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DESULFURIZATION OF COAL IN A FLUIDIZED BED REACTOR AT ELEVATED TEMPERATURES

Gaurang Bhalchandra Haldipur

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RESEARCH INSTITUTE
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Preface

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Desulfurization of coal in a fluidized bed reactor at elevated temperatures

by

Gaurang Bhalchandra Haldipur

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ABSTRACT

The results of an experimental investigation of a fluidized bed process for the gaseous desulfurization of Iowa coal are presented. The experiments were conducted in a batch fluidized bed reactor under essentially isothermal conditions. A special technique was used for rapidly preheating the coal to the reaction temperature.

The effectiveness of hydrogen and oxygen in the removal of sulfur from coal was evaluated at temperatures in the range of 220°-410°C, and compared with the desulfurization achieved due to thermal pyrolysis of coal. A statistical parametric study was done to determine the effects of temperature, type of treatment gas and the ash content on weight loss, volatile matter loss and sulfur removal from coal. The reactions of organic and pyritic sulfur were shown to be very temperature sensitive. The removal of organic sulfur is effected only by the thermal decomposition reactions during pyrolysis. Pyritic sulfur reacts appreciably with oxygen or hydrogen at 400°C.

The gases evolved from coal due to devolatilization, combustion and desulfurization were analyzed on a mass spectrometer. The sulfurous species identified in the gas were sulfur dioxide, hydrogen sulfide and traces of carbon oxysulfide. Significant quantities of carbon monoxide and carbon dioxide are formed during the oxygen treatment of coal.

Other gaseous species which were detected were hydrogen, methane, propane, and ethane. After removal of the sulfurous gases and carbon dioxide, the heating value of the gas evolved from coal was estimated to be 400 to 900 Btu./scf.

The specific sulfur content (lb. S./MM Btu.) of the char residue from the runs was not appreciably different from the feed coal. It was shown that if the evolved gas is desulfurized and used as a fuel with the char, the specific sulfur content of the overall product could be significantly reduced.

INTRODUCTION

With ever increasing demands on fossil fuels as a source of energy and ever decreasing supplies of crude petroleum, it has now become imperative to develop new processes to harness the energy from coal. The utilization of coal is however, impaired by the presence in coal of sulfur which, after combustion, forms sulfur dioxide, a major air pollution irritant. The U.S. Environmental Protection Agency, EPA, has established air quality standards which define the maximum allowable concentrations of pollutants in the atmosphere. The current Federal Standard for emissions of sulfur dioxide is 1.2 lb./MM Btu. for new coal fired steam generators larger than 250 MM Btu./hr. Individual states have established their own emission standards for existing facilities. In the State of Iowa, the sulfur dioxide emission rules limit its emission to 6 lb./MM Btu. from coal burning plants with a base energy load of 500 MM Btu./hr. or greater.

The reduction of sulfur emissions from coal burning operations can be effectuated in a number of ways. Aside from the employment of low sulfur fuels, the traditional approach has been aimed at removal of the offending pollutants from the stack gases. This route is fraught with many problems, such as the low concentrations of sulfur dioxide in the flue gas, and the tremendous gas flow rates involved. It has been estimated that for a 600 mega watt power plant, the throughput of stack gases amounts to 2 to 3 million cu. ft./min. (52). Hence, physical and chemical techniques to eliminate sulfur from coal prior to combustion promise attractive economic alternatives to stack gas desulfurization.

It is generally accepted that sulfur occurs in coal in three forms: (1) in organic chemical combinations and, therefore, as an integral part of the coal substance itself; (2) as iron pyrites and/or marcasites; and (3) as sulfates, which generally are of calcium and iron. In view of the nature and the abundance of the organic sulfur in coal it is readily apparent that chemical methods of sulfur removal present the only practical means of efficient desulfurization prior to coal combustion.

The purpose of this investigation was to develop a good understanding of a chemical treatment method for desulfurizing high sulfur bituminous coal. The envisaged process involved treating this coal with an oxidizing or reducing gas in a fluidized bed reactor at elevated temperatures. The objectives of the research were: (a) to investigate the reactions between treatment gases and the sulfur species in coal at various temperatures, (b) to do a parametric study of the process and determine the effects of the type and composition of treatment gas, reaction temperature and the ash content in the coal, (c) to identify and estimate the concentrations of all gaseous species evolving due to the reactions of coal pyrolysis, desulfurization and combustion, and, (d) to suggest possible kinetic models which could describe the reactions of the coal sulfur species.

A bench scale batch reactor was developed to investigate the desulfurization of coal under essentially isothermal conditions. A novel device was used to rapidly heat the coal to the reaction temperature thereby simulating the conditions obtained in a continuous reactor. The conclusions drawn from this investigation could be used to provide a basis for the design of a scaled-up continuous process for the gaseous desulfurization of bituminous high sulfur coal.

LITERATURE REVIEW

Before sulfur dioxide emissions became a major air pollution hazard, research work was directed towards removing sulfur from coal to produce metallurgical coke. This was necessary since sulfur in steel causes "hot shortness" and thus adversely affects the hardness properties of steel. A literature review of coal desulfurization processes can therefore be classified chronologically into sulfur removal during carbonization in coke ovens, sulfur removal from carbonized products, that is, char and coke, and finally processes for producing sulfur-free coal to serve as a boiler fuel.

Although several attempts have been made to elucidate the kinetics and mechanisms of coal desulfurization reactions, much of the reported work tends to be speculative in nature or restricted to a very qualitative treatment. To date, only one in-depth study has been made of the kinetics of coal desulfurization in the presence of reactive gases (50,52). This work and the literature about the kinetics of desulfurizing pyrites will be reviewed separately.

Sulfur Removal in Coke Ovens

Carbonization without added gases

Summarizing the work of various experimenters, Thiessen (49) reported the following average percentages of sulfur gasified upon carbonization of coal: 52 percent (Parr), 42 to 52 percent (McCallan), 42 percent (Campbell), 33 percent (Aronov), 53 percent (Bone and Himus), 48 percent (Thiessen). Thiessen also determined a relationship between the total sulfur in the coke (S_k) and the pyritic sulfur (S_p) and organic sulfur (S_o) in the coal, and it was found to be:

$$S_k = 0.62\ S_p + 0.45\ S_o \tag{1}$$

This equation suggests that the organic sulfur is more readily converted to volatile product gases than is the pyritic sulfur.

Using radioactive tracers, Eaton et al. (14) studied the relative gasification of pyritic and organic sulfur in a coke oven. After a 15 hr coking period with a synthetic coal mixture, 35 percent of the pyritic sulfur was removed, and 27 percent of the organic and sulfate sulfur was converted to volatile products. The organic sulfur had a tendency to be gasified first, but the pyritic sulfur gasification rate became more predominant in the latter stages. It was also shown that a large fraction of the pyritic sulfur which does not leave the coke is converted to solid solution sulfur.

Powell (32) made a study of the behavior of the various sulfur forms upon carbonization. He determined that (1) the pyrites start to decompose at 300°C and are completely converted to pyrrhotite (Fe_7S_8) and hydrogen sulfide at 600°C, (2) the reduction of sulfates to sulfides is complete at 600°C, (3) one third to one quarter of the organic sulfur is converted to hydrogen sulfide, (4) only a small part of the organic sulfur appears as volatile organic compounds, and occurs at low temperatures, (5) a portion of the pyrrhotite disappears at 500°C, the sulfur apparently reacting with the carbon to yield a solid product, (6) carbon disulfide is formed as a secondary reaction between hot coke and hydrogen sulfides and (7) the secondary reaction of hydrogen with the pyritic and organic sulfur is very significant in the overall volatilization process.

Brewer and Ghosh (11,18) carbonized four coals containing 7.54, 3.35, 2.41 and 2.11 percent sulfur and studied the product distribution. The majority of the sulfur was evolved as hydrogen sulfide. However, up to 20 percent of the sulfur containing gases appeared as mercaptans, with minor yields of carbonyl sulfide, carbon disulfide and thiophenes. No analysis was performed for sulfur dioxide. The addition of carbonates to the coal greatly increased the amount of sulfur which could be leached out of the coke after carbonizing, but did not appreciably alter the amount of sulfur gasified.

Sulfur dioxide, however, was shown to represent some 30 percent of the sulfur containing gases in the carbonate addition runs.

Gollmar (20) and Powell (33) have reported that the gases from commercial coke ovens contain from 90 to 95 percent of the sulfur as hydrogen sulfide, except for relatively high sulfur coals. About two-thirds of the remainder appears as carbon disulfide, with smaller proportions of mercaptans, thiophenes, carbonyl sulfide and other minor organic sulfur compounds. From the findings of Huff and Holz, Powell (33) also surmised that the hot coke reacts with hydrogen sulfide to form a carbon-sulfur complex; when a sufficient concentration of the complex builds up it dissociates into volatile carbon disulfide.

The rate of sulfur gasification during carbonization of Colorado Crested Butte Coal at 480°C was investigated by Stone et al. (48). They employed a novel technique of injecting the pulverized coal into a preheated bed of fluidized sand. Although this technique avoided the common practice of using a relatively long period to heat the coal to test temperature, they had difficulty with a rather large drop in the temperature of the bed after injection of the coal. The initial sulfur gasification rate was found to be fairly constant for the first 50 sec. but after 4 min., the rate dropped to half the initial rate.

Chowdhury et al. (12) attempted carbonization of Assam coals containing 2.7-7.8 percent sulfur, a major portion of which was in the organic form. They found that pyrolytic desulfurization could be improved by first impregnating the coals with sodium bicarbonate. The chlorides of sodium, magnesium, zinc and tin were also effective. When the Assam coals were treated with sodium bicarbonate at 750°C for 65 min, it was found that 83-92 percent of the sulfur was removed.

Cernic-Simic (44) carbonized coals of different ranks, having different percentages of ash, and different quantities of sulfur at 500°, 600° and 900°C. The results showed that the rank of the coal influences the amount of volatile matter released which in turn influences the amount of sulfur removed from coal. The quantity and the composition of the mineral matter in coal were shown to be principal factors that determine the behavior of coal sulfur during carbonization. It was shown that compounds of calcium and iron present in ash retain much of the sulfur that normally leaves with the gas.

Given and Jones (19) studied the change in sulfur distribution upon carbonization of a bituminous coal containing 2.46 percent total sulfur. In order to show the interconversion of the different forms of sulfur they worked at a series of temperatures from 200° to 700°C. The data revealed that between 200° and 300° there appears to be some gain in organic sulfur and loss of pyrite even though no ferrous sulfide could be detected. It was therefore concluded that the organic material reduces pyrite, forming unstable sulfur containing groups which subsequently are lost as volatile matter. They further worked with carbonization using 27 substances as additives, of which all but three were organic. These included various alcohols and sugars, which would give water and possibly olefins on pyrolysis, several high polymers which on pyrolysis should give monomers capable of picking up sulfur, and some aromatic and aliphatic oxygen compounds that might take up sulfur to give a stable but volatile heterocyclic compound. The reduction in sulfur content due to the presence of the additive was appreciable for four substances, benzene-1, 2, 4, 5-tetra-carboxylic anhydride, p-terphenyl, sodium borohydride and ammonium chloride.

Carbonization with added gases

Steam Snow (47) carbonized a coal containing 5.34 percent total sulfur, crushed to 20x40 mesh size, for 4 hr. at test temperatures from 300° to 1000°C. At 600°C, using a steam to coal ratio of 0.18 g.mole/g., 65 percent sulfur conversion was obtained with 34 percent organic loss. His results for nitrogen at the same gas to coal ratio were 51 and 30 percent respectively for sulfur and organic gasification. At 1000°C and a gas to coal ratio of 0.22, the sulfur gasification was 84 percent for steam and 57 percent for nitrogen. The organic conversion with steam was not measured, but evidently was almost double the value of 43 percent for nitrogen.

Mangelsdorf and Broughton (26) conducted a series of experiments very similar to but less extensive than those of Snow. They used a coal containing 2.26 percent sulfur, crushed to pass through an 8 mesh screen. They found that at a steam to coal ratio of 0.8 g.mole/g. during a 5 hr. carbonizing treatment at 600°C, 44 percent sulfur elimination was obtained as compared to 33 percent with heat alone. The organic conversion was 40 percent as compared to 28 percent with no added gas.

