

FINAL SCIENTIFIC/TECHNICAL REPORT

Project Title: Advancing Coal Catalytic Gasification to Promote Optimum Syngas Production

Type of Report: Final Scientific/Technical

Reporting Period Start Date: October 1, 2014

Reporting Period Start Date: July 31, 2017

Principal Authors: Dr. Francine Battaglia, Dr. Foster Agblevor, Dr. Michael Klein, and Dr. Reza Sheikhi

Date of Report: October 31, 2017

Award Number: DE-FE0024013

Submitting Organization: Virginia Polytechnic Institute and State University
Office of Sponsored Programs
300 Turner Street NW, Suite 4200 (MC 0170)
Blacksburg, Virginia 24061

Subcontractors: Utah State University
Office of Research and Graduate Studies
1415 Old Main Hall
Logan, Utah 84322

University of Delaware
Research Office
210 Hullihen Hall
Newark, Delaware 19716

Northeastern University
Research Administration and Finance
960 Renaissance Park
Boston, Massachusetts 02115

DISCLAIMER

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 does 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.

Abstract

An investigation was pursued to improve the use of low rank sub-bituminous coal by using suitable catalysts to advance gasification and create cleaner synthesis gas. Bench- and pilot-scale experiments were performed to measure key reactive properties and verify the use of red mud catalyst. The experiments provided reaction data for the development of kinetic models and validation data for CFD simulations. The reaction kinetics were analyzed to provide an understanding of the major pathways involved and identify the necessary reaction mechanisms needed for the computational models. The reaction kinetics model was implemented into the computational fluid dynamics (CFD) code MFiX to simulate, predict and validate the chemistry model with the experiments. It was shown that red mud as a catalyst lowered methane formation during coal gasification. Additional benefits were that red mud destroyed tars formation, promoted water gas shift reaction resulting in a syngas rich in hydrogen. In the presence of red mud catalyst, biomass feedstocks high in ash did not form clinker in the fluidized bed because it prevented the formation of eutectic mixtures. The reaction kinetics model was reasonably robust and the CFD predictions using the model were in good agreement with the experiments.

Table of Contents

Abstract	iii
1. Executive Summary	1
2. Gasification experiments.....	3
2.1 Methods.....	3
2.1.1 <i>Materials</i>	3
2.1.2 <i>Experimental methods</i>	8
2.2 Results.....	11
2.2.1 <i>Bench-scale fluidized bed reactor</i>	11
2.2.2 <i>Pilot-scale fluidized bed reactor</i>	20
3. Modeling of the kinetics of product formation	22
3.1 Methods.....	22
3.1.1 <i>Lumped Modeling</i>	22
3.1.2 <i>Attribute Reaction Modeling</i>	22
3.2 Results.....	27
3.3 Model analysis	29
4. CFD Simulations.....	32
4.1 Methods.....	32
4.2 Results.....	32
5. Conclusions.....	40
List of Tables.....	41
List of Figures	43
Bibliography	44
Appendix	46

1. Executive Summary

Coal is one of the major sources of fossil fuels used for power generation in the USA. It is also the most polluting fuel and its use contributes significantly to environmental pollution and greenhouse gas emissions. Gasification of coal can be an alternative approach to mitigate pollutant emissions. Syngas produced from coal gasification can be used for electricity generation, chemical feedstocks, or for production of synthetic natural gas. Gasification of coal using steam and catalysts provides more flexibility in the control of the hydrogen to carbon monoxide ratios, which are critical in converting syngas into transportation fuels such as gasoline and diesel through the Fischer-Tropsch process. The current needs are to control and minimize methane concentrations formed during coal gasification. Doing so will facilitate better use of power plants for polygeneration applications.

Effective gasification of coal requires efficient robust catalysts which can tolerate sulfur and other elements that normally deactivate catalysts. Red mud is a by-product of the Bayer process (refining bauxite to produce alumina), which is obtained when bauxite is treated with hot sodium hydroxide. Bauxite usually contains 30–54% of alumina (Al_2O_3), silica, iron oxides, TiO_2 and other clayey materials. For every ton of alumina extracted, more than a ton of RM is produced. Alumina plants worldwide annually generate around 120 million tons of red mud (RM). The RM is disposed in clay-lined dams or dykes. The high alkalinity of red mud (pH 9-13) may have a potential negative impact on the surrounding groundwater and environment if not properly disposed. Red mud is a complex mixture of metallic oxides such as ferric oxide, aluminum oxide, titanium dioxide, magnesium oxide, calcium oxide, silicon oxide, and other minor compounds, in addition to the residual sodium hydroxide used in the extraction process.

Catalytic applications of red mud have been extensively reviewed by Sushil and Batra (2008). This material has been investigated by several researchers for catalytic applications such as hydrodechlorination (Ordonez et al., 2001), hydrogenation of anthracene (Alvarez et al., 1995; Alvarez et al., 1999), pyrolysis of waste plastics and waste oils (Cakici et al., 2004; Lopez et al., 2011), hydrogenation and liquefaction of rye straw (Kloperies et al., 1990), upgrading of hemp-seed pyrolysis oils (Karimi et al., 2010), and acetic acid (Karimi et al., 2010). In most of these applications red mud was activated through acid treatment and other modifications. However, there has not been any systematic investigation of using red mud as coal gasification catalyst. The ultimate goal of these studies is to develop catalytic gasification process to convert coal into clean fuels using red mud as catalyst.

In this report we present evidence of the investigation of red mud as an effective gasification catalyst for conversion of coal and coal/biomass mixtures to synthesis gas. The report includes coal gasification in the presence of steam, carbon dioxide, coal/biomass mixtures and combinations thereof to produce synthesis gas of high hydrogen content. A bench-scale and pilot-scale fluidized bed will be used to investigate the use of red mud catalyst with coal and assess the scale-up of the effects. It will be shown that reformulated red mud is a robust catalyst that does not lose its activity after several regenerations. It is an effective catalyst and destroys tars formed during coal gasification. Red mud catalyst also promotes water gas shift reaction resulting in a syngas rich in hydrogen. In the presence of red mud catalyst, biomass feedstocks high in ash do not form clinker in fluidized bed because it prevents the formation of eutectic mixtures.

A reaction kinetics model was created based on the available experimental data. The model developed for gasification of coal in a neutral (nitrogen) and reactive (carbon dioxide) environment provided a good fit for the experimental data. The kinetics models were varied to determine the robustness and a verification and validation study helped identify the best model. The size of the model is usable for implementation in a computational fluid dynamics (CFD) code, and it captured and summarized the kinetics behind the raw gasification data very well.

The reaction kinetics model was implemented into the CFD code Multiphase Flow with Interphase eXchanges (MFiX). Detailed analysis of the CFD simulations revealed that the drying and pyrolysis reactions were the dominant processes experienced in the fluidized beds, even when carbon dioxide was used as the fluidizing agent. Comparison of the chemistry model results for systems under carbon dioxide to those of the experiments demonstrated that carbon monoxide production is under-predicted by the model, while the quantity of carbon dioxide in the reactor effluent is over-predicted. However, the overall effluent comparisons were in good agreement with the experiments and consistent with other published literature.

The outcome of this research has provided substantial evidence that red mud can be successfully used as a catalyst and improves the gasification of low rank coals to reduce the production of unwanted pollutants.

2. Gasification experiments

2.1 Methods

2.1.1 Materials

The red mud (RM) was supplied by Sherwin Alumina Co LLC, (Gregory, TX). The “as received” red mud is a very soft clayey material that crumbles easily into fine powder when dried. In order to successfully use red mud for fluidized bed gasification of coal, the material has to be reformulated with binders and attrition resistant material. Thus red mud was reformulated with various amounts of proprietary binders and attrition resistant component. After reformulation, the material was first dried at 105 °C overnight to drive off the moisture. The material was then calcined at 650 °C for 5 hours. After calcination, it was ground and sieved to appropriate particle size (125–180 μm) for the fluidized bed gasification studies. The ground and sieved material was then characterized for various properties. The red mud was also modified by the addition of Ni. This was accomplished by dissolving nickel nitrate in water and impregnating the RM with the precipitate. The impregnated sample was first dried at 105 °C overnight and then calcined as described above. Various proportions of nickel were added to the RM.

The various sample preparations were evaluated for attrition resistance by measuring the amount of fine particles produced in a 30 hour period during cold continuous fluidization in a replica glass fluidized bed reactor. After fluidization for 30 hours, the catalyst was sieved and the fine particles below 125–180 μm were attributed to the attrition of larger particles.

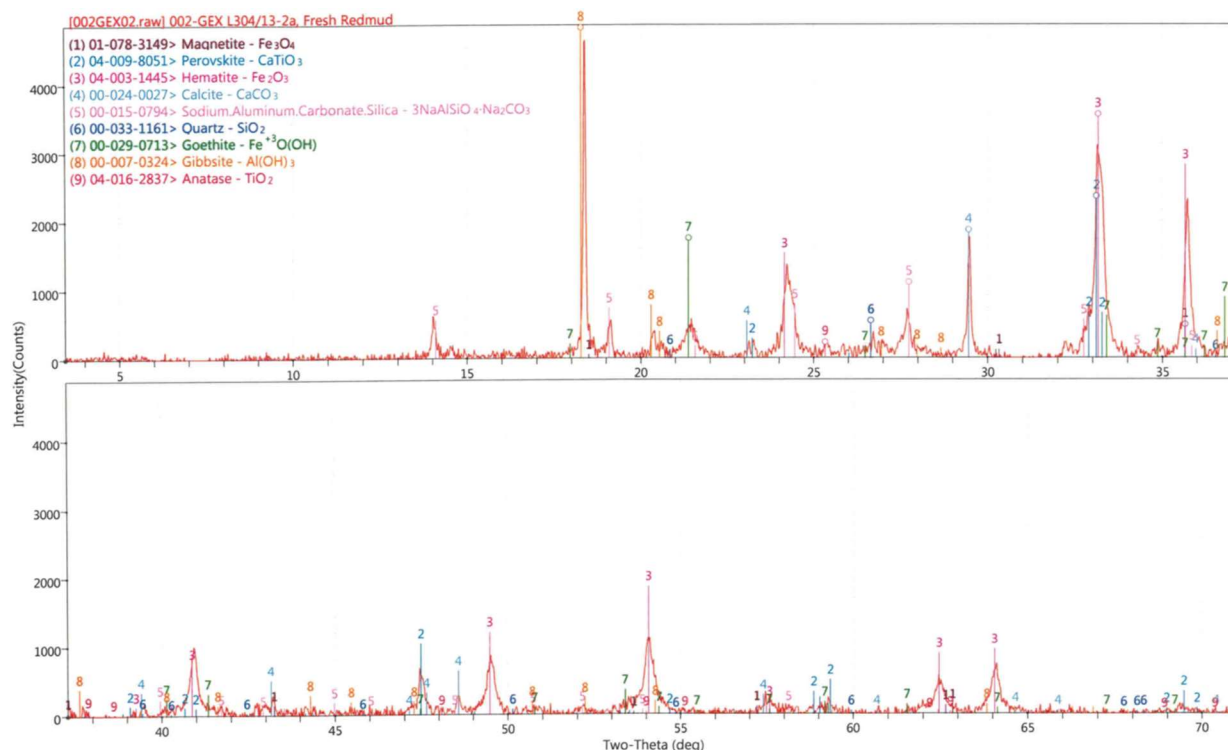
The Brunauer–Emmett–Teller (BET) method was used to measure the specific surface areas of the catalyst using Quantachrome BET surface analyzer (Quantachrome Instruments, Boyton Beach, FL). The specific surface area (BET) of dried and ground RM was about 30 m^2/g . The pore size distribution and pore volumes of the catalyst were also calculated from the BET measurements.

The chemical composition of the red mud was determined by X-ray diffraction (XRD) and X-ray fluorescence (XRF) (Hazen Research, Inc., Golden, CO) as well as inductively coupled plasma spectroscopy (ICP). The XRD analyses were performed using a Bruker D8 Davinci Advance XRD instrument with a Lynxeye detector using 35 kV/40 mA with cobalt radiation. The patterns were converted to Cu K α 1/K α 2 for phase identification. The morphology of RM catalyst particles was also analyzed using scanning electron microscope (SEM).

The sub-bituminous coal used for studies was provided by University of Utah Institute of Clean and Secure Energy (ICSE), Salt Lake City, UT. The samples as-received was a pulverized coal powder (<90 μm). The proximate and ultimate composition of the sub-bituminous coal used for these studies is shown in Table 2.1. This composition is typical of Utah sub-bituminous coal. The corn stover had very high ash content probably because of the method of feedstock harvest which could have included extraneous materials which could account for such high values. This high content has potential negative effect during the gasification of the coal /corn stover mixtures. As expected the ash content of the poplar wood was very low. The volatile matter content for the corn stover was higher than that of the coal but lower than that for the poplar wood. The coal had the highest fixed carbon content while the poplar wood had the lowest. Sulfur content for the coal was highest while the wood had no sulfur within the detection limit of the organic elemental analyzer. As expected, the coal had the highest carbon content while the corn stover had the lowest. The higher heating values (HHV) of the three feedstocks showed coal having the highest value while the corn stover was the lowest. Thus the choice of the three feedstock is such that they reflect a wide range potential feedstock variation that could be encountered in a potential plant that could co-feed biomass and coal.

Table 2.1. Proximate and ultimate composition of coal and biomass feedstocks used for the gasification studies.

Parameter	Coal	Corn stover	Poplar wood
Proximate composition			
Moisture (wt%)	24	5.14	6.55
Ash (wt%)	4.94	8.51	0.43
Fixed carbon (wt%)	38.01	14.60	11.85
Volatiles (wt%)	31.36	71.75	81.17
Ultimate composition			
Carbon (wt%)	53.72	43.07	46.33
Hydrogen (wt%)	6.22	5.77	6.04
Nitrogen (wt%)	0.78	1.26	0.10
Sulfur (wt%)	0.23	0.04	0.00
Oxygen (wt%)	34.11	41.35	47.1
HHV (MJ/kg)	21.12	17.21	18.60

**Fig. 2.1. X-ray powder diffraction pattern of fresh red mud.**

The fresh RM supplied by Sherwin Alumina Co LLC, was composed of: magnetite (Fe_3O_4), hematite (Fe_2O_3), perovskite (CaTiO_3), calcite (CaCO_3), sodium aluminum carbonate silica $3\text{NaAlSiO}_4 \cdot \text{Na}_2\text{CO}_3$, quartz (SiO_2), goethite ($\text{FeO}(\text{OH})$), gibbsite ($\text{Al}(\text{OH})_3$), and anatase (TiO_2) (Fig. 2.1). A typical composition of the RM formulation was: Fe_2O_3 (30-60 wt%); Al_2O_3 (10-20 wt%); SiO_2 (3-50 wt%); Na_2O (2-10 wt%); CaO (2-8 wt%); TiO_2 (0.1-25 wt%). For the Sherwin RM the composition was Fe_2O_3 (54 wt%), Al_2O_3 (13.5 wt%), SiO_2 (8.9 wt%), CaO (8.9 wt%), TiO_2 (6.2 wt%), Na_2O_3 (5.8 wt%). A comprehensive X-ray fluorescence analysis of the red mud is also shown in Table 2.2.

Table 2.2. X-ray florescence analysis of fresh red mud.

SAMPLE NUMBER:		L304/13-2			
SAMPLE IDENTIFICATION:		Fresh Redmud			
PARAMETER	%	PARAMETER	%	PARAMETER	%
Iron	43	Lead	0.02	Cesium	<0.02
Aluminum	7.8	Thorium	0.02	Barium	<0.03
Calcium	7.7	Niobium	0.02	Praseodymium	<0.02
Titanium	5.1	Scandium	0.01	Neodymium	<0.02
Sodium	4.7	Gallium	0.006	Samarium	<0.02
Silicon	3.4	Vanadium	<0.007	Europium	<0.02
Manganese	0.8	Cobalt	<0.006	Terbium	<0.02
Phosphorus	0.73	Germanium	<0.002	Dysprosium	<0.03
Sulfur	0.32	Arsenic	<0.01	Holmium	<0.01
Zirconium	0.31	Selenium	<0.003	Erbium	<0.006
Chromium	0.23	Bromine	<0.002	Ytterbium	<0.02
Magnesium	0.21	Rubidium	<0.002	Hafnium	<0.01
Chlorine	0.20	Molybdenum	<0.002	Tantalum	<0.009
Cerium	0.11	Ruthenium	<0.006	Tungsten	<0.008
Lanthanum	0.11	Palladium	<0.006	Rhenium	<0.02
Yttrium	0.10	Silver	<0.006	Iridium	<0.007
Nickel	0.09	Cadmium	<0.006	Platinum	<0.006
Potassium	0.09	Indium	<0.006	Gold	<0.006
Zinc	0.09	Tin	<0.007	Mercury	<0.005
Strontium	0.05	Antimony	<0.008	Thallium	<0.007
Gadolinium	0.04	Tellurium	<0.01	Bismuth	<0.004
Copper	0.03	Iodine	<0.02	Uranium	<0.004

Thermogravimetric analysis (TGA) of fresh red mud showed a minor peak due to water loss that occurred at about 100 °C and two major decomposition peaks (Fig. 2.2). The first major weight loss and shoulder that occurred between 200 and 350 °C, were attributed to the decomposition of Gibbsite ($\text{Al}(\text{OH})_3$) and Goethite ($\text{FeO}(\text{OH})$) (Eq. 2.1-2.2). The second major weight loss that occurred between 600 and 700 °C was attributed to the decomposition of calcite (CaCO_3) (Eq. 2.3). These decomposition information was used to justify the calcination of the, fresh red mud catalyst at 700 °C in a muffle furnace overnight to convert the Gibbsite, Goethite, calcium hydroxide, and Calcite into Al_2O_3 , Fe_2O_3 , and CaO respectively before being used for the gasification. If the calcination step is avoided, the red mud catalyst will release water and carbon dioxide during coal gasification process, which will affect the final mass balance:



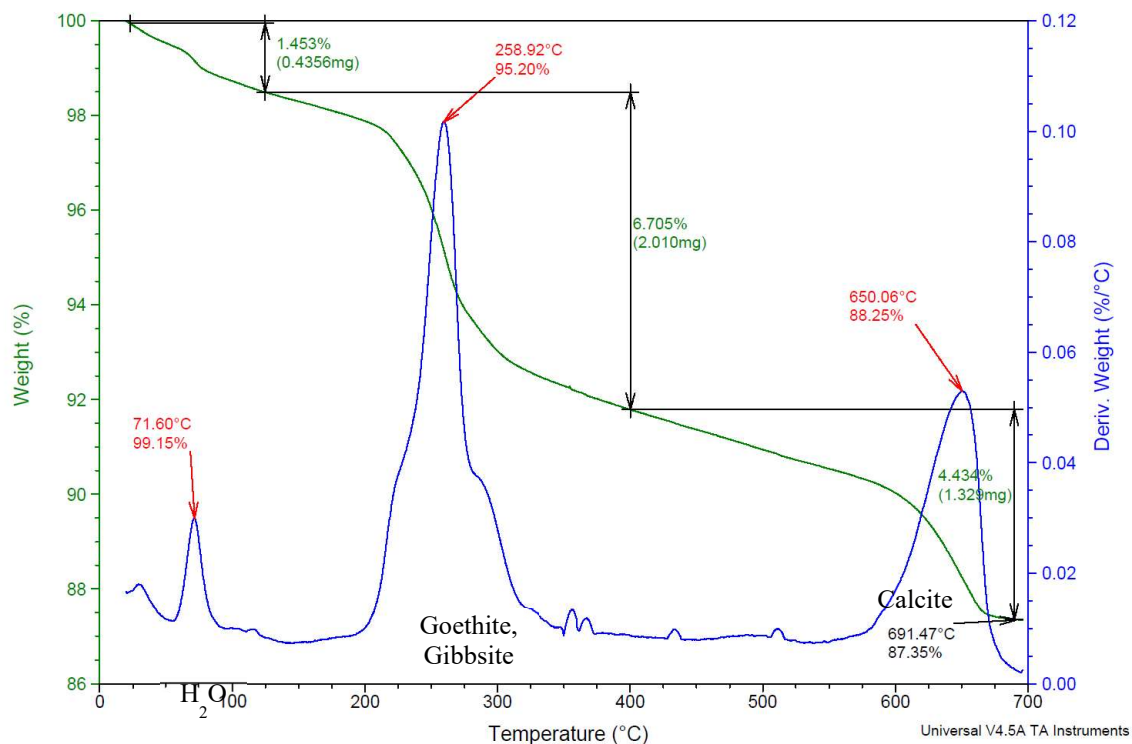


Fig. 2.2. TGA of fresh Red Mud supplied by Sherwin Alumina Co LLC, (Gregory, TX).

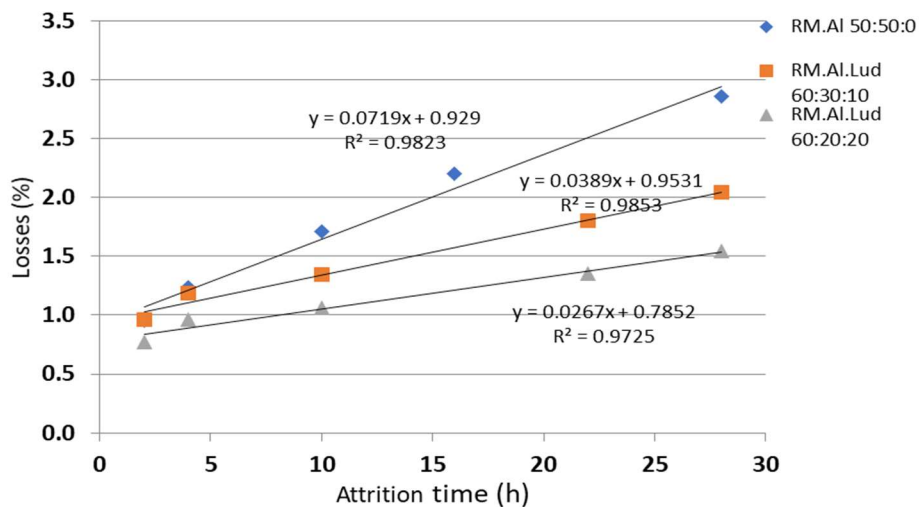


Fig. 2.3. Attrition properties of various red mud catalyst formulations.

Table 2.3. Characteristics of formulated and original red mud catalyst.

