

Distribution of Sulfur During Coal Pyrolysis in a High Pressure Entrained-Flow Reactor

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Introduction

An understanding of the fundamental and interrelated processes involved in coal pyrolysis/gasification is essential in order to advance gasification technologies. Therefore, it is necessary to generate data on the effect of coal properties and operating conditions on coal devolatilization behavior under conditions similar to those in advanced-concept gasifiers; typically, a high-temperature and high pressure environment for entrained coal particles.

The thermal decomposition of raw coal produces solid char/coke plus some liquid (tar) and gaseous products.⁽¹⁾ Tars are vapors at the pyrolysis temperature, but are usually heavy liquids or solids at room temperature. The chars, which usually account for between 30-70% of the original coal, consist mainly of carbon, along with small amounts of H, O, N and S as well as the ash which results from the mineral matter. The quantity and quality of the char, tar and gases produced during pyrolysis depend on the chemical and physical properties of the coal (i.e. coal type, particle size, etc.) as well as on the pyrolysis conditions (i.e. temperature, pressure, etc.).⁽¹⁾

Due to the environmental impact of the emission of SO₂ during combustion, pre-combustion processing may be necessary to reduce the sulfur content of so-called "high sulfur coals". Desulfurization of coal prior to combustion can be achieved by one or more of the following methods.⁽²⁻⁴⁾ 1) Advanced physical cleaning -- this method involves a variety of approaches (i.e. froth flotation, float-sink, etc.) for reduction of pyrite in the coal based on the differences between the density of pyrite (5.0g/cm³) or marcasite (4.87 g/cm³)⁽⁵⁾ and the organic matrix (1.2-1.5 g/cm³).⁽⁶⁾ 2) Chemical coal cleaning -- based on the concept of breaking the chemical bonds of the organic sulfur by exposing the coal usually to molten chemicals such as sodium hydroxide. 3) Conversion of the coal to low-sulfur liquid and gaseous fuels -- based on liquefaction and gasification technologies.

According to the literature, there are three commonly recognizable forms of sulfur in coal: sulfate, pyrite and organic sulfur. Although the distribution of various forms of sulfur is less often determined than the total sulfur, their presence can have a significant effect on coal utilization. However, the degree to which the sulfur can be reduced and/or removed from the coal by the above techniques is strongly dependent on the forms of sulfur present in the coal. Therefore, accurate analytical data on the forms of sulfur is a requirement for improving removal processes.

Pyrolysis has been used by some researchers to study the behavior and distribution of sulfur in coal.⁽⁷⁻¹²⁾ Some investigators have also used pyrolysis in order to study the chemistry and kinetics of reactions involving sulfur-containing compounds in coal.⁽¹³⁻¹⁵⁾ The purpose of the current work was to determine the distribution of the total sulfur between the products of pyrolysis (tars and chars) and the various forms of sulfur in the chars from pyrolysis of a subbituminous coal in a high pressure entrained-flow reactor.

Experimental

A schematic diagram of the entrained-flow reactor used in this study is shown in Figure 1. This reactor is capable of subjecting pulverized coal particles to temperatures and pressures as severe as 1373 K and 1000 psig, respectively. It is also equipped with a computerized data

acquisition system for rapid data collection and monitoring of the experimental conditions. The operating principle and procedure have been described elsewhere.^(16,17)

Pyrolysis experiments were performed on pulverized and sized samples, ~57 μm mean diameter, of Montana Rosebud Subbituminous coal at 1189 K, 100-900 psig applied N_2 pressure and 0.1-1.7s residence time. The collectable products of pyrolysis, both solid and the material trapped on the filter, were extracted in conventional Soxhlet apparatus using tetrahydrofuran (THF) as the solvent. The extracted material represented the tars from pyrolysis while the THF insoluble material represented the char. The gaseous products from pyrolysis were analyzed qualitatively and quantitatively at steady-state operation by an on-line Carle gas chromatograph capable of monitoring the following gases: H_2 , N_2 , O_2 , H_2S , CO , CO_2 , CH_2 , C_2H_4 , C_2H_6 , H_2O , SO_2 , and C_3+C_4 hydrocarbons. An infrared gas analyzer was used to continuously monitor the CO concentration in the outlet gas stream. This was needed to determine when steady state operation had been reached.