Roy and Goswami (35,36) studied the effect of steam on the removal of sulfur from Assam coal (-20+40 mesh) in the presence of potential inorganic catalysts. Catalysts used were silica, sodium silicate in jelly form, hydrated alumina and bauxite. A mixture of coal (containing 4.57 percent sulfur) and 5 percent silica was carbonized for 6 hr. at 850°C with steam yielding 42 percent coke and 1.2 percent sulfur. Among all the catalysts tried silica appeared to be the best desulfurizing agent.

Air Postnikow et al. (31) used air to gasify sulfur from mixtures of carbonaceous pyrites (44 percent sulfur) and premium coal. Using a batch technique for charging the solids, they established that (1) hydrogen sulfide was first formed and then sulfur dioxide came over in the latter stages, (2) carbon disulfide evolution reached a maximum at 1000°C, where it represented up to 30 percent of the total sulfur, and was favored by an increase in the amount of carbonaceous matter present and a decrease in the air supply, and (3) elemental sulfur formation was extremely favorable with yields up to 80 percent being favored by moderate temperatures (up to 800°C), a minimum amount of carbonaceous matter present and an optimum oxygen to sulfur ratio for each set of conditions.

Other gases The work of Snow (47) is probably the most extensive. He found the following order of effectiveness for sulfur gasification between 600° and 1000°C, at a gas to coal ratio of 0.20 g.mole/g. and for a 4-6 hr. treatment; hydrogen, ammonia, water gas, nitrogen, carbon dioxide, carbon monoxide, methane and ethylene. The efficiency of steam fell between hydrogen and ammonia. Mangelsdorf and Broughton (26) found water gas to be the most efficient at 600°C of the various gases they tested, with no appreciable carbon loss at a gas to coal ratio of 0.8.

Brewer and Ghosh (11) concluded that ammonia was the most efficient gas they investigated for removing sulfur. During carbonization of a 20x30 mesh Illinois coal containing 3.55 percent total sulfur at 800°C, they found sulfur gasification of 52 percent using an ammonia to coal ratio of 0.009 g.mole/g. and 67 percent for ratios of 0.026 and 0.034. Hydrogen and nitrogen under the same conditions at a gas to coal ratio of 0.018 gave sulfur gasifications of 38 and 37 percent respectively. The effects of added sodium carbonate, sodium bicarbonate, calcium, iron, aluminum and silicon oxides were determined. The aluminum oxide had a slight catalytic effect with ammonia, while the other oxides tended to retard the sulfur gasification.

Roy and Goswami (35,36) studied the efficiency of coal gas for the removal of sulfur from Assam coal in the presence of catalysts. With coal gas alone, carbonization for 6 hr. at 800°C reduced the sulfur from 4.57 percent in coal to 1.97 percent in coke. With 5 percent silica, the sulfur was reduced to 1.51 percent. Calcium oxide gave a maximum desulfurization of 54 percent. Other catalysts investigated were magnesium chloride and aluminum oxide which yielded cokes containing 1.69 and 1.41 percent sulfur respectively.

Sulfur Removal from Carbonized Products

Treatment with steam

Working with various cokes with sulfur contents ranging from 0.82 to 3.37 percent, Powell (33) found that by steaming the cokes at temperatures from 200° to 800°C for periods of time from 15 min. to 6 hr., they caused considerable desulfurization to occur. No carbon gasification took place below 500°C, and only 15 percent was lost due to reaction at 800°C during a 6 hr. period. They concluded that the optimum conditions for 35x60 mesh coke were 700°C and a 2 hr. steaming period using 1.11 g.mole steam/g. coke. Longer periods of steaming had little or no effect on the sulfur gasification, while at 800°C, any desulfurization advantage was offset by higher carbon burnoffs. It was determined that the sulfide sulfur was easy to remove, while the organic sulfur (sulfur in solid solution) was removed only with large carbon conversions. Using 3x7 in. industrial-size coke and steaming at a gas to coal ratio of 2.22 for 4 hr., they obtained average conversions at 750°C of 13 percent using natural steam flow, 14 percent using alternating steam and vacuum on the coal and 20 percent using alternating vacuum and 100 psig steam flow.

Pexton and Cobb (30) found that excess steam was an effective desulfurization agent at 800°C, but higher temperatures or low steam rates seriously reduced the preferential sulfur gasification. The sulfide sulfur was gasified quite easily, but the organic sulfur was removed only upon relatively large carbon conversions.

Treatment with air and steam

Fuchs and Wunderlich (17) investigated the effect of air and steam mixtures on the removal of sulfur from coke. The cokes contained 1.60 and 1.38 percent sulfur and were treated at 500° and 600°C for 5 min. The results at the two temperature levels for either coke were about the same, although carbon burnoff indicated that 500°C was the optimum temperature. Using a 1:2 air to steam mixture at a gas to coke ratio of 0.4, 13 percent sulfur gasification was obtained; with a 3:2 air to steam mixture at a gas to coke ratio of 1.0, 15 percent of the sulfur was removed.

Treatment with hydrogen

Gray et al. (21) studied the hydrodesulfurization of Illinois No. 6 coal char at about 1600°F. The char initially contained about 2 percent organic sulfur and 1 percent inorganic sulfur (mainly ferrous sulfide) from pyrolysis of pyrite. It was found that the removal of the organic sulfur was rapid and limited primarily by the equilibrium between hydrogen sulfide in the gas and sulfur in the char. The reaction of ferrous sulfide with hydrogen proceeds more slowly than would be expected from equilibrium. The authors therefore concluded that the rate limiting step is either the inherent gas-solid kinetics, or the diffusion of hydrogen sulfide through the reacted shell of iron surrounding the ferrous sulfide. They also observed that about 10 percent of the sulfur content of the char was not removed even by prolonged hydro-treatment; but it was possible to remove over 80 percent in 20 min. Thus a high ratio of hydrogen to hydrogen sulfide necessitates the use of a hydrogen sulfide acceptor to provide a commercially feasible process.

Batchelor et al. (2) investigated the basic kinetics of the desulfurization of char with hydrogen in a batch fluidized reactor at various temperatures and pressures. They further elucidated the inhibitive action of hydrogen sulfide by developing characteristic total inhibition isotherms which define the point of total inhibition of the desulfurization process. A comparison of the final sulfur values observed in the batch fluidized bed runs with those calculated from the equilibrium or total inhibition basis revealed that at partial pressures of hydrogen above 1.5 atm and for beds of char larger than 70 g. the desulfurization is equilibrium controlled. For shallow beds, kinetics and not equilibrium determined the amount of desulfurization. Further rate data on char hydrodesulfurization were collected with a continuous fluidized bed treating raw Arkwright char (containing 1.47 percent total sulfur) at temperatures ranging from 1200 to 1600°F and total pressures of 1.37 to 6.04 atm. The data suggested that the net rate of desulfurization is determined by the competition between two processes -- thermal fixation of the sulfur to produce a more stable form and its rate of removal by hydrogen while in the labile form. Because thermal fixation occurred more rapidly the higher the temperature, the authors suggested an optimum temperature of 1450°F at low pressures of the order of 1 atm for maximum desulfurization.

Robinson and Green (34) have demonstrated that the effectiveness of the hydrodesulfurization process for coal chars is significantly improved, in turn, by the physical beneficiation of the parent coal and by the acid pretreatment of the product char. These treatments were effective in removing iron and calcium constituents which appeared to contribute to the severity of the hydrogen sulfide inhibition. The optimum desulfurization temperature which was determined for the chars of the West Kentucky coal used in the study appeared to be in the range of 1700° and 1800°F. However, the authors pointed out that this optimum temperature may vary with the method of char preparation. The hydrodesulfurization kinetics was explained as a rapid evolution of sulfur on the char surface followed by the slower removal of sulfur in the char interior. Since similar rates were obtained from tests conducted at 1600° and 1700°F, it was believed that the kinetics are probably not controlled by a chemical reaction mechanism. Also, tests conducted with a -60+80 mesh char were not appreciably different from similar tests conducted with the same char which was ground to a -200 mesh particle size. These data were in accordance with a product-shell diffusion mechanism postulated by Gray et al. (21).

Treatment with hydrogen and steam

Zielke et al. (53) studied the preferential gasification of low temperature coke sulfur by steam and hydrogen mixtures at 870°C. The coke used was a 48x30 mesh coal char which contained 1.92 percent sulfur. The initial desulfurization rate was found to be six to eight times the initial carbon gasification rate. They found that the higher the percentage of hydrogen, the greater is the efficiency of desulfurization at a given gas to char ratio. The effect of pressure up to 6 atm was not especially significant. Sulfur conversions of 85 percent were obtained with gas to char ratios of 2.0 g.mole/g. with carbon burnoffs of about 20 percent. These authors also pointed out the severe thermodynamic limitations of the process. According to their data the equilibrium mole fraction of hydrogen sulfide at 870°C for the steam-iron sulfide reaction is 1.4 percent; while for the hydrogen-iron sulfide reaction it is 1.8 percent. In general they found that steam was effective for removing the sulfide sulfur, but hydrogen was necessary to react with the organic sulfur in the char.

Sulfur Removal from Coal

Treatment with air and steam

Jacobs and Mirkus (23) studied the effect of process variables on the fluid bed desulfurization of an agglomerating high-sulfur Illinois No. 6 seam coal. A coal sample containing 4.90 percent total sulfur consisting of 1/16 in. size particles was treated with nitrogen-air-steam mixtures over a range of temperatures, steam-air compositions and residence time distributions. The results indicated that desulfurization is profoundly influenced by particle size. The authors suggest that diffusion is a limiting factor in the reaction kinetics. The limiting diffusion could be a film type or a particle type in which the reactants must travel through the capillary structure. The finer particles would have a greater external surface as well as a shorter capillary path. The results also indicated that desulfurization is very sensitive to residence time below 8 min. and much less affected by longer times. This would suggest the presence of two phases of desulfurization. In the devolatilization phase, the sulfur content drops rapidly to around 60 percent in about 8 min., followed by a chemical reaction phase in which the sulfur content drops off slowly and steadily. Chemical reaction occurs when the porous char structure, no longer permeated with hydrocarbon rich gases, comes in contact with the fluidizing medium, so that sulfur is oxidized. Further it was found that steam is a relatively unimportant factor since even with no steam in the fluidizing medium, considerable desulfurization occurred. The data showed a small but consistent improvement in sulfur removal, with increasing steam content, indicating that the presence of steam is slightly more conducive to sulfur removal than nitrogen. Moreover, desulfurization is not very sensitive to the air content of the fluidizing medium. Although sulfur removal in the chemical reaction phase is probably an oxidation reaction, its rate did not seem sensitive to oxygen partial pressure. More than 60 percent air could not be used without excessive combustion of the material; with less than 5 percent air, the coal fused because of insufficient preoxidation. In addition the authors found that the percent desulfurization increased with increase in temperature, however, above 800°F additional sulfur removal was counteracted by gasification and attendant loss of char yield. It is believed that there is competition for oxygen in the fluid bed among the carbon, the solid state sulfur and the gas phase hydrocarbons. At lower temperatures, the evolving gas might be preferentially oxidized, while at higher temperatures the increasingly active carbon reaction might prevail.

Blum and Cindea (7) and Blum et al. (8,9,10) worked on both fluidized and fixed bed desulfurization of PALV noncoking coals using steam-air mixtures at various reacting conditions to determine an optimum set of process variables. In the fixed bed experiment the powdered coal (0-1 mm.) was treated with a steam-air mixture of 85:15 weight ratio. The reaction vessel was placed in a molten alkaline nitrite bath at 380°C, air flow being 27 ℓ/hr. and steam 204 g./hr. The desulfurization of coal from 2.62 to 1.79 percent total sulfur was accompanied by a considerable decrease in volatile matter from 42.7 to 22.6 percent. Working with a 40 mm diameter fluidized bed reactor, the authors achieved a reduction in sulfur content from 4.9 to 2.7 percent at the following optimum working conditions: (1) reaction temperature - 510°C, (2) residence time - 18 min., (3) fluidizing velocity - 26 cm./sec., (4) mean particle size - 1.6 mm., (5) composition of air-steam-nitrogen fluidizing gas: 16.3-31.1-52.6 percent. The experimental results demonstrated that the oxidation of pyrite in coal by a steam-air mixture is similar to the oxidation process for pure pyrite. Hence, the authors deduced that the rate of oxidation of pyrites in coal is not influenced by the large surrounding carbonaceous mass. Further they postulated a new operating hypothesis which assumes that the desulfurization process by gases consists of two distinct stages: (a) the period of material preparation, consisting essentially of the creation of an increased porosity and a large accessible surface and (b) the period of chemical attack, comprising a chemical reaction between sulfur and the oxidizing agent and the growth of the accessible surface by gasification. Thus, this rate mechanism more or less corroborates the work done earlier by Jacobs and Mirkus.