Catalyst type	BET (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Formulated Fresh RM	93.3	0.30	10.8
Regenerated Formulated RM	53.9	0.21	12
Original RM	30.2	n/a	n/a

The attrition test results shown in Fig. 2.3 revealed that the attrition of various red mud formulations vary very widely. For the extremely hard materials with high attrition properties, the pore size and specific surface area of the particles decreased considerably and were not effective for coal gasification studies.

A typical BET specific surface area of the original RM was 30 m²/g while after formulation it increased to almost three times the original (Table 2.3). The BET specific surface area however decreased after regeneration of the catalyst. After several regenerations the BET specific surface area stabilized as shown in Fig. 2.4. The loss in surface area after regeneration was attributed to agglomeration and chemical reaction between the alumina and calcium oxide to form calcium aluminosilicate. The pore size increased with regeneration while the pore volume decreased (see Table 2.3 and Fig. 2.5).

The change in BET specific surface area is also corroborated by the SEM data on the morphology of the catalyst. The fresh catalyst had very small grains and hence the larger specific surface area. However, after regeneration, the grain sizes were large probably due to agglomeration of some of the catalyst particles (see Fig. 2.6). The activity of the catalyst did not appear to be affected by the loss of specific surface area after regeneration. As shown by the gasification studies, the activity of the catalyst remained constant after several regenerations and gasification studies under various gasification atmospheres.

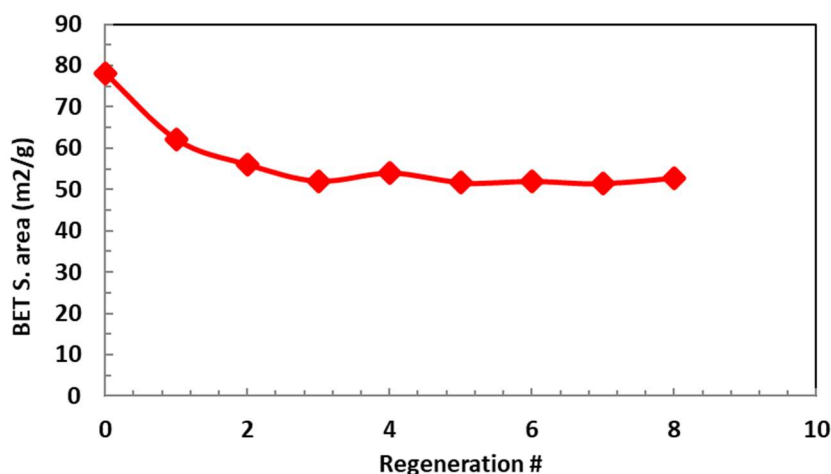


Fig. 2.4. Effect of catalyst regeneration on BET specific surface area.

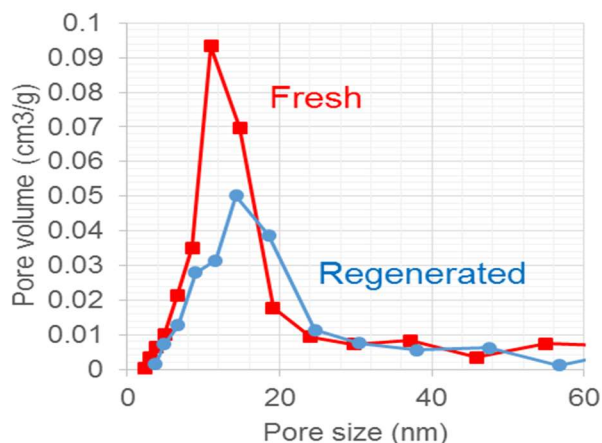


Fig. 2.5. Pore size and volume distribution of formulated fresh and regenerated red mud catalyst.

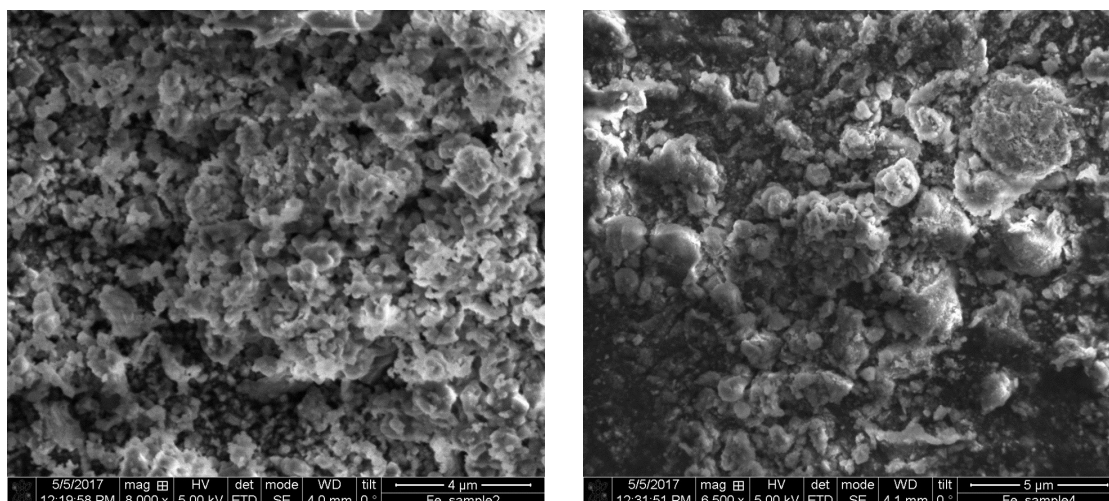


Fig. 2.6. SEM of fresh and regenerated formulated catalysts (left) fresh catalyst; (right) regenerated catalyst.

2.1.2 Experimental methods

The gasification of the coal was conducted under various atmospheres including, nitrogen, steam, carbon dioxide and carbon dioxide/steam mixtures. The gasification procedures used were similar except the gases used as the fluidizing gas. The coal gasification experiments were performed in a bench-scale bubbling fluidized-bed reactor designed to operate under a wide range of operating conditions at atmospheric pressure (Figure 7). The gasification of the coal feedstock was conducted in a 2-in (51 mm) diameter and 20-in (508 mm) high fluidized bed reactor. Red mud (120 g) was used as a bubbling fluid bed medium. The ratio of catalyst (red mud) to coal was 1:1 and weight hourly space velocity (WHSV) of 1/h. The gasification was conducted at 700, 800, and 900 °C, at atmospheric pressure. When the fluidized bed stabilized at the target temperature, the fluidizing gas was introduced into the reactor via preheating zone containing Berl saddles and heating continued until the bed was fully stabilized with respect to temperature. The coal was introduced into the reactor at a rate of 120 g/h using a volumetric twin-screw feeder (Model: K2VT20, K-Tron, Pitman, NJ).

In case of steam gasification, the amount of steam and steam flow rate required to ensure fluidization of silica sand or red mud was determined by collecting steam condensate through metering steam into the reactor when empty. Steam was regulated using a stainless steel high-flow metering valve (Model: SS-4L2-MH, Swagelok®, Salt Lake City, UT). Nitrogen gas was used to convey the coal feed into the reaction zone. To prevent steam condensation, the bottom of the reactor was preheated with a heating mantle to 300 °C.

When nitrogen was used as the fluidizing gas the nitrogen flow rates were decreased with increasing temperature. Thus, for 700 °C, 1.8 L/min of nitrogen was used from top and 1.0 L/min from bottom; for 800 °C, 1.6 L/min of nitrogen were used from top and 0.8 L/min from bottom; for 900 °C, 1.4 L/min of nitrogen was used from top and 0.6 L/min from bottom. Feed rate, gas flow rate, steam flow rate, and bed temperature were kept constant throughout the experiment.

The gasification products exiting the reactor were first separated with a hot gas filter (HGF) to collect the char and some entrained catalyst. The HGF was maintained at 400 °C to avoid condensation of vapors going through it. The vapors and non-condensable gases (NCG) exiting the HGF were then passed through two condensers kept below 10 °C to condense the gasification vapors. The condensers were cooled using an 18-liter Haake A82 Temperature Bath/Recirculator (Haake, Karlsruhe, Germany). The coolant was a mixture of 50/50 ethylene

glycol and water. The NCG and aerosols were further passed through an electrostatic precipitator (ESP) maintained at 30 kV to condense aerosols. The NCG leaving the ESP were then passed through an F72C Series oil removing coalescing filter (NORGREN, Littleton, CO, USA). The clean NCG were passed through a totalizer/mass flow meter where the mass flow rate (nitrogen and gasification products) and the total mass flow (liters) were measured with a Top-Trak™ mass flow meter/totalizer, before being analyzed online with a Varian 490-Micro GC gas chromatograph (Agilent Technologies, Santa Clara, CA, USA). Each experiment was conducted continuously for two hours.

A fraction of the NCG (0.1 L/min) exiting the mass flow meter/totalizer was connected to a Varian 490-micro GC system for online analysis. The NCG was automatically sampled every 10 min for the duration of the experiment. The micro GC was equipped with two modules: a 10 m Molsieve 5 Å (MS) column, and a 10 m porous polymer (PPU) column. Each column had a thermal conductivity detector. The MS was used to analyze hydrogen, methane, and carbon monoxide (CO), while carbon dioxide (CO₂) and C₁–C₄ hydrocarbons were analyzed on the PPU column.

The gasification of the coal on red mud catalyst was also investigated on a pilot scale fluidized bed reactor that had a capacity of 2 kg/h, which is 10 times the size of the bench scale studies. The schematic diagram of the pilot plant unit is shown in Fig 8. The coal used for these studies was similar to the one used on the bench scale studies, but the temperatures investigated was limited 800-830 °C because of the design limitations of this unit. In these studies both one pass and gas recycle were investigated. Catalyst to coal ratio and steam feed rate were varied. In this unit, distilled water was injected into the reaction zone using a peristaltic pump set at various feed rates, but the coal feed rate was kept constant. Experiments lasted as long as 5 hours to ensure a steady state was achieved. Gas samples for online analysis were taken from a slip stream and injected into an Agilent 490 microGC described above. Gas samples were taken every ten minutes for analysis.

The gasification products were first passed through a hot gas filter maintained at 400 °C to collect unreacted char and carryover fine catalyst. After the hot gas filtration, the product gases were passed through two shell and tube heat exchangers maintained at 10 °C, a Venturi scrubber, an electrostatic precipitator, and a coalescing filter before being fed into a gas compressor that compressed the gas to 60 psi for recycling into the reactor. Part of the recycle gas was purged and flared to minimize gas build in the system. The reactor was first fluidized with nitrogen and then gradually the nitrogen was replaced with recycled gasification products. For each experiment, either 800 g or 1600 g red mud catalyst was used for the gasification. The coal feed rate was 1 kg/h.

After each run, the catalyst was regenerated in a muffler furnace for 5 hours and reused. After the coke burnoff from the surface of the catalyst, no permanent deactivation was observed. Thus one batch of catalyst could be used for as many runs as necessary except make-up catalyst of about 1% that was added after each regeneration of the catalyst. This make-up catalyst was to compensate for losses due to attrition.

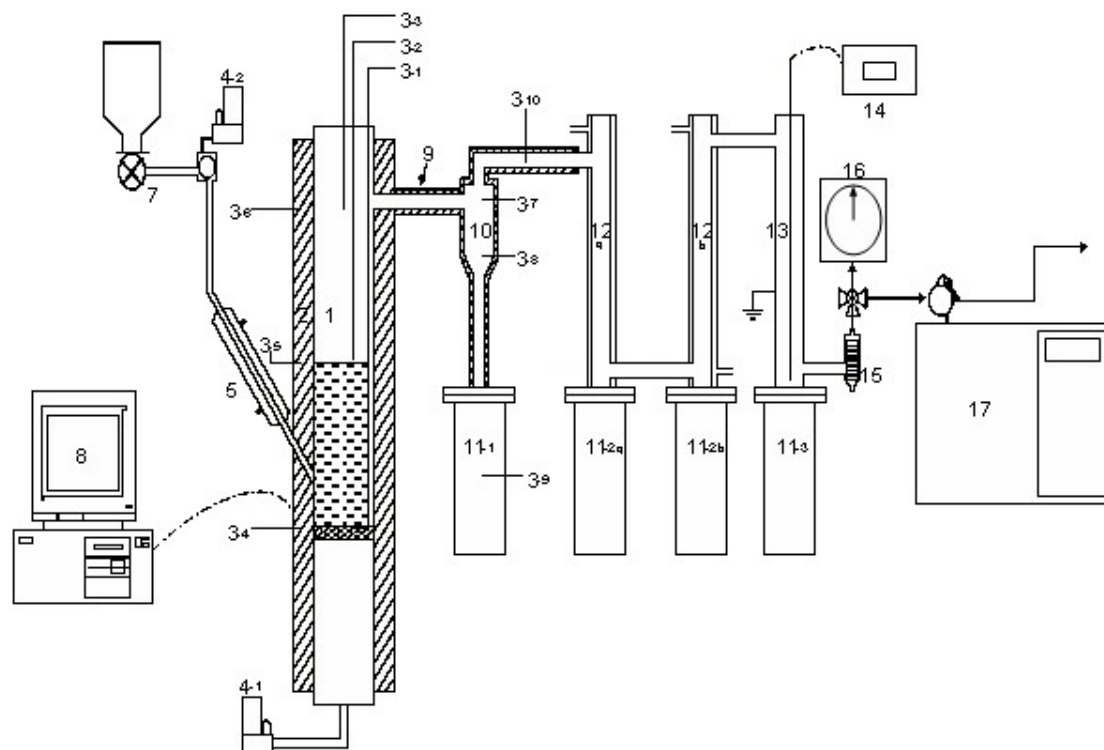


Fig. 2.7. Schematic diagram of bench scale fluidized bed reactor unit: 1- reactor, 2-furnace, 3-thermocouple, 4-mass flow controller, 5-jacketed air-cooled feeder tube, 6-hopper, 7-screw feeder, 8-computer, 9-heating tape, 10-hot gas filter, 11-reservoir, 12-condenser, 13-electrostatic precipitator, 14-AC power supply, 15-coalescing filter, 16-wet gas meter, 17-gas chromatograph.

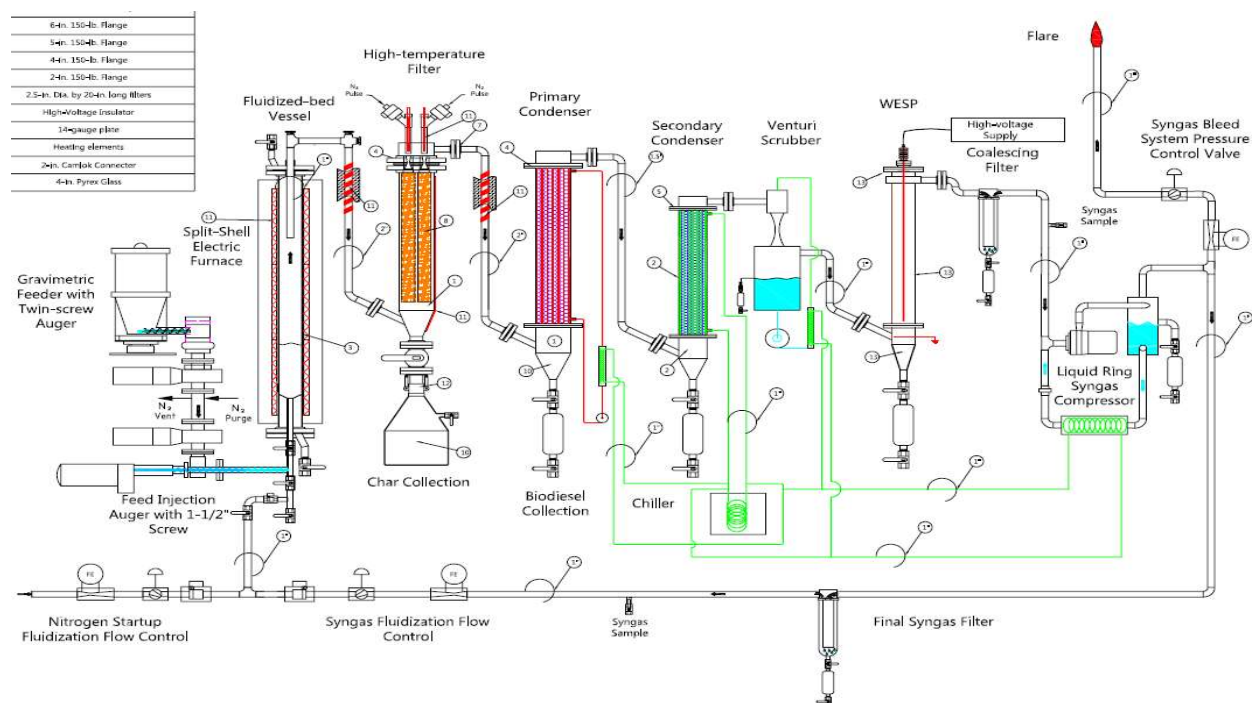


Fig. 2.8. Schematic of pilot plant fluidized bed gasification unit.

2.2 Results

2.2.1 Bench-scale fluidized bed reactor

Gasification under on red mud in nitrogen atmosphere. The gasification of coal on red mud was strongly influence by the gasification environment and the moisture content of the coal (wet or dry). In Table 2.4, wet coal containing about 24 wt% moisture and dried coal were gasified at 700, 800 and 900 °C. When the coal was dry, the yield of gas was very high reaching up to 71 wt% in one pass gasification, however when the coal was wet, the gas yield decreased to 49.42 wt%. The differences in the gas yields were attributed to thermal effect. In the case of the wet coal, a fraction of the thermal energy was used to vaporize the moisture which was later recovered as liquid in the condenser. In the case of the dry coal, the amount of thermal energy used for vaporizing the moisture was used to gasify the coal and hence the large difference in the syngas yields. In comparison to wet coal gasified on sand in nitrogen atmosphere, the gas yields were significantly higher especially at 700 °C where the gas yield on RM was twice that from sand (Table 2.4). This large difference at 700 °C was attributed to contribution from water gas shift reaction (WGSR) discussed in detail below. At the higher gasification temperatures, the differences in gas yield were not as large as that at 700 °C because WGSR reaction at higher temperatures was considerably reduced and therefore less hydrogen was produced.

The composition of the syngas was strongly influenced by both the moisture content and the gasification temperature (Table 2.5). The major differences in the gas compositions were in the hydrogen and carbon monoxide contents and consequently in the H₂:CO ratios. At the lower temperature (700 °C) the hydrogen contents of the gases were very high for the wet coal gasification products and very low for the dry coal. The differences were attributed to the water gas shift reaction (WGSR) that occurred in the presence of the water associated with the wet coal, where:



Thus, wet coal gasification product gas was enriched in H₂ and the CO decreased because it was partially converted to CO₂ as shown by the reaction in Eq. (2.5). It is known that iron compounds catalyze WGSR, thus it appeared that the iron oxides in the RM catalyzed this reaction. This assertion was corroborated by passing steam and CO over heated RM in a fluidized bed reactor using the RM as the fluidizing media. The major products detected with gas chromatograph were H₂ and CO₂ with small fractions of hydrocarbons, thus confirming the hypothesis of WGSR during the wet coal gasification. In the case of the dry coal, the amount of moisture was extremely low (~1 wt%) and therefore H₂ production was lower and CO levels were much higher and hence the lower H₂:CO ratio. However, at higher temperatures, WGSR is known to be considerably reduced and this was also observed for the RM. Thus with increase in coal gasification temperature from 700 to 800 and 900 °C, the H₂:CO ratios decreased considerably because less CO was converted into H₂ and CO₂. The CO₂ content of the wet coal syngas was consistently higher than that of the dry coal while the CO content of the wet coal syngas was consistently lower than that of the dry coal syngas.

Methane was the other gas produced in significant quantities, which was different for the wet and dry coals (see Table 2.5). The wet coal produced less methane than the dry coal. The dry coal syngas methane content was 1.4 to 1.7 times higher than that of the wet coal at 700 °C and 800 °C, but at 900 °C, the methane contents were similar. The production of other hydrocarbon species was considerably low for both the dry and wet coal. Thus, the RM did not appear to influence the production of low molecular weight hydrocarbons.

Table 2.4. Product yields in the gasification of as received coal (wet coal) and dried coal on red mud and wet coal on sand. Yields expressed as wt% moisture free basis.

Temp, °C	Wet Coal				Dried Coal			
	Moisture	Liquid	Char	Gas by diff.	Moisture	Liquid	Char	Gas by diff.
700	24.19	29.58	43.20	27.22	0.71	12.06	60.64	27.30
800	24.33	27.57	42.78	29.65	0.56	8.24	38.74	53.02
900	24.94	20.97	29.61	49.42	0.71	2.69	25.51	71.80
Wet coal gasification on sand in nitrogen atmosphere								
700	24.34	31.65	54.0	14.25				
800	24.33	52.38	26.73	20.72				
900	24.35	45.14	15.00	38.96				

Table 2.5. Coal gasification in nitrogen over red mud medium. Gas composition (mol %) for wet and dried coal gasification under N₂ on red mud. Wet coal is defined as the “as-received coal”.

Gas composition (mol %) for wet coal gasification under N₂ on red mud (24% moisture in coal)												
Temp (°C)	H ₂ :CO	H ₂	CH ₄	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	O ₂	N ₂	Total Gases
700	3.5:1	5.03	0.81	1.44	1.99	0.23	0.06	0.12	0.07			
800	2.5:1	5.94	0.86	2.37	2.93	n/a	0.04	0.07	0.01			
900	1.6:1	8.26	0.94	5.16	3.01	0.35	0.01	0.01	0.002	0.04	80.05	97.83
Gas composition (mol %) for dried coal gasification under N₂ on red mud (1% moisture in coal)												
700	1.3:1	2.90	1.13	2.20	2.52	0.43	0.09	0.19	0.05	0.04	90.12	99.65
800	1.4:1	5.57	1.46	4.08	2.91							
900	1:1.1	5.53	0.99	6.01	2.41	0.20	0.005	0.001	0.00	0.07	83.40	98.62

The yield of gasification products of the wet coal using red mud (Table 2.6) was surprisingly different from that of the dry coal (Table 2.7). In this case, the gas yields were relatively very high. At 700 °C, the gas yield was 27.30 wt% which was similar to the wet coal gasification system. However, when the gasification temperature was increased to 800 °C, the gas yield increased to 53 wt% which is almost double the yield at 700 °C. When the gasification temperature was further increased to 900 °C, the gas yield increased to 71.8 wt%. Clearly the gasification of the coal was greatly enhanced by temperature increase in the presence of the red mud catalyst. The catalytic activity increased with increase in gasification temperature.