Proximate analyses were performed on the raw coal and the chars using a Leco MAC-400 analyzer. Ultimate analyses were also performed on raw coal, chars and tars using a Leco CHN-600 analyzer. Total sulfur contents of the raw coal, tars and chars were determined by a Leco SC-132 sulfur analyzer. Sulfate and pyritic sulfur in the raw coal and the chars were determined according to the American Society for Testing and Materials (ASTM) standard procedure D-2492.⁽¹⁸⁾ Organic sulfur for the raw coal and chars was calculated by subtracting the percentage sums of sulfate and pyritic sulfur from the total sulfur. Higher heating values were measured for both the raw coal and the chars using a Parr model 1241 adiabatic bomb calorimeter. Full analyses of the Montana Rosebud coal are shown in Table 1.

Coal particle residence times in the furnace were determined using a computer flow model. The governing equations have been discussed elsewhere.^(16,17) Weight loss due to the coal devolatilization was calculated by using ash as a tracer. Tar yields (~5-15%) were measured from the total amount of THF solubles collected and expressed as weight percent of coal (daf) fed into the reactor. Total gas yields were calculated from the difference between the weight loss and tar yield.

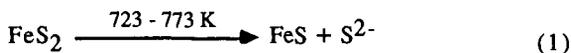
Results and Discussion

Pyrolysis results on weight loss, tar and gas yields and gaseous compositions have been reported and discussed in detail elsewhere.^(16,19,20) Total and forms of sulfur (daf) for the raw coal and selected chars from pyrolysis of Montana Rosebud coal at 1189 K, 100-900 psig applied N_2 pressure and 0.3-1.7s residence time are shown in Table 2. Total sulfur analyses of the corresponding tars are also shown in Table 2.

A comparison of the total sulfur (daf) contents of the chars and tars (Table 2) clearly indicates that the sulfur in the chars is always higher than the sulfur in the tars produced from the pyrolysis experiments. In most cases the sulfur content of the tars was about 50% lower than the sulfur content of the corresponding char and the raw coal. It was observed that as the residence time of pyrolysis increased, the sulfur content of the tar increased, as shown in Figure 2.

The reason for the increase in the sulfur content of the tar with increasing pyrolysis residence time might be the higher rate of decomposition of pyrite in the coal and the secondary reactions between the decomposition product and the tar molecules in the gas phase. This is supported by the data in Figure 3. As can be seen, the pyritic sulfur content of the chars decreases as the pyrolysis residence time increases.

It has been shown by Given et al.⁽²¹⁾ and others that pyrites decompose between 724-773 K. The produced ferrous sulfide and free sulfur (S^{2-}) then react with the organic matrix of the tars and chars by crosslinking according to the following reactions.^(14,22)



The effect of pressure on the pyritic sulfur content of the chars produced from pyrolysis of Montana Rosebud subbituminous coal is shown in Figure 4. As the pressure increases, the pyritic sulfur content of the chars increases. This indicates that increasing the pyrolysis pressure reduces the rate of the pyrite decomposition reactions.

Reductions in the total sulfur content of the coal were calculated according to the following equation:^(10,12)

$$\% S_t = \left\{ (S_t)_{\text{Raw Coal}} - [(S_t)_{\text{Char}} \times (\text{char yield})] / (S_t)_{\text{Raw Coal}} \right\} \times 100$$

The effect of residence time on the percent reduction in total sulfur is shown in Figure 5. As the pyrolysis residence time increases, the percent reduction in sulfur content of the coal increases, meaning a higher reduction in total sulfur can be achieved by increasing the pyrolysis residence time. This is supported by the data in Figure 2. The decrease in pyritic sulfur with increasing residence time is most likely the reason behind the increase in the percent reduction in the total sulfur content with increasing pyrolysis residence time.