Sinha and Walker (45,46) investigated the desulfurization of different types of coal and coal char with various gases at temperatures ranging from 350° to 600°C. Air, nitrogen, carbon monoxide and mixtures of steam and carbon monoxide were employed. The best results were obtained with air. Thus when air was used, more than 90 percent of the pyritic sulfur was removed in 10 min. at 450°C. Under these conditions there was a loss in sample weight of 5 to 17 percent and a decrease in calorific value of 8 to 16 percent except for one sample where the decrease was 28 percent. These losses were mainly due to the escape and/or oxidation of part of the volatile matter.

Oxley (29) studied the flash carbonization of pulverized coal in fluidized beds, and was able to measure the selectivity of steam-oxygen mixtures used for preferentially removing the sulfur from coal by oxidation. In his investigation, the pulverized coal was passed through a bed of relatively coarse sand heated by external heaters to temperatures ranging from 490° to 675°C. The amounts of sulfur and carbonaceous matter gasified were determined for a Diester Table reject sample containing approximately 8 percent sulfur, most of it pyritic. It was observed that the selectivity of the process increases at first with temperature and then decreases. At 620°C, approximately 80 percent of the sulfur was removed from the coal with an attendant loss of 26 percent of the organic combustible matter. The off gases had an undetermined fuel value which Oxley pointed out could be recovered by recombination with the coal product in a boiler after scrubbing out the sulfur containing portions of the off gases.

A patent issued to Schroeder (39) describes a process which treats coal with a mixture of steam and oxygen at 482° to 816°C. This yields a useful combustible gas and a char with reduced sulfur content. No details are reported of the extent of desulfurization and the heating value of the gas.

Treatment with hydrogen

Maa et al. (25) measured inhibition isotherms for the hydrodesulfurization of Western Kentucky No. 9 coal. Their experiments involved fluidizing 10 g. batches of crushed and sieved coal (-25+140 mesh) in a 22 mm I.D. quartz reactor up to a temperature of 870°C. The release of hydrogen sulfide during heatup under nitrogen and at the run temperature under hydrogen, or hydrogen--hydrogen sulfide mixtures was estimated by gas chromatography. Inhibition isotherms (equilibrium between sulfur in the char and gaseous hydrogen sulfide) were measured at 600° and 870°C. At the lower temperature the isotherm was found to be independent of the hydrogen sulfide concentration in the gas stream and the char sulfur content remained constant at 2.6 percent. At 870°C the sulfur content of the char was greater than that of the original coal when gas mixtures of 1, 3, and 6 percent hydrogen sulfide in hydrogen were used indicating the necessity of maintaining a low hydrogen sulfide concentration for sulfur removal. In pure hydrogen, sulfur removal increased continuously from 47 percent at 600°C to 84 percent at 870°C. For pyrolysis under nitrogen, sulfur removal was 40 percent at 600°C and increased to 59 percent at 740°C. In addition to the inhibition isotherms, sulfur-form transformation diagrams were constructed for coal treated with the above mentioned gases. Pyritic sulfur, which comprised 40 percent of the sulfur in the original coal, was completely converted to ferrous sulfide at 600°C in hydrogen, and 740°C in nitrogen. At 870°C the sulfur content of the char produced under hydrogen was 1.1 percent and consisted of 48.4 percent ferrous sulfide, 43.4 percent organic sulfur, and 8.2 percent sulfate.

Block et al. (6) studied the effect of hydrogen treatment on the sulfur removal from ten high volatile bituminous coals. The equipment consisted of a stainless steel boat holding the coal samples in amounts from 0.5 to 10 g. and the whole assembly was placed in a stainless steel tube heated by an electric tube furnace. Their results indicated that hydrogen was not effective below 850°C but at 900°C, 86 percent of the total sulfur was expelled, with 94 percent of the inorganic and 76 percent of the organic sulfur removed. Without any oxidative pretreatment the sulfur was much more difficult to remove, apparently due to a destruction of the microporous structure of the coal. After oxidative pretreatment at 300°C for 10 min. followed by treatment with hydrogen at 900°C, as much sulfur was removed in 4 min. as was removed in 60 min. without pretreatment. For temperature swelling coals with large quantities of organic sulfur, heating at 300°C appeared to permit rapid discharge of the organic as well as the inorganic sulfur of the coal to produce a char with a fuel value similar to that of the untreated coal.

Samoilenko et al. (38) studied the effect of Raney nickel catalyst on the hydrodesulfurization of Donetsk coals. The amount of catalyst used was 2.5 percent and it reduced the sulfur content by as much as 26 percent of its initial level. Methods of recovering the spent catalyst were not indicated. The authors believe that much of the catalytic activity is due to the hydrogen absorption on nickel and its subsequent release during the course of reaction in a highly reactive atomic form.

Batchelor et al. (3,4,5) have patented a process to desulfurize granular, noncoking coal by heating a mixture of coal and a hydrogen sulfide acceptor consisting of manganese oxide on an inert carrier at 1100° to 1600°F. This process further involves separation of coal and acceptor and the latter is then reoxidized by heating in air. When this cycle is repeated, the acceptor gradually loses its activity. This is restored by cooling and removing a part of the acceptor which is heated at 50°-200°C in a closed vessel with a mineral acid, such as nitric acid to leach out substantially all of the manganese as a soluble salt. The support material is then heated in contact with manganese salts in acid solution to vaporize the acid solution and deposit the salts on the support material. This is then oxidized and reused.

A process patented by Lee and Schorra (24) involves treating an equal volume mixture of sulfur bearing coal and calcined limestone of 16-80 mesh size with hydrogen at 600°-800°C and atmospheric pressure. The inventor claims that substantially all the pyritic and nearly 34 percent of organic sulfur are removed by this process.

In another patent McKinley and Henke (27) claims a process to achieve between 40-70 percent desulfurization without excessive devolatilization. It entails contacting a comminuted, high sulfur bearing coal and hydrogen under a pressure of 300-350 atm for a period of about 90 min. Processing details are not explained in this patent.

In a patent awarded to Selmeczi and Vlnaty (41), a process is described where coal, premixed with 3-30 percent iron oxides, is heated in a reducing atmosphere at 1200°-1700°F for 5-60 min. The iron is separated by gravitational or magnetic methods and the char is subjected to an oxidizing atmosphere at 800-1100°F to yield a finished char containing 0.6-0.7 percent sulfur.

Essenhigh (15) has patented a process in which coal is desulfurized by hydrogen in the presence of calcium oxide in a dual channel cascade reactor. Further operating details are not mentioned.

Desulfurization Thermochemistry

The process chemistry and kinetics of coal desulfurization are complicated by the large number of parallel and consecutive reactions possible and the variety of end products which can be formed. When coal is subjected to elevated temperatures, a spontaneous pyrolysis occurs which leads to a simultaneous rearrangement of the coal lamallae and release of tars and volatile matter. Very little is known about the exact mechanism of these reactions but most authors agree that pyrolysis proceeds by the following steps (22,49,52)

$$P \xrightarrow{\text{fast}} M \xrightarrow{\text{fast}} \underset{G_1}{\overset{}{\underset{+}{R}}} \xrightarrow{\text{slow}} \underset{G_2}{\underset{+}{S}} \qquad (2)$$

where P = original coal

M = "metaplast" or fluid coal

R = semicoke

G_1 = primary volatile products (mainly tars)

S = coke

G_2 = secondary volatile products (mainly hydrogen, carbon monoxide and methane)

It is believed that this process is affected by the rate of heating and the general consensus is that a faster heating rate yields more tar and less volatile matter in the form of gases.

The reactions of coal sulfur at elevated temperatures are undoubtedly affected by the course of the pyrolysis reactions. Organic sulfur is chemically bonded to the coal matrix and, hence, one can expect some release of this sulfur due to pyrolysis and subsequent reaction with the volatile products. Pyritic and sulfate sulfur may be finely disseminated in the coal and these species can also react with the gases evolved by pyrolysis.

The forms in which organically bonded sulfur occurs in coal are poorly defined. Hence, the reactions of organic sulfur in the presence of various gases cannot be studied from the standpoint of thermodynamic feasibility. In the case of pyritic sulfur there is a more fortunate situation in that the feasibility of pyrite reactions can be predicted in a given temperature range. The reactions of sulfate sulfur have not been studied because the amount of this type of sulfur in coal is usually insignificant.

Reduction of iron pyrites

The following reactions could occur when iron pyrites (FeS_2) are contacted with steam and hydrogen.

$$FeS_2 + H_2 = FeS + H_2S \tag{3}$$

$$FeS + H_2O = FeO + H_2S \tag{4}$$

$$FeS + H_2 = Fe + H_2 \tag{5}$$

$$FeS_2 = FeS + S \tag{6}$$

Thermodynamic equilibrium constants (K) can be calculated using the free energies of formation of the various reacting species as reported by Dutta and Bhattacharyya (13).

Figure 1 shows the variation of the equilibrium constant with temperature for reactions 3 to 6. It is obvious from this plot that only reaction 3 is thermodynamically feasible at temperatures above 340°K.

Some investigators (21,34,52) have reported the reduction of ferrous sulfide by hydrogen at temperatures greater than 825°K. However, the equilibrium constant for this reaction at these temperatures is rather small as can be seen from

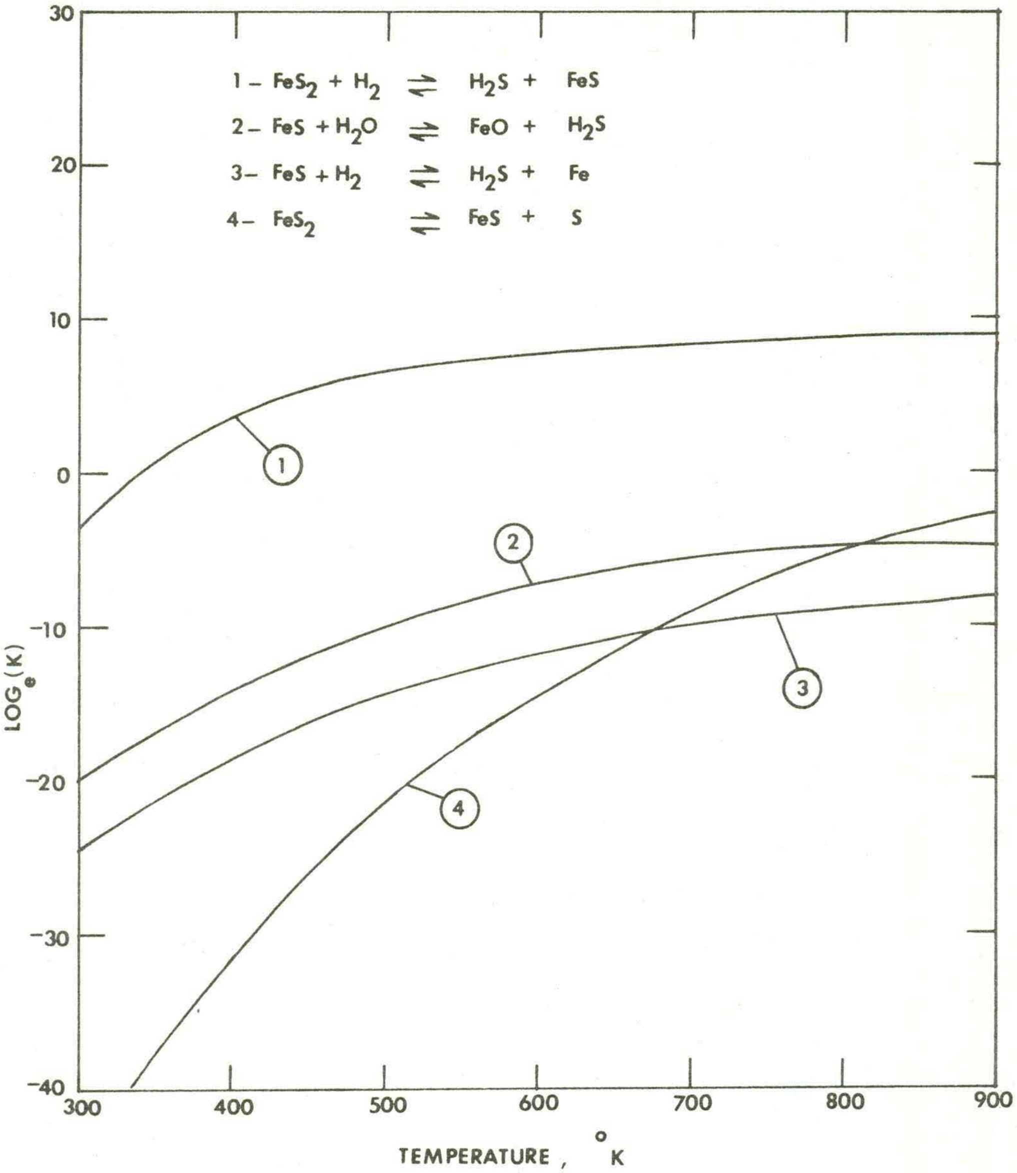

Figure 1. Equilibrium constants for the reducing reactions of iron pyrites

Figure 1. This would suggest that ferrous sulfide could exist in a more reactive form like pyrrhotite (Fe_nS_n+1, n≥5) which could react with hydrogen.