The composition of the dried coal gas product was much different from that of the wet coal. The H₂:CO ratio of the dry coal varied from 1.31 to 0.92 (Table 2.7) compared to 3.5 to 1.6 for the wet coal. The absence of water reduced the WGS and the H₂ content of the gas was relatively low compared to the wet coal gas product. CO production was greatly enhanced since there was very little water available for the WGS. It also appeared that a component of the red mud catalyzed the gasification of the coal. CO₂ production was less in the dry coal than in the wet coal probably because there was less WGS taking place because of the low water content of the coal.

Methane (CH₄) production was similar at 700 and 800 °C, but at 900 °C, the CH₄ production decreased considerably for both the wet (Table 2.6) and dry coal (Table 2.7), but it was more pronounced for the dry coal than the wet coal. CH₄ production through the methanation pathway depends on the availability of H₂; interestingly, at 700 °C when there was a relatively large amount of hydrogen in the wet coal gas, the amount of CH₄ produced was only slightly higher than that of the dry coal. Thus, the reaction producing CH₄ does not appear to depend on the water present in the coal; it appears to derive from the fragmentation of hydrogen rich-component of the coal. After the gasification, the red mud was magnetic because of the conversion of the hematite component of the red mud to the magnetite component.

Table 2.6. Gas yield and composition of wet coal (24 wt% moisture) gasified on red mud catalyst and sand in nitrogen atmosphere. Ratios are on mole basis.

Temp (°C)	Sand gasification of wet coal				Red mud gasification of wet coal			
	Gas yield (%)	H ₂ /CO	CO ₂ /CO	CH ₄ /CO	Gas yield (%)	H ₂ /CO	CO ₂ /CO	CH ₄ /CO
700	14.25	2.1	1.49	0.62	27.22	3.50	1.17	0.56
800	20.72	2.1	1.26	0.44	29.65	2.50	1.24	0.36
900	38.96	1.5	0.40	0.24	49.42	1.60	0.58	0.18

Table 2.7. Gas yield and compositions of wet and dry coal (<2 wt% moisture) gasified on red mud catalyst in nitrogen atmosphere.

Temp (°C)	Red mud gasification of wet coal				Red mud gasification of dry coal			
	Gas yield (%)	H ₂ /CO	CO ₂ /CO	CH ₄ /CO	Gas yield (%)	H ₂ /CO	CO ₂ /CO	CH ₄ /CO
700	27.22	3.5	1.17	0.56	27.3	1.31	1.14	0.51
800	29.65	2.5	1.24	0.36	53.0	1.36	0.71	0.35
900	32.30	1.8	0.80	0.26	71.8	0.92	0.40	0.16

Table 2.8. Composition of gases (mol %) from coal gasification on RM in N₂ and Steam.

Gaseous products for coal gasification on RM in N ₂									
Temp, °C	H ₂ : CO	H ₂	CH ₄	CO	CO ₂	C ₂ -C ₄	O ₂	N ₂	ΣGases
700	3.5 : 1	5.032	0.809	1.442	1.988	0.480	0.059	89.690	99.50
800	2.5 : 1	5.939	0.862	2.373	2.933	0.121	0.036	86.521	98.79
900	1.6 : 1	8.264	0.938	5.161	3.010	0.367	0.040	80.052	97.83
Composition of gaseous products from coal gasification on RM in Steam									
700	4.7 : 1	8.563	1.195	1.826	5.258	0.703	0.058	81.954	99.56
800	2.4 : 1	16.94	1.641	7.069	6.725	0.785	0.027	66.017	99.21
900	1.8 : 1	24.17	1.944	13.81	8.298	0.555	0.027	49.949	98.76

During the gasification of coal on RM under steam atmosphere the classic water-gas shift reaction (WGSR) was observed. This process involves reaction of carbon monoxide and water vapors to produce carbon dioxide and hydrogen (Eq. 2.5). Thus, the production of H₂ and CO₂ increased considerably in case of coal gasification on RM under steam compared with the base coal gasification on RM under N₂ (Table 2.8). As expected, the concentration of carbon dioxide increased due to WGSR. The syngas was significantly enriched in H₂ when the coal was gasified under steam on RM. These results bode well for upgrading of the syngas for applications such as electricity generation, chemical feedstocks, or for production of synthetic natural gas. Also, the ratios of H₂:CO obtained at 800 and 900 °C are suitable for the Fischer-Tropsch process.

Coal gasification with steam on red mud. The gasification of coal using steam has been extensively reported in literature. Steam gasification has been used to increase the syngas yield due to the gasification reaction:



From this reaction the H₂/CO ratio is 1.0. If partial oxidation is used for the gasification, then more CO is produced from the reaction:



Table 2.9. Product yields of coal gasification (wt %) in steam and nitrogen.

Temp(°C)	Coal on RM in N ₂				Coal on RM in Steam			
	Moist.	Liquid	Solid	Gas	Moist.	Liquid	Char	Gas
700	24.19	29.58	43.20	27.22	23.96	19.36	54.06	26.58
800	24.33	27.57	42.78	29.65	22.52	17.08	40.81	42.11
900	24.94	20.97	29.61	49.42	21.55	13.94	31.87	54.19

Table 2.10. Water content in the liquid formed during coal gasification on RM under steam.

Temp, °C	Trial 1	Trial 2	Trial 3	Average
700	100.052	99.862	99.273	99.73±0.41
800	97.987	97.682	98.143	97.94±0.23
900	99.088	99.195	100.506	99.60±0.79

The overall gas yields for gasification under steam conditions were higher than those under nitrogen atmosphere for 800 and 900 °C (Table 2.9), but were the same for the reaction at 700 °C. Although the yields of gaseous products at 700 °C were similar for both the nitrogen and steam atmospheres, the steam syngas was richer in hydrogen than the corresponding one from nitrogen.

The baseline coal gasification on RM under nitrogen (Table 2.10) at 700 °C produced 6.0 g of tar and the water content of liquid product from condenser 1 was 96%; at 800 °C, 1.0 g of tar was produced and the water content of the liquid product was 98%; at 900 °C, no tar was observed in condensers 1, 2, and ESP. However, water content of the liquid product collected from condenser 1 at 900 °C was 98%.

During coal gasification on RM under steam only 1.0 g of tar was produced at 700 °C compared to 6.0 g produced under nitrogen atmosphere. Furthermore, at 800 and 900 °C the tar produced was below detection limit of the Karl Fischer titrator and the liquids products collected from condenser 1 were close to 100% water for the two temperature range (Table 2.10). The data therefore supports the hypothesis that RM in the presence of steam promotes better cracking of the tar during coal gasification. This is a very important finding for the coal gasification, since tar formation during coal gasification is a common problem in the technology and extensive gas cleanup technologies are needed to make the gas cleaner for other applications.

Coal gasification with carbon dioxide. In addition to the gasification of coal on red mud in steam and nitrogen atmospheres, some coal was also gasified with carbon dioxide (CO₂) and carbon dioxide/steam mixtures. In the CO₂ atmosphere, the overall gasification of coal on red mud at 700 °C and 800 °C were reduced in comparison with gasification in nitrogen atmosphere (Table 2.11). Hydrogen production decreased while CO production increased, consequently the H₂/CO ratio was less than 1.0 (see Table 2.12). However, methane production was more than double that produced during gasification in nitrogen atmosphere probably because of methanation of CO₂. The methanation reaction could also explain the reduction in hydrogen production since this reaction involves consumption of hydrogen as shown in Equation 8 below.



The introduction of steam in the CO₂ showed a dramatic improvement in the gasification of the coal. The gas yield at 800 °C was 19% for the CO₂ atmosphere compared to 39.6% for

steam/CO₂ and 42.1% for steam only. The improvement in the yield of gases was mainly due the effect of the steam since the steam alone at 800 °C had a slightly higher gas yield than the steam/CO₂ combination (see Table 2.11). The effect of steam/CO₂ mixture was most dramatic at 900 °C, where the gas yield increased from 39.6% at 800 °C to 78.1% at 900 °C. It appeared at 900 °C the CO₂ also contributed to the gasification of the coal since the steam/CO₂ mixture produced a higher yield of gas than the steam only (54%).

Table 2.11. Product yields in the gasification of coal in nitrogen, carbon dioxide, steam and steam/carbon dioxide mixture on red mud

Wet coal gasification in N₂ on red mud				
Temp (°C)	Moisture (wt%)	Liquid (wt%)	Char (wt%)	Gas (wt%) by difference
700	24.19	29.58	43.20	27.22
800	24.33	27.57	42.78	29.65
900	24.93	20.97	29.61	49.42
Wet coal gasification in CO₂ on red mud				
700	25.02	44.10	40.87	15.03
800	24.11	37.03	43.56	19.41
Wet coal gasification in steam on red mud				
800	22.52	17.08	40.81	42.11
900	21.55	13.94	31.87	54.19
Wet coal gasification in steam/CO₂ mixture on red mud				
800	24.90	26.34	34.03	39.63
900	21.99	15.84	5.76	78.40

Table 2.12. Composition of major compounds (mol%) in coal gasification products at various temperatures in nitrogen and carbon dioxide on red mud.

Wet coal gasification in N₂ on red mud				
Temp (°C)	H₂:CO	H₂	CO	CH₄
700	3.5:1	5.03	1.44	0.81
800	2.5:1	5.94	2.37	0.86
900	1.6:1	8.26	5.16	0.94
Wet coal gasification in CO₂ on red mud				
700	0.42:1	3.18	7.63	1.42
800	0.32:1	6.11	18.97	1.81
Wet coal gasification in steam on red mud				
800	2.4:1	16.94	7.07	1.64
900	1.8:1	24.17	13.81	1.94
Wet coal gasification on steam/CO₂ mixture on red mud				
800	0.77:1	19.43	25.05	1.94
900	0.51:1	17.88	34.91	2.20

The steam/CO₂ mixture improved the hydrogen production so that the H₂/CO ratio at 800 °C improved from 1:3.1 to 1:1.3 (see Table 2.12) compared to 1.8:1 for steam alone. At 900 °C, there was more CO production due to the CO₂ effect and the H₂/CO ratio was 1:1.95 compared to 1.8:1.0 for the steam only gasification. The gas produced in the combination therefore was richer in CO than the steam only. The methane production was only slightly higher than that produced when only steam was used for the gasification. The tar cracking of the steam/CO₂ mixture was also similar to the steam only gasification on red mud. The aqueous phase obtained from the gasification was over 99.6% water according to Karl Fischer water content of the liquid product.

Coal gasification on regenerated red mud. During gasification of coal with red mud, the catalyst gradually deactivated and this was observed by the change in the H₂/CO ratios. As catalyst deactivated the H₂ concentration decreased and the H₂/CO decreased. However, the catalyst activity was restored by regeneration through burning in a muffler furnace at 700 °C for five hours. The process burnt off coke deposited on the surface of the catalyst. After regeneration, the activity of the catalyst was fully restored. The RM catalyst was regenerated more than twenty times and it was still active. Fig. 2.4 shows that the BET specific surface area of the RM catalyst stabilized after three regenerations. However, make-up catalyst was added to the original catalyst because of attrition losses.

Modification of red mud with nickel. The red mud catalyst was impregnated with nickel to take advantage of the reported nickel and nickel oxide catalytic activity for coal gasification. In this process the red mud was impregnated with 10-20 wt% nickel. However, the gasification of the coal with the modified red mud at 700, 800, and 900 °C in nitrogen atmosphere did not show any significant improvement in either the gas yield or the gas composition. The lack of activity of the nickel/red mud was attributed to perhaps the rapid oxidation of the nickel back to nickel oxide which was inactive in the gasification of the coal or the lack of good contact between the nickel and the coal. This process will need further work to be able to explain the poor activity of the incorporation of the nickel into the red mud.

Gasification of coal/biomass mixtures on red mud. One of the goals of these studies was to determine the influence of RM on the gasification of biomass/coal mixtures. We observed earlier that gasification of corn stover and other herbaceous biomass feedstocks that had high potassium content formed clinker during the gasification process at high temperatures (900 °C) on silica sand. The clinker formation was attributed to the reaction of silica sand with potassium to form a low melting eutectic mixture and the subsequent agglomeration of the sand particles that gradually defluidized the silica sand bed (Fig. 2.9).

When red mud was used to replace the silica sand for gasification of biomass and coal/biomass mixtures the gasification of corn stover on red mud produced very interesting results; unlike the gasification on the sand which formed clinker at 900 °C, no clinker formation was observed when red mud was used to replace the silica sand. Similar results were obtained when switchgrass and poplar wood feedstocks were also gasified on the red mud catalyst. It is interesting that although the red mud also contained silica, the presence of other oxides in the red mud prevented the formation of the eutectic mixture and therefore no clinker was formed in the process. The gasification using red mud in place silica sand for the coal/corn stover (90/10) and other biomass feedstocks (switchgrass, poplar wood) all showed improved yields of gaseous products at all temperatures.

The coal/corn stover gasification (Table 2.13) on red mud showed improved gas yields compared to the gasification on sand. At 700 °C, gas yield improved by 33%, while at 800 and 900 °C, gas yields improved by 49% and 43% respectively. These large improvements in gas

yields were attributed to secondary gasification reactions taking place on the red mud surface. These secondary reactions are reflected in the higher H_2/CO ratios observed (Table 2.14). It appears that in this case, just like the case of coal gasification alone, there was water gas shift reaction which increased the gas yields. Also interesting is the fact that the red mud appeared to be effective in destroying the tars and therefore increasing the gas yield further in addition to the water gas shift reaction. The gas yields for the dry coal/corn stover mixture were higher than those of the wet coal/corn stover mixtures and the sand at all three gasification temperatures. The H_2/CO ratios were very similar for the three gasification temperatures for the wet coal, but were higher than that for the dry coal (Table 2.14).

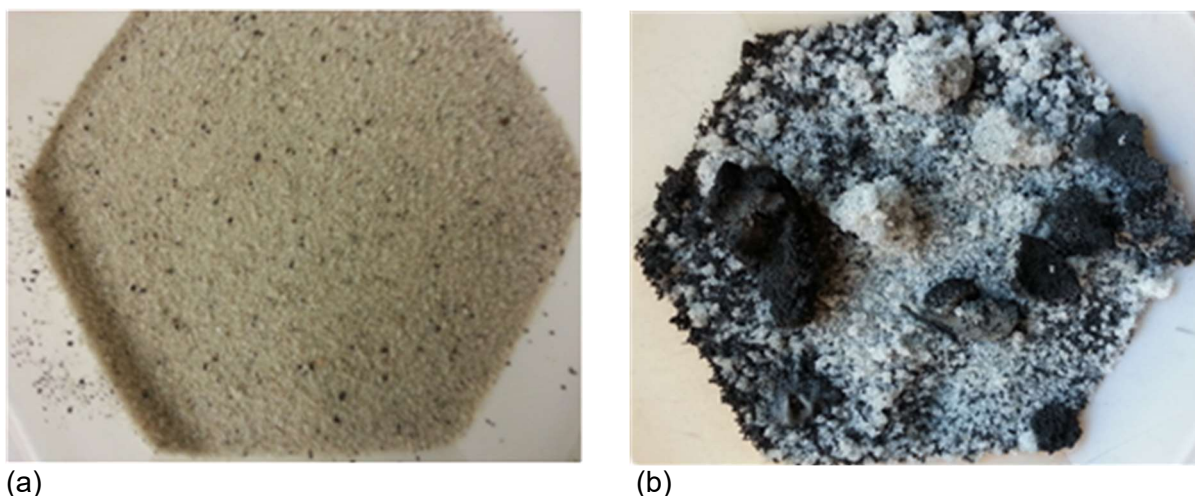


Fig. 2.9. Clinker formation in silica sand at high temperature gasification of corn stover: a) fresh silica sand; b) clinker formation after gasification.

Table 2.13. Product yields on coal/corn stover (90/10) gasification on sand and red mud.

Wet coal/corn stover gasification in N_2 on sand				
	Moisture in coal (wt%)	Liquid (wt%)	Char (wt%)	Gas by difference (wt%)
700	22.00	37.63	48.61	13.66
800	22.00	34.75	44.84	19.47
900	22.00	29.22	42.62	27.74
Wet coal/corn stover (90/10) gasification in N_2 on red mud				
700	17.25	43.36	37.82	18.82
800	21.67	33.26	37.76	28.98
900	20.57	30.57	29.68	39.75
Dry coal/corn stover (90/10)				
700	1.49	18.66	49.26	32.08
800	1.12	9.25	39.66	51.09
900	1.46	5.22	41.79	52.99

Table 2.14. Composition of coal/corn stover gasification products (mole %) on sand and red mud

Wet coal/corn stover (90/10) gasification in N ₂ on sand							
Temp (°C)	H ₂ :CO						
700	0.77:1						
800	1.04:1						
900	1.32:1						
Wet coal/corn stover (90/10) gasification in N ₂ on red mud							
Temp (°C)	H ₂ :CO	H ₂	CO	CO ₂	CH ₄	C ₂ -C ₅	N ₂
700	1.5:1	2.67	1.83	0.82	2.23	0.58	87.10
800	1.4:1	5.91	4.08	1.38	3.12	0.75	83.63
900	1.5:1	9.13	5.95	1.45	3.33	0.63	77.59
Dry coal/corn stover (90/10) gasification in N ₂ on red mud							
700	1.1:1	3.36	2.99	1.25	3.05	0.84	87.10
800	1.0:1	5.16	5.05	1.61	8.91	0.89	83.34
900	1.1:1	8.99	8.48	1.70	2.10	0.68	

Table 2.15. Product yields of wet and dry coal/switchgrass (90/10) gasification on red mud

Wet coal/switchgrass (90/10) gasification on red mud				
Temp (°C)	Coal moisture (wt%)	Liquid (wt%)	Char (wt%)	Gas by difference
700	20.23	36.53	52.30	11.17
800	22.11	27.03	49.55	23.42
900	21.53	14.79	28.45	56.76
Dry coal/switchgrass gasification on red mud				
700	1.83	9.97	57.70	32.33
800	2.33	9.31	47.87	42.82
800	1.48	3.73	35.08	61.19

The gasification of wet coal/switchgrass (90/10) mixture also showed similar trend as the corn stover mixture gasification in that gas yields increased with increasing temperature (Table 2.15). However gas yields for coal/switchgrass mixtures were lower at 700 and 800 °C, but at 900 °C, the coal/switchgrass mixture produced much higher gas. The difference was attributed to the nature of the ash in the two feedstocks. The switchgrass ash could probably catalyze the gasification reaction as noted in published literature.

The gasification of dry coal/switchgrass mixture produced more gas than the wet coal mixture. This trend was similar to that of corn stover and the dry coal itself. However, the major challenge is the added cost of drying the coal before the gasification. A techno-economic assessment has to be performed on the data to assess if pre-drying the coal before the gasification is worth the effort, especially at the lower gasification temperatures.

The H₂/CO ratios also followed a similar trend as that for the corn stover. The wet coal produced more hydrogen than the dry coal and hence the H₂/CO ratios were always greater than 1 (Table 2.16). On the contrary, the H₂/CO ratios for the dry coal were always low and at 900 °C, there was more CO produced than H₂.

The gasification of wet coal/poplar wood showed similar trends like that of corn stover and switchgrass (Table 2.17). At lower gasification temperatures, the gas yields were low but increased with increasing temperature. The gas yields at 900 °C for the poplar wood was

higher than those for the switchgrass and corn stover probably because of the lower ash content of this feedstock. The dry coal/poplar wood mixture also showed much higher gas yield than the wet coal/poplar wood mixture. However, this difference was only significant at 700 and 800 °C, but at 900 °C, there was not much difference in the gas yields from the two feedstock mixtures.

The H₂/CO ratios for the wet coal/poplar wood mixtures were much higher than those for the switchgrass and corn stover coal mixtures (Table 2.18). The coal/poplar wood mixture produced more hydrogen than the other feedstocks. This higher hydrogen generation for the woody biomass was also observed by Yathavan and Agblevor (2013) for pinyon juniper pyrolysis on red mud. The rationale for more hydrogen generation from the woody biomass is not very clear.

