of experimental proceedings, and gas flow rate values to be input and providing a repository for syngas product data collection and analysis. The LEFR experimental setup ensures precise and controlled conditions for the study, allowing for a comprehensive exploration of the desired processes.

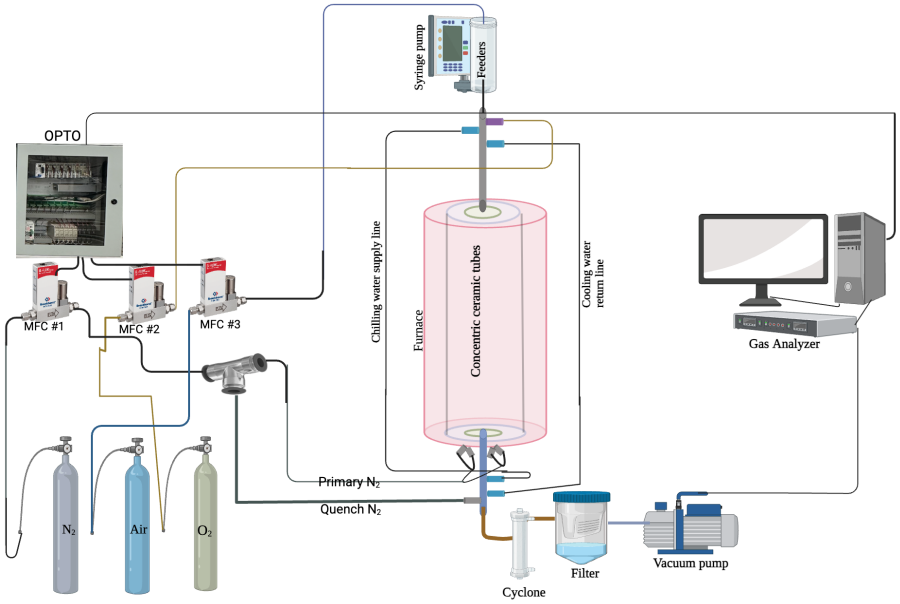

Figure 1. Schematic diagram of Laminar Entrained Flow Reactor (LEFR)

2.2 Experimental Procedure

The setup begins with a thorough system check, verifying the functionality of the cooling water system. Simultaneously, the LEFR is gradually heated to a predefined temperature, either 1300°C or 1400°C, with a heating rate of 14°C/min at a constant ambient pressure of 0.85 bar, while the gas analyzer (California Analytical Instruments) is calibrated using calibration gas, ensuring a seamless transition as the LEFR readies itself. Coal and HDPE plastic samples are kept within an electric oven, maintaining them at a constant temperature of 64°C, well below HDPE's melting point, before loading into the feeder. Dried samples of the desired particle size are carefully weighed, with the remaining samples promptly returned to the oven to prevent moisture-induced variations. Blended samples, 5%, 10%, and 30% HDPE with coal balance, are mixed vigorously for 15 minutes to ensure homogeneity.

Once the preparations are complete, the samples are loaded into the feeder, and any potential leftover materials are removed from the injection probe, collection probe, and cyclone. Subsequently, the gas cylinders are turned on, and a nitrogen flow is directed into the LEFR for 40 minutes, establishing an inert environment within the system to prepare for the experiment. Moving on to the experiment, the feeder is securely hung on the injection probe once the predetermined set point temperature is attained. Reacting gases (N_2 and O_2) are carefully adjusted to the desired flow rates using mass flow controllers (MFCs). A stoichiometry ratio (SR) of 0.5 was chosen for the gasifying gas (O_2), and the flow rate of O_2 is adjusted for experiments including HDPE to maintain the SR at 0.5. The gas transfer pump is initiated and adjusted to maintain a balance of reactor and atmospheric pressure to avoid leakage, and the experiment officially commences as the syringe pump is set to the specified fuel flow rate of 5g/hr. Fuel begins flowing into the LEFR typically after 5-10 minutes, and real-time data logging of syngas composition is facilitated with the aid of the Opto-22 control system.