Oxidation of iron pyrites

Iron pyrites could be oxidized to a variety of products by a number of parallel reactions. Some of these reactions which are predominant in the temperature range of 400°-900°K are listed below and their equilibrium constants (K) have been plotted as functions of temperature in Figure 2.

$$FeS_2 + 3O_2 = FeSO_4 + SO_2 \tag{7}$$

$$FeS_2 + \frac{11}{4}O_2 = \frac{1}{2}Fe_2O_3 + 2SO_2 \tag{8}$$

$$FeS + 2O_2 = FeSO_4 \tag{9}$$

$$FeS + \frac{7}{4}O_2 = \frac{1}{2}Fe_2O_3 + SO_2 \tag{10}$$

$$FeS + \frac{3}{2}O_2 = FeO + SO_2 \tag{11}$$

$$FeS_2 + O_2 = FeS + SO_2 \tag{12}$$

It is clear from Figure 2 that all these reactions are exothermic in nature and are thermodynamically feasible in the temperature range 400°-900°K.

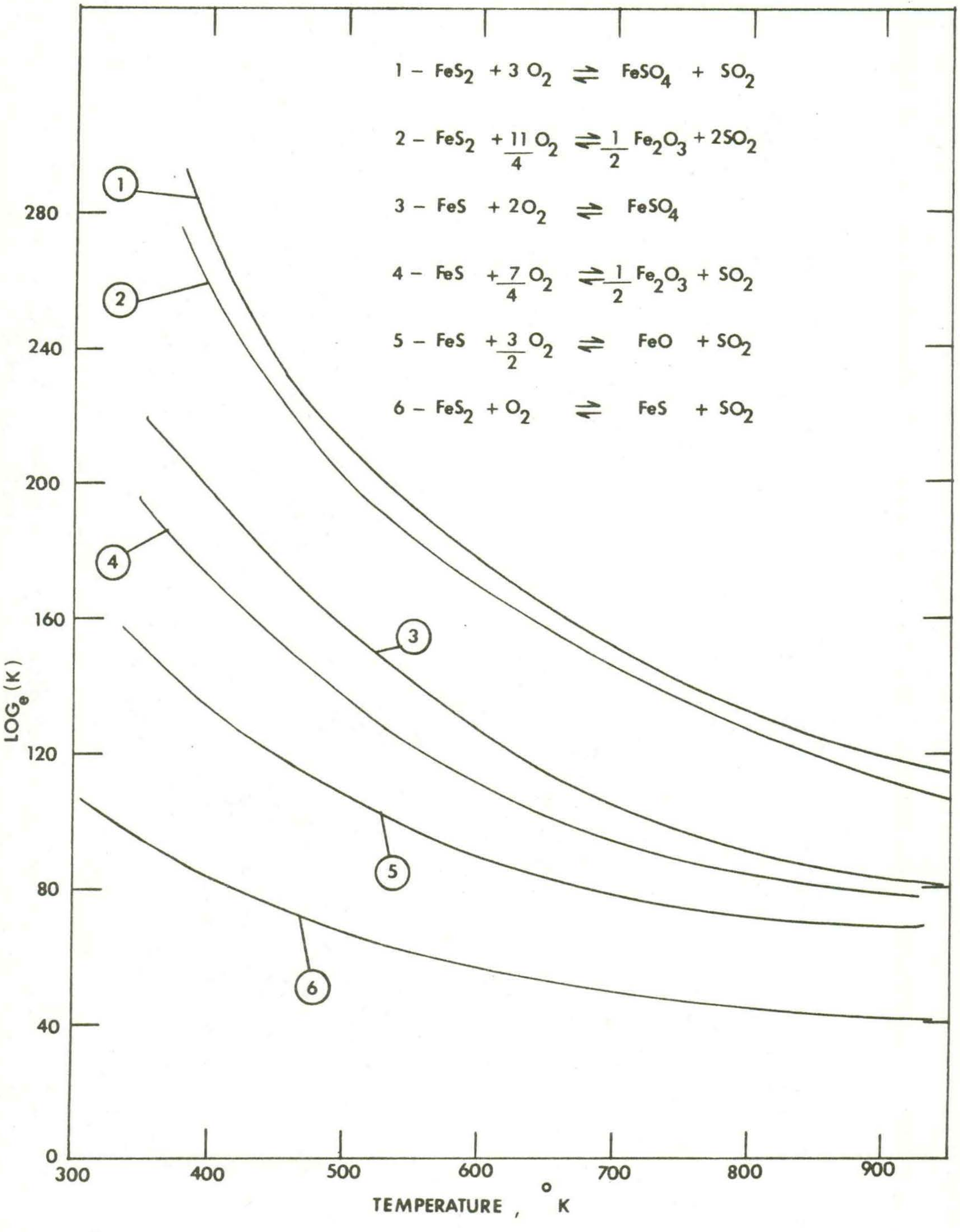

Figure 2. Equilibrium constants for the oxidizing reactions of iron pyrites

Desulfurization Kinetics

A common feature of all the early investigations of coal desulfurization has been the use of the classical, time honored method of chemical kinetics in which the extent of conversion was measured as a function of time for series of experiments, each series at a different but constant temperature. Unfortunately, this method is severely limited when applied to such a complex process as coal desulfurization because of the occurrence of a number of parallel chemical reactions, both at the desired reaction temperature and during the nonisothermal preheating period when the sample is brought to the reaction temperature. Hence, the observed result is the overall end result of a superposition of reactions.

Furthermore, the structure of organic sulfur is unknown and this makes it impossible to study the kinetics of coal desulfurization from the standpoint of a reaction mechanism.

In order to circumvent these problems Yergey et al. (52) used a nonisothermal experimental method to investigate the kinetics of coal and pyrite desulfurization in reducing and oxidizing atmospheres. In their experiments, gases were flowed over a plug of solids heated in a furnace at a controlled rate. The composition of the gases leaving the system was monitored continuously by a quadropole mass spectrometer. The results showed where activated adsorption and desorption and chemical reaction of various species occurred and the corresponding temperatures of such occurrences. The data were analyzed to provide values of the rate constant, activation energy, frequency factor and reaction order of different reactions. Important kinetic parameters for the principal hydrodesulfurization reactions and the temperatures at which they are significant are reproduced in Table 1.

Three species of organically combined sulfur were observed and kinetic parameters corresponding to the hydrodesulfurization reactions of these species were determined.

The reduction of iron pyrites to ferrous sulfide was studied by Schwab and Philinis (40). Hydrogen at a high flow rate was passed at atmospheric pressure through beds of iron pyrites particles. The results indicated a first order (with respect to hydrogen) reaction. Measurements were made at 450°, 477° and 495°C and an activation energy of 30 kcal/mole was obtained. Later Shen and Smith (42) proposed a shrinking core model for this reaction and fitted the data of Schwab and Philinis to their model. It was found that at temperatures less than 450°C a chemical reaction rate controlling mechanism gave good agreement with the data. At higher temperatures the data showed good correlation with a product-layer (FeS) diffusion controlling mechanism.

The kinetics of oxidative desulfurization have been

Table 1. Kinetic data for hydrodesulfurization of coal (Yergey et al. (52))

Reaction	Order[a]	k_o^b	E kcal/mole	Effective temperature range, °C
$(Org\text{-}S)_I + (Org\text{-}S)_{II} + H_2 \rightarrow H_2S$	1	2×10^6	22.0	220-427
$FeS_2 + H_2 \rightarrow FeS + H_2S$	1/2	1.3×10^{11}	42.1	402-552
$FeS + H_2 \rightarrow Fe + H_2S$	1	9.7×10^8	43.1	552-677
$(Org\text{-}S)_{III} + H_2 \rightarrow H_2S$	2	1.3×10^{11}	56.1	627-827
$Fe + H_2S \rightarrow FeS + H_2$	1	6.5×10^4	18.0	527-833
$Char + H_2S \rightarrow H_2S + (C\text{-}S)$	1	2.3×10^8	32.0	577-727

[a] Reaction order with respect to S-containing species.

[b] Frequency factor, units are $(atm)^{-1}(min)^{-1}$ for a first order reaction.

studied less extensively. Vestal et al. (50) showed that pyrite adsorbs oxygen strongly at 307° and 557°C respectively and evolves sulfur dioxide at 527° and 557°C. The evolution at 527°C seemed to be related to oxygen adsorption at 307°C. Thus it would appear that evolution of sulfur dioxide from pyrite occurs by two processes. When coal was subjected to an oxidizing atmosphere, sulfur dioxide evolution was observed corresponding to reactions of the following sulfur species in order of increasing temperatures $(\text{Org-S})_{I}$, $(\text{Org-S})_{II}$, FeS_2, FeS, $(\text{Org-S})_{III}$.

EXPERIMENTAL INVESTIGATION

Apparatus

Figure 3 shows a schematic flow diagram for the apparatus used in this investigation. It consisted of a fluidized bed reactor, a solids injector, a fluidized sand bath, a gas preheater, and a gas handling, sampling and analysis system.

Feed gases were metered through rotameters, combined, and the mixture was passed through the gas preheater which raised the gas to the reaction temperature. The hot gas then passed into a fluidized bed reactor which was placed in an electrically heated fluidized sand bath. Hot gases laden with tar and moisture from the reactor passed through a glass cyclone where the elutriated fines were separated and then to a tar trap where tar and moisture were condensed. The condensate was separated out in the tar trap, while the product gases were passed through a glass wool filter to eliminate any condensate mist. The dried and filtered gas then passed through a sparger into an aqueous absorbent where the sulfurous gases were absorbed and then discharged into the atmosphere. Gas samples were withdrawn at regular intervals from the dried and filtered gas stream into evacuated gas sampling flasks and were analyzed after the completion of a run with a mass spectrometer.