Table 2.16. Composition of gasification products (mol%) of coal/switchgrass (90/10) mixture on red mud

Wet coal/switchgrass (90/10) gasification on red mud							
Temp (°C)	H ₂ :CO	H ₂	CO	CO ₂	CH ₄	C ₂ -C ₅	N ₂
700	1.6:1	3.52	2.22	2.95	0.72	0.68	89.09
800	1.9:1	7.94	4.13	3.53	1.18	0.67	82.12
900	1.3:1	10.74	8.30	3.16	1.11	0.39	75.97
Dried coal/switchgrass (90/10) gasification on red mud							
700	1.4:1	4.19	2.93	2.91	0.99	0.64	87.53
800	1.1:1	7.08	6.71	3.37	1.79	0.96	79.93
900	0.95:1	9.39	9.91	1.59	1.49	0.56	76.54

Table 2.17. Product yields of wet and dry coal/poplar wood (90/10) gasification on red mud

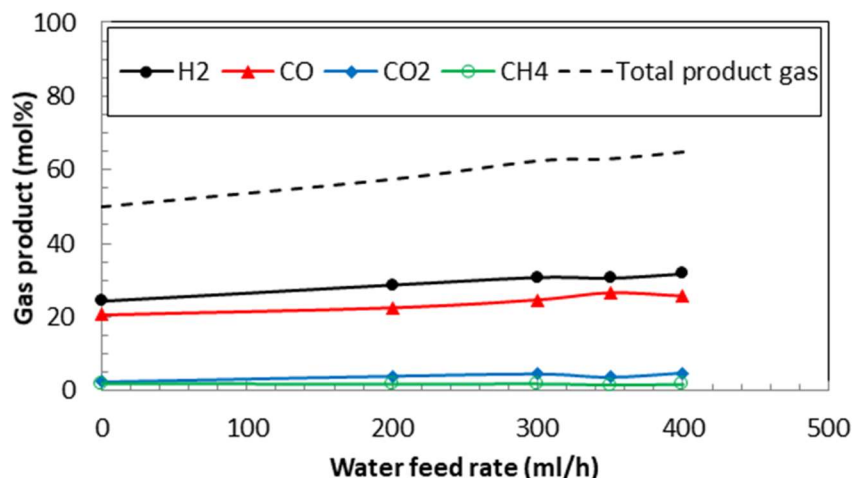
Wet coal/poplar wood (90/10) gasification on red mud				
Temp (°C)	Moisture (wt%)	Liquid (wt%)	Char (wt%)	Gas by difference (wt%)
700	21.49	33.63	58.08	8.29
800	22.32	22.13	39.22	38.65
900	21.91	12.71	24.44	62.85
Dry coal/poplar wood (90/10) gasification on red mud				
700	1.37	12.10	57.61	30.29
800	1.18	6.63	45.06	48.29
800	1.32	2.98	36.51	60.51

Table 2.18. Composition of gasification products (mol%) of coal/poplar wood on red mud

Wet coal/poplar wood (90/10) gasification on red mud							
Temp (C)	H ₂ :CO	H ₂	CO	CO ₂	CH ₄	C ₂ -C ₅	N ₂
700	2.1:1	4.30	2.06	2.70	0.98	0.60	88.88
800	2.0:1	8.24	4.21	2.98	1.11	0.61	82.18
900	1.3:1	11.90	9.52	3.23	1.12	0.38	72.40
Dried coal/poplar wood (90/10) gasification on red mud							
700	1.2:1	3.84	3.12	2.96	1.21	0.73	87.37
800	1.0:1	6.59	6.50	3.07	1.45	0.77	81.13
900	0.87:1	9.90	11.28	2.04	1.57	0.57	74.51

Table 2.19. Composition of gasification products of coal gasification on red mud catalyst (mole%)

Mode	H ₂ :CO	H ₂	CO	CO ₂	CH ₄	C ₂ -C ₅	N ₂
No recycle	1.7:1	12.55	7.44	3.78	1.83	0.06	73.97
Gas recycle	1.2:1	22.26	18.32	3.5	2.68	0.11	51.96

**Fig. 2.10. Effect of water feed rate into reactor on pilot scale gas composition.**

2.2.2 Pilot-scale fluidized bed reactor

The first set of experiments was conducted to determine the influence of gas recycling on the syngas composition. In this case, the wet coal gasification was run for one hour without product gas recycling and no steam was added to the reactor. Fresh nitrogen was continuously added to the reactor to maintain the fluidization. Gas samples were taken every 10 min and analyzed on microGC. Table 2.19, shows the average gas composition with and without recycling. Clearly without gas recycling the H₂ content was higher, but the volume of the product gas was small. As product gas recycling was introduced, the product gas yield increased and the CO content increased more than the increase in H₂ content, but the CO₂ content was almost constant. Both the CO and CH₄ contents doubled due to the recycling but the H₂ content was less than double. Since the CO₂ content was constant but the CO more than double, we hypothesized that the gasification was due to the reaction of CO₂ with carbon:



There could be some contribution from water gas shift reaction that also produced some H₂. Thus, the recycling is an effective way of increasing the CO content of the gaseous products. The Karl Fischer moisture analysis of the aqueous products collected showed that there was about 5 wt% organic compounds in the liquid which were attributed to tars.

The pilot scale gasification was also carried out using steam as the variable while keeping the coal feed rate constant and recycling the gaseous products. The steam was fed into the reactor using peristaltic pump. In one set of experiments, the water injection rate was kept between 200 ml/h to 450 ml/h. In a second set of experiments, the water injection rate was varied from 570 ml/h to 1285 ml/h. In each case, the gaseous products were recycled and a purge stream was flared continuously into the atmosphere. The influence of water feed rate on the gas composition is shown in Fig. 2.10. For Fig. 2.10, when the water feed rate was low the

H₂, CO, and CO₂ contents increase to almost a maximum of 32 mole% for H₂ and 26 mole% for the CO. However, the H₂/CO ratios for all the feed rates were constant at 1.2:1. This clearly suggests that the gas product recycling had a stronger effect than the water feed rate. The water feed rate however, changed the total volume of product gas generated. The higher water feed rates generated more products compared to the low feed rate (Fig. 2.10). When the water feed rate was increased to as much as 1028 ml/h, the maximum total volume of gas produced was the same as that produced at 400 ml/h and the H₂ mole% was the same. However, the CO mole% decreased slightly so that the H₂/CO ratio increased to 1.4:1. The excess amount of water appeared to quench the reaction. At such high water feed rate, a higher reaction temperature would be required to show any significant effect on the reaction. The char yield on the pilot scale was between 23 to 30 wt%. The aqueous phase was visually very clear and the organic compound content determined by Karl Fischer water titration was less than 1%. Thus, it is clear that the small scale data was reproducible.

When the amount of catalyst fed into the reactor was reduced from 1600 g to 800 g, while the coal feed rate was constant, this changed the weight hourly space velocity (WHSV) from 0.625/h to 1.25/h. This change in WHSV greatly influenced the amount of organic compounds detected in the aqueous products. At WHSV of 0.625/h, the amount of organic compounds detected in the aqueous phase was less than 1% while when the WHSV was increased to 1.25/h, the organic compounds detected in the aqueous phase was 4.67%. Thus, it is clear that the control of the WHSV is a critical parameter in reducing the amount of tar formed during the gasification using red mud catalyst.

3. Modeling of the kinetics of product formation

3.1 Methods

The kinetic network modeling portion of the project was meant to capture the intrinsic kinetics of the experimentalists' work in such a way that the team modeling the computational fluid dynamics could utilize this knowledge in their own models. The initial goal was to establish a lumped model that contained few enough "species" that the CFD calculations were tenable, but more than enough to provide detail and nontriviality. A secondary goal was to utilize an attribute reaction modeling approach to increase the complexity of the model with hopes of either developing a direct link with the CFD or as a way to generate simulated data to help tune the lumped model.

3.1.1 Lumped Modeling

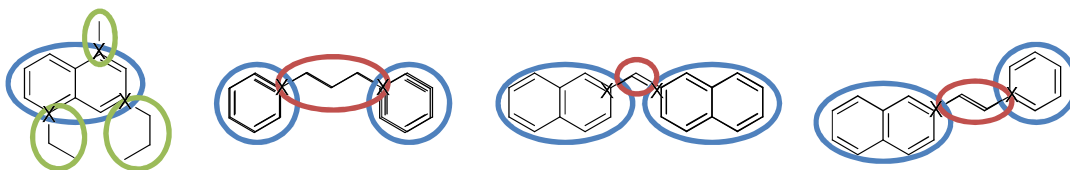
As the bridge between experimental results and CFD modeling, the lumped model served as a keystone for the project. Over the course of the project, the form of the lumped model changed many times in order to better fit the data and the needs of the CFD team. Using the raw data for the dry coal experiments in CO₂, we were able to attempt to retune the model and employed a multistep, combined, lumped approach. First, the drying step was removed because the rate of drying was much higher than the other reactions, and the wet coal was used as a input stream for H₂O into the system. The coal now had two paths forward, one towards a hydrogen rich char, and one toward a tar. The char then could transform into a more carbonaceous form of char by losing hydrogen. The tar could also precipitate into the carbonaceous char as shown in the reaction network:

- 1) Coal $\rightarrow$ 30.3 CharH + 0.1 CH₄ + 1.4 CO + 0.69 CO₂ + 0.95 H₂ + 9.5 H₂O
- 2) Coal $\rightarrow$ 4.7 Tar + 1.3 CO₂ + 4.4 H₂O
- 4) Tar $\rightarrow$ 12.0 CharC + 0.96 CH₄ + 1.5 H₂ + 1.1 H₂O
- 5) CharH $\rightarrow$ 2 CharC + 0.5 H₂
- 6) CharC + H₂O $\rightarrow$ CO + H₂
- 7) CharC + CO₂ $\rightarrow$ 2 CO
- 8) CharC + 2 H₂ $\rightarrow$ CH₄
- 9) CO + H₂O $\leftrightarrow$ CO₂ + H₂

The initial coefficients for the pyrolysis of coal and tar condensation were obtained through direct analysis of the dry coal in N₂ experiment (which should most closely resemble pure pyrolysis). Experimental data was not available for the make-up of the solids reported, so instead of establishing a random factor to break down the reported solids into the two types of char, the Coal, CharC, and CharH lumps were combined into a single solids lump for the purpose of the tuning objective function. The final form of the model using the multi-step, combined, lumped approach was able to reach a reasonable state of parity. A set of tests were performed using the model in which the chemistry of the devolatilization and condensation reactions were varied. Finally, a model fitness regimen was performed to validate the model. All of the results will be presented in the Results section. The infrastructure of the model has been implemented such that further analysis of co-gasification as well as an analysis of red mud would be possible, provided an appropriate set of data for modeling purposes is provided.

3.1.2 Attribute Reaction Modeling

The attribute reaction modeling methodology is an attempt to molecularly model a complex system that can potentially contain an untenable number of important species and isomers by breaking the species into a finite set of attributes. These attributes fall into three categories:



- **Cores** – Largely defined as rings or closely bound ring clusters
- **Side Chains** – Paraffinic or olefinic chains that lead from cores, but do not connect to other cores
- **Inter-unit Links** – Paraffinic or olefinic chains that lead from cores, and do connect to other cores

The proposed structures of the system species easily break down into smaller pieces via these attribute classifications: the Wiser model for coal (Fig. 3.1), the Freudenberg model for lignin (Fig. 3.2), the cellulose molecule (Fig. 3.3), and the hemicellulose molecule (Fig. 3.4).

After breaking down the structures into attributes, there are on the order of 17 ($O(17)$) unique cores, $O(14)$ unique inter-unit links, and $O(12)$ unique side chains. Each attribute will be reacted independently in the kinetic model. Therefore, the concentrations of these attributes will fluctuate with reaction, but the molecular detail of the model can always be reassembled via a juxtaposition of the attributes concentrations. The full factorial construction of the molecular detail would lead to tens, if not hundreds, of thousands of molecules even given a reasonable set of construction criteria and rules. The multiple orders of magnitude in species savings leads to fewer ODEs, which in turn leads to quicker calculation time.

The attribute reaction model for the pyrolysis of sub-bituminous coal begins with an analysis of the initial coal. Although the Wiser model of coal had been put forward earlier, the Smith model was better suited for the structures within sub-bituminous coal. As such, the Smith model led to 42 different Core structures, 17 Side Chain structures, and 8 Intercore Linkages.

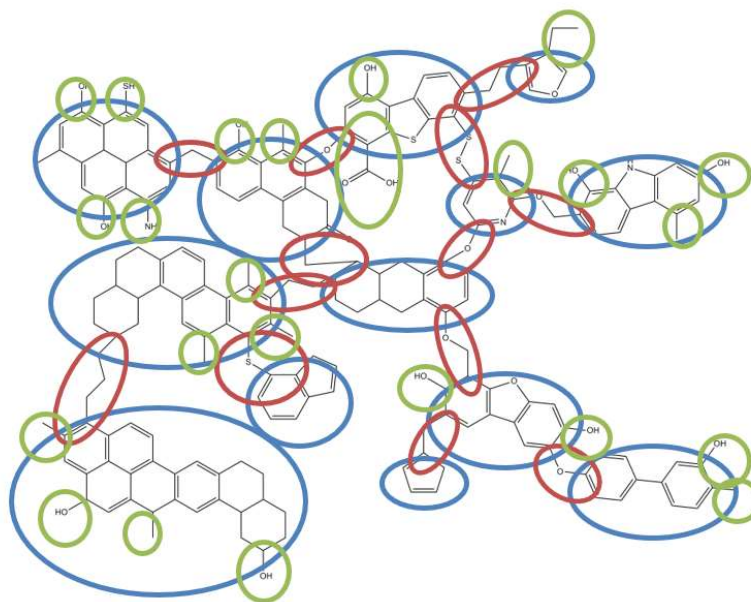


Fig. 3.1. The Wiser model of coal broken into attributes

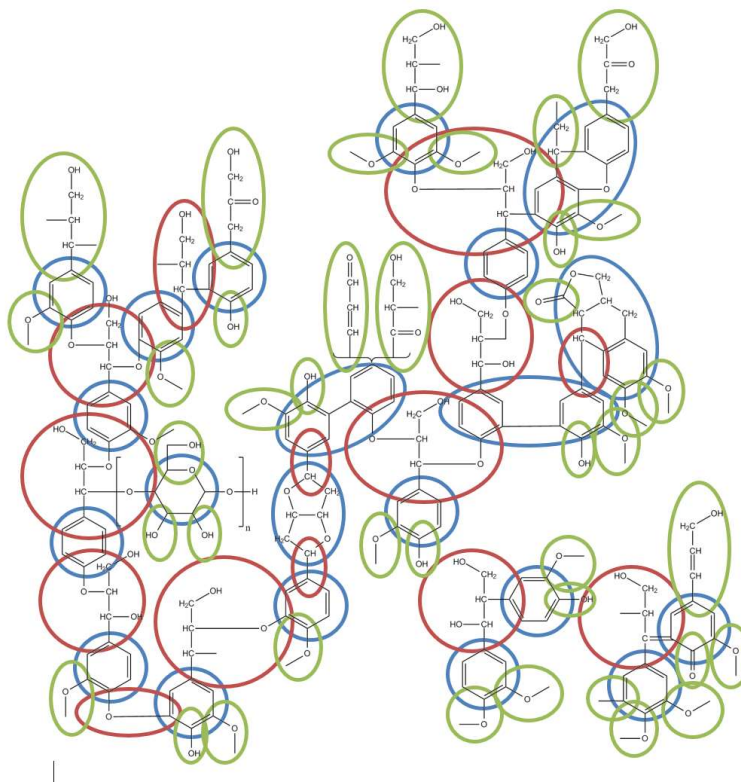


Fig. 3.2. The Freudenberg model of lignin broken into attributes

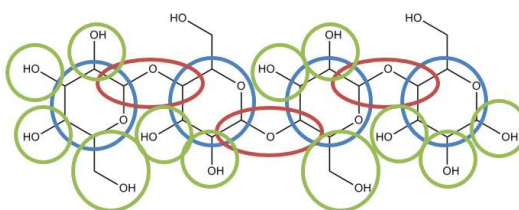


Fig. 3.3. A representative cellulose molecule broken into attributes

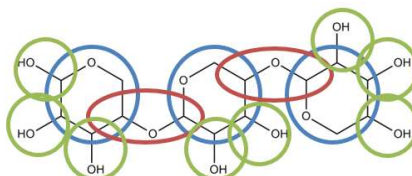


Fig. 3.4. A representative hemicellulose molecule broken into attributes

Using the ultimate analysis of the coal along with other published properties (NMR, Density, XPS, etc.) of sub-bituminous coals with similar ultimate analyses, we were able to use the in-house Composition Model Editor (CME) to tune the probability distribution functions that underlie the structures of the attributes, and ultimately produce the probabilities of each. The SMILES code for each attribute and its probability is listed in Table 3.1 through Table 3.3.

Table 3.1. Core structures and probabilities in sub-bituminous coal

Core ID	SMILES Code	Probability
Core1	<chem>CC(H)C(H)CC(H)C(H)C(H)CC(H)C(H)C(H)C:</chem>	0.003123
Core2	<chem>CC(H)C(H)C(H)C(H)CC(H)C(H)S</chem>	0.020101
Core3	<chem>CCC(H)C(H)CC(H)C(H)C(H)CC(H)C(H)CC(H)CC(H)C(H)C(H)C(H)C:C:</chem>	0.012497
Core4	<chem>CCC(H)C(H)CC(H)C(H)C(H)C(H)CCC(H)C(H)CC(H)C(H)C(H)C(H)</chem>	0.004482
Core5	<chem>C(H)C(H)C(H)C(H)C(H)N</chem>	0.015355
Core6	<chem>CC(H)C(H)CC(H)C(H)C(H)CC(H)C(H)CC(H)C(H)C(H)C:C:</chem>	0.004794
Core7	<chem>CCC(H)C(H)C(H)C(H)C(H)CC(H2)C(H2)CC(H)C(H)C(H)C(H)</chem>	0.004365
Core8	<chem>CC(H)CC(H)C(H)CC(H)CC(H)C(H)C(H)CC(H)CC(H)C(H)CC(H)CC(H)C(H)C(H)C(H):C:C:C:C:C:C:</chem>	0
Core9	<chem>CC(H)C(H)C(H)C(H)CC(H)C(H)C(H)N</chem>	0.01001
Core10	<chem>CC(H)C(H)C(H)C(H)CC(H2)C(H2)C(H2)</chem>	0.004952
Core11	<chem>CCC(H)C(H)CC(H)C(H)C(H)NCCC(H2)CCSC(H)C(H)CC(H)C(H)</chem>	0.002165
Core12	<chem>CCCC(H)C(H)C(H)C(H)COCC(H)C(H)CC(H2)OC(H2)</chem>	0.000203
Core13	<chem>CCC(H)C(H)CC(H)CC(H)C(H)C(H)C(H)CCC(H)C(H)CC(H)CC(H)C(H)C(H)C(H)C:C:</chem>	0.00635
Core14	<chem>CC(H)C(H)C(H)C(H)CC(H2)OC(H2)</chem>	0.004584
Core15	<chem>CCN(H)C(H)C(H)CC(H)C(H)CC(H2)C(H2)C(H2)O</chem>	0.010642
Core16	<chem>CC(H)C(H)C(H)C(H)CC(H2)C(H2)C(H2)C(H2)</chem>	0.029803
Core17	<chem>CC(H)C(H)CC(H)C(H)C(H)CC(H)C(H)C(H)C(H)C(H)C(H)</chem>	0.003871
Core18	<chem>CC(H)CC(H)C(H)C(H)C(H)CC(H)CC(H)C(H2)C(H2)C(H2)C(H)C(H2)C(H2)</chem>	0.011658
Core19	<chem>CC(H)C(H)CC(H)C(H)CC(H)C(H)CC(H)C(H)CC(H)C(H)C:C:C:C:C:C:</chem>	0
Core20	<chem>C(H2)C(H2)C(H2)C(H2)C(H2)</chem>	0.478258
Core21	<chem>CCCC(H)C(H)C(H)C(H)COCC(H)C(H)CC(H2)CC(H)CCC(H)C(H)C(H)C(H)CO</chem>	0.001639
Core22	<chem>CC(H)CC(H)C(H)C(H)C(H)CNCC(H)C(H)C(H)C(H)</chem>	0.006831
Core23	<chem>C(H)C(H)C(H)C(H)C(H)C(H)</chem>	0.195498
Core24	<chem>CC(H)C(H)C(H)C(H)CC(H)C(H)C(H)C(H)</chem>	0.016249
Core25	<chem>CC(H)C(H)C(H)C(H)CC(H2)SC(H2)</chem>	0.002249
Core26	<chem>CC(H)N(H)C(H)CC(H2)C(H2)C(H2)C(H2)</chem>	0.014582
Core27	<chem>C(H2)C(H2)C(H2)C(H2)C(H2)O</chem>	0
Core28	<chem>CCC(H)C(H)C(H)C(H)CC(H2)CC(H)C(H)C(H)C(H)</chem>	0.003871
Core29	<chem>C(C(H)C(H)C(H)C(H)C(H)C(H))C(C(H)C(H)C(H)C(H)C(H))</chem>	0.047475
Core30	<chem>CCC(H)C(H)C(H)C(H)CC(H)C(H)CN(H)C(H)C(H)</chem>	0.015265
Core31	<chem>CCCC(H)C(H)C(H)C(H)CC(H)C(H)CN(H)CC(H)C(H)C(H)C(H)</chem>	0.013754
Core32	<chem>CCC(H)C(H)C(H)C(H)CN(H)CC(H)C(H)C(H)C(H)</chem>	0.015265
Core33	<chem>CC(H)C(H)C(H)CC(H)C(H)C(H)CC(H2)C(H2)C:</chem>	0.003123
Core34	<chem>CCC(H)C(H)CC(H)C(H)C(H)C(H)CCOCC(H)C(H)C(H)C(H)</chem>	0.013446
Core35	<chem>CCC(H)CC(H2)C(H2)C(H2)C(H2)CC(H)CC(H)C(H)CCC(H)C(H)C(H)C(H)CN(H)</chem>	0.00397
Core36	<chem>CCCC(H)C(H)C(H)C(H)CC(H)C(H)CC(H)CC(H2)CC(H)CC(H)C(H)C(H)C(H)C(H)C(H)CC(H)C(H2)C(H2)C:</chem>	0.00158
Core37	<chem>CCC(H)CCC(H)CC(H2)C(H2)C(H2)CC(H)COCC(H)CC(H)C(H)CC(H2)C(H)C(H2)C(H2)C(H2)C(H2)C(H)C(H2)</chem>	0.002199
Core38	<chem>CCC(H)C(H)C(H)C(H)COCC(H)C(H)C(H)C(H)</chem>	0.002996
Core39	<chem>CC(H)CC(H)CC(H)C(H)SCC(H2)C(H2)C(H)C(H2)CC(H)CC(H2)C(H2)C(H2)</chem>	0.006678
Core40	<chem>CCC(H)C(H)C(H)C(H)CSCC(H)C(H)C(H)C(H)</chem>	0.014649
Core41	<chem>CCC(H)C(H)C(H)C(H)CC(H)C(H)CC(H)C(H)C(H)C(H)</chem>	0.013727
Core42	<chem>CC(H)CC(H)CC(H)C(H)C(H)C(H)CC(H)CC(H)CC(H)C(H)C(H)C(H)</chem>	0.004482

Table 3.2. Side chain structures and probabilities in sub-bituminous coal

SIDE CHAIN ID	SMILES CODE	PROBABILITY
SC1	<chem>C(H3)O(H)</chem>	0
SC2	<chem>O(C(H3)C(H3))</chem>	0.018963
SC3	<chem>C(C(H3)H2)O(C(H3))</chem>	0.064909
SC4	<chem>C(H4)</chem>	0.000004
SC5	<chem>C(Cl.H2)C(H3)</chem>	0.02423
SC6	<chem>C(H3)C(H3)</chem>	0.001313
SC7	<chem>C(C(H3)C(H3)Cl.H)</chem>	0.082938
SC8	<chem>C(C(H3)C(H3)H2)</chem>	0.012894
SC9	<chem>C(C(H3)Cl.H)C(C(H3)H2)</chem>	0.169643
SC10	<chem>C(C(H3)H2)C(C(H3)H2)</chem>	0.044137
SC11	<chem>C(C(C(H3)Cl.H)C(C(H3)H2)H2)</chem>	0.255463
SC12	<chem>C(C(C(H3)H2)C(C(H3)H2)H2)</chem>	0.090278
SC13	<chem>C(C(C(H3)H2)H2)C(C(C(H3)H2)H2)</chem>	0.135948
SC14	<chem>S(H2)</chem>	0
SC15	<chem>C(H3)S(H)</chem>	0
SC16	<chem>S(C(H3)C(H3))</chem>	0.022447
SC17	<chem>C(C(H3)H2)S(C(H3))</chem>	0.076835

Table 3.3. Inter-core linkage structures and probabilities in sub-bituminous coal

INTERCORE LINKAGE ID	SMILES CODE	PROBABILITY
IL1	<chem>C(H4)</chem>	0.000027
IL2	<chem>C(H3)C(H3)</chem>	0.009106
IL3	<chem>C(C(H3)C(H3)H2)</chem>	0.089447
IL4	<chem>C(C(H3)H2)C(C(H3)H2)</chem>	0.306175
IL5	<chem>O(H2)</chem>	0.000039
IL6	<chem>C(H3)O(H)</chem>	0.013391
IL7	<chem>O(C(H3)C(H3))</chem>	0.131544
IL8	<chem>C(C(H3)H2)O(C(H3))</chem>	0.450272

Table 3.4. Core attribute reaction families and counts

REACTION FAMILY	REACTION COUNT
ACYCLICTHERMALCRACKING	822
ALCOHOLDEHYDRATION	8
ALDEHYDEHYDROGENATION	7
CYCLICTHERMALCRACKING	813
DECARBONYLATION	11
DECARBOXYLATION	5
RINGOPENING	149
SATURATION2H	40
GRAND TOTAL	1855

These feed structures were then used as the input for the reaction network generation routine in the in-house INGen software. The cores underwent pyrolysis reactions resulting in the following number of reactions and reaction families (Table 3.4). These 1855 reaction resulted in a total of 1048 cores structures found in the effluent. The side chains and inter-core linkage structures were subjected to pyrolysis reaction routines, the results of which are presented in Table 3.5. These 39 reactions resulted in a total of 39 chain structures found in the effluent.