Finally, data collection and analysis commence. The CAI gas analyzer ZRE4 with four sampling gas units, including CO_2, CO, CH_4, and O_2, is used to sample the gas products. Data is gathered and evaluated over a 30-minute runtime for each experimental run, encompassing the measurement and documentation of the mass of the sample that traverses the LEFR and the mass of residual materials deposited in the cyclone. Furthermore, the carbon content in the collected residual material is analyzed using the LECO SC832 Carbon and Sulfur analyzer. Syngas composition data is extracted from the Opto-22 file repository and incorporated into the data analysis, ensuring the integrity and accuracy of the experimental results. Conditions for the experiments are summarized in Table 1.

Table 1. Experimental parameters for the LEFR tests.

Parameter	Values
Reactor temperature (°C)	1300, 1400
Fuel feed rate (g/h)	5
Stoichiometric ratio of O_2	0.5
Fuel particle size (micron)	90-125, 150-180
Estimated residence time (s)	5, 7

2.3 Post-experimental analysis of carbon conversion

Below is a mathematical equation for estimating the percentage of coal carbon conversion Y, based on measurable values. The variable C_{char}^{carbon} represents the weight fraction of carbon found in the collected char, determined using the LECO SC832 carbon and sulfur analyzer. The variable C_{coal}^{ash} stands for the weight fraction of ash in the dry coal, obtained through proximate analysis, and C_{coal}^{carbon} signifies the weight fraction of carbon in the dry coal. When applying this equation to calculate carbon conversion in a blended mixture of coal and HDPE, it is assumed that all carbon in the residual char originates from the coal, while carbon in the HDPE transforms into volatile components. It is also assumed that the char comprises only carbon and ash, i.e. that C_{char}^{ash} (not used in the expression) equals 1 – C_{char}^{carbon}.

$$Y = \left[1 - \left(\frac{C_{char}^{carbon} C_{coal}^{ash}}{(1 - C_{char}^{carbon}) C_{coal}^{carbon}}\right)\right] \times 100 \quad (1)$$

2.4 Uncertainty in data collection and analysis

The dataset employed in this investigation was acquired through a comprehensive collection process spanning three consecutive days for each variable under scrutiny. Rigorous analytical procedures were applied, utilizing a margin of error measurement within the range of ±2 standard errors (±2 SEM) or, equivalently, a 95% confidence interval. This meticulous approach was adopted to guarantee high accuracy in the analysis, thereby minimizing any potential bias inherent in the gathered data.

3. Results and Discussion

Competitive oxidation is explored in the co-gasification of coal and HDPE in the context of four critical parameters: reactor temperature, plastic concentration, residence time, and particle size, offering insights

into their individual contributions and nuanced interplay. This systematic investigation is critical for understanding the synergistic effects of HDPE and coal, which is necessary for unraveling the complexity of their co-gasification. By studying these parameters, valuable insights into the intricate dynamics driving the simultaneous oxidation of coal and HDPE are gained, providing a comprehensive view of the complexities of their collaborative gasification process.

3.1 Effect of gasifier temperature

The temperature significantly influences solid fuel gasification, impacting the process and resulting gas quality. Temperature impacts thermochemical reactions within the gasifier, affecting conversion efficiency and gas composition. The five most important reactions in a gasification system are shown below. It should be noted that steam gasification (Reaction 3) is important and is 3-4 times faster than CO_2 gasification (Reaction 2), but the dry feed approach used in the LEFR studies provided little steam for the reaction. Elevated temperatures accelerate gasification, promoting the release of hydrogen and carbon monoxide and reducing tar and methane content for improved gas quality. Temperature also affects the rate and equilibrium of gas-phase reactions, including the water-gas shift reaction (Reaction 5), which is driven to the left at higher temperatures. In this study, the crucial role of temperature is further elucidated through experiments using blends of coal and HDPE plastic in varying mass ratios (95:5, 90:10, and 70:30) alongside pure coal as feedstock. In the case of temperature effect, blends of mass ratio 90:10, 70:30, and pure coal were used, having established with other factors that there was negligible difference between 5% and 10% plastic concentration in the blended mixture.