The effect of pressure on the percent reduction in the total sulfur content of the coal is shown in Figure 6. It was observed that as the pyrolysis pressure increased, the percent reduction in the total sulfur content decreased. In other words, increasing the pyrolysis pressure reduces the percent total sulfur reduction. This behavior is probably due to the fact that increasing the pyrolysis pressure reduces the decomposition of pyrite, Figure 4, which in turn affects the overall percent reduction in the sulfur content of the chars.

It has been reported that H_2S is the dominant sulfur-containing species produced by high-temperature (>1073 K) pyrolysis.^(14,15,22) H_2S is the result of desulfurization reactions between the H_2 , generated by the decomposition of the coal matrix during pyrolysis, and pyrites according to the following equations:



However, some of the produced H_2S reacts with the tars and chars as soon as they are formed and becomes organically bonded to the products. This is due to the availability of active carbon sites in the chars produced during devolatilization of the coal matrix, and in the reactive organic species formed during secondary cracking reactions of the tars. This is supported by the fact that the secondary cracking reactions of the tars increase as the pyrolysis residence time increases, and the data in Figure 2, which indicate that as the pyrolysis residence time increases the total sulfur in the tars increases.

Conclusions

Based on the information available in the literature and the data presented here on the pyrolysis of Montana Rosebud subbituminous coal the following can be concluded:

- 1) Total sulfur in the tars produced during pyrolysis is residence time dependent.
- 2) Forms of sulfur in the chars produced from pyrolysis revealed that pyritic sulfur is most affected by the pyrolysis conditions (residence time and pressure).
- 3) A higher percent reduction in total sulfur can be achieved by increasing the pyrolysis residence time.
- 4) Increasing the pyrolysis pressure reduces the percent total sulfur reduction.
- 5) The dominant species from the decomposition of pyrite in the coal at high-temperatures is H_2S . However, some of the evolved H_2S reacts with the chars and tars, especially at higher residence times.

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Table 1.

Characteristics of Montana Rosebud Subbituminous Coal

<u>Proximate Analysis</u>	<u>(wt%, dry)</u>
Moisture	--
Ash	10.31
Volatile Matter	36.50
Fixed Carbon	53.19
<u>Ultimate Analysis</u>	
Ash	--
Carbon	83.89
Hydrogen	3.72
Nitrogen	1.38
Total Sulfur	1.12
Oxygen (by diff.)	9.89
<u>Forms of sulfur</u>	
Pyritic	0.217
Sulfatic	0.092
Organic	0.814
Total	1.123
Heating Value (Btu/lb, daf)	13929

Table 2.

Sulfur Analyses of the Tars and Chars From Pyrolysis of Montana Rosebud Subbituminous Coal at 1189 K, 100-900 psig N₂ Pressure and 0.3-1.7s Residence Times.

Sample(a)	Total Sulfur (wt%, daf)		Forms of Sulfur (wt%, daf)		
	Tar	Char	Pyritic	Sulfatic	Organic(b)
Raw Coal	--	--	0.217	0.092	0.814
100-0.3	0.54	0.92	0.209	0.101	0.608
100-1.0	0.82	1.16	0.098	0.079	0.983
100-1.7	0.97	0.88	0.044	0.073	0.766
178-0.3	0.75	1.17	0.220	0.132	0.822
178-1.0	0.70	0.89	0.121	0.154	0.608
178-1.7	0.97	0.99	0.008	0.076	0.902
309-0.3	0.51	1.01	0.144	0.119	0.748
309-1.0	0.90	0.96	0.125	0.120	0.709
309-1.7	1.02	1.18	0.021	0.166	0.989
530-0.3	0.40	0.84	0.272	0.151	0.520
530-1.0	0.68	1.17	0.190	0.142	0.833
900-1.0	0.62	1.42	0.304	0.162	0.954