Table 3.5. Chain attribute reaction families and counts

REACTION FAMILY	REACTION COUNT
ACYCLICTHERMALCRACKING	25
ALCOHOLDEHYDROGENATION	3
ALDEHYDEHYDROGENATION	3
CYCLICTHERMALCRACKING	1
DECARBONYLATION	3
HDS_4H	4
GRAND TOTAL	39

The reaction network and initial concentrations were used to construct an ODE based model for the pyrolysis of the sub-bituminous coal, but in order to tune the rate parameters to the effluent properties, these attributes would need to be reconstructed into concentrations of molecular species. Largely, this reconstruction is accomplished by the juxtaposition of the attributes. For instance, there is x probability that a single aromatic ring exists, y probability that it does not have an inter-core link, and z probability that the side chain has one double bond. The concentration of such a species would be $x \cdot y \cdot z$, but, it was determined that a full set of individual species properties was necessary for the CFD calculation. Although a given juxtaposition calculation could be performed in under a second, the number of calculations necessary, and the continued call for these calculations through the CFD mesh was unusable.

The original call for using the attribute reaction model to supply synthetic data for the lumped model would necessitate a well-tuned ARM model. Without a detailed analysis of the Tar and Solid products coming from the experimental reactor, such a model was not possible without making assumptions that would negate the effect of creating the model in the first place. These unfortunate facts along with the skewing of the timeframe for the successful creation of the lumped model led to an eventual abandonment of the ARM methodology for this project.

3.2 Results

Using the multistep, combined, lumped approach the set of reactions, coefficients, and Arrhenius parameters were finalized (Table 3.6) and sent on to the CFD team. The restrictions were lessened for the optimization engine of the tar lump by decreasing the effectiveness of its weight (by increasing α) on the objective function. In addition, a tighter fit was permitted for the CO and H₂ lumps by decreasing their weights (α). The form of the objective function is listed below along with the weighting factors listed in Table 3.7.

$$OBJ = \sum_i^n \left(\frac{exp_i - mdl_i}{\alpha exp_i} \right)^2 \quad (3.1)$$

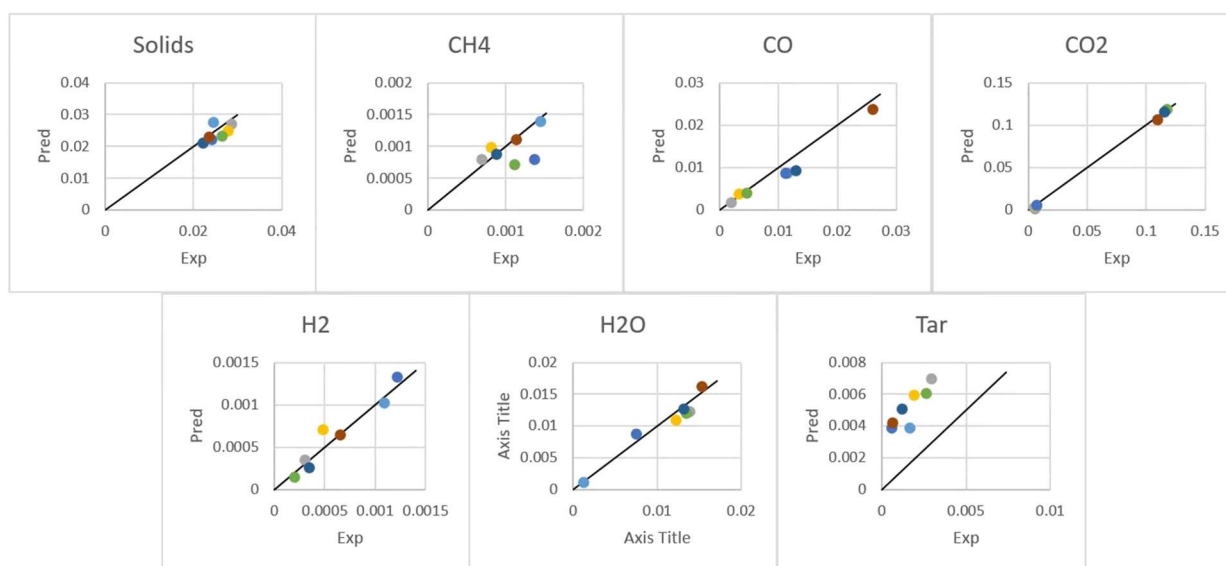
Upon the completion of tuning, the overall model displayed a much better fit than the previous quarter's work for all seven data sets (which included the reactive CO₂ environment). Below you can see from (a) the individual parity plots (a visual measure of predicted versus experimental data) that there is good agreement (save for the Tar). When viewed as a whole (b), wherein each lump is plotted on together, the points lie nicely along the 45° line, signifying a successful model. Previous attempts showed the CO₂ lumps far from that line of parity.

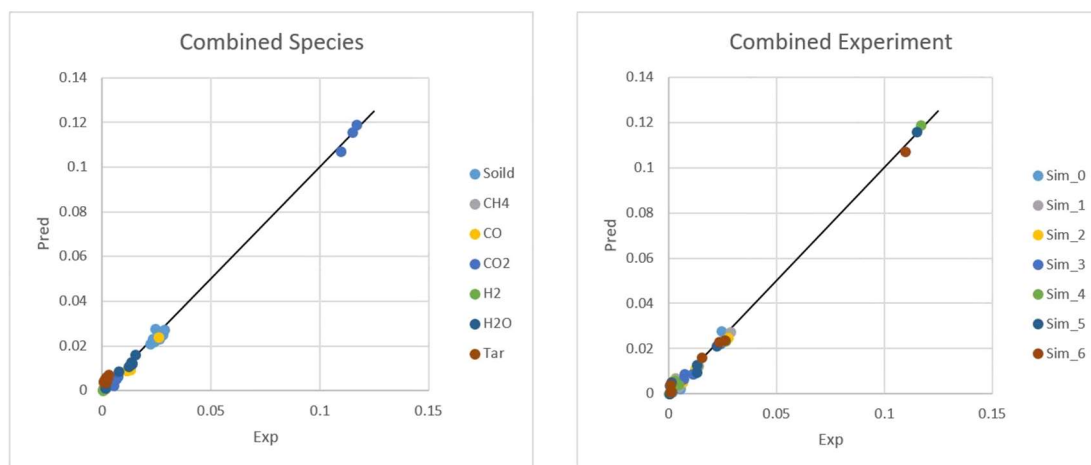
Table 3.6. Final reaction set

#	Reaction	Type	logA	E*
1	Coal $\rightarrow$ 25.8 CharH + CH ₄ + 8.2 CO + 1.9 CO ₂ + 10.8 H ₂ + 0.11 H ₂ O	Pyrolysis	4.70	24.20
2	Coal $\rightarrow$ 4.7 Tar + 1.3 CO ₂ + 4.4 H ₂ O	Pyrolysis	-0.37	1.69
3	Tar $\rightarrow$ 11.5 CharC + 1.5 CH ₄ + 0.45 H ₂ + 1.1H ₂ O	Condensation	2.22	11.39
4	CharH $\rightarrow$ 2 CharC + $\frac{1}{2}$ H ₂	Pyrolysis	4.77	29.48
5	CharC + H ₂ O $\rightarrow$ CO + H ₂	Gasification	-0.22	3.37
6	CharC + CO ₂ $\rightarrow$ 2 CO	Gasification	-0.0020	0.030
7	CharC + 2 H ₂ $\rightarrow$ CH ₄	Gasification	-6.77	9.93
8	CO + H ₂ O $\leftrightarrow$ CO ₂ + H ₂	Water-Gas-Shift	2.45	1.22

Table 3.7. The lump parameters with weighting factors.

Lump	MW (g/mol)	Density (g/L)	OBJ Lump	OBJ Weight α
Coal	1000	1300	Solid	1
CharH (C ₂ H)	25	2000		
CharC (C)	12	2000		
Tar	182	---	Tar	100
H ₂ O	18	---	H ₂ O	1
CH ₄	16	---	CH ₄	1
CO	28	---	CO	0.1
CO ₂	44	---	CO ₂	1
H ₂	2	---	H ₂	0.1

**Fig. 3.5.** Parity plots for coal modeling for each species. The 45° line demonstrates how close the actual data (abscissa) matches with the model (ordinate).



(a)

(b)

	Temp °C	Environmental Gas	Fuel
Sim_0	900	N ₂	Dry Coal
Sim_1	700	N ₂	Wet Coal
Sim_2	800	N ₂	Wet Coal
Sim_3	900	N ₂	Wet Coal
Sim_4	700	CO ₂	Wet Coal
Sim_5	800	CO ₂	Wet Coal
Sim_6	900	CO ₂	Wet Coal

Fig. 3.6. Parity plots for coal modeling for (a) combination of the species and (b) the combination for different conditions. The 45° line demonstrates how close the actual data (abscissa) matches with the model (ordinate). The table corresponds to the cases listed in the legend.

3.3 Model analysis

Following our completion of the reaction model, further hypothetical model tests were considered by changing the coefficients in the devolatilization and condensation reactions. We studied the effect of removing some of the CH₄ from the Coal → CharH and Tar → CharC reactions and rebalancing the equations. Table 3.8 presents the general set of reactions and summarizes the coefficients and Arrhenius parameters.

For the first coefficient change, Case 2, 0.5 was removed from the coefficient of CH₄ of both Rxn 1 and Rxn 3. For Rxn 1, the mass and element balance was then corrected by adjusting the coefficients for CharH (C₂H) and H₂. For Rxn 3, the mass balanced was fixed by adjusting CharC (C) and H₂. For Case 3, only 0.25 CH₄ was removed from the Rxn 1 and Rxn 3 baseline coefficients and adjusted the other parameters appropriately. Case 4 considered the removal of 0.5 CH₄ from Rxn 1 and Rxn 3 baseline coefficients, but rather than using H₂ to achieve mass and element balance, we affected the H₂O content for Rxn 1. By raising H₂O, it was necessary to cut CO₂ to account for the oxygen and performed further balancing steps (keeping the coefficient for CO constant). Finally, Case 5 also removed 0.5 CH₄ from the Rxn 1 and Rxn 3 baseline coefficients, used H₂O as the first step to correct for hydrogen in Rxn 1, but instead of correcting for Oxygen with CO₂ (as in Case 4), we used CO while holding CO₂ coefficient constant.

Table 3.8. Reaction equations and corresponding type.

#	Reaction	Type
1	$\text{Coal} \rightarrow a \text{ CharH} + b \text{ CH}_4 + c \text{ CO} + d \text{ CO}_2 + e \text{ H}_2 + f \text{ H}_2\text{O}$	Pyrolysis
2	$\text{Coal} \rightarrow g \text{ Tar} + h \text{ CO}_2 + i \text{ H}_2\text{O}$	Pyrolysis
3	$\text{Tar} \rightarrow j \text{ CharC} + k \text{ CH}_4 + l \text{ H}_2 + m \text{ H}_2\text{O}$	Condensation
4	$\text{CharH} \rightarrow 2 \text{ CharC} + \frac{1}{2} \text{ H}_2$	Pyrolysis
5	$\text{CharC} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$	Gasification
6	$\text{CharC} + \text{CO}_2 \rightarrow 2 \text{ CO}$	Gasification
7	$\text{CharC} + 2 \text{ H}_2 \rightarrow \text{CH}_4$	Gasification
8	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	Water-Gas-Shift

Table 3.9. Coefficients for reactions shown in Table 3.8

coefficient	Case 1	Case 2	Case 3	Case 4	Case 5
<i>a</i>	26.9	27.15	27.03	27.4	27.65
<i>b</i>	1.4	0.9	1.15	0.9	0.9
<i>c</i>	6.6	6.6	6.6	6.6	5.6
<i>d</i>	1.9	1.9	1.9	1.4	1.9
<i>e</i>	8.5	9.38	8.94	8.25	8.13
<i>f</i>	1.1	1.1	1.1	2.1	2.1
<i>g</i>	4.7	4.7	4.7	4.7	4.7
<i>h</i>	1.3	1.3	1.3	1.3	1.3
<i>i</i>	4.4	4.4	4.4	4.4	4.4
<i>j</i>	11.5	12	11.75	12	12
<i>k</i>	1.5	1.0	1.25	1.0	1.0
<i>l</i>	0.4	1.4	0.9	1.4	1.4
<i>m</i>	1.1	1.1	1.1	1.1	1.1

Table 3.10. Arrhenius parameters for reactions shown in Table 3.8.

Case 1		Case 2		Case 3		Case 4		Case 5	
logA	E*	logA	E*	logA	E*	logA	E*	logA	E*
3.796	20.019	2.559	14.868	3.264	17.572	2.805	15.567	2.63	14.493
0.72	6.786	1.637	10.468	1.232	8.962	1.623	10.229	1.675	10.579
0.73	5.216	1.281	6.673	1.371	7.814	1.617	8.397	1.695	8.633
11.595	65.706	14.268	81.854	14.298	81.129	11.342	71.41	13.292	102.624
8.477	31.654	10.656	43	10.966	44.615	13.72	58.779	14.32	61.751
3.809	11.631	3.743	12.516	4.566	15.41	5.905	22.055	6.055	22.833
-3.987	46.84	-3.811	16.094	-7.084	41.208	-6.032	56.103	-4.918	9.785
3.8	7.082	5.024	12.965	4.439	10.343	5.39	14.808	4.777	12.139

Table 3.11. Objective function values for the coefficient trials

Case	OBJ
Case 1	1.19
Case 2	1.41
Case 3	1.18
Case 4	1.29
Case 5	1.26

The best fit occurred when the coefficients were slightly decreased for CH₄ for both Rxn 1 and Rxn 3 (lower is better). However, this fit was nominally close to the original fit which obtained its values from studying literature produced results of similar cases, and therefore we are comfortable using the baseline values.

In order to further evaluate models, a statistical analysis was performed on each of the models fitness and likelihood. It was decided to use the previous five cases as starting points, and tune the model using equal weights on all the components. The final results are shown in the appendix based on the tuning. As can be seen from the statistics summary in Table 3.12, the objective function value was lowest for our initial baseline coefficients and it also had the lowest valued P-Test. The P-Test helps to test the model validity and compare various models. As all the models had the same structure, we did not anticipate great differences in the P-Test. The lowest R² value was actually attributed to the second case, but they were all fairly close to one another. The parity plots are nearly identical, as shown in Fig. 3.7. Therefore, we have concluded that the form of the model is correct, and that for the range of conditions we had data for, the model fitness is excellent.

Table 3.12. Statistic summary for the coefficient trials

Case	P-Test	OBJ	R ²
Case 1	9.68E-16	1.81	6.74
Case 2	6.80E-14	2.38	6.66
Case 3	1.14E-15	1.83	6.74
Case 4	6.27E-15	2.04	6.71
Case 5	1.20E-15	1.84	6.74

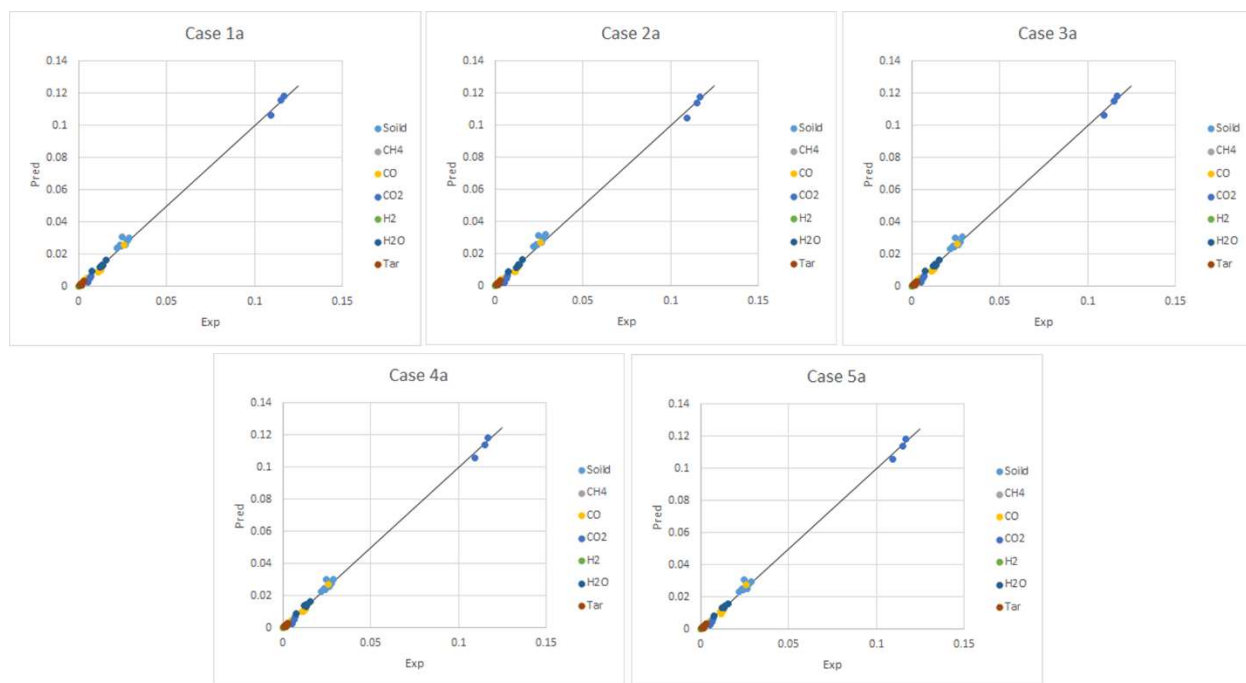


Fig. 3.7. Parity plots for cases 1a-5a.

4. CFD Simulations

4.1 Methods

The Multiphase Flow with Interphase Exchanges (MFiX) software package was employed for the development of a computational modeling strategy to simulate coal gasification on sand in the Task 1 bubbling fluidized bed reactor. The multi-fluid modeling functionality of MFiX was invoked for the calculation of flow quantities. The Task 3 chemistry model was applied to simulations of coal gasification under atmospheres of nitrogen and carbon dioxide at 700, 800, and 900 °C. Two additional chemistry models, the METC Gasifier Advanced Simulation Model (MGAS) and the C3M HPTR pyrolysis model (HPTR), were also applied to the system of interest to assist in improving the Task 3 model. Kinetic and stoichiometric parameters for both the MGAS and HPTR models were taken from the Carbonaceous Chemistry for Computational Modeling (C3M) software package using the Powder River Basin subbituminous coal fuel setting. Because the HPTR model is solely for the pyrolysis reaction the remaining reaction model were taken from the MGAS model.

Each of the three chemistry models was implemented into 2-D Cartesian simulations of the reactor described by Task 1. Those simulations were performed for a total of ten seconds, with the flow of coal being initiated after 2 seconds of simulation time. Delayed injection of coal was used to allow the bed material to develop a realistic hydrodynamic condition prior to fuel introduction. Thermochemical properties for gas phase species were taken from the Burcat and Ruscic database which is the default in MFiX. Properties for pseudo-species, such as coal and ash, were taken from C3M.

Time series of all effluent gas mass fractions were inspected following completion of the simulations to ensure that a steady effluent composition had developed during the allotted simulation time. Those inspections revealed that cases where the operating temperature was 800 and 900 °C were able to achieve a steady effluent composition; however, the 700 °C simulations still exhibited local transience in some effluent mass fractions. The 700 °C simulations were extended for an additional two seconds, which proved sufficient to attain a stable effluent composition.

4.2 Results

Table 4.1 and Table 4.2 show comparisons of MGAS-simulated gas mole fractions on a N_2/H_2O /Tar-free basis with those observed in the experiments, along with the relative errors of the simulated results. Inspection of Table 4.1 and Table 4.2 shows that use of the MGAS chemistry model produces significant over-prediction of methane when compared to the experiments. Examination of the model equations reveals that the tar-cracking reaction stoichiometry heavily favors production of methane.

Table 4.3 and Table 4.4 show comparisons of the experimental and HPTR-simulated gas mole fractions on a N_2/H_2O /Tar free basis. It can be seen from Tables 3 and 4 that use of the HPTR pyrolysis model in place of the MGAS pyrolysis and tar-cracking models produces marked improvement in quantitative agreement between the simulations and the experiments. Inspection of Table 3 reveals that the HPTR model nearly exactly recovers the experimental gas composition for nitrogen gasification at 900 °C; however, agreement diminishes with decreasing temperature, as the carbon monoxide and carbon dioxide production trends diverge at the lower temperatures. The information contained in Table 4 shows that, under carbon dioxide, the HPTR model exhibits progressively worsening agreement in carbon dioxide and carbon monoxide prediction as temperature increases. This observation may be attributed to insufficient activity of the CO_2 -char gasification reaction predicted by the model, an assertion that is substantiated by consistent, monatomic over-prediction of carbon dioxide production and under-prediction of carbon monoxide production.