Partial oxidation:	$C + ½\ O_2 \rightarrow CO$	$\Delta H = -111$ kJ/mol	(R1)
CO2 gasification:	$C + CO_2 \leftrightarrow 2\ CO$	$\Delta H = 173$ kJ/mol	(R2)
Steam gasification:	$C + H_2O \leftrightarrow CO + H_2$	$\Delta H = 173$ kJ/mol	(R3)
Methanation:	$C + 2H_2 \rightarrow CH_4$	$\Delta H = -75$ kJ/mol	(R4)
Water-gas shift reaction:	$CO + H_2O \leftrightarrow H_2 + CO_2$	$\Delta H = -41$ kJ/mol	(R5)

The effect of temperature on coal carbon conversion and the CO/CO_2 ratio is depicted in Figure 2 for different plastic concentrations. The conversion of coal carbon increased slightly (1-3 %-units) at 1400°C relative to 1300°C. At the higher temperature, the CO/CO_2 ratio is markedly higher. The temperature effect has been found to be statistically significant and predicts 39% variability in CO/CO_2 ratio ($p < .001$). Possible contributions to higher CO/CO_2 are enhanced CO gasification (Reaction 2) and the reverse water-gas shift reaction (Reaction 5, with left-side species favored). The endothermic gasification reactions (Reactions 2 and 3) play a pivotal role in the reduction zone of the reactor, where temperature exerts a more pronounced influence than oxidation. The higher heating value of HDPE (19,800 BTU/lb) could, in theory, further amplify the temperature impact since the flame temperature would be higher than for coal at an equal stoichiometric ratio. However, with 20% plastic at 5 g/h total feed, the increased heat input is less than 5 Watts, which is negligible compared to the heat input from the electric furnace.

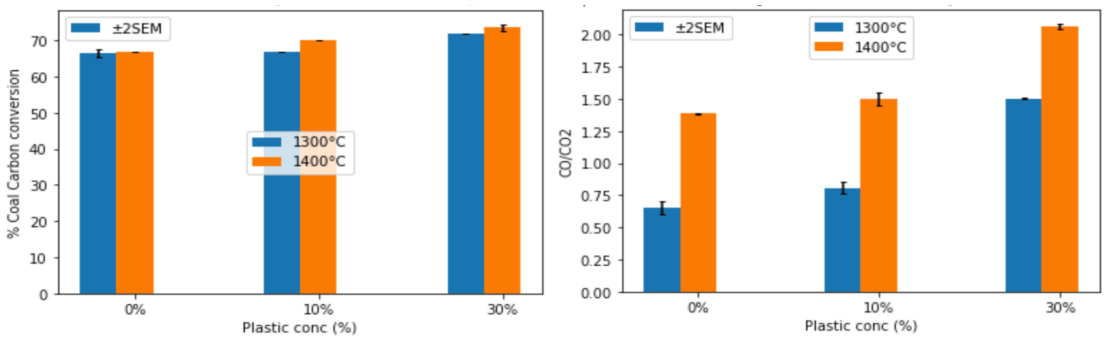

Figure 2. Effect of gasifier temperature on (left) the coal carbon conversion and (right) the CO/CO2 ratio.

The limited influence of temperature on coal carbon conversion is difficult to reconcile with the significant influence on CO/CO_2 ratio. For example, the 0% plastic case shows CO/CO_2 increasing from about 0.65 to 1.4 as the temperature increases from 1300 to 1400°C. Simple water-gas shift equilibrium evaluation indicates that such a temperature increase would increase the ratio only from 0.65 to about 0.67, which alone cannot explain the much higher CO/CO_2 ratio. Additional carbon conversion also cannot explain the large difference. The marginally higher coal carbon conversion at 1400°C would consume a portion of the CO_2 to form two CO molecules as per Reaction 2, but at best, a carbon conversion increase from 65% to 67% would increase the CO/CO_2 ratio from 0.65 to about 0.81.