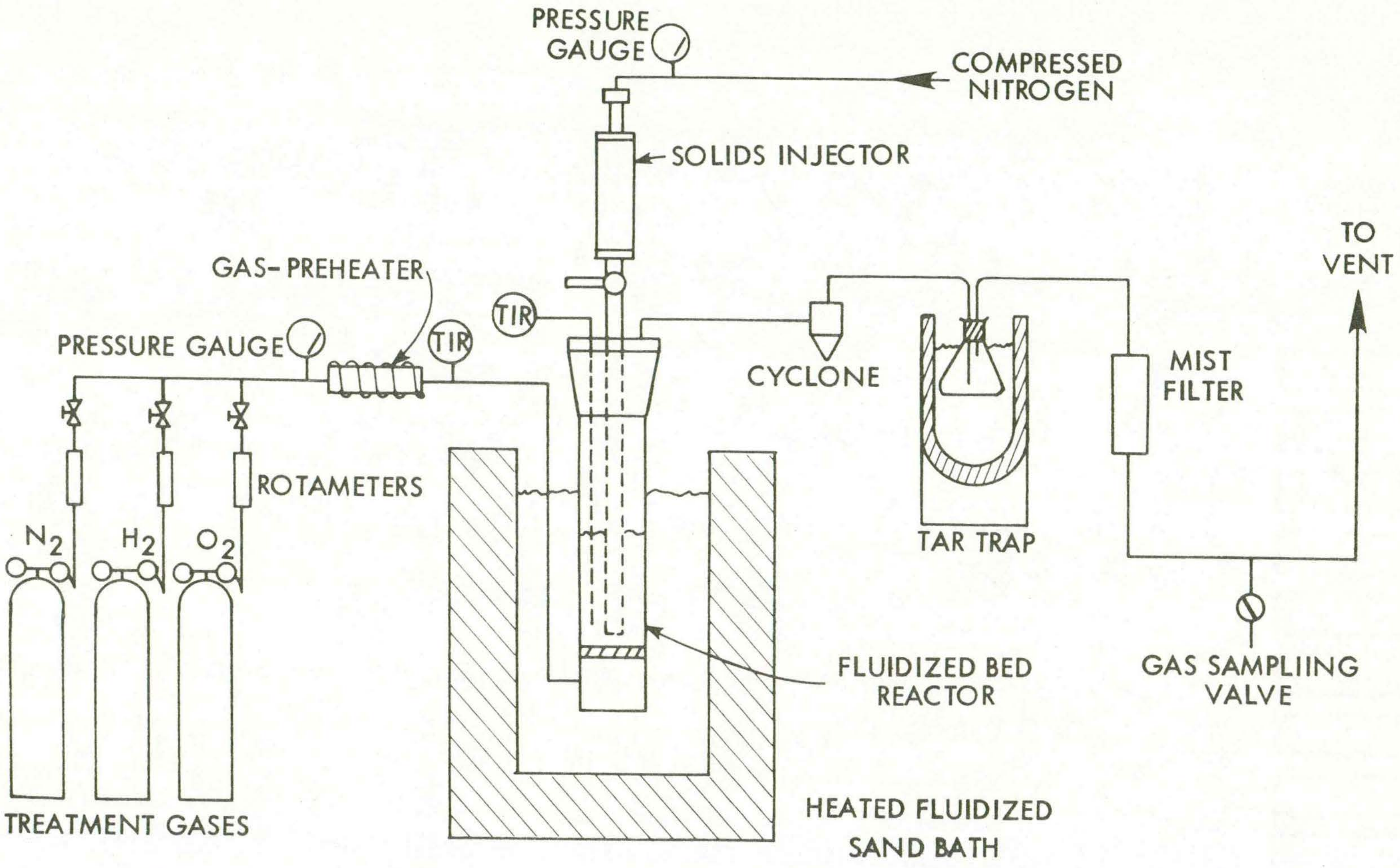

Figure 3. Flow diagram of apparatus

Gas preheater

The gas preheater was a 72 in. long, 0.375 in. I.D. stainless steel tube wound into a 4 in. diameter coil. This coil was housed in a cylindrical chamber heated by Kanthal resistance elements. The temperature of the outlet gas was measured by a 20 gauge chromel-alumel thermocouple sheathed in a 0.125 in. I.D. stainless steel hypodermic tube. The gas temperature was controlled manually by regulating the voltage supplied to the resistance elements using a variable transformer.

Fluidized sand bath

The fluidized sand bath was a 3 kW, 240 V. laboratory model supplied by Cole-Parmer Instrument Company, Chicago, Illinois. The bath utilized -80+120 mesh size Alundum particles as a medium which was fluidized by air. The granular Alundum was heated by three nichrome heaters and the bath temperature could be controlled by varying the voltage supplied to the heaters. The temperature of the bath was measured by a 20 gauge chromel-alumel thermocouple sheathed in a ceramic tube which was immersed in the bath. Finer control of the bath temperature was obtained by varying the flow rate of air through the Alundum. The maximum operating temperature of the bath was 600°C.

Fluidized bed reactor

The bench scale reactor was constructed from a 2 in. I.D., 13 in. long stainless steel pipe. The bed was supported by a 20 micron pore size sintered stainless steel plate (supplied by Newmet Products, Pequabuck, Connecticut) which acted as a gas distributor. This plate was wedged to the bottom of the reactor by a stainless steel cap which screwed on to the bottom of the reactor. The feed gas was delivered to the reactor by a 0.25 in. stainless steel pipe.

The top of the reactor was enclosed by a flared conical cap having a 15° taper and a height of 3 in. The flared top served as a solids disengaging zone for the exit gases. On this cap were mounted a thermowell, an off gas line and the solids injector. The thermowell was a 0.125 in. I.D., 15 in. long hypodermic tube which encased a 20 gauge chrome-alumel thermocouple. Temperature measurements were taken with a Honeywell multipoint potentiometric recorder.

Solids injector

The solids injector consisted of a 2 in. I.D. Plexiglas tube, 9.5 in. in height, the bottom of which was connected to a 0.5 in. ball valve. The other end of the ball valve was connected to a 0.375 in. diameter stainless steel tube which was welded to the flared cap of the reactor. When the reactor was assembled this tube extended to within 2 in. of the distributor plate. The Plexiglas injector was enclosed by a cap which was connected to a line for supplying nitrogen at 5 lb./sq.in. The flow of nitrogen was controlled by a quick opening valve.

Gas handling system

The gas handling system consisted of a cyclone and catch pot, tar trap, condensate filter, and sampling arrangement.

The cyclone was fabricated of glass and had a principal diameter of 1.5 in. The catch pot, also made of glass, was attached to the bottom of the cyclone by a ball and socket joint for easy detachment. The tar trap was a 500 mℓ. Erlenmeyer flask which was kept immersed in crushed Dry Ice in a Dewar flask. The flask was stoppered and was provided with tubes for the entry and exit of gases. The condensate filter consisted of a plug of glass wool packed into a 1 in. I.D., 6 in. long glass tube. The gas stream leaving the condensate filter was split by means of a glass tee. One of the openings in the tee was connected to a rubber hose which carried the gases to the gas absorber. The other opening of the tee was attached to a short piece of flexible hose, which could be clamped shut by a surgical clamp. Gas samples were withdrawn in evacuated 250 mℓ. gas sampling bulbs. These bulbs were provided with tubes which could be connected to the sampling tee.

Gas analysis

The gas analysis system consisted of a sampling manifold attached to a mass spectrometer and a gas absorber.

The mass spectrometer used was a magnetic type, model MS10 made by Associated Electrical Industries Ltd., Manchester, England. Samples were introduced into the sampling manifold and were leaked into the analyzer tube of the mass spectrometer through a 6 ft. length of 0.013 in. I.D. capillary tubing made of austenitic stainless steel. A block diagram showing the various operational features of the MS10 unit is shown in Figure 4.

Optimum conditions for operation of the mass spectrometer were a trap current of 50 microamperes, an electron accelerating voltage of +70 V. with respect to the cage, and an ion-repeller voltage of +1 V. with respect to the cage.

The mass spectrometer output was recorded with a Moseley 7035-A model X-4 recorder supplied by the Hewlett-Packard Company, Cupertino, California.

The gas absorber consisted of a 4 ℓ. beaker containing an alkaline solution of hydrogen peroxide of known volume and concentration. Off gases were bubbled into this solution by means of sintered glass spargers. The undissolved gases were vented to the atmosphere.

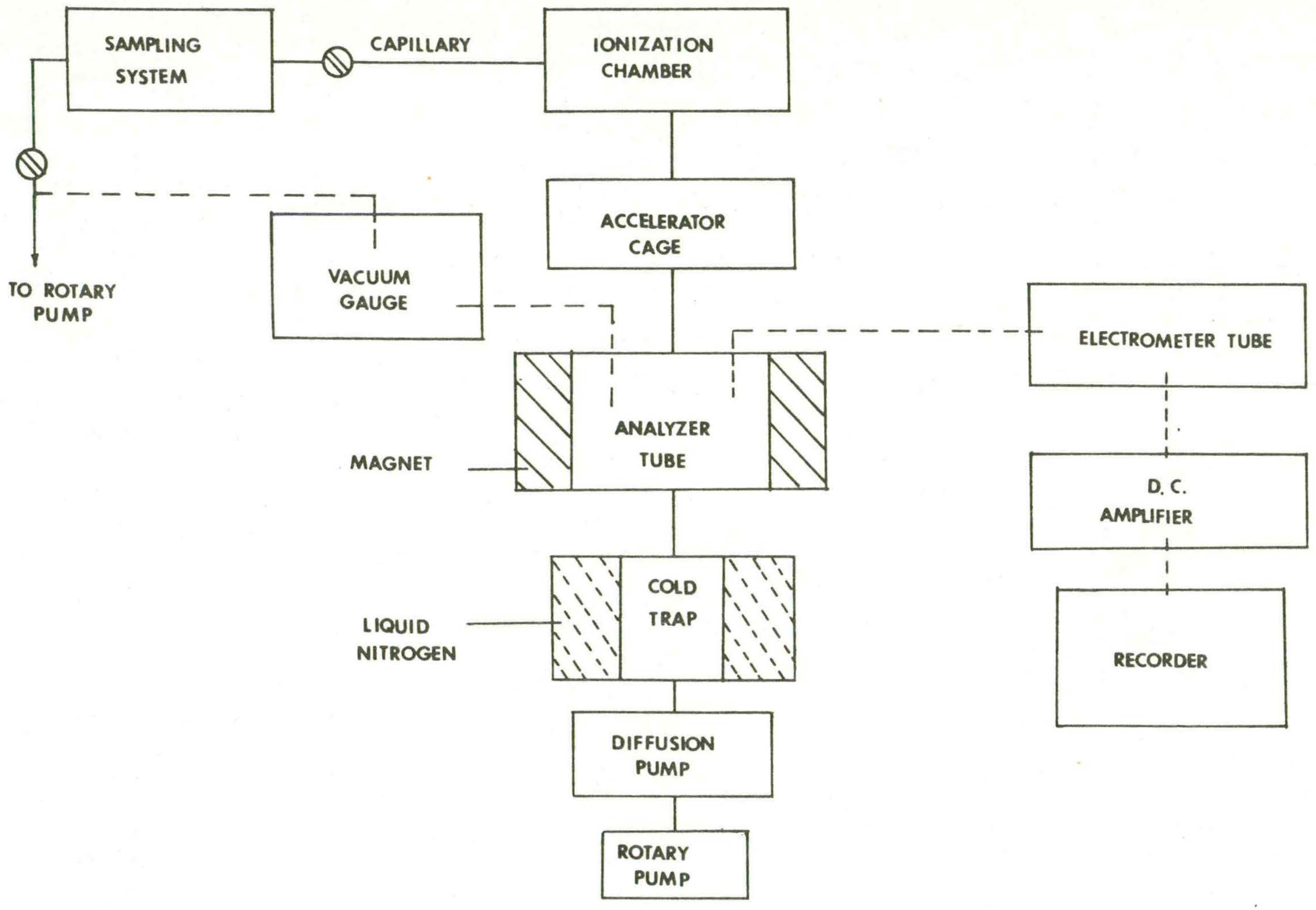

Figure 4. Block diagram of the mass spectrometer

Materials

Reactor feedstock

Series I For this series of runs two types of materials were used, that is, Run of Mine (R.O.M.) coal and Deashed coal.

A consignment of lump coal was obtained from the Jude coal mine (Iowa), crushed in a jaw-crusher, and then closely screened using U.S. standard testing sieves. The particle size cut used was in the -20+40 mesh range. After sieving, the coal was split into two fractions by using a sample splitter. One fraction was designated as R.O.M. coal and then stored in an air-tight container. The other fraction was immersed in a liquid medium whose specific gravity was equal to 1.3 g./cu.cm. The liquid medium was a mixture of hexane and tetrachloroethylene whose relative proportions were adjusted to yield a mixture with the desired specific gravity. The float product was skimmed off the liquid using a perforated ladle and then dried in an oven at about 75°C. The dried coal was then stored in an air-tight container. Since this material floated in a liquid having a specific gravity of 1.3 g./cu.cm. its ash and pyritic sulfur content was appreciably different from that in the parent R.O.M. coal. Hence, this coal was called Deashed coal. The proximate analysis and the sulfur distribution of representative samples of these materials are presented in Table 2.