Table 4.1. Experimental and Simulated Gas Mole Fractions for MGAS under N₂

<i>Spec.</i>	700 °C			800 °C			900 °C		
	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>
H ₂	39.97	29.44	26.34 %	44.24	29.44	33.46 %	47.65	29.44	38.21 %
CO	14.77	17.23	16.63 %	21.10	17.23	18.34 %	31.87	17.24	45.93 %
CH ₄	11.88	46.18	288.76 %	10.01	46.18	361.57 %	6.95	46.17	564.83 %
CO ₂	33.38	7.15	78.58 %	24.65	7.15	71.00 %	13.53	7.15	47.18 %

Table 4.2. Experimental and Simulated Gas Mole Fraction for MGAS under CO₂

<i>Spec.</i>	700 °C			800 °C			900 °C		
	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>
H ₂	3.28	4.04	23.41 %	5.19	4.07	21.50 %	8.49	4.03	52.55 %
CO	5.36	2.37	55.79 %	13.89	2.39	82.76 %	24.35	2.38	90.23 %
CH ₄	2.32	6.34	173.08 %	1.65	6.39	286.09 %	1.85	6.32	241.37 %
CO ₂	89.04	87.24	2.02 %	79.27	87.14	9.94 %	65.31	87.27	33.63 %

Table 4.3. Experimental and Simulated Gas Mole Fractions for HPTR under N₂

<i>Spec.</i>	700 °C			800 °C			900 °C		
	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>
H ₂	39.97	32.94	17.58 %	44.24	41.69	5.76 %	47.65	46.29	2.86 %
CO	14.77	32.34	118.94 %	21.10	30.99	46.89 %	31.87	30.30	4.94 %
CH ₄	11.88	10.82	8.93 %	10.01	10.14	1.39 %	6.95	9.78	40.88 %
CO ₂	33.38	23.90	28.40 %	24.65	17.17	30.35 %	13.53	13.63	0.72 %

Table 4.4. Experimental and Simulated Gas Mole Fractions for HPTR under CO₂

<i>Spec.</i>	700 °C			800 °C			900 °C		
	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>	<i>Exp.</i>	<i>Sim.</i>	<i>Rel. Err.</i>
H ₂	3.28	2.87	12.55 %	5.19	4.80	7.47 %	8.49	6.38	24.84 %
CO	5.36	2.82	47.44 %	13.89	3.58	74.19 %	24.35	4.22	82.65 %
CH ₄	2.32	0.94	59.49 %	1.65	1.17	29.40 %	1.85	1.35	27.10 %
CO ₂	89.04	93.38	4.87 %	79.27	90.45	14.10 %	65.31	88.04	34.81 %

Table 4.5 and Table 4.6 show comparisons of the experimental and Task 3 model simulated gas mole fraction on a N₂/H₂O/Tar free basis. Inspection of Table 5 reveals good agreement between the experiments and simulations in the case of hydrogen production; however, methane formation is consistently over-predicted. Table 6 shows that carbon monoxide production is consistently under-predicted for Task 3 model simulations of the carbon dioxide gasification systems. Again, this observation may be attributed to insufficient activity of the CO₂-char gasification reaction predicted by the model.

Comparative assessment of the models was achieved by inspecting the mean relative error for each investigated system. Table 4.7 shows the mean relative error for each model under each of the investigated atmospheres and temperatures. Inspection of Table 4.7 reveals that the HPTR model provides the most accurate results of all of the investigated models for each operating condition; a finding most likely attributable to the specialized method used in the determination of the pyrolysis reaction stoichiometric coefficients. Detailed inspection of Tables 4 and 6 reveals that the Task 3 model does provide more accurate results in the determination of carbon monoxide production for systems under carbon dioxide. That observation indicates that the kinetic rate expression and parameters employed by the Task 3 model for the

determination of CO₂-char gasification rate are more applicable to the system of interest than those used by the HPTR, i.e. MGAS, models. The aggregate of these results suggest that while the HPTR model does outperform the Task 3 model for each investigated case, this finding is likely the result of the HPTR pyrolysis model accuracy propagating through the simulated solution. It follows that the Task 3 model may experience improved accuracy through tuning the pyrolysis stoichiometry, using the HPTR pyrolysis coefficients as a starting point.

After the HPTR model was identified as the most suitable for simulating the system of interest, the results for the HPTR cases were further analyzed to better understand the modeling technique. Fig. 4.1 shows time-averaged axial profiles of gas species mole fractions for the HPTR model simulations under (a) nitrogen and (b) carbon dioxide, respectively, for three operating temperatures. Inspection of the figures reveals that both the nitrogen and carbon dioxide atmospheres produce very similar results at all temperatures, with the obvious exception of the fluidizing gas species. It can be seen in these figures that each system experiences surge in gas evolution in the immediate vicinity of the coal injection site, followed by slight dilution by the gas carrier stream. This behavior becomes increasingly pronounced as temperature increases, which is likely caused by the increased permanent gas production of the HPTR pyrolysis stoichiometry with increasing temperature.

Table 4.5. Experimental and simulated gas mole fractions for Task 3 model under N₂

Spec.	700 °C			800 °C			900 °C		
	Exp.	Sim.	Rel. Err.	Exp.	Sim.	Rel. Err.	Exp.	Sim.	Rel. Err.
H ₂	39.97	37.87	5.23 %	44.24	45.72	3.35 %	47.65	56.68	18.96 %
CO	14.77	22.46	52.02 %	21.10	27.60	30.81 %	31.87	26.01	18.41 %
CH ₄	11.88	27.11	128.23 %	10.01	16.53	65.18 %	6.95	9.54	37.42 %
CO ₂	33.38	12.56	62.39 %	24.65	10.15	58.83 %	13.53	7.77	42.60 %

Table 4.6. Experimental and simulated gas mole fractions for Task 3 model under CO₂

Spec.	700 °C			800 °C			900 °C		
	Exp.	Sim.	Rel. Err.	Exp.	Sim.	Rel. Err.	Exp.	Sim.	Rel. Err.
H ₂	3.28	6.07	85.42 %	5.19	10.02	93.03 %	8.49	16.22	90.97 %
CO	5.36	3.68	31.27 %	13.89	6.09	56.13 %	24.35	7.47	69.30 %
CH ₄	2.32	4.35	87.26 %	1.65	3.60	117.52 %	1.85	2.71	46.22 %
CO ₂	89.04	85.89	3.54 %	79.27	80.29	1.29 %	65.31	73.60	12.70 %

Table 4.7. Mean relative errors for each chemistry model at each operating condition

Model	Atmosphere	Temperature		
		700 °C	800 °C	900 °C
MGAS	N ₂	102.58 %	121.09 %	174.04 %
	CO ₂	63.57 %	100.07 %	104.45 %
HPTR	N ₂	43.46 %	21.10 %	12.35 %
	CO ₂	31.09 %	31.29 %	42.35 %
Task 3	N ₂	61.97 %	39.54 %	29.35 %
	CO ₂	51.87 %	66.99 %	54.80 %

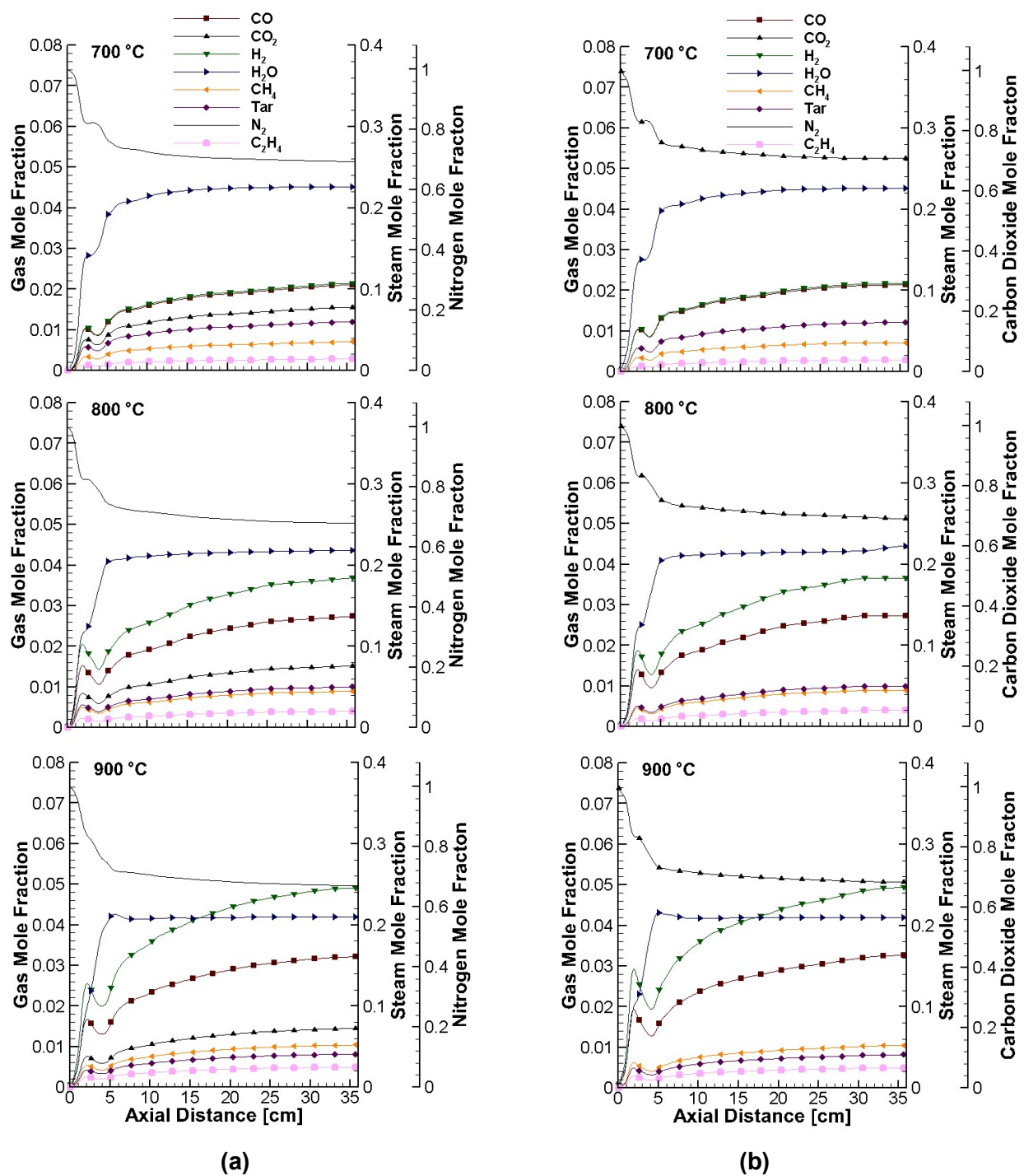


Fig. 4.1. Axial profiles of gas mole fractions for HPTR predictions under (a) N_2 and (b) CO_2

Fig. 4.2(a-b) shows time-averaged contour plots of gas volume fraction for the HPTR simulations under nitrogen and carbon dioxide, respectively. Fig. 4.3(a-b) depicts time-averaged contour plots of sand volume fraction for the HPTR simulations under nitrogen and carbon dioxide, respectively. Fig. 4.4(a-b) shows time-averaged contour plots of coal volume fraction for the HPTR simulations under nitrogen and carbon dioxide, respectively. The aggregate information conveyed by these figures is that both the nitrogen and carbon dioxide systems exhibit nearly identical hydrodynamic behavior at each operating temperature. Inspection of Fig. 4.2 reveals the presence of a gas void in the vicinity of the injection site.

Fig. 4.4 reveals the quantity of coal particles diminishing within the bed region with increasing temperature; however, this observation is likely exacerbated at the 700 °C operating temperature by the time-averaging region being 10-12 s, to allow for a steady effluent composition to develop, instead of the 8-10 s used for the 800 and 900 °C operating temperatures. Comparison the operating temperatures for each atmosphere reveals slightly less coal material in the bed region at the higher temperature, which is likely caused by increased entrainment brought about by the higher gas velocity experienced by the 900 °C systems.

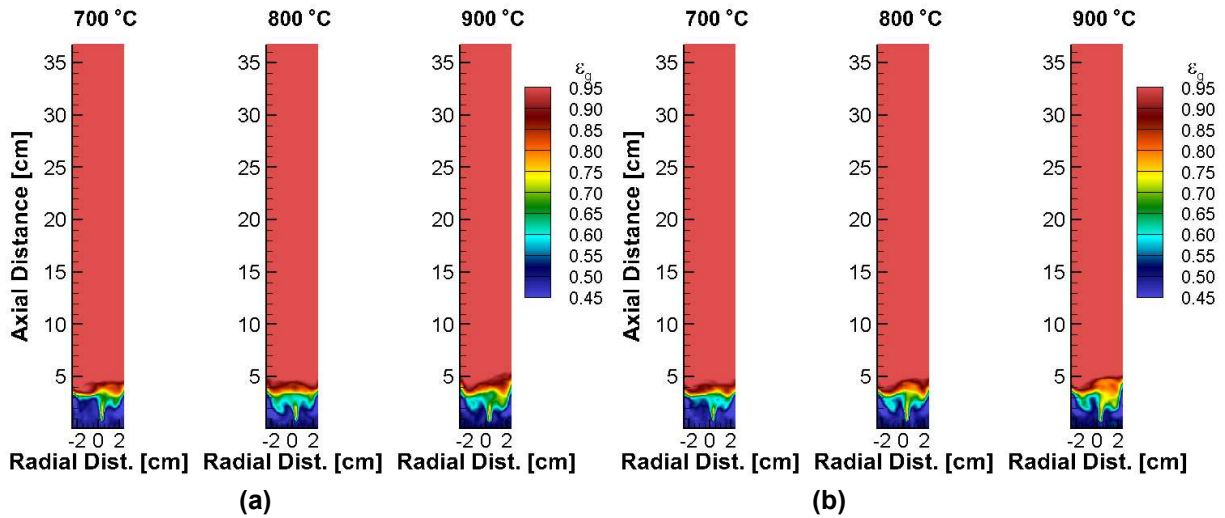


Fig. 4.2. Contours of gas volume fraction for HPTR predictions under (a) N₂ and (b) CO₂

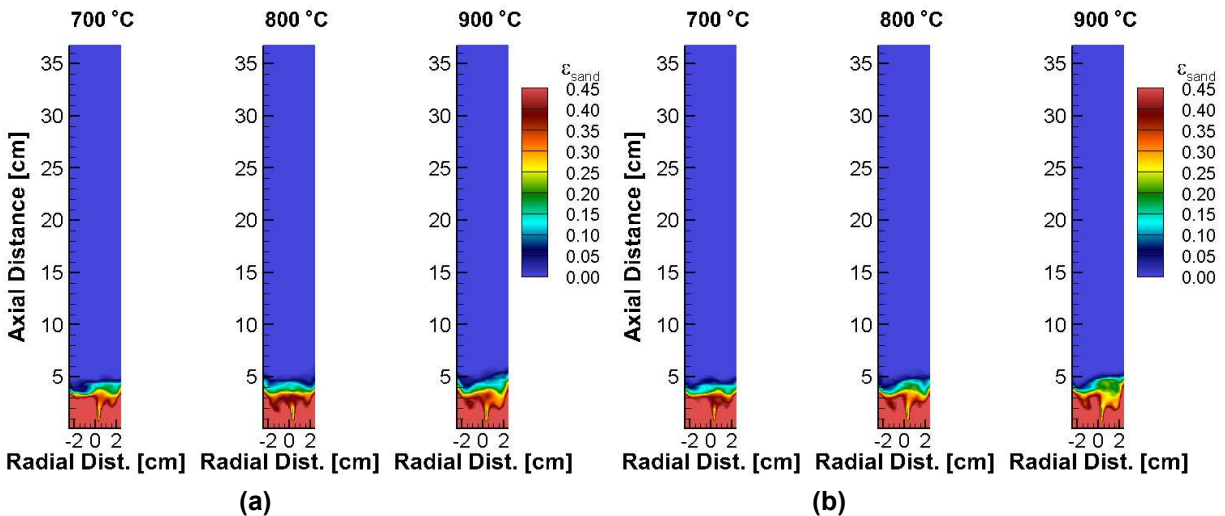


Fig. 4.3. Contours of sand volume fraction for HPTR predictions under (a) N₂ and (b) CO₂

Fig. 4.5(a-b) depicts time-averaged contour plots of drying reaction rate for the HPTR simulations under nitrogen and carbon dioxide, respectively. Inspection of the figure reveals that similar drying behavior is experienced under both investigated atmospheres. It can be observed from these figures that moisture release is most prevalent in the immediate vicinity of the injection site and that the maximal rate of the drying process increases with increasing temperature. Fig. 4.5 also shows increased activity of the drying reaction at the top of the bed for the lower two operating temperatures. A likely cause for this behavior is that the moisture content of the coal material is more quickly depleted at the 900 °C temperature.

Fig. 4.6(a-b) shows time-averaged contour plots of pyrolysis reaction rate for the HPTR simulations under nitrogen and carbon dioxide, respectively. Inspection of these figures shows that the bulk of the pyrolysis process is confined to the bed with diminishing activity along the axial length of the vessel. Furthermore, the pyrolysis reaction of the HPTR model appears to be largely temperature independent, which is likely the result of the low activation energy of 4.69 kcal/mol used in the kinetic rate expression. Comparison of Fig. 4.6 reveals very similar pyrolysis behavior is experienced under both atmospheres.

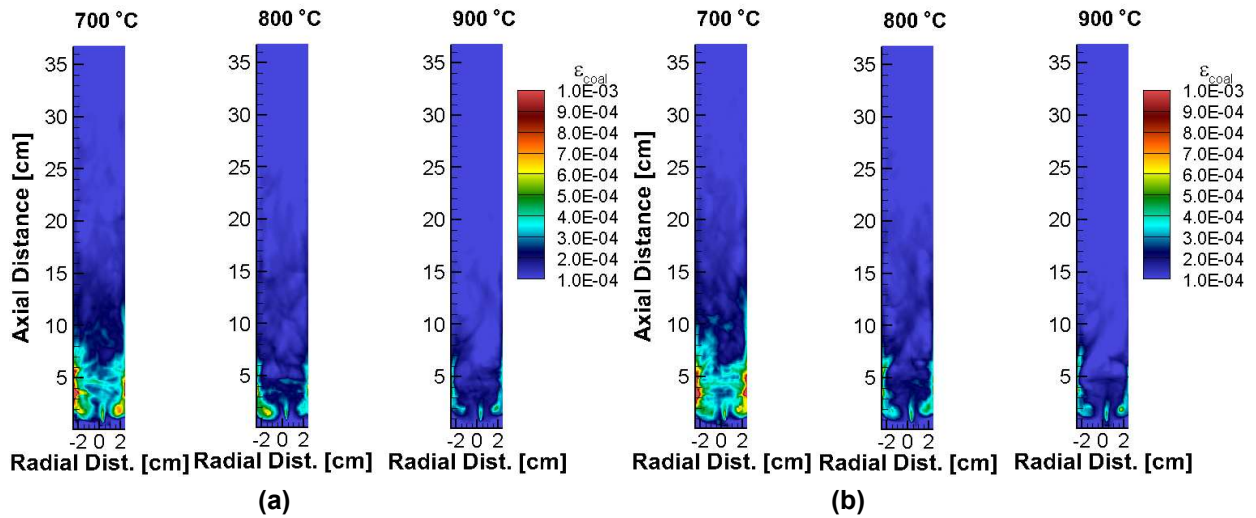


Fig. 4.4. Contours of coal volume fraction for HPTR predictions under (a) N₂ and (b) CO₂

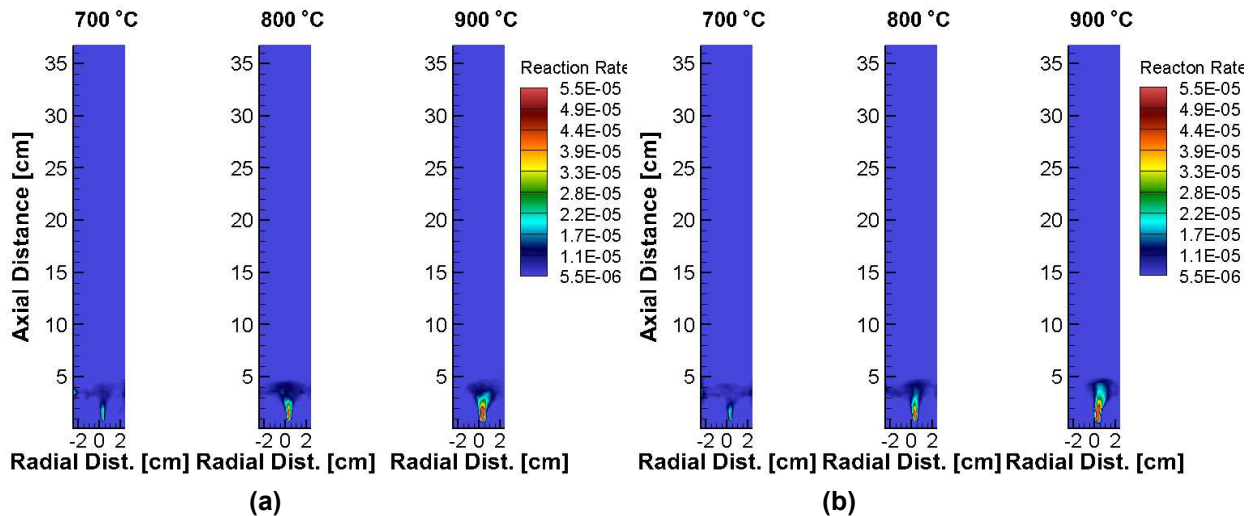


Fig. 4.5. Contours of drying reaction rate for HPTR predictions under (a) N₂ and (b) CO₂