The coal gasification process is not as simple as Reactions 1 through 5 suggested. As coal is heated, the structure breaks down to release primary volatiles, which are mainly organic, often polyaromatic hydrocarbon "tars" that contain much of the carbon. Those molecules subsequently break down via thermal cracking as well as oxidative and reforming reactions similar to reactions 1 through 4 above. Higher temperatures and longer residence times promote those reactions. Although we do not have direct evidence, it seems reasonable that the temperature increase from 1300 to 1400°C resulted in more breakdown and high production of CO. As noted later, increasing the residence time in the reactor yielded results of minimal influence on coal carbon conversion but higher CO/CO_2 ratios. It is also worth noting that due to the nature of the LEFR furnace, the entire length is not at the setpoint temperature. Rather, that is the maximum temperature in the axial direction with the top and bottom about 100°C lower (Li, 2010). So, the coal volatiles are overall exposed to a lower average temperature than the reactor setpoint.

3.2 Effect of Plastic Concentration

The introduction of plastics may enhance coal carbon conversion by facilitating the release of additional volatiles during gasification while reducing the fraction of the feedstock that is slow-to-convert fixed carbon. A controlled study was performed to systematically investigate this phenomenon, isolating the influence of increasing HDPE plastic concentration in coal/plastic mixtures on CO/CO_2 ratio and coal carbon conversion while holding other factors constant. HDPE, chosen for its prevalence as the second most utilized plastic in the United States, served as the focal point of our investigation. The tests were performed with a constant SR of 0.5, with the O_2/feed ratio adjusted to account for the higher O_2 demand per mass of the HDPE. The mass flow of O_2 fed is shown in Figure 3 as a function of sample HDPE concentration.

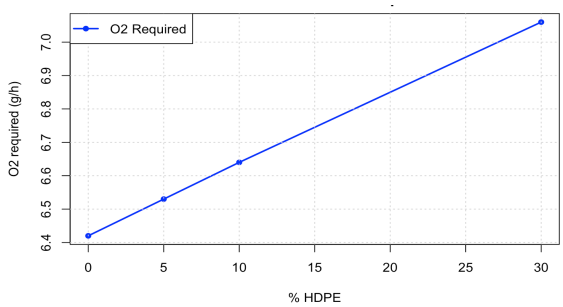

Figure 3. Mass flow rate of O_2 versus the percent HDPE in the sample.

The findings, as illustrated in Figure 4, demonstrate a minor effect of HDPE on coal carbon conversion and a pronounced influence on the CO/CO_2 ratio. As observed in our thermogravimetric study, HDPE completely volatilizes by about 500°C, so displacing a portion of the coal with plastic results in more volatiles and less fixed carbon. To maintain the SR of 0.5, more O_2 was fed as the plastic fraction in the sample increased (Figure 3). This heightened O_2 consumption fosters increased CO_2 formation during devolatilization, favoring CO_2 char gasification and contributing to an augmented CO/CO_2 ratio.

However, the slight increase in char conversion cannot explain the significant increase in CO/CO_2 ratio as the plastic fraction increases. It seems more likely that the explanation relates to the chemistry and conversion of volatile matter from the plastic. Plastic thermally decomposes to form a wide mix of hydrocarbons, including the original monomer (e.g., ethylene in the case of HDPE), alkanes, alkenes (olefins), alkynes, and even aromatics. Because plastics do not contain oxygen, CO and CO_2 are not possible primary volatile products. Rather, oxygen must react with the gas-phase hydrocarbons resulting from the thermal breakdown of the plastic. The specific reactions and mechanisms associated with the oxidation of the volatiles are not known, and by extension, it is not clear whether CO or CO_2 is a favored oxidation product. Volatiles from the rapid thermal breakdown of plastics undoubtedly have a different composition than volatiles resulting from the heating of coal particles. It may be that subsequent oxidation of plastics volatiles yields more CO and a correspondingly higher CO/CO_2 ratio than coal volatiles. Regardless of the specific mechanism, the trend observed in Figure 4 is clear, which is that under the conditions studied, increasing plastic increases the CO/CO_2 ratio.

