

RESPONSE SURFACE MODEL PREDICTIONS FOR THE FLASH PYROLYSIS OF MONTANA ROSEBUD COAL

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Abstract

Experiments covering a broad range of reaction conditions are being conducted to determine and model the effects of coal gasification environment on product yields. The research uses a 3-inch I.D., down-flow entrained reactor that turbulently mixes preheated gases with coal to achieve high particle heating rates. As part of the test program, a pyrolysis series reacting Montana Rosebud coal in a nitrogen-argon atmosphere was completed. A 3-variable, composite factorial experimental design was used in which reaction conditions ranged from 1,500° to 2,500°F temperature, 100 to 900 psig pressure, and 2.19 to 10.00 seconds gas residence time. Quadratic response surface models were used to analyze the product yield and composition data as a function of the reaction conditions. Trends predicted by some of the statistically significant regression models are presented and discussed.

Introduction

For advancement to continue towards tailored, economic, and environmentally sound coal conversion technologies, further understanding of reaction mechanisms and product formations in relation to processing conditions and the physical and chemical structure of coal is needed. Devolatilization and associated phenomena are especially important in entrained gasification and pulverized coal combustion due to the small particle sizes, high temperatures, and short residence times involved. Although numerous studies have been conducted, recent reviews have concluded that there is little experimental verification at high-temperature, high-pressure conditions that exist in some current and advanced processes (1,2). Therefore, this project was initiated to determine the effects of gasification environment on product yields over a broad range of mild to severe conditions. A broad-range study was chosen to aid in the detection of reaction mechanism changes and to help integrate results from other related investigations.

Experimental

A down-flow entrained reactor designed to be able to preheat reactant gases to 3,000°F along the horizontal axis and maintain the reaction mixture at 2,500°F along the vertical axis at pressures up to 1,000 psig is used for the research. Details of the reactor and experimental system have been previously presented (3,4). The reactor is uniquely characterized by a mixing configuration that turbulently combines argon-conveyed coal with highly preheated reactant gases and subsequently transitions the flow to laminar-like before it enters a 3-inch I.D., 4-foot long alumina reaction tube. The turbulent, nearly adiabatic mixing between reactant gases and coal results in high particle heating rates approaching 10⁵°F per second. In addition to being essential for properly studying the phenomena of interest, this enables reaction temperatures to be reached near the exit of the nozzle and provides the potential for achieving axial isothermal temperature profiles in the reaction tube.

A comprehensive test program with Montana Rosebud subbituminous coal is being conducted. The program is organized into three major test classes to study inert, steam, and carbon dioxide environments, and an additional class to investigate char gasification reactions. The classes are further subdivided into test series to

investigate other variables. The Class 3A pyrolysis tests reported here were conducted in an inert environment of 75 mole percent nitrogen and 25 mole percent argon and consisted of a composite factorially designed series to investigate the effects of reaction temperature, pressure, and gas residence time. The composite factorial experimental design enabled a wide range of conditions to be studied with 15 different tests and permitted the use of response surface and statistical techniques for data analyses. To help ensure that each test point carried about the same weight, uniform variable spacing was used for testing and analyzing. The variable levels and respective codes are given in Table 1. To facilitate the ability of the quadratic response surface models to adequately represent the true response surfaces, the temperature levels were equally spaced reciprocally as absolute temperature, and the pressure and gas residence time levels were equally spaced logarithmically as absolute pressure and seconds, respectively.

TABLE 1. Composite Factorial Variable Levels

Variable	Levels				
METC Test Code	1	2	3	4	5
Factorial Code	-2	-1	0	1	2
Temperature, °F	1,500	1,681	1,898	2,165	2,500
Pressure, psig	100	178	309	530	900
Gas Residence Time, sec	2.19	3.20	4.68	6.84	10.00

Experimentally, the gas environment, gas-coal ratio (400 scf/lb), and total material fed to the reactor during steady-state conditions were held essentially constant throughout the test series. A 200 x 270 mesh fraction of Montana Rosebud coal with an average particle diameter of 57 microns was used. Expressed as weight percent, the average ultimate analysis of the coal was 64.1 carbon, 4.4 hydrogen, 17.9 oxygen, 1.1 nitrogen, 1.0 sulfur, 10.4 ash, and 1.0 moisture; and the average volatile matter content was 40.6.