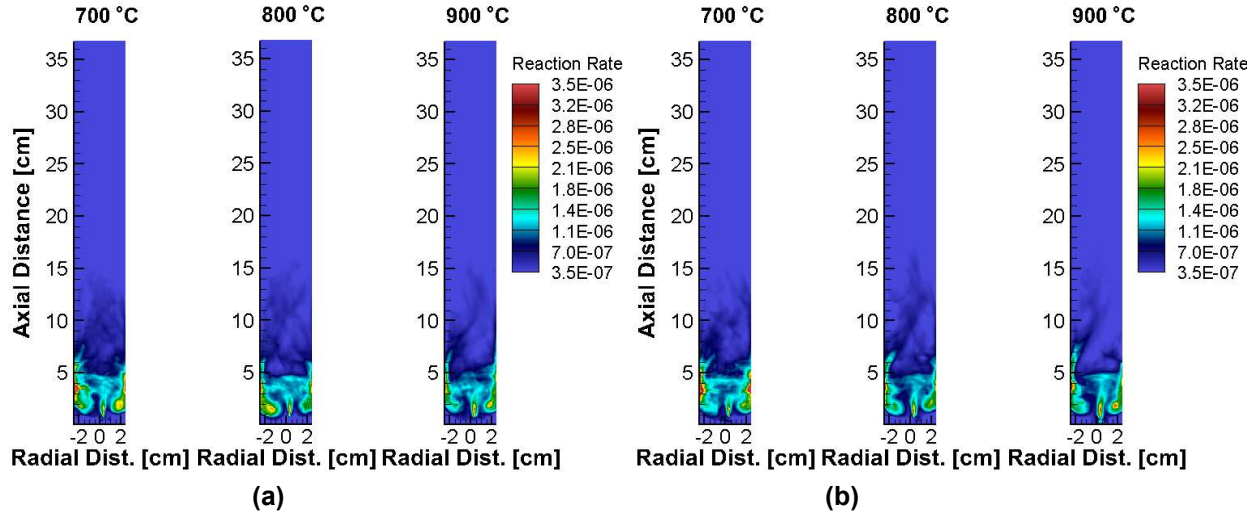


Fig. 4.6. Contours of pyrolysis reaction rate for HPTR predictions under (a) N_2 and (b) CO_2

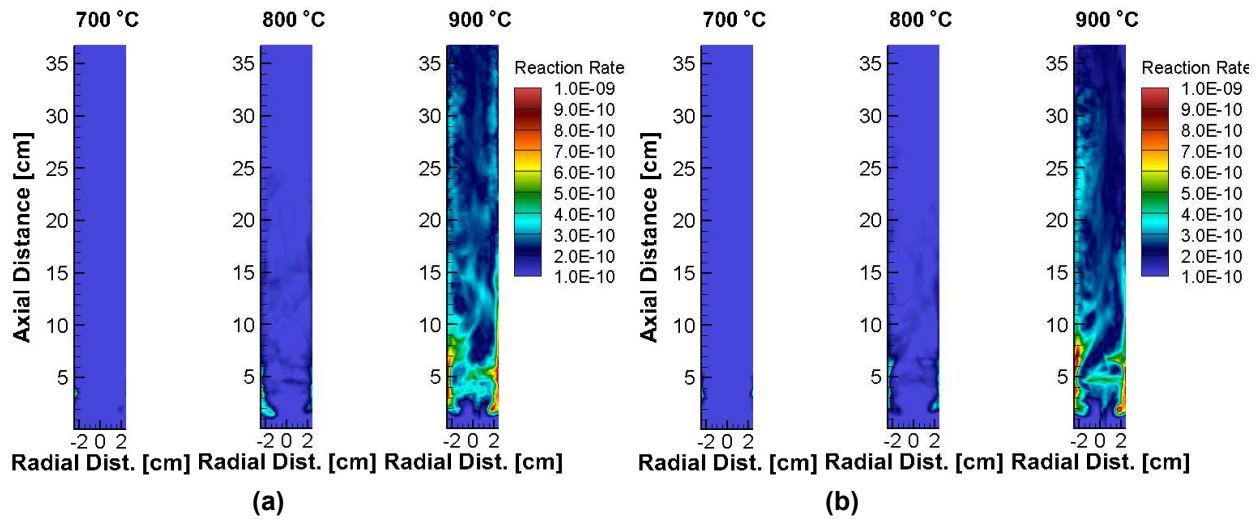


Fig. 4.7. Contours of steam gasification rate for HPTR predictions under (a) N_2 and (b) CO_2

Fig. 4.7(a-b) depicts time-averaged contour plots of the steam gasification reaction rate for the HPTR simulations under nitrogen and carbon dioxide, respectively. Inspection of the figure reveals similar activity in steam gasification is experienced under both of the investigated atmospheres. It can be seen in these figures that very little steam gasification activity is apparent at the 700 and 800 °C temperatures. While the 900 °C operating temperature does exhibit some activity in steam gasification comparison, of the reaction rates in shown in Fig. 4.7 to those of the drying and pyrolysis reactions shows that initial stage reactions are dominant.

Fig. 4.8(a-b) show time-averaged contour plots of the carbon dioxide gasification reaction rate for the HPTR simulations under nitrogen and carbon dioxide, respectively. The behavior exhibited by the carbon dioxide gasification reaction is similar to that of the steam gasification reaction in that very little reaction activity is apparent at the 700 and 800 °C temperatures. At the 900 °C operating temperature, some activity of the carbon dioxide gasification reaction is apparent under nitrogen; however, the highest rates are observed under carbon dioxide. Again,

while the 900 °C operating temperature under carbon dioxide does exhibit activity in carbon dioxide gasification, comparison of the reaction rates shown in Fig. 4.5 and Fig. 4.6 to those of the drying and pyrolysis reactions shows that initial stage reactions are dominant over carbon dioxide gasification as well.

Fig. 4.9(a-b) depicts time-averaged contour plots of the water-gas shift reaction rate for the HPTR simulations under nitrogen and carbon dioxide, respectively. It can be seen from the figures that some forward water-gas shift is experienced by the nitrogen systems; while the direction of water-gas shift swings from forward to reverse as temperature increases for the carbon dioxide systems.

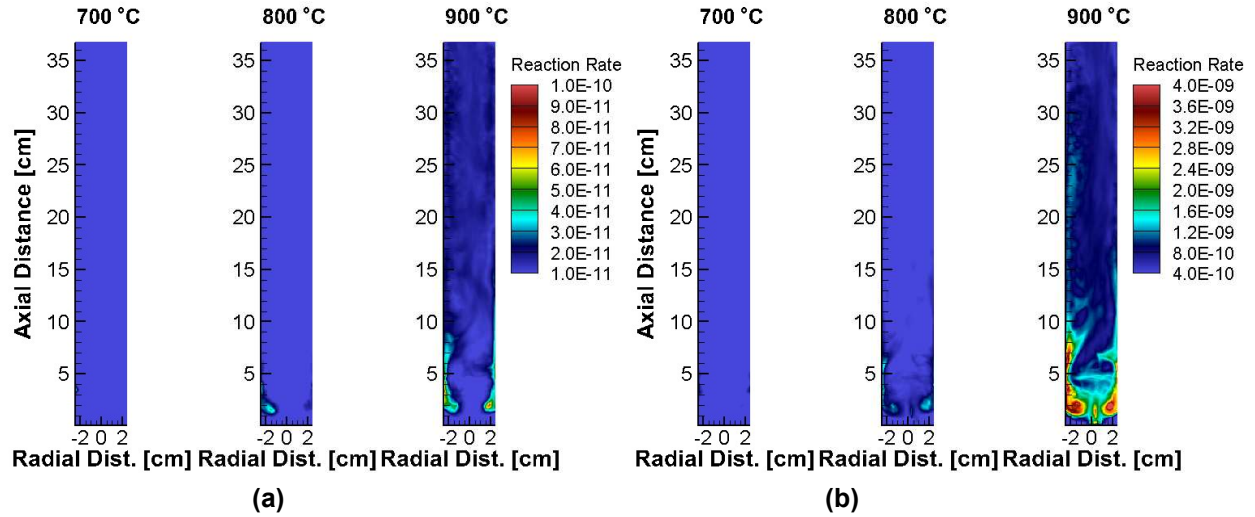


Fig. 4.8. Contours of CO₂ gasification rate for HPTR predictions under (a) N₂ and (b) CO₂

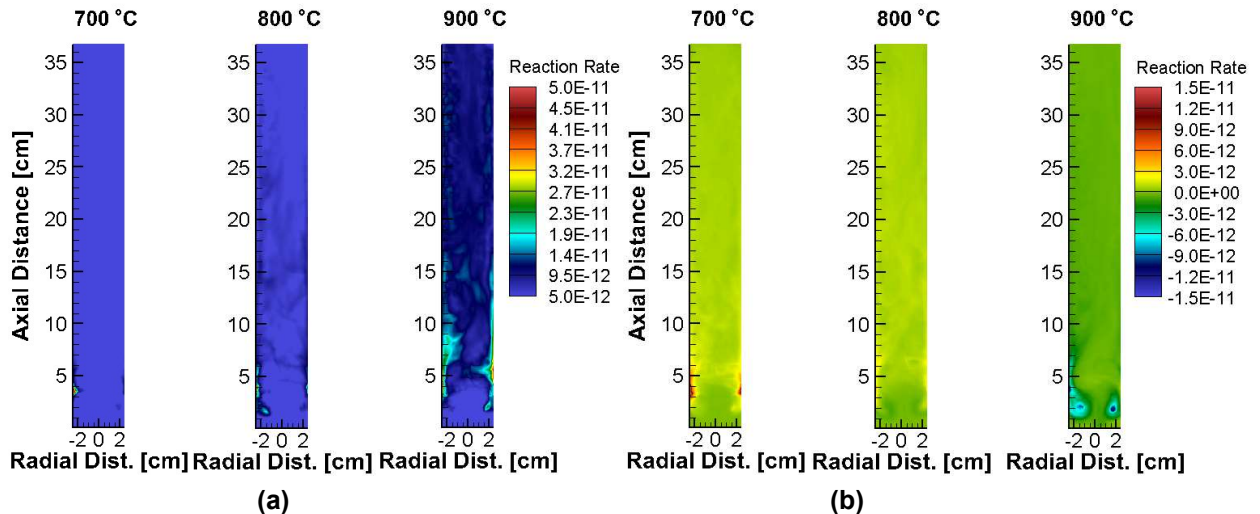


Fig. 4.9. Contours of water-gas shift rate for HPTR predictions under (a) N₂ and (b) CO₂

5. Conclusions

In this report we present evidence of the investigation of red mud as an effective gasification catalyst for conversion of coal and coal/biomass mixtures to synthesis gas. The report includes coal gasification in the presence of steam, carbon dioxide, coal/biomass mixtures and combinations thereof to produce synthesis gas of high hydrogen content. It will be shown that reformulated red mud is a robust catalyst that does not lose its activity after several regenerations. It is an effective catalyst and destroys tars formed during coal gasification. Red mud catalyst also promotes water gas shift reaction resulting in a syngas rich in hydrogen.

When red mud was used to replace the silica sand for gasification of biomass and coal/biomass mixtures the gasification of corn stover on red mud produced very interesting results; unlike the gasification on the sand which formed clinker at 900 °C, no clinker formation was observed when red mud was used to replace the silica sand. Similar results were obtained when switchgrass and poplar wood feedstocks were also gasified on the red mud catalyst. It is interesting that although the red mud also contained silica, the presence of other oxides in the red mud prevented the formation of the eutectic mixture and therefore no clinker was formed in the process. The gasification using red mud in place silica sand for the coal/corn stover (90/10) and other biomass feedstocks (switchgrass, poplar wood) all showed improved yields of gaseous products at all temperatures.

For the pilot-scale experiments, reducing the amount of catalyst fed into the reactor from 1600 g to 800 g, while the coal feed rate was constant, changed the weight hourly space velocity (WHSV) from 0.625/h to 1.25/h. This change in WHSV greatly influenced the amount of organic compounds detected in the aqueous products. At WHSV of 0.625/h, the amount of organic compounds detected in the aqueous phase was less than 1% while when the WHSV was increased to 1.25/h, the organic compounds detected in the aqueous phase was 4.67%. Thus, it is clear that the control of the WHSV is a critical parameter in reducing the amount of tar formed during the gasification using red mud catalyst.

A reaction kinetics model was created based on the available experimental data. The model developed for gasification of coal in a neutral (nitrogen) and reactive (carbon dioxide) environment provided a good fit for the experimental data. The kinetics models were varied to determine the robustness and a verification and validation study helped identify the best model. The size of the model is usable for implementation in a computational fluid dynamics (CFD) code, and it captured and summarized the kinetics behind the raw gasification data very well.

The reaction kinetics model was implemented into the CFD code Multiphase Flow with Interphase eXchanges (MFiX). Detailed analysis of the HPTR simulations revealed that the drying and pyrolysis reactions were the dominant processes experienced by the systems, even when carbon dioxide was used as the fluidizing agent. Comparison of the HPTR model results for systems under carbon dioxide to those of the experiments demonstrated that carbon monoxide production is under-predicted by the model, while the quantity of carbon dioxide in the reactor effluent is over-predicted. This observation, coupled with the information conveyed by the contours of carbon dioxide gasification reaction rate, suggests that the HPTR model is under-predicting the activity of the carbon dioxide gasification reaction.

The outcome of this research has provided substantial evidence that red mud can be successfully used as a catalyst and improves the gasification of low rank coals to reduce the production of unwanted pollutants.

List of Tables

Table 2.1. Proximate and ultimate composition of coal and biomass feedstocks used for the gasification studies.....	4
Table 2.2. X-ray florescence analysis of fresh red mud.....	5
Table 2.3. Characteristics of formulated and original red mud catalyst.....	6
Table 2.4. Product yields in the gasification of as received coal (wet coal) and dried coal on red mud and wet coal on sand. Yields expressed as wt% moisture free basis.	12
Table 2.5. Coal gasification in nitrogen over red mud medium. Gas composition (mol %) for wet and dried coal gasification under N ₂ on red mud. Wet coal is defined as the “as-received coal”.	12
Table 2.6. Gas yield and composition of wet coal (24 wt% moisture) gasified on red mud catalyst and sand in nitrogen atmosphere. Ratios are on mole basis.	13
Table 2.7. Gas yield and compositions of wet and dry coal (<2 wt% moisture) gasified on red mud catalyst in nitrogen atmosphere.....	13
Table 2.8. Composition of gases (mol %) from coal gasification on RM in N ₂ and Steam.....	13
Table 2.9. Product yields of coal gasification (wt %) in steam and nitrogen.....	14
Table 2.10. Water content in the liquid formed during coal gasification on RM under steam.	14
Table 2.11. Product yields in the gasification of coal in nitrogen, carbon dioxide, steam and steam/carbon dioxide mixture on red mud.....	15
Table 2.12. Composition of major compounds (mol%) in coal gasification products at various temperatures in nitrogen and carbon dioxide on red mud.....	15
Table 2.13. Product yields on coal/corn stover (90/10) gasification on sand and red mud.....	17
Table 2.14. Composition of coal/corn stover gasification products (mole %) on sand and red mud.....	18
Table 2.15. Product yields of wet and dry coal/switchgrass (90/10) gasification on red mud	18
Table 2.16. Composition of gasification products (mol%) of coal/switchgrass (90/10) mixture on red mud.....	19
Table 2.17. Product yields of wet and dry coal/poplar wood (90/10) gasification on red mud	19
Table 2.18. Composition of gasification products (mol%) of coal/poplar wood on red mud.....	19
Table 2.19. Composition of gasification products of coal gasification on red mud catalyst (mole%)	20
Table 3.1. Core structures and probabilities in sub-bituminous coal	25
Table 3.2. Side chain structures and probabilities in sub-bituminous coal	26
Table 3.3. Inter-core linkage structures and probabilities in sub-bituminous coal	26
Table 3.4. Core attribute reaction families and counts.....	26
Table 3.5. Chain attribute reaction families and counts	27
Table 3.6. Final reaction set.....	28
Table 3.7. The lump parameters with weighting factors.....	28

Table 3.8. Reaction equations and corresponding type.....	30
Table 3.9. Coefficients for reactions shown in Table 3.8	30
Table 3.10. Arrhenius parameters for reactions shown in Table 3.8.	30
Table 3.11. Objective function values for the coefficient trials	30
Table 3.12. Statistic summary for the coefficient trials.....	31
Table 4.1. Experimental and Simulated Gas Mole Fractions for MGAS under N ₂	33
Table 4.2. Experimental and Simulated Gas Mole Fraction for MGAS under CO ₂	33
Table 4.3. Experimental and Simulated Gas Mole Fractions for HPTR under N ₂	33
Table 4.4. Experimental and Simulated Gas Mole Fractions for HPTR under CO ₂	33
Table 4.5. Experimental and simulated gas mole fractions for Task 3 model under N ₂	34
Table 4.6. Experimental and simulated gas mole fractions for Task 3 model under CO ₂	34
Table 4.7. Mean relative errors for each chemistry model at each operating condition.....	34
Table 0.1. Case 1a (equally weighted) parameters and coefficients.....	46
Table 0.2. Case 1a (equally weighted) statistics.....	46
Table 0.3. Case 2a (equally weighted) parameters and coefficients.....	47
Table 0.4. Case 2a (equally weighted) statistics.....	47
Table 0.5. Case 3a (equally weighted) parameters and coefficients.....	48
Table 0.6. Case 3a (equally weighted) statistics.....	48
Table 0.7. Case 4a (equally weighted) parameters and coefficients.....	49
Table 0.8. Case 4a (equally weighted) statistics.....	49
Table 0.9. Case 5a (equally weighted) parameters and coefficients.....	50
Table 0.10. Case 5a (equally weighted) statistics.....	50

List of Figures

Fig. 2.1. X-ray powder diffraction pattern of fresh red mud.....	4
Fig. 2.2. TGA of fresh Red Mud supplied by Sherwin Alumina Co LLC, (Gregory, TX).....	6
Fig. 2.3. Attrition properties of various red mud catalyst formulations.....	6
Fig. 2.4. Effect of catalyst regeneration on BET specific surface area.....	7
Fig. 2.5. Pore size and volume distribution of formulated fresh and regenerated red mud catalyst.....	7
Fig. 2.6. SEM of fresh and regenerated formulated catalysts (left) fresh catalyst; (right) regenerated catalyst.....	8
Fig. 2.7. Schematic diagram of bench scale fluidized bed reactor unit: 1- reactor, 2-furnace, 3- thermocouple, 4-mass flow controller, 5-jacketed air-cooled feeder tube, 6-hopper, 7-screw feeder, 8-computer, 9-heating tape, 10-hot gas filter, 11-reservoir, 12-condenser, 13- electrostatic precipitator, 14-AC power supply, 15-coalescing filter, 16-wet gas meter, 17-gas chromatograph.....	10
Fig. 2.8. Schematic of pilot plant fluidized bed gasification unit.....	10
Fig. 2.9. Clinker formation in silica sand at high temperature gasification of corn stover: a) fresh silica sand; b) clinker formation after gasification.....	17
Fig. 2.10. Effect of water feed rate into reactor on pilot scale gas composition.....	20
Fig. 3.1. The Wisser model of coal broken into attributes.....	23
Fig. 3.2. The Freudenberg model of lignin broken into attributes.....	24
Fig. 3.3. A representative cellulose molecule broken into attributes.....	24
Fig. 3.4. A representative hemicellulose molecule broken into attributes.....	24
Fig. 3.5. Parity plots for coal modeling for each species. The 45° line demonstrates how close the actual data (abscissa) matches with the model (ordinate).....	28
Fig. 3.6. Parity plots for coal modeling for (a) combination of the species and (b) the combination for different conditions. The 45° line demonstrates how close the actual data (abscissa) matches with the model (ordinate). The table corresponds to the cases listed in the legend.....	29
Fig. 3.7. Parity plots for cases 1a-5a.....	31
Fig. 4.1. Axial profiles of gas mole fractions for HPTR predictions under (a) N ₂ and (b) CO ₂	35
Fig. 4.2. Contours of gas volume fraction for HPTR predictions under (a) N ₂ and (b) CO ₂	36
Fig. 4.3. Contours of sand volume fraction for HPTR predictions under (a) N ₂ and (b) CO ₂	36
Fig. 4.4. Contours of coal volume fraction for HPTR predictions under (a) N ₂ and (b) CO ₂	37
Fig. 4.5. Contours of drying reaction rate for HPTR predictions under (a) N ₂ and (b) CO ₂	37
Fig. 4.6. Contours of pyrolysis reaction rate for HPTR predictions under (a) N ₂ and (b) CO ₂	38
Fig. 4.7. Contours of steam gasification rate for HPTR predictions under (a) N ₂ and (b) CO ₂	38
Fig. 4.8. Contours of CO ₂ gasification rate for HPTR predictions under (a) N ₂ and (b) CO ₂	39
Fig. 4.9. Contours of water-gas shift rate for HPTR predictions under (a) N ₂ and (b) CO ₂	39

Bibliography

- Alvarez, J.; Ordonez, S.; Rosal, R.; Sastre, H.; Diez, F.V., A new method for enhancing the performance of red mud as a hydrogenation catalyst, *Applied Catalysis A: General*, 180, 399-409 (1999).
- Boyle, E.J., Sams, W.N., Syamlal, M., and Cho, S.M., MFI Validation Studies December 1994 to November 1995, DOE/FETC-97/1042, National Energy Technology Laboratory, Department of Energy.
- Cakici, A.I., Yanik, J., Ucar, S. J., Utilization of red mud as catalyst in conversion of waste oil and waste plastics to fuel, *Mater Cycles Waste Manag.*, 6, 20-26 (2004).
- Cantera website, <http://code.google.com/p/cantera>.
- Echekki, T., Multiscale methods in turbulent combustion: strategies and computational challenges, *Comput. Sci. Discovery*, 2(1): 013001 1–40 (2009).
- Estejab,* B. and Battaglia, F., “Assessment of Drag Models for Geldart A Particles in Bubbling Fluidized Beds”, *ASME J. Fluids Eng.*, 138(3):031105, pp.1-12, 2016. doi:10.1115/1.4031490
- Estejab,* B., Nyendu,* G., Agblevor, F., and Battaglia, F., “Coal-biomass mixing characteristics in a bubbling fluidized bed of Geldart A particles”. *Chem. Eng. Res. Desg.*, 120(4), pp. 1-14 2017. doi:10.1016/j.cherd.2017.01.025
- Hindmarsh, A. C., ODEPACK, A Systematized Collection of ODE Solvers, in Stepleman, R. S. et al., editor, *Scientific Computing*, pp. 55–64, North-Holland, Amsterdam, 1983.
- Hou, Z., Bennett, C.A., Klein, M.T. and Virk, P.S., Approaches and Software Tools for Modeling Lignin Pyrolysis, *Energy Fuels*, 24 (1): 58-67 (2010).
- Joshi, P.V., Molecular and Mechanistic Modeling of Complex Process Chemistries. *Chemical Engineering*, Ph.D. Thesis, University of Delaware (1998).
- Karimi, E., Briens, C., Berruti, F., Moloodi, S., Tzanetakis, T., Thomson, M.J., Schlaf, M., Red mud as a catalyst for the upgrading of hemp-seed pyrolysis bio-oil, *Energy & Fuels*, 24, 6586–6600 (2010).
- Klopries, B.; Hodek, W.; Bander mann, F., Catalytic hydroliquefaction of biomass with red mud and CoO MoO₃ catalysts, *Fuel*, 69, 448–455 (1990).
- Kodama, T., Aoki, A., Ohtake, H., Funatoh, A., Shimizu, T., Kitayama, Y., Thermochemical CO₂ Gasification of Coal Using a Reactive Coal-In₂O₃ System, *Energy & Fuels*, 14, 202-211 (2000).
- López, A., De Marco, I., Caballero, B.M., Laresgoiti, M.F., Adrados, A., Aranzabal, A., Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud, *Applied Catalysis B: Environmental*, 104, 211–219 (2011).
- Mizan, T. I. and M. T. Klein, Computer-assisted Mechanistic Modeling of n-Hexadecane Hydroisomerization Over Various Bifunctional Catalysts, *Catal. Today*, 50:159-172 (1999).