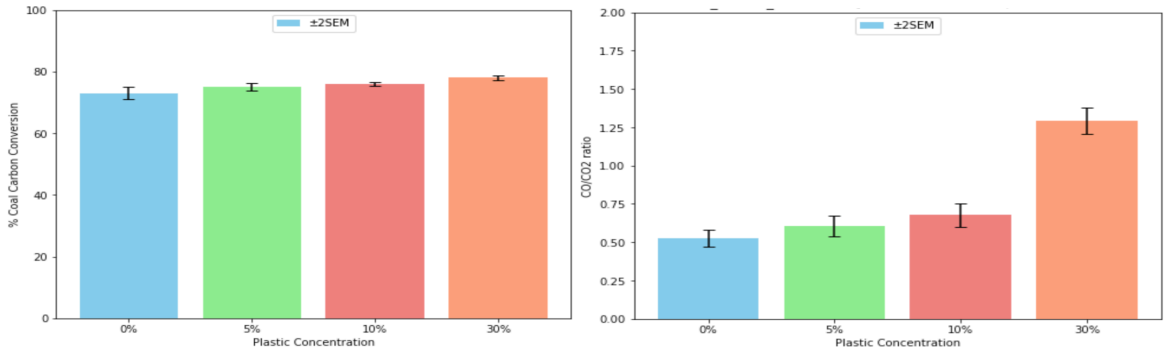

Figure 4. Effect of plastic concentration on (a) Coal Carbon Conversion and (b) CO/CO2 ratio.

3.3 Effect of Particle Size

The importance of particle size on carbon conversion and resulting syngas composition in gasification is well-recognized, particularly when dealing with heterogeneous materials like HDPE and highly volatile

bituminous coal with distinct bulk density and surface area to volume ratio (SA/V). In this study, maintaining uniform particle size across coal and HDPE blends (mass ratios of 95:5, 90:10, and 70:30) was crucial for accurate analysis. Employing particle sizes of 90-125µm and 150-180µm resulted in lower carbon conversion and CO/CO_2 ratio, as seen in Figure 5. This phenomenon can be attributed to the smaller SA/V of larger particles, limiting reactive sites and hindering effective pore diffusion, leading to lower char reactivity. Conversely, smaller particle sizes enhance reactivity, fostering higher coal carbon conversion and CO/CO_2 ratios. While the CO/CO_2 ratio's sensitivity to particle size variation is not pronounced due to the proximity of the two sizes used, particle size emerges as a significant predictor, explaining 78% of carbon conversion variability ($p < .001$).

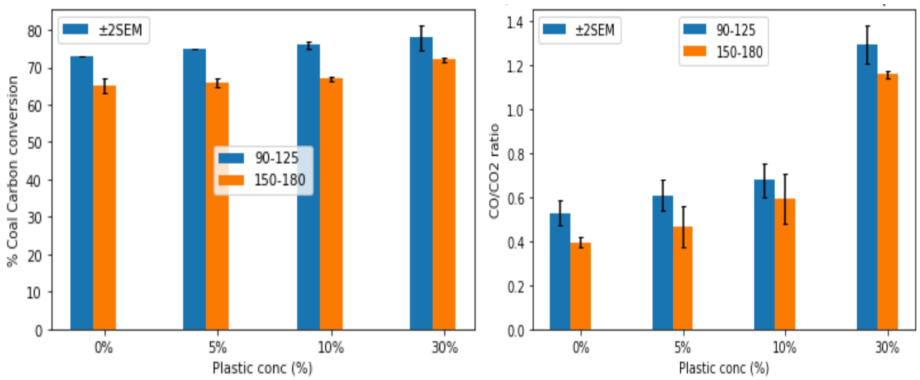

Figure 5. Effect of particle size on (left) coal carbon conversion and (right) CO/CO_2 ratio.

3.4 Effect of Residence Time

The gasification efficiency of solid fuel hinges on particle residence time in the reactor, influenced by reaction pathway length and gas velocity. In our study with a defined 890 mm pathway, gas velocity is modulated by flow rates and reactor temperature. Adjustments in residence time primarily involve pre-heated N2 flow. Coal particle residence time will be somewhat shorter than the gas residence time since the free-fall velocity of particles through the hot gas is non-zero, but for the particle size and char density used, the Stokes number is calculated to be less than 1, indicating that inertial forces are much less than viscous forces and that the particles can be assumed to follow the gas flow (Li, 2010). Two residence times (5 and 7 seconds) were chosen for this research. As depicted in Figure 6, a discernible pattern unfolds, wherein an increase in residence time, coupled with heightened plastic concentration, leads to elevated CO/CO_2 ratios and slightly enhanced carbon conversion. Increased residence time with higher plastic concentration correlates with enhanced carbon conversion and CO/CO_2 ratio, significantly impacting gasification processes. The residence time and increased plastic concentration account for 96% variability in carbon conversion and CO/CO_2 ratio ($p < .001$).