Results and Discussion

The overall material balance accountability of coal to product gases, liquids, and chars was greater than 98 weight percent. Quadratic response surface models which considered linear, quadratic, and interaction effects were used to analyze 50 variables. The Statistical Analysis System (SAS) computer program was used to perform the least squares regressions (5). Thirty-six variables had potentially adequate regression model fits at the 0.05 significance level or higher. Some regression model predictions of product yields and compositions from this test series have been previously reported (6). Only the regression models for elemental retentions in char will be discussed here.

Table 2 lists the experimental elemental char retentions, defined as the weight percentage of each major coal element that remained in the char, for this test series. The test numbers are derived from the METC test codes for the variable levels given in Table 1. The "3A" identifies the test class and is followed by three numbers which sequentially identify the temperature, pressure, and gas residence time levels. A fourth number is used when a test condition is repeated and represents the repetition number. Thus, Table 2 also illustrates the 15 different variable combinations involved with the composite factorial design and shows

that the center point condition (i.e., 3A333) was repeated 4 times to determine experimental variation. Test No. 3A333-1 failed and therefore does not appear in the table.

Nitrogen was the only elemental retention that could not be adequately represented by a quadratic response model at the 0.06 significance, or alpha, level or higher. Of the four that could be adequately represented, all had statistically significant predicted temperature effects to at least the 0.07 alpha level, only hydrogen and sulfur retentions had significant predicted pressure effects to at least the 0.04 alpha level, and all but oxygen retention had significant predicted gas residence time effects to at least the 0.08 alpha level. The significance levels provided the criteria for selecting which regression models and what variable ranges were used for predictive purposes. In general, full experimental ranges were used when significance values were 0.05 or higher, and only small variations around the center point of the experimental design were used when significance values were between 0.05 and 0.10.

Figure 1 shows how the predicted carbon, hydrogen, oxygen, and sulfur retentions in char vary with reaction temperature at the experimental center point pressure and gas residence time conditions. Oxygen is the least retained (i.e., most converted) element, and is predicted to be essentially absent in the char at temperatures above 2,000°F. Hydrogen retention decreases steadily with temperature and begins to approach zero at the highest temperature. This behavior most likely reflects thermally induced dehydrogenation and condensation of the larger aromatic structures in the char. Carbon and sulfur retentions both initially decrease, but then increase at higher temperatures. This behavior mostly accounts for a similar trend in char yield, which was also shown to pass through a minimum (6). The tendency for carbon retention to increase at higher temperatures is probably due to the increased cracking of volatile species, either in the hotter, outer regions of the particles as they devolatilize or in the extraparticle environment. The possibility of decreased yields at higher temperatures due to secondary reactions was recognized prior to this experimental confirmation (7). The tendency for sulfur retention to increase may be due to the high-temperature reaction of hydrogen sulfide with char to form thiophenic structures, as has been reported (8), or capture of the sulfur by ash components.

Figure 2 indicates an interaction between temperature and pressure effects on hydrogen retention. The nature of the predicted pressure effect changes with reaction temperature and decreases in magnitude as temperature increases. The pressure effect is relatively unimportant at higher temperatures. At lower temperatures, however, hydrogen retention increases faster with pressure than hydrogen yield decreases which, if there is no pressure effect on carbon retention as indicated by a poor significance level, implies that the overall hydrogen-carbon ratio of the nonchar products decreases. Thus, in very general and relative terms, pressure may tend to shift the aromatic hydrocarbon spectrum to heavier components at lower temperatures, but has little or no effect at higher temperatures due to extremely low organic yields. This behavior may be due to equilibrium considerations or reflect pressure effects on the sequence of secondary cracking reactions.

Figure 3 shows that near the experimental center point temperature and at the center point gas residence time, sulfur retention is predicted to maximize in roughly the 200 to 300 psig pressure range. At lower pressures, sulfur retention decreases slightly with temperature and, conversely, increases slightly with temperature at the higher pressures. The occurrence of maxima and the inverted temperature dependencies suggest the presence of multiple phenomena. Candidate explanations could include some of the possible effects of pressure on the following: (1) reaction rates of sulfur species with char and ash, (2) initial distribution of devolatilized sulfur species, (3) sequence and rates of secondary reactions, (4) coal and char physical changes during devolatilization that affect reactant accessibility,

and (5) various sulfur absorption equilibriums. Planned analyses of the chars to obtain the proportion of organic and inorganic sulfur forms may clarify these trends.

Figure 4 shows how the predicted hydrogen and carbon retentions vary with gas residence time near the experimental center point temperature and at the center point pressure. Hydrogen retention decreases just slightly with residence time and has a comparatively much greater sensitivity to temperature. The decrease is probably due to an annealing-like phenomena which results in the slow dehydrogenation and condensation of aromatic structures in the char. The predicted trends show that the dehydrogenation rate increases with temperature. Carbon retention is predicted to increase with time at the lower temperatures, but decrease with time at the highest temperature. Furthermore, carbon retention increases with temperature at gas residence times less than approximately 3.5 seconds, but decreases with temperature at longer residence times. The explanation for this behavior is not clear, but may possibly involve the relative kinetics of some of the cracking and gasification reactions and the initial cracking sequence. Initially, more intraparticle cracking of volatile species may be occurring during devolatilization as temperature increases, and, hence, carbon retention increases with temperature at the shortest residence times. The volatile species that escaped intraparticle cracking at the lower temperatures may then, with time, continue cracking in the extraparticle environment and lead to a gradual increase in carbon retention. Because significant cracking may have already occurred at the highest temperature, there would be little material left for long-term extraparticle cracking and, hence, no tendency for carbon retention to increase. However, gasification reactions of the char with carbon dioxide and water formed during pyrolysis would have the opportunity to proceed and may account for the gradual conversion of carbon at the highest temperature. At the lower temperatures, the gasification reactions may not be fast enough to counter deposition resulting from cracking reactions, and thus, carbon retention continues to increase. To validate these explanations, more data are needed for yields at residence times under 2 seconds and for cracking rates of various light hydrocarbons in the presence of char at the experimental conditions.

Figure 5 shows that sulfur retention in char is very sensitive to gas residence time and relatively insensitive to temperature. The trends indicate that a low-sulfur char is initially produced, but increases in sulfur content as time proceeds. This implies that a large percentage of the sulfur in the coal is initially released to the extraparticle environment and that various mechanisms then return some of the sulfur to the char. Various organic sulfur compounds crack into hydrogen sulfide and carbon disulfide, and these as well as the hydrogen sulfide initially formed from pyrite probably back react with the char and ash components. Depending on the initial forms of the devolatilized sulfur and relative reaction rates, these trends could predominantly reflect the kinetics of either hydrogen sulfide absorption reactions or organic sulfur compound cracking reactions. The suggested asymptote at approximately 75 percent sulfur retention possibly reflects approach to equilibrium or an absorption limit of the ash. Further analyses of sulfur forms in the chars may indicate the dominant effects.

Conclusions

A composite factorial experimental design and response surface methods were successfully applied to study the flash pyrolysis of Montana Rosebud coal over wide ranges of temperature, pressure, and gas residence time. Statistically significant regression models were used to predict product yield and composition trends. The regression model predictions reported here for elemental retentions in char lead to the following conclusions: (1) char yields increased at the higher temperatures investigated due to carbon deposition from the cracking of volatiles and sulfur absorption by char and ash components, (2) carbon, hydrogen, and oxygen retentions

were most sensitive to temperature and sulfur retention was most sensitive to residence time, (3) pressure may tend to shift the aromatic hydrocarbon spectrum to heavier components at the lower temperatures investigated, (4) sulfur retention was likely affected by multiple phenomena, (5) char annealing effects and continued cracking of light hydrocarbons were present in the residence time range studied, and (6) a low-sulfur char was initially produced, but increased in sulfur content with time to an apparent asymptotic value due to back reactions of sulfur species with the char and ash.

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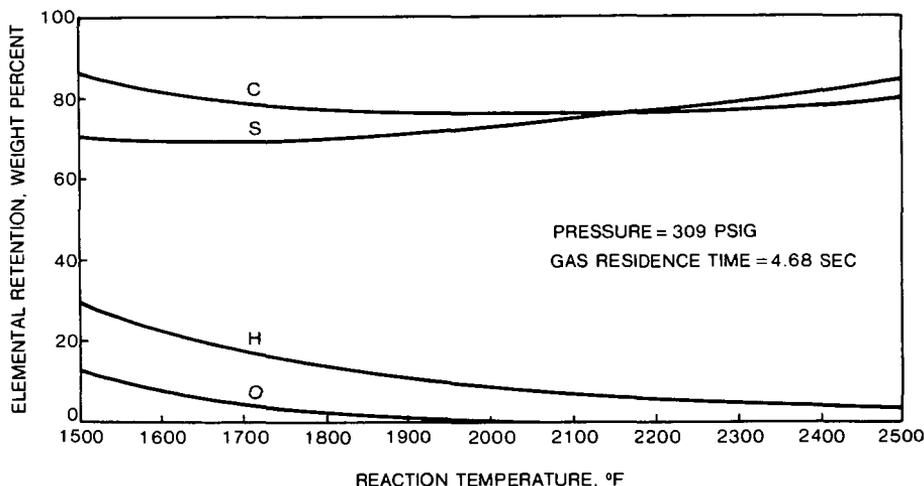