Series II Here again two types of materials were used, that is, R.O.M. coal and Deashed coal. The parent coal was also obtained from Jude mine. However this batch of coal was mined at a later date than the batch used in Series I. The particle size fractions and the method of deashing used were identical to those described for Series I. The proximate analysis and the sulfur distribution of the materials for the Series II runs are given in Table 3.

Series III The feedstock used for this set of runs consisted of iron pyrites obtained from the ICO mine (Iowa). Lump pyrites were crushed by a jaw-crusher and the material was screened using U.S. standard testing sieves. The two size fractions which were separated for use were a -40+60 mesh cut and a -80+100 mesh cut which had a total sulfur content of 55.80 percent and 58.00 percent, respectively.

Inert bed material

The material used for the fluidized bed in the reactor had to satisfy three criteria. First, it had to be an inert solid which would not react with the treatment gas nor interact with the coal or pyrite. Second, it had to be granular and nonagglomerating in order to provide a well mixed fluidized bed and facilitate rapid heat transfer to the feed solids. Third, in order to minimize particle segregation

Table 2. Solids analysis of feedstock for Series I

	R.O.M. Coal		Deashed Coal	
Type of Analysis	As received	Moisture and ash free	As received	Moisture and ash free
Proximate analysis				
Moisture	6.35%	---	2.24%	---
Volatile matter	41.14%	51.53%	46.03%	48.52%
Fixed carbon	38.68%	48.47%	48.84%	51.48%
Ash	13.83%	---	2.90%	---
Total sulfur	6.43%	8.06%	4.95%	5.22%
Sulfate sulfur	0.49%	0.62%	0.39%	0.41%
Pyritic sulfur	2.40%	3.01%	0.60%	0.63%
Organic sulfur	3.54%	4.43%	3.97%	4.18%
Heating value				
Btus./lb.	10981	13756	13428	14155

Table 3. Solids analysis of feedstock for Series II

Type of Analysis	R.O.M. Coal As received	R.O.M. Coal Moisture and ash free	Deashed Coal As received	Deashed Coal Moisture and ash free
Proximate analysis				
Moisture	5.37%	---	4.04%	---
Volatile matter	40.61%	50.76%	45.60%	48.98%
Fixed carbon	39.41%	49.24%	47.50%	51.02%
Ash	14.61%	---	2.86%	---
Total sulfur	8.06%	10.08%	6.25%	6.82%
Sulfate sulfur	0.76%	0.95%	0.38%	0.41%
Pyritic sulfur	2.87%	3.59%	0.60%	0.64%
Organic sulfur	4.43%	5.54%	5.37%	5.77%
Heating value				
Btus./lb.	10860	13575	12992	13955

and to ensure homogeneous fluidization it was necessary that both the inert bed material and the reactor feedstock have similar fluidizing velocities.

With these criteria in mind it was decided to use silica sand as the bed material. Grade 37 sand (supplied by Martin Marietta Co., Cedar Rapids, Iowa) was screened into various fractions using U.S. standard testing sieves. A 2 in. I.D. fluidization column made of Plexiglas was used to conduct fluidizing tests on the reactor feed materials and various size fractions of sand. Table 4 presents the values obtained for the minimum fluidizing velocities of the sand and feed material employed in each series of runs.

General Procedures

Experimental procedure

In preparing for a run, a representative sample of the desired reactor feedstock was obtained by using a riffle separator. This sample was weighed out and kept aside for charging to the reactor.

The fluidized sand bath was readied for the run by turning on the air flow for fluidization and the power supply to the resistance heaters. It usually took about 3 hr. to raise the temperature of the bath to 350°C.

The reactor was charged with a weighed quantity of sand

Table 4. Fluidizing velocities of bed and reactor feed materials

Series	Bed Material	Umf[a] cm./sec.	Feed Material	Umf[a] cm./sec.
I	-40+50 sand	13.2	-20+40 R.O.M. coal	15.0
I	-40+50 sand	13.2	-20+40 Deashed coal	14.5
II	-40+50 sand	13.2	-20+40 R.O.M. coal	14.0
II	-40+50 sand	13.2	-20+40 Deashed coal	13.1
III	-20+30 sand	17.1	-40+60 Pyrite	18.2
III	-60+80 sand	5.4	-80+100 Pyrite	5.1

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[a] Superficial air velocity at incipient fluidization.

of the desired particle size. The reactor tube was then fitted with the flared cap and thermocouple. A high temperature anti-sieze compound was applied to the threads to insure easy removal of the cap at the end of a run. The assembled reactor was then lowered into the sand bath and clamped securely.

The gas inlet tube of the reactor was coupled to the gas preheater and the heating elements of the preheater were energized. During the heat-up period when the sand in the fluidized bed reactor was brought to the desired reaction temperature, air was used as a fluidizing agent. This was done by attaching a compressed air supply line through a diaphragm pressure reducing valve to the preheater gas inlet. The air velocity was kept close to the minimum fluidizing velocity of the sand.

Next, the gas handling system was readied. The cyclone, tar trap, condensate mist filter, and connecting glass lines were weighed and then assembled. The inlet to the cyclone was connected to the reactor off gas line. The tar trap was embedded in crushed Dry Ice contained in a Dewar flask. All glass equipment upstream of the tar trap was lagged with heating tapes which were then energized.

A solution was made up of 500 mℓ. of 30 percent hydrogen peroxide, 200 mℓ. of 30 percent ammonium hydroxide and 2300 mℓ. of distilled water. This solution was placed in the absorber and the hose carrying the reactor off gases was coupled to the sparger.

While the system was being assembled, the gas sampling bulbs were individually evacuated by the rotary pumps of the mass spectrometer. After evacuation, the residual pressure in the bulbs was about 40 microns of mercury.

Once the reactor was heated to within 10°C of the desired temperature, the air supply was cut off and replaced by the treatment gas mixture. Feed gas flow rates were set at the desired levels by adjusting the appropriate rotameters.

When the temperature of the preheated gas and that of the sand in the reactor came to steady state, the system was considered ready for injection of the reactor feed material. For the rest of the experiment the power supply settings for all heating elements in the system remained fixed.

The solids injector was now attached to the top of the reactor and the reactor feed material was poured into the injector. The material was compacted by tapping the sides of the injector tube. This was found to improve the flow characteristics of the granular solids. The injector tube was then closed with the cap and pressurized with nitrogen by opening the quick opening valve attached to the cap. The ball valve was then opened and the feed material flowed under nitrogen pressure into the preheated bed of sand in the reactor. This injection marked the beginning of a run. The ball valve was then closed and the injector removed from the reactor.

Gas samples were taken at discrete time intervals by attaching the sampling bulbs to the flexible hose connected to the sampling tee and withdrawing gas until the pressure inside the bulb equalized with the pressure of the gas stream.

At the end of a run, the power supplies for the sand bath and preheater were switched off, and after shutting off the gas flow, the reactor was uncoupled from the process lines and removed from the sand bath. The reactor tube was then doused with cold water to cool the reactor to room temperature. The reactor contents were then collected, weighed and sieved to separate the sand from the reacted residue. The latter was ground in a Mikro-Samplmill to -60 mesh size and then analyzed for the sulfur distribution, heating value and proximate analysis.

The material collected in the cyclone catch pot constituted the fines carry over. Tar was condensed mainly in the tar trap but some of it also collected on the walls of the glass tubing, the cyclone, and the condensate mist filter. Hence, the glass equipment was weighed and the difference between the final and initial weights yielded the weight of tar and moisture evolved during the run.

Operation of the mass spectrometer

Gas samples collected in the sampling bulbs during a run were analyzed with the mass spectrometer. The following species were expected in the off gas due to coal devolatilization, desulfurization and combustion.

(1) Hydrogen (H_2)
(2) Oxygen (O_2)
(3) Nitrogen (N_2)
(4) Carbon dioxide (CO_2)
(5) Carbon monoxide (CO)
(6) Methane (CH_4)
(7) Ethane (C_2H_6)
(8) Propane (C_3H_8)
(9) Hydrogen sulfide (H_2S)
(10) Sulfur dioxide (SO_2)
(11) Carbon oxysulfide (COS)

Since the sampling point was situated downstream of the tar trap, the gas was essentially free of moisture and tar. Hence, the gas was not analyzed for benzene, napthalene and other aromatic fractions commonly present in tar.

The purpose of using a mass spectrometer was to identify the types and concentrations of the gaseous species and to estimate quantitatively the total moles of each species produced during a run.

In order to fulfill the second objective it was necessary to have a reference element whose flow rate was known during the course of a run. A convenient element for this purpose was nitrogen. In all runs the treatment gas consisted of a mixture of a reactive gas and nitrogen whose molar flow rates were known. Hence, it was possible with the mass spectrometer to determine the concentration of the gaseous species of interest relative to the concentration of nitrogen. Thereby, knowing the molar throughput of nitrogen, it was possible to obtain the molar yields of the other gaseous species. The assumption made was that the devolatilization of coal did not yield any appreciable amount of nitrogen. This was consistent with the findings of Groom (22) who reported that the yield of nitrogen from devolatilization was insignificant compared to other gases.

Sampling system The gases contained in the sampling bulbs were introduced into the mass spectrometer by means of a specially fabricated sampling system shown in Figure 5. This manifold was needed for two reasons. First, the pressure inside the analyzer tube of the mass spectrometer was of the order of 10^{-6} cm. of mercury. Hence, this necessitated a device which could isolate small volumes of gas from the bulb in a leak-proof fashion and deliver it at sub-atmospheric pressure through the capillary tube into the mass spectrometer. Second, the calibration factors of various gases analyzed with a mass spectrometer are dependent on the total

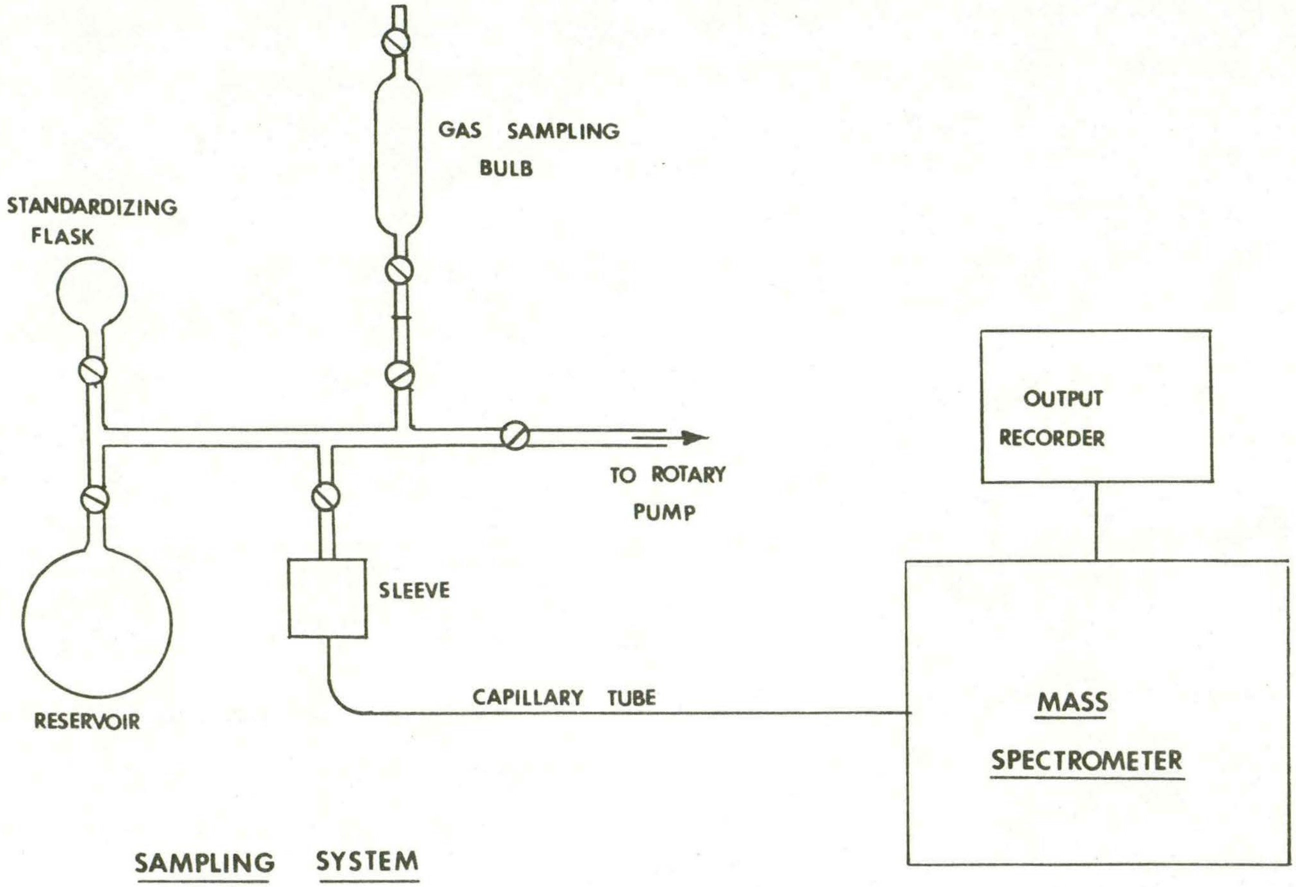

Figure 5. Block diagram of the sampling system

pressure of the gas sample. Hence, this required a fairly large reservoir which would damp out pressure fluctuations arising from gas withdrawal through the capillary tube.