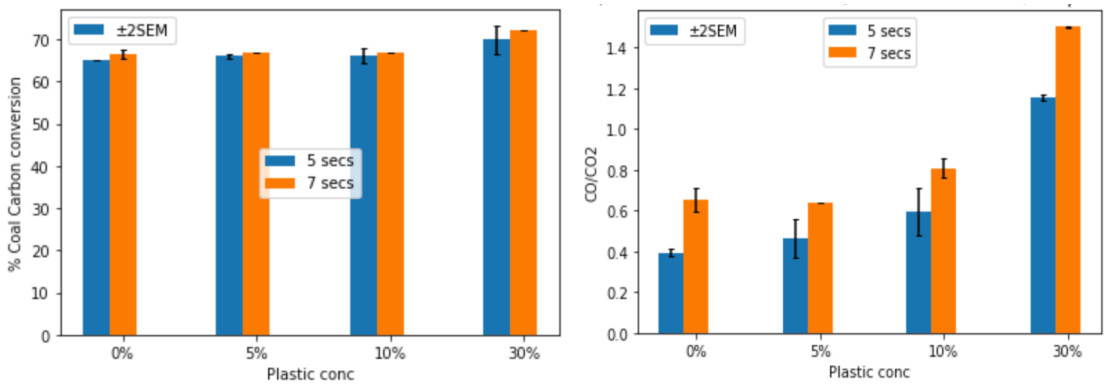

Figure 6. Effect of particle size on (left) coal carbon conversion and (right) CO/CO_2 ratio.

4. Conclusions

Results of the LEFR tests revealed that elevated temperature, smaller particle size, and longer residence time enhance coal-based carbon conversion. Introducing plastic, maintaining mass flow and stoichiometric ratio resulted in slightly higher coal carbon conversion. Higher plastic concentration notably increases the CO/CO_2 ratio, surpassing explanations based on temperature or reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). LEFR tests demonstrated lower coal conversion than an industrial gasifier due to a dilute environment (low pressure, high N_2 concentration), no steam or water feed, and limitations in capturing complex gas-phase chemistry in the reactor's temperature profile and residence time. Future investigations will explore tar production and reaction mechanisms, exploring varied O_2/feedstock ratios, temperatures, and residence times.

5. Acknowledgements

This work was funded in part by Eastman Chemical Company and also by the U.S. Department of Energy under award number DE-FE0032042. This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness. or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise docs not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References

Burra, K. G. ; G., Ashwani K. (2018). Synergistic effects in steam gasification of combined biomass and plastic waste mixtures. *Applied Energy*, *211*(NA), 230–236. https://doi.org/10.1016/j.apenergy.2017.10.130

Fazil, A., Kumar, S., & Mahajani, S. M. (2022). Downdraft co-gasification of high ash biomass and plastics. *Energy*, *243*, 123055. https://doi.org/10.1016/j.energy.2021.123055

Li, S., Wu, Y., & Whitty, K. J. (2010). Ash Deposition Behavior during Char−Slag Transition under Simulated Gasification Conditions. *Energy & Fuels*, *24*(3), 1868–1876. https://doi.org/10.1021/ef901480e

Pinto, F., Franco, C., AndreÂ, R. N., Miranda, M., Gulyurtlu, I., & Cabrita, I. (2002). *Co-gasi®cation study of biomass mixed with plastic wastes*.

Zaccariello, L. ; B., D. ;. Morrone, B. ;. Mastellone, M. L. (2022). Hydrothermal Carbonization: A Pilot-Scale Reactor Design for Bio-waste and Sludge Pre-treatment. *Waste and Biomass Valorization*, *13*(9), 3865–3876. https://doi.org/10.1007/s12649-022-01859-x