- O'Brien, T.J., Syamlal, M., and Guenther, C., Computational Fluid Dynamic Simulations of Chemically Reactive Fluidized Bed Processes, in Third International Conference on CFD in the Minerals and Process Industries, CSIRO, Melbourne, Australia (2003).
- Ordenez, S., Sastre, H., Diez, F.V., Catalytic hydrodechlorination of tetrachloroethylene over red mud, *J. Hazardous Materials B*, 81, 103-114 (2001).
- Pope, S.B. and Ren, Z., Efficient Implementation of Chemistry in Computational Combustion, *Flow Turbul. Combust.*, 82(4): 437–453 (2009).
- Silaen A. and Wang, T., Effect of turbulence and devolatilization models on coal gasification simulation in an entrained-flow gasifier, *International Journal of Heat and Mass Transfer* 53, 2074–2091 (2010).
- Slezak, A., Kuhlman, J.M., Shadle, L.J., Spenik, J., and Shi, S., CFD simulation of entrained-flow coal gasification: Coal particle density/size fraction effects, *Powder Technology* 203, 98–108 (2010).
- Soncini, R. M., N. C. Means, and N. T. Weiland, "Co-pyrolysis of low rank coals and biomass: Product distributions," *Fuel*, vol. 112, pp. 74-82, 2013.
- Sushil, S.; Batra, V.S., Catalytic applications of red mud, an aluminium industry waste: A review, *Applied Catalysis B: Environmental*, 81, 64-77 (2008).
- Syamlal, M. and Bissett, L.A., METC Gasifier Advanced Simulation Model (MGAS) Model, DOE/METC-92/4108, National Energy Technology Laboratory, Department of Energy (1992).
- Syamlal, M., Rogers, W., and O'Brien, T.J., MFIX Documentation: Theory Guide. Technical Note, DOE/METC-95/1013, NTIS/DE95000031, National Energy Technology Laboratory, Department of Energy, See also <http://www.mfix.org>.
- Wei, W., Bennett, C.A., Tanaka, R., Hou, G. and Klein, M.T., Detailed Kinetic Models for Catalytic Reforming, *Fuel Processing Technology*, 89:344–349 (2008).
- Wei, W., Bennett, C.A., Tanaka, R., Hou, G. Klein, M.T., Jr. and Klein, M.T., Computer Aided Kinetic Modeling with KMT and KME, *Fuel Processing Technology*, 89:350–363 (2008).
- Xie, N., Battaglia, F. and Fox, R.O., Simulations of multiphase reactive flows in fluidized beds using in situ adaptive tabulation, *Combust. Theor. Model.*, 8 (2):195- 209 (2004).
- Yan, X. and Maas, U., Intrinsic low-dimensional manifolds of heterogeneous combustion processes, *Proc. of the Combustion Institute*, 28(2): 1615-1621 (2000).
- Yathavan, B.K. and F.A. Agblevor, Catalytic pyrolysis of pinyon juniper using red mud and HZSM-5, *Energy & Fuels*, 2013, 27(11), 6858-6865.
- Zhang, Y., Ashizawa, M., Kajitani, S., Hara, S., Modeling of Catalytic Gasification Kinetics for of Coal Char and Carbon, *Fuel*, 89, 417-422 (2010).

Appendix

In order to further evaluate models, we ran a statistical analysis on each of the models fitness and likelihood. We decided to use the previous five cases as starting points, and tune the model using equal weights on all the components. The final results are listed below:

Table 0.1. Case 1a (equally weighted) parameters and coefficients

#	Rxn	Type	logA	E*
1	Coal $\rightarrow a$ CharH + b CH ₄ + c CO + d CO ₂ + e H ₂ + f H ₂ O	Pyrolysis	3.888	20.436
2	Coal $\rightarrow g$ Tar + h CO ₂ + i H ₂ O	Pyrolysis	-0.408	2.455
3	Tar $\rightarrow j$ CharC + k CH ₄ + l H ₂ + m H ₂ O	Condensation	1.962	9.710
4	CharH $\rightarrow 2$ CharC + $\frac{1}{2}$ H ₂	Pyrolysis	9.562	54.930
5	CharC + H ₂ O $\rightarrow$ CO + H ₂	Gasification	9.005	34.979
6	CharC + CO ₂ $\rightarrow 2$ CO	Gasification	3.975	12.403
7	CharC + 2 H ₂ $\rightarrow$ CH ₄	Gasification	-2.441	38.637
8	CO + H ₂ O $\leftrightarrow$ CO ₂ + H ₂	Water-Gas-Shift	3.404	5.144
	a 26.90 e 8.50 i 4.40 m 1.10			
	b 1.40 f 1.10 j 11.50			
	c 6.60 g 4.70 k 1.50			
	d 1.90 h 1.30 l 0.40			

Table 0.2. Case 1a (equally weighted) statistics

	Sum of squared observations	Sum of squared deviations	R-Squared	Standard deviation of data	Sum of deviations	Avg of deviations
Solid_Unweighted	4.49E-03	4.96E-05	9.89E-01	1.23E-03	1.39E-02	1.99E-03
Solid_Weighted	7.00E+00	8.29E-02	9.88E-01	5.01E-02	5.66E-01	8.08E-02
CH4_Unweighted	8.35E-06	3.05E-07	9.63E-01	9.61E-05	1.13E-03	1.62E-04
CH4_Weighted	7.00E+00	2.61E-01	9.63E-01	8.90E-02	1.07E+00	1.53E-01
CO_Unweighted	1.12E-03	1.62E-05	9.86E-01	7.00E-04	8.36E-03	1.19E-03
CO_Weighted	7.00E+00	1.61E-01	9.77E-01	6.99E-02	9.71E-01	1.39E-01
CO2_Unweighted	3.90E-02	2.30E-05	9.99E-01	8.34E-04	1.11E-02	1.58E-03
CO2_Weighted	7.00E+00	3.99E-01	9.43E-01	1.10E-01	1.12E+00	1.60E-01
H2_Unweighted	3.54E-06	5.95E-08	9.83E-01	4.24E-05	5.32E-04	7.60E-05
H2_Weighted	7.00E+00	2.87E-01	9.59E-01	9.32E-02	1.15E+00	1.65E-01
H2O_Unweighted	9.81E-04	5.81E-06	9.94E-01	4.20E-04	4.98E-03	7.12E-04
H2O_Weighted	7.00E+00	9.05E-02	9.87E-01	5.24E-02	5.94E-01	8.48E-02
Tar_Unweighted	2.40E-05	1.41E-06	9.41E-01	2.07E-04	1.87E-03	2.67E-04
Tar_Weighted	7.00E+00	5.29E-01	9.24E-01	1.27E-01	1.24E+00	1.77E-01
OverAll_Unweighted	4.56E-02	9.63E-05	6.86E+00	3.52E-03	4.19E-02	5.99E-03
OverAll_Weighted	4.90E+01	1.81E+00	6.74E+00	5.91E-01	6.72E+00	9.59E-01
DOF	33					
P-Test	9.68E-16					
Q-Test	1					

Table 0.3. Case 2a (equally weighted) parameters and coefficients

#	Rxn	Type	logA	E*
1	Coal $\rightarrow a$ CharH + b CH ₄ + c CO + d CO ₂ + e H ₂ + f H ₂ O	Pyrolysis	6.372	34.768
2	Coal $\rightarrow g$ Tar + h CO ₂ + i H ₂ O	Pyrolysis	0.118	3.943
3	Tar $\rightarrow j$ CharC + k CH ₄ + l H ₂ + m H ₂ O	Condensation	2.076	8.719
4	CharH $\rightarrow 2$ CharC + $\frac{1}{2}$ H ₂	Pyrolysis	12.445	70.480
5	CharC + H ₂ O $\rightarrow$ CO + H ₂	Gasification	6.713	22.873
6	CharC + CO ₂ $\rightarrow 2$ CO	Gasification	5.151	19.515
7	CharC + 2 H ₂ $\rightarrow$ CH ₄	Gasification	-2.765	36.901
8	CO + H ₂ O $\leftrightarrow$ CO ₂ + H ₂	Water-Gas-Shift	3.908	7.050
	a 27.15 e 9.38 i 4.40 m 1.10			
	b 0.90 f 1.10 j 12.00			
	c 6.60 g 4.70 k 1.00			
	d 1.90 h 1.30 l 1.40			

Table 0.4. Case 2a (equally weighted) statistics

	Sum of squared observations	Sum of squared deviations	R-Squared	Standard deviation of data	Sum of deviations	Avg of deviations
Solid_Unweighted	4.49E-03	7.82E-05	9.83E-01	1.54E-03	1.91E-02	2.73E-03
Solid_Weighted	7.00E+00	1.28E-01	9.82E-01	6.24E-02	7.71E-01	1.10E-01
CH4_Unweighted	8.35E-06	4.55E-07	9.45E-01	1.17E-04	1.51E-03	2.16E-04
CH4_Weighted	7.00E+00	3.27E-01	9.53E-01	9.96E-02	1.35E+00	1.94E-01
CO_Unweighted	1.12E-03	1.62E-05	9.86E-01	7.01E-04	8.87E-03	1.27E-03
CO_Weighted	7.00E+00	2.11E-01	9.70E-01	8.00E-02	1.08E+00	1.55E-01
CO2_Unweighted	3.90E-02	4.54E-05	9.99E-01	1.17E-03	1.47E-02	2.10E-03
CO2_Weighted	7.00E+00	7.10E-01	8.99E-01	1.47E-01	1.56E+00	2.23E-01
H2_Unweighted	3.54E-06	1.06E-07	9.70E-01	5.66E-05	6.24E-04	8.91E-05
H2_Weighted	7.00E+00	3.83E-01	9.45E-01	1.08E-01	1.20E+00	1.71E-01
H2O_Unweighted	9.81E-04	4.88E-06	9.95E-01	3.85E-04	4.83E-03	6.90E-04
H2O_Weighted	7.00E+00	5.96E-02	9.91E-01	4.25E-02	5.18E-01	7.39E-02
Tar_Unweighted	2.40E-05	1.47E-06	9.39E-01	2.11E-04	1.84E-03	2.63E-04
Tar_Weighted	7.00E+00	5.62E-01	9.20E-01	1.31E-01	1.23E+00	1.76E-01
OverAll_Unweighted	4.56E-02	1.47E-04	6.82E+00	4.18E-03	5.15E-02	7.36E-03
OverAll_Weighted	4.90E+01	2.38E+00	6.66E+00	6.69E-01	7.72E+00	1.10E+00
DOF	33					
P-Test	6.80E-14					
Q-Test	1					

Table 0.5. Case 3a (equally weighted) parameters and coefficients

#	Rxn	Type	logA	E*
1	Coal $\rightarrow a$ CharH + b CH ₄ + c CO + d CO ₂ + e H ₂ + f H ₂ O	Pyrolysis	4.463	23.070
2	Coal $\rightarrow g$ Tar + h CO ₂ + i H ₂ O	Pyrolysis	0.756	7.398
3	Tar $\rightarrow j$ CharC + k CH ₄ + l H ₂ + m H ₂ O	Condensation	1.888	8.931
4	CharH $\rightarrow 2$ CharC + $\frac{1}{2}$ H ₂	Pyrolysis	15.705	89.227
5	CharC + H ₂ O $\rightarrow$ CO + H ₂	Gasification	12.996	55.911
6	CharC + CO ₂ $\rightarrow 2$ CO	Gasification	5.255	18.649
7	CharC + 2 H ₂ $\rightarrow$ CH ₄	Gasification	-2.046	22.085
8	CO + H ₂ O $\leftrightarrow$ CO ₂ + H ₂	Water-Gas-Shift	3.713	6.985
	<i>a</i> 27.03 <i>e</i> 8.94 <i>i</i> 4.40 <i>m</i> 1.10			
	<i>b</i> 1.15 <i>f</i> 1.10 <i>j</i> 11.75			
	<i>c</i> 6.60 <i>g</i> 4.70 <i>k</i> 1.25			
	<i>d</i> 1.90 <i>h</i> 1.30 <i>l</i> 0.90			

Table 0.6. Case 3a (equally weighted) statistics

	Sum of squared observations	Sum of squared deviations	R-Squared	Standard deviation of data	Sum of deviations	Avg of deviations
Solid_Unweighted	4.49E-03	4.26E-05	9.91E-01	1.14E-03	1.17E-02	1.67E-03
Solid_Weighted	7.00E+00	7.02E-02	9.90E-01	4.61E-02	4.73E-01	6.76E-02
CH4_Unweighted	8.35E-06	3.24E-07	9.61E-01	9.91E-05	1.20E-03	1.72E-04
CH4_Weighted	7.00E+00	2.85E-01	9.59E-01	9.30E-02	1.14E+00	1.63E-01
CO_Unweighted	1.12E-03	1.04E-05	9.91E-01	5.61E-04	6.84E-03	9.77E-04
CO_Weighted	7.00E+00	1.20E-01	9.83E-01	6.04E-02	8.50E-01	1.21E-01
CO2_Unweighted	3.90E-02	2.36E-05	9.99E-01	8.45E-04	1.09E-02	1.56E-03
CO2_Weighted	7.00E+00	4.39E-01	9.37E-01	1.15E-01	1.19E+00	1.70E-01
H2_Unweighted	3.54E-06	6.41E-08	9.82E-01	4.41E-05	5.53E-04	7.90E-05
H2_Weighted	7.00E+00	2.65E-01	9.62E-01	8.97E-02	1.10E+00	1.57E-01
H2O_Unweighted	9.81E-04	5.53E-06	9.94E-01	4.09E-04	5.06E-03	7.23E-04
H2O_Weighted	7.00E+00	7.60E-02	9.89E-01	4.80E-02	5.56E-01	7.95E-02
Tar_Unweighted	2.40E-05	1.51E-06	9.37E-01	2.14E-04	1.93E-03	2.76E-04
Tar_Weighted	7.00E+00	5.74E-01	9.18E-01	1.32E-01	1.30E+00	1.86E-01
OverAll_Unweighted	4.56E-02	8.40E-05	6.86E+00	3.31E-03	3.82E-02	5.46E-03
OverAll_Weighted	4.90E+01	1.83E+00	6.74E+00	5.84E-01	6.62E+00	9.46E-01
DOF	33					
P-Test	1.14E-15					
Q-Test	1					

Table 0.7. Case 4a (equally weighted) parameters and coefficients

#	Rxn	Type	logA	E*
1	Coal $\rightarrow a$ CharH + b CH ₄ + c CO + d CO ₂ + e H ₂ + f H ₂ O	Pyrolysis	5.058	25.788
2	Coal $\rightarrow g$ Tar + h CO ₂ + i H ₂ O	Pyrolysis	1.773	11.397
3	Tar $\rightarrow j$ CharC + k CH ₄ + l H ₂ + m H ₂ O	Condensation	1.539	6.807
4	CharH $\rightarrow 2$ CharC + $\frac{1}{2}$ H ₂	Pyrolysis	22.202	126.788
5	CharC + H ₂ O $\rightarrow$ CO + H ₂	Gasification	16.961	76.450
6	CharC + CO ₂ $\rightarrow 2$ CO	Gasification	6.324	24.316
7	CharC + 2 H ₂ $\rightarrow$ CH ₄	Gasification	-2.700	41.480
8	CO + H ₂ O $\leftrightarrow$ CO ₂ + H ₂	Water-Gas-Shift	4.566	11.044
	<i>a</i> 27.40 <i>e</i> 8.25 <i>i</i> 4.40 <i>m</i> 1.10			
	<i>b</i> 0.90 <i>f</i> 2.10 <i>j</i> 12.00			
	<i>c</i> 6.60 <i>g</i> 4.70 <i>k</i> 1.00			
	<i>d</i> 1.40 <i>h</i> 1.30 <i>l</i> 1.40			

Table 0.8. Case 4a (equally weighted) statistics

	Sum of squared observations	Sum of squared deviations	R-Squared	Standard deviation of data	Sum of deviations	Avg of deviations
Solid_Unweighted	4.49E-03	3.87E-05	9.91E-01	1.08E-03	1.04E-02	1.48E-03
Solid_Weighted	7.00E+00	6.33E-02	9.91E-01	4.38E-02	4.14E-01	5.91E-02
CH4_Unweighted	8.35E-06	4.38E-07	9.48E-01	1.15E-04	1.40E-03	2.00E-04
CH4_Weighted	7.00E+00	3.27E-01	9.53E-01	9.95E-02	1.25E+00	1.78E-01
CO_Unweighted	1.12E-03	6.52E-06	9.94E-01	4.45E-04	5.87E-03	8.39E-04
CO_Weighted	7.00E+00	7.84E-02	9.89E-01	4.87E-02	6.88E-01	9.82E-02
CO2_Unweighted	3.90E-02	3.14E-05	9.99E-01	9.76E-04	1.24E-02	1.77E-03
CO2_Weighted	7.00E+00	5.55E-01	9.21E-01	1.30E-01	1.31E+00	1.88E-01
H2_Unweighted	3.54E-06	9.37E-08	9.74E-01	5.33E-05	6.31E-04	9.01E-05
H2_Weighted	7.00E+00	3.19E-01	9.54E-01	9.84E-02	1.12E+00	1.60E-01
H2O_Unweighted	9.81E-04	7.72E-06	9.92E-01	4.84E-04	5.94E-03	8.49E-04
H2O_Weighted	7.00E+00	6.73E-02	9.90E-01	4.52E-02	5.29E-01	7.56E-02
Tar_Unweighted	2.40E-05	1.68E-06	9.30E-01	2.25E-04	2.15E-03	3.07E-04
Tar_Weighted	7.00E+00	6.31E-01	9.10E-01	1.38E-01	1.40E+00	2.00E-01
OverAll_Unweighted	4.56E-02	8.66E-05	6.83E+00	3.38E-03	3.88E-02	5.54E-03
OverAll_Weighted	4.90E+01	2.04E+00	6.71E+00	6.04E-01	6.71E+00	9.58E-01
DOF	33					
P-Test	6.27E-15					
Q-Test	1					

Table 0.9. Case 5a (equally weighted) parameters and coefficients

#	Rxn	Type	logA	E*
1	Coal $\rightarrow a$ CharH + b CH ₄ + c CO + d CO ₂ + e H ₂ + f H ₂ O	Pyrolysis	2.897	15.725
2	Coal $\rightarrow g$ Tar + h CO ₂ + i H ₂ O	Pyrolysis	1.236	9.040
3	Tar $\rightarrow j$ CharC + k CH ₄ + l H ₂ + m H ₂ O	Condensation	3.103	14.177
4	CharH $\rightarrow 2$ CharC + $\frac{1}{2}$ H ₂	Pyrolysis	8.357	113.594
5	CharC + H ₂ O $\rightarrow$ CO + H ₂	Gasification	15.943	70.596
6	CharC + CO ₂ $\rightarrow 2$ CO	Gasification	6.852	26.614
7	CharC + 2 H ₂ $\rightarrow$ CH ₄	Gasification	-4.118	94.701
8	CO + H ₂ O $\leftrightarrow$ CO ₂ + H ₂	Water-Gas-Shift	4.600	11.432
	<i>a</i> 27.65 <i>e</i> 8.13 <i>i</i> 4.40 <i>m</i> 1.10			
	<i>b</i> 0.90 <i>f</i> 2.10 <i>j</i> 12.00			
	<i>c</i> 5.60 <i>g</i> 4.70 <i>k</i> 1.00			
	<i>d</i> 1.90 <i>h</i> 1.30 <i>l</i> 1.40			

Table 0.10. Case 5a (equally weighted) statistics

	Sum of squared observations	Sum of squared deviations	R-Squared	Standard deviation of data	Sum of deviations	Avg of deviations
Solid_Unweighted	4.49E-03	4.73E-05	9.89E-01	1.20E-03	1.24E-02	1.78E-03
Solid_Weighted	7.00E+00	7.88E-02	9.89E-01	4.89E-02	5.04E-01	7.19E-02
CH4_Unweighted	8.35E-06	3.41E-07	9.59E-01	1.02E-04	1.09E-03	1.55E-04
CH4_Weighted	7.00E+00	2.75E-01	9.61E-01	9.13E-02	9.84E-01	1.41E-01
CO_Unweighted	1.12E-03	9.51E-06	9.92E-01	5.37E-04	6.31E-03	9.02E-04
CO_Weighted	7.00E+00	7.25E-02	9.90E-01	4.69E-02	6.11E-01	8.73E-02
CO2_Unweighted	3.90E-02	3.17E-05	9.99E-01	9.80E-04	1.29E-02	1.85E-03
CO2_Weighted	7.00E+00	4.99E-01	9.29E-01	1.23E-01	1.32E+00	1.88E-01
H2_Unweighted	3.54E-06	9.05E-08	9.74E-01	5.24E-05	6.44E-04	9.20E-05
H2_Weighted	7.00E+00	2.78E-01	9.60E-01	9.19E-02	1.14E+00	1.63E-01
H2O_Unweighted	9.81E-04	4.11E-06	9.96E-01	3.53E-04	4.26E-03	6.09E-04
H2O_Weighted	7.00E+00	3.70E-02	9.95E-01	3.35E-02	4.20E-01	6.00E-02
Tar_Unweighted	2.40E-05	1.63E-06	9.32E-01	2.22E-04	1.98E-03	2.83E-04
Tar_Weighted	7.00E+00	5.95E-01	9.15E-01	1.34E-01	1.27E+00	1.81E-01
OverAll_Unweighted	4.56E-02	9.47E-05	6.84E+00	3.44E-03	3.97E-02	5.67E-03
OverAll_Weighted	4.90E+01	1.84E+00	6.74E+00	5.70E-01	6.24E+00	8.92E-01
DOF	33					
P-Test	1.20E-15					
Q-Test	1					