(a) Pressure-Residence Time

(b) By Difference

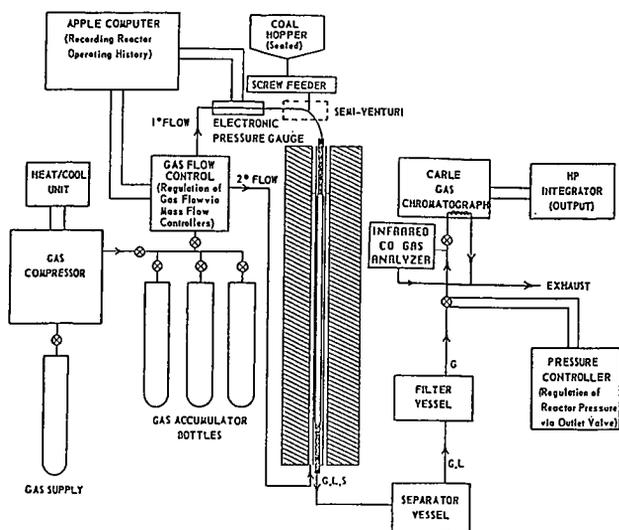


Figure 1. Configuration of High Pressure Entrained-Flow Reactor

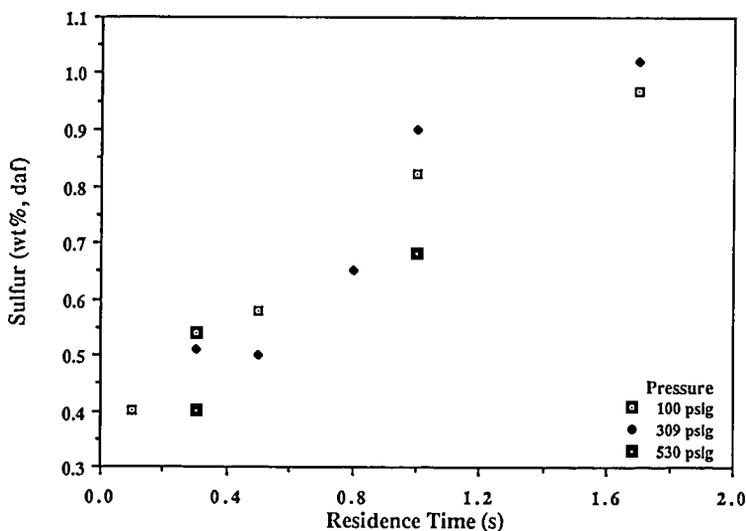


Figure 2. Effect of Residence Time on Total Sulfur (daf) of Tars from Pyrolysis of Montana Rosebud Coal at 1189 K

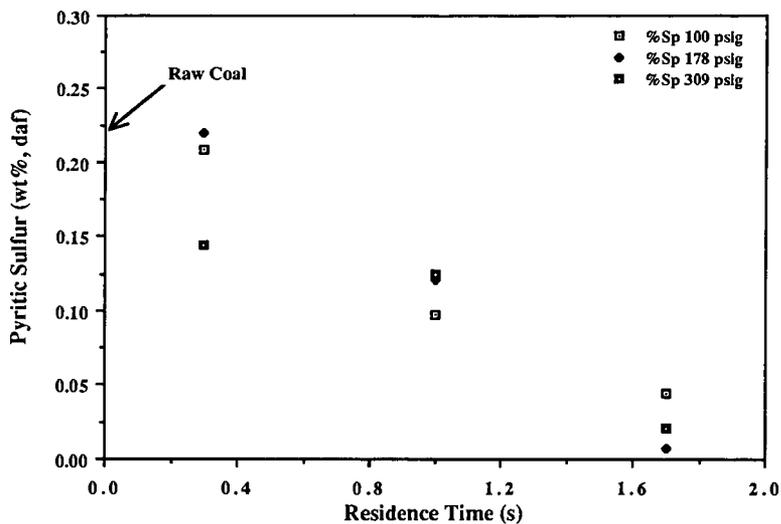


Figure 3. Effect of Residence Time on Pyritic Sulfur of the Chars from Pyrolysis of Montana Rosebud Coal at 1189 K