Figure 1. Regression Model Prediction for Elemental Retention in Char vs. Reaction Temperature, Class 3A Nitrogen-Montana Rosebud Coal Tests, METC Advanced Gasification Facility Entrained Reactor

TABLE 2. Elemental Char Retention, Weight Percent, Class 3A
 Nitrogen -- Montana Rosebud Coal Tests, METC
 Advanced Gasification Facility Entrained Reactor

Test No.	Temperature, F°	Pressure, psig	Gas Residence Time, sec.	Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur
3A133	1,500	309	4.68	85.9	31.7	11.0	89.6	67.9
3A222	1,681	178	3.20	75.1	16.3	7.3	69.3	66.2
3A224	1,681	178	6.84	82.9	15.8	13.3	36.2	70.9
3A242	1,681	530	3.20	78.1	19.6	11.1	69.8	47.1
3A244	1,681	530	6.84	85.6	19.7	5.8	76.6	70.1
3A313	1,898	100	4.68	78.1	6.7	1.5	80.4	62.3
3A331	1,898	309	2.19	77.0	12.7	5.5	73.5	41.1
3A333	1,898	309	4.68	77.5	11.0	0.1	89.5	67.6
3A333-2	1,898	309	4.68	76.6	10.0	2.4	58.9	71.4
3A333-3	1,898	309	4.68	76.3	11.5	0.2	70.5	76.5
3A333-4	1,898	309	4.68	75.5	11.9	0.5	68.2	70.6
3A335	1,898	309	10.00	76.4	8.0	1.6	76.9	74.5
3A353	1,898	900	4.68	76.3	12.5	11.2	67.6	51.1
3A422	2,165	178	3.20	76.2	8.0	1.1	80.2	59.0
3A424	2,165	178	6.84	71.3	2.6	0	41.4	66.4
3A442-1	2,165	530	3.20	78.0	5.2	0.7	62.4	68.6
3A444	2,165	530	6.84	78.0	6.5	3.9	56.4	71.4
3A533	2,500	309	4.68	80.5	3.0	0	49.4	89.0

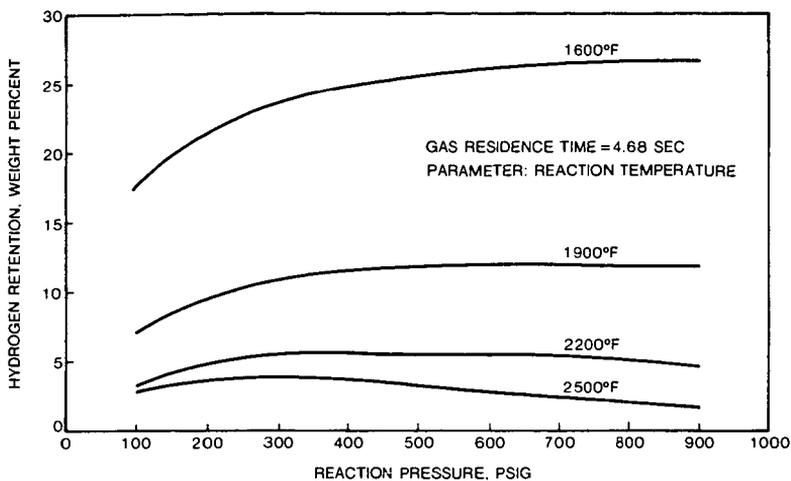


Figure 2. Regression Model Prediction for Hydrogen Retention in Char vs. Reaction Pressure, Class 3A Nitrogen-Montana Rosebud Coal Tests, METC Advanced Gasification Facility Entrained Reactor

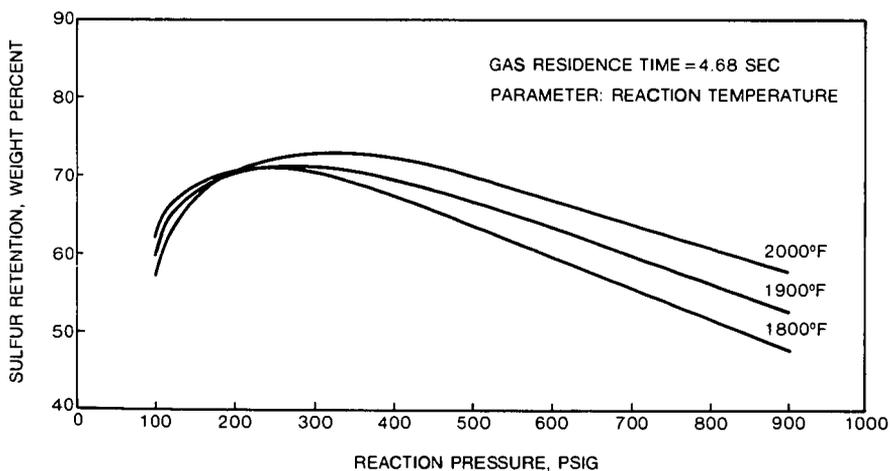


Figure 3. Regression Model Prediction for Sulfur Retention in Char vs. Reaction Pressure, Class 3A Nitrogen-Montana Rosebud Coal Tests, METC Advanced Gasification Facility Entrained Reactor

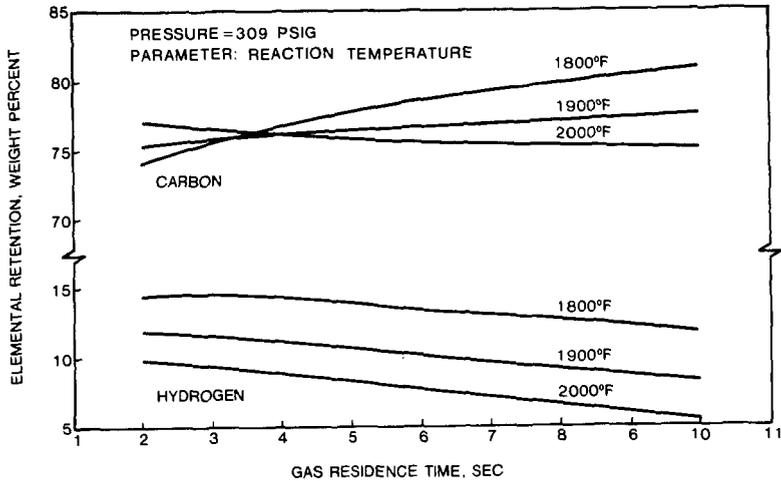


Figure 4. Regression Model Prediction for Carbon and Hydrogen Retention in Char vs. Gas Residence Time, Class 3A Nitrogen-Montana Rosebud Coal Tests, METC Advanced Gasification Facility Entrained Reactor

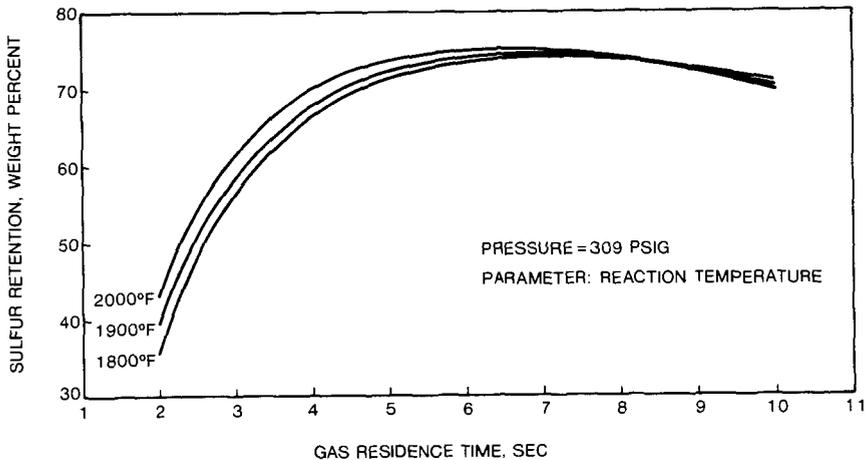


Figure 5. Regression Model Prediction for Sulfur Retention in Char vs. Gas Residence Time, Class 3A Nitrogen-Montana Rosebud Coal Tests, METC Advanced Gasification Facility Entrained Reactor