The operation of the sampling system is clarified by referring to Figure 5. Before introducing a gas sample, the system including the capillary tube was completely evacuated by the rotary pump. After this preliminary evacuation, the capillary, reservoir and standardizing flask were isolated by closing appropriate valves. The gas sampling bulb was then attached to the manifold. After evacuating the glass stems of any residual air, the rotary pump was closed off and the pressure in the sampling bulb was equalized with that in the standardizing flask. The valve on the bulb was then closed and the gas in the standardizing flask was expanded into the reservoir. After closing the valve on the reservoir, the standardizing flask was evacuated and the entire procedure was repeated. Thereby it was possible to remove two equal volumes of gas from the sampling bulb and expand them in the reservoir using the standardizing flask as an intermediate container. After this, the valves on the standardizing flask and the sampling bulb were evacuated and the rotary pump was closed off to the manifold. The reservoir was now opened to the capillary tube through which the gas flowed into the mass spectrometer.

Calibration and gas analysis In the current investigation the gas analysis was performed for the eleven gases listed above. Each gas produced its own characteristic spectrum of ionized fragments completely independent of all the other gases present. Thus, the mass spectrum of the mixture of gases was a linear superposition of the spectra of all the components present. Hence, in order to compute the analysis of a gas mixture, it was necessary to know the mass spectra of each of the component gases. These spectra were obtained by running samples of the pure gases through the instrument and, from the individual spectra found, the relative intensity of each component gas at various mass/charge ratios was determined.

The response factor for each component gas was determined by running 50:50 mixtures of nitrogen and the gas and estimating the ratio of the response of nitrogen to that of the component gas.

The mass spectral analysis of a gas sample from a typical experiment yielded peaks for mass/charge ratios ranging from 2 to 64. The relative molar concentration of each gas component was then obtained by solving a set of simultaneous equations to resolve the spectra into contributions from individual gases. These contributions were then multiplied by the appropriate response factors to obtain the molar concentration of each component with respect to the reference element nitrogen. All calculation procedures were incorporated in a computer program which performed the computations necessary to determine the volume percent of each component in the reactor off gas sample and its cumulative molar yield.

Titrimetric estimation of sulfur removal

Although the mass spectral analysis gave the yields of various sulfurous gases obtained during a run, a check was needed to guard against gross experimental or analytical error. This check on the cumulative yields of hydrogen sulfide, sulfur dioxide and carbon oxysulfide was provided by titrimetric estimation of the sulfate ions present in the absorbent solution. The solution was titrated with standard barium chlorate solution using thorin as an indicator. Details of this analytical procedure are reported by Fritz and Yamamura (16).

Chemical analysis of solids

The reactor feedstock and the residue after a run were chemically analyzed for mositure, ash, volatile matter and fixed carbon. Sulfur determinations were performed to obtain the concentration of total sulfur, pyritic sulfur and sulfate sulfur. The organic sulfur content was determined by difference. The heating values of coal and char were estimated with a bomb calorimeter.

All these chemical analyses conformed to the standards laid down by the American Society for Testing and Materials. Details of these analytical procedures are given elsewhere (1).

EXPERIMENTAL CONDITIONS AND RESULTS

The experimental program was broken down into three independent series of runs whose respective objectives are outlined below. The results of these three series of runs are presented separately.

In Series I, a scheme of experiments was devised to study the effects of temperature, type of treatment gas, and the ash content on the devolatilization and desulfurization of coal. The char residues from the reactor were chemically analyzed to provide a sulfur distribution and proximate analysis. These experiments did not include a time variant analysis of the reactions involved.

Series II consisted of runs performed to study the reactions of coal devolatilization, combustion, and desulfurization as a function of time. In this series mass spectral and titrimetric procedures were utilized for analyzing reactor off gases.

The runs in Series III were similar to those in Series II except that the feedstock was not coal but iron pyrites. An attempt was made to study the kinetics of the desulfurization of iron pyrites by monitoring the concentration of different sulfurous gas species in the off gas.

Series I Experiments

Factorial design of experiments

A set of experiments was designed to statistically examine the effects of various treatment gases, reaction temperatures and ash contents on different dependent parameters such as weight loss, volatile matter loss, and sulfur removal. The factorial design of experiments consisted of a 2x4x3 hierarchical or nested classification with three stages namely, type of coal, type of treatment gas and the reaction temperature.

The first stage had two types of coal and these were R.O.M. coal and Deashed coal. The method of preparing the two coals and the procedure used to obtain a representative sample for each experiment were discussed above. The major difference between the two coals was the ash or mineral matter content.

The second stage of the design was made up of four different treatment gases. Actually three reactive gases and one inert gas were employed. The inert gas was used to demonstrate the effects of the spontaneous pyrolytic reactions occurring in the coal at elevated temperatures. For the purpose of statistical analysis, the gases were called:

(a) hydrogen (85 percent concentration in nitrogen)

(b) low oxygen (3.8 percent concentration in nitrogen)

(c) high oxygen (9.5 percent concentration in nitrogen)

(d) nitrogen (100 percent)

Thus for each type of coal the design consisted of a block of experiments using a reducing atmosphere (with hydrogen), two blocks using oxidizing atmospheres (with low and high oxygen) and one using an inert atmosphere (with nitrogen).

In the third stage of the factorial design, three temperature levels were employed. For the statistical study these levels were designated as high, intermediate and low and they corresponded to approximate reactor temperatures of 400°, 325° and 240°C. Two replications of runs were attempted in all the blocks at the high and low temperature levels. Temperatures greater than 400°C were not included in the factorial design since preliminary runs had shown conclusively that at higher temperatures coal softening leads to agglomeration which is detrimental to the operation of the fluidized bed.

Operating conditions

The experimental procedure adopted for the 40 runs in this series deviated to some extent from the general procedure outlined above. First, the mass spectrometer and the gas absorber were not employed in these runs since a gas analysis was not required. Second, the tar trap was not used and, hence, the yields of tar and moisture were not determined.

In the experimental set-up, the reactor off gases, after passing through the cyclone, were vented to the atmosphere.

In each run 50 g. of coal were injected into a preheated bed of sand. Since 400 g. of sand were used, the ratio of sand to coal was 8. As soon as the coal had descended into the bed, some carry over of solids was noticed in the cyclone. The initial carry over was due to the action of the compressed nitrogen used in the solids injector tube. The weight of the coal actually treated was obtained by subtracting the weight of the coal recovered in the cyclone, from the weight of the feed.

The purpose of the preheated sand in the reactor was to provide a source of heat which would rapidly heat the coal to the reaction temperature. With the exception of the high temperature runs where a high oxygen concentration was used in the treatment gas, the coal rapidly attained the temperature of the bed and remained steady for the duration of the experiment. Thus these runs were assumed to have been conducted under essentially isothermal conditions. The thermal behavior of the reactor and other operating conditions are presented in Tables 5 and 6. Time variant temperature profiles in the reactor for typical runs are shown in Figure 6. In regard to this diagram, time zero represents the time when coal was injected.

The runs conducted at high temperatures using high oxygen

Table 5. Operating conditions for runs in Series I, R.O.M. coal[a]

Run no.	Wt. of coal treated g.	Concen. of treatment gas	Thermal behavior: Temp. drop on coal injection, °C	Thermal behavior: Coal preheat time, min.	Thermal behavior: Av. temp. during run, °C	Superficial gas velocity,[b] cm./sec.
H-1	49.6	85.1% H_2	42	9	232	29.7
H-8	50.0	85.1% H_2	25	9	243	30.7
H-4	49.9	85.1% H_2	50	5	321	35.3
H-2	46.9	85.1% H_2	50	6	396	39.8
H-9	50.0	85.1% H_2	28	9	402	40.1
N-3	49.9	100% N_2	22	6	235	28.6
N-13	49.9	100% N_2	39	6	235	28.6
N-11	50.0	100% N_2	39	6	324	33.6
N-8	50.0	100% N_2	47	8	396	37.6
N-9	50.0	100% N_2	25	7	399	37.8

---

[a] All runs were conducted for a duration of 30 min.

[b] Calculated at the temperature of the feed gas.

Table 5. (continued)

Run no.	Wt. of coal treated g.	Concen. of treatment gas	Thermal behavior Temp. drop on coal injection, °C	Coal preheat time, min.	Av. temp. during run, °C	Superficial gas velocity, cm./sec.
O-1	49.7	3.8% O_2	34	7	232	29.2
O-22	49.8	3.8% O_2	34	8	235	29.4
O-7	49.5	3.8% O_2	28	5	321	34.4
O-2	45.2	3.8% O_2	42	12	412	29.6
O-17	50.0	3.8% O_2	45	13	411	39.6
O-8	49.7	9.5% O_2	22	7	243	29.4
O-11A	49.8	9.5% O_2	22	7	236	29.0
O-4	49.2	9.5% O_2	39	9	332	36.1
O-18	47.1	9.5% O_2	45	6	449	39.0
O-20	48.9	9.5% O_2	39	7	435	39.0

Table 6. Operating conditions for runs in Series II, Deashed coal[a]

Run no.	Wt. of coal treated g.	Concen. of treatment gas	Thermal behavior Temp. drop on coal injection, °C	Thermal behavior Coal preheat time, min.	Thermal behavior Av. temp. during run, °C	Superficial gas velocity,[b] cm./sec.
H-5	50.0	85.1% H_2	17	6	229	29.8
H-6	49.9	85.1% H_2	17	7	227	29.7
H-3	49.9	85.1% H_2	33	7	322	35.4
H-7	50.0	85.1% H_2	47	6	396	39.8
H-10	50.0	85.1% H_2	39	9	399	39.9
N-4	49.8	100% N_2	17	6	235	30.2
N-7	49.9	100% N_2	28	9	242	30.6
N-12	50.0	100% N_2	31	9	316	35.0
N-5	49.9	100% N_2	47	7	413	40.8
N-10	50.0	100% N_2	46	9	399	39.9

---

[a] All runs were conducted for a duration of 30 min.

[b] Calculated at the temperature of the feed gas.

Table 6. (continued)

Run no.	Wt. of coal treated g.	Concen. of treatment gas	Thermal behavior			Superficial gas velocity,[b] cm./sec.
			Temp. drop on coal injection, °C	Coal preheat time, min.	Av. temp. during run, °C	
O-10	49.8	3.8% O_2	19	9	235	29.4
O-12	49.9	3.8% O_2	17	8	246	30.0
O-21	49.9	3.8% O_2	28	7	324	34.5
O-15	49.8	3.8% O_2	44	8	402	39.0
O-19	50.0	3.8% O_2	25	7	410	39.5
O-9	49.8	9.5% O_2	14	6	235	29.0
O-13	49.9	9.5% O_2	31	6	249	29.8
O-5	49.5	9.5% O_2	33	6	324	34.0
O-14	48.8	9.5% O_2	33	6	460	38.9
O-16	49.2	9.5% O_2	42	6	427	38.9

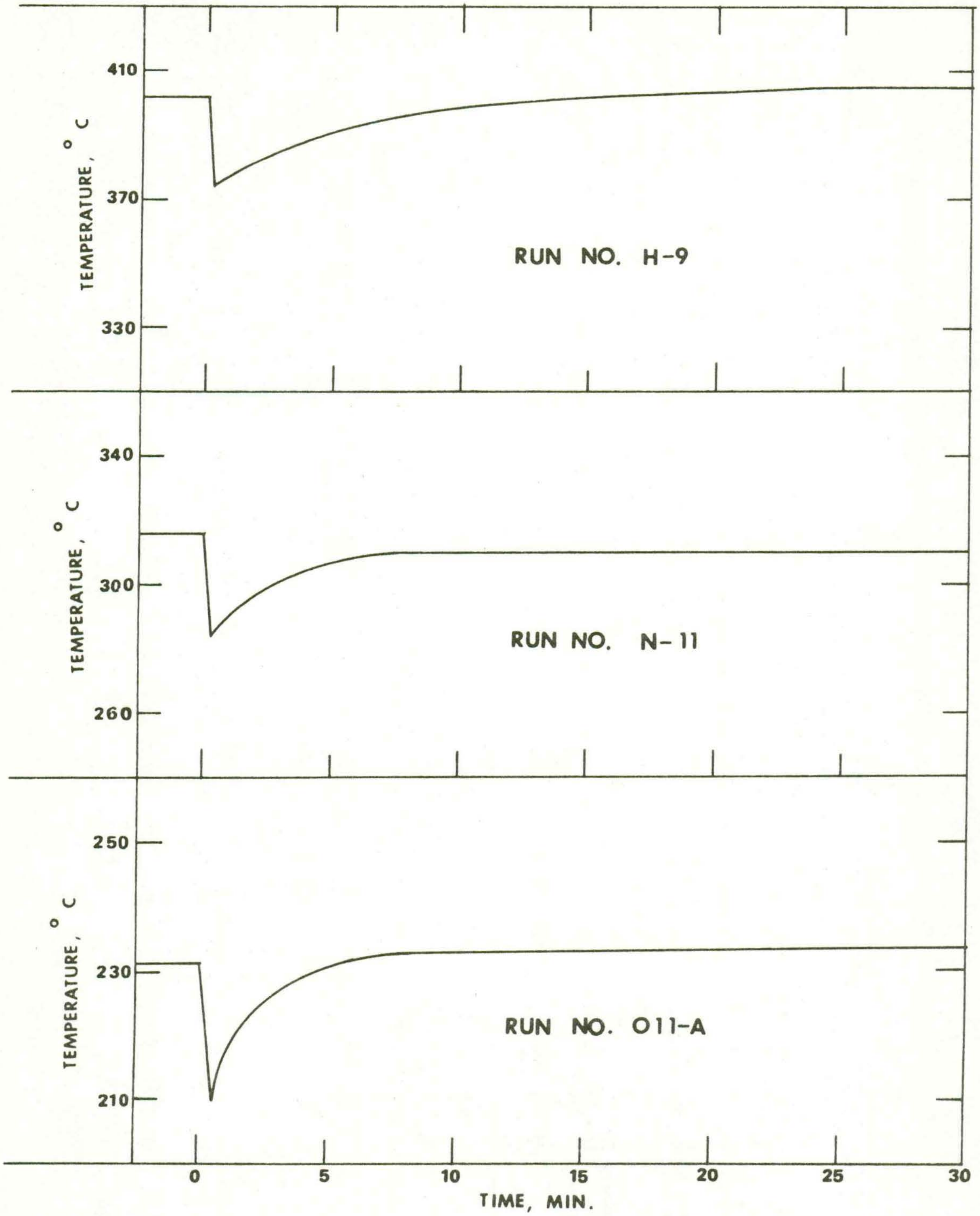

Figure 6. Typical time variant temperature profiles in the reactor, Series I

gas were not truly isothermal. This is evident on examining Figure 7 which shows the temperature variation in the reactor before and after injection of coal. The nonisothermal behavior was probably due to runaway combustion of the coal within the bed and the temperature rise was caused by the substantial exothermic heat of reaction. Since these runs did not conform to the isothermal requirements laid down in the factorial design, they were not included in the statistical analysis. However, for purpose of comparison, the data from these runs have been plotted in the graphs that follow. The temperature coordinate of these data points corresponds to the temperatures in the reactor midway through the run.

Experimental results

In order to get meaningful results from these runs, it was necessary to make a systematic statistical analysis. This ensured that any conclusions drawn from the study would take into consideration the random errors in the observations and the scatter inherent in the data.

Statistical analysis The lay-out of experiments consisted of a 2x4x3 hierarchy which generated 24 treatment blocks. The third stage of the hierarchy was temperature level where the high and low levels were replicated twice. Thus there were two observations in each of 16 treatment blocks at high and low temperature levels. The intermediate

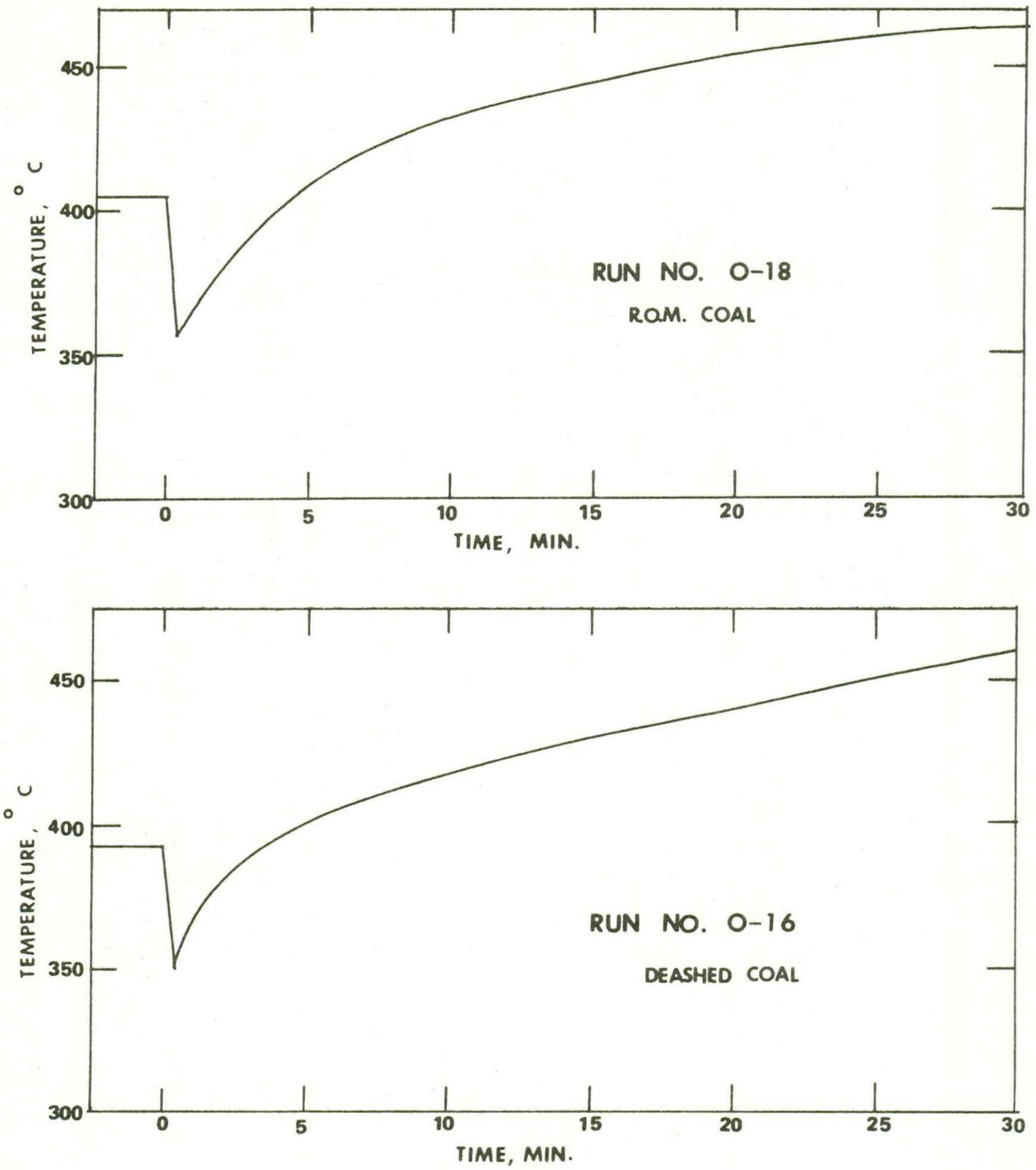

Figure 7. Time variant temperature profiles showing nonisothermal behavior, Series I

temperature level was not duplicated, hence, each of these treatment blocks had only one observation.

The first step in the procedure was to determine the mean and variance of the observations in each of the doubly replicated treatment blocks. Then the overall variance (s^2) was determined by equation 13.

$$s^2 = \frac{\sum_{k=1}^{m} [(n_k - 1) s_k^2]}{\sum_{k=1}^{m} (n_k - 1)} \qquad (13)$$

where m = total number of blocks having duplications

s_k^2 = variance in the kth treatment block

n_k = number of observations in a doubly replicated block (n_k=2)

A contrast could then be set up between any two treatment blocks, each containing two replications. The significance of the contrast was tested by using Scheffé's test for multiple comparisons (28). The method adopted is shown below for a generalized case.

The contrast was set up as the following null hypothesis (H_o).

$$H_o\colon \ W_a - W_b = 0 \qquad (14)$$

where W_a, W_b = treatment means at identical temperature levels

The variance (V) for this contrast is given by equation 15.

$$V = V(W_a) + V(W_b) \tag{15}$$

where $V(W_i) = s^2$ (16)

$i = a,b$

s^2 = overall variance given by equation 13

The critical value, C, for the test is given by equation 17.

$$C = \sqrt{\nu_1 f_{\nu_1,\nu_2,(1-\alpha)} V} \tag{17}$$

where ν_1 = (total number of blocks available for contrasts)-1

ν_2 = total number of blocks with two replications

α = level of significance

f = F distribution statistic

The criterion for rejecting the null hypothesis, H_o, is given by inequality 18.

$$\left|\overline{W}_a - \overline{W}_b\right| > C \tag{18}$$

where $\bar{W}_a, \bar{W}_b$ = estimated sample means for the blocks under comparison.

Scheffé's test for contrasts was used only for those treatment blocks which contained replicated observations. Hence this test was not used to compare means at the intermediate temperature levels.

The statistical procedure shown above was employed for the analysis of various parameters of devolatilization and desulfurization.

Weight loss The percent weight loss for any experiment was defined as

$$\% \text{ weight loss} = 100 \left[\frac{\text{Wt. of coal treated} - \text{Wt. of residue}}{\text{Wt. of coal treated}} \right] \tag{19}$$

Table 7 gives the values of the mean observations for the percent weight loss in all the treatment blocks. The overall variance which was obtained from the 14 blocks containing two replications was 8.1. Since the high temperature runs using high oxygen treatment gas were excluded the total number of blocks available for contrasts was 14. The critical value, C, was estimated to be 14.6 at a level of significance, α, of 0.1.

Scheffé's test showed that there were no significant

Table 7. Mean weight loss (%) for different treatments, Series I

Temp. level	Treatment gas			
	N_2	H_2	low O_2	high O_2
		R.O.M. coal		
Low	11.6	11.8	11.7	10.0
Intermediate	14.0[a]	15.0[a]	16.0[a]	18.5[a]
High	31.6	33.6	30.7	--
		Deashed coal		
Low	5.0	3.9	2.2	2.6
Intermediate	7.2[a]	9.0[a]	8.2[a]	9.9[a]
High	33.9	39.3	28.0	--

[a] Blocks containing only one observation.

differences between treatment blocks due to the type of coal or the type of treatment gas. This meant that any apparent differences between treatment means at the same temperature level were masked by the random error in the observations.

Figure 8 shows the variation of the percent weight loss with the reaction temperature. On examining this graph it can be seen that at the low and intermediate temperature levels the weight loss obtained with R.O.M. coal was slightly greater than that obtained with Deashed coal. However at the