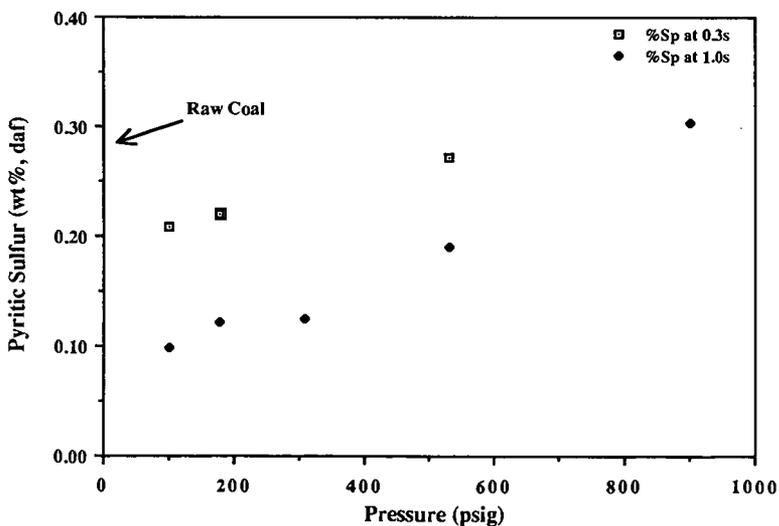


Figure 4. Effect of Pressure on Pyritic Sulfur of the Chars from Pyrolysis of Montana Rosebud Coal at 1189 K

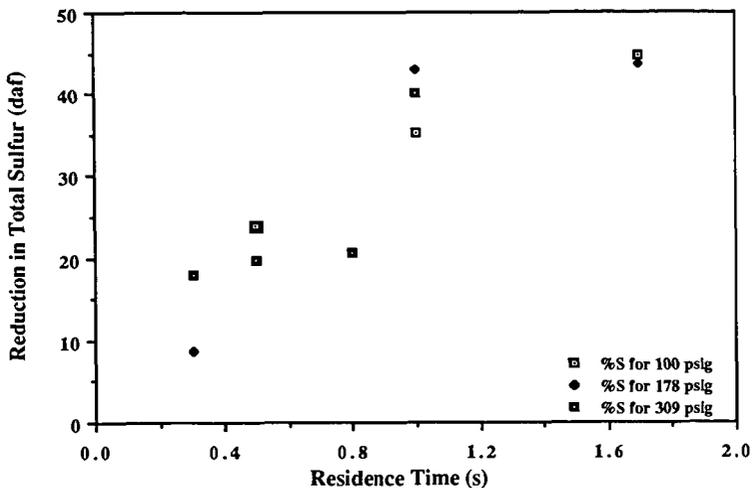


Figure 5. Effect of Residence Time on Percent Reduction in the Total Sulfur of Montana Rosebud Coal Pyrolyzed at 1189 K

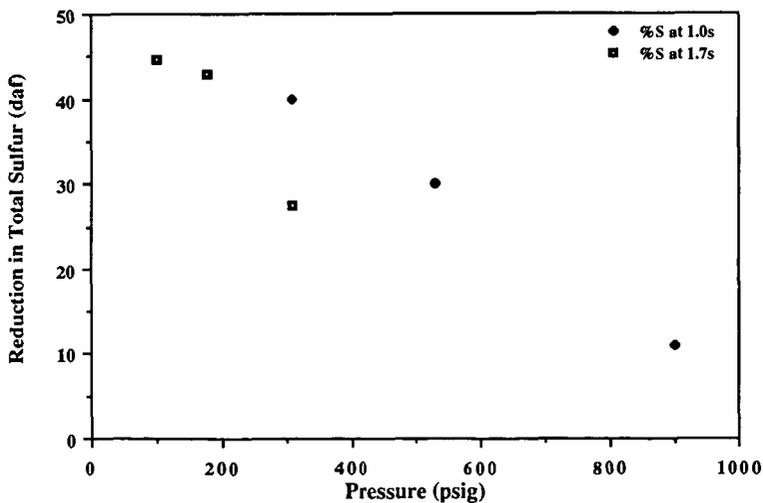


Figure 6. Effect of Pressure on Percent Reduction in the Total Sulfur of Montana Rosebud Coal Pyrolyzed at 1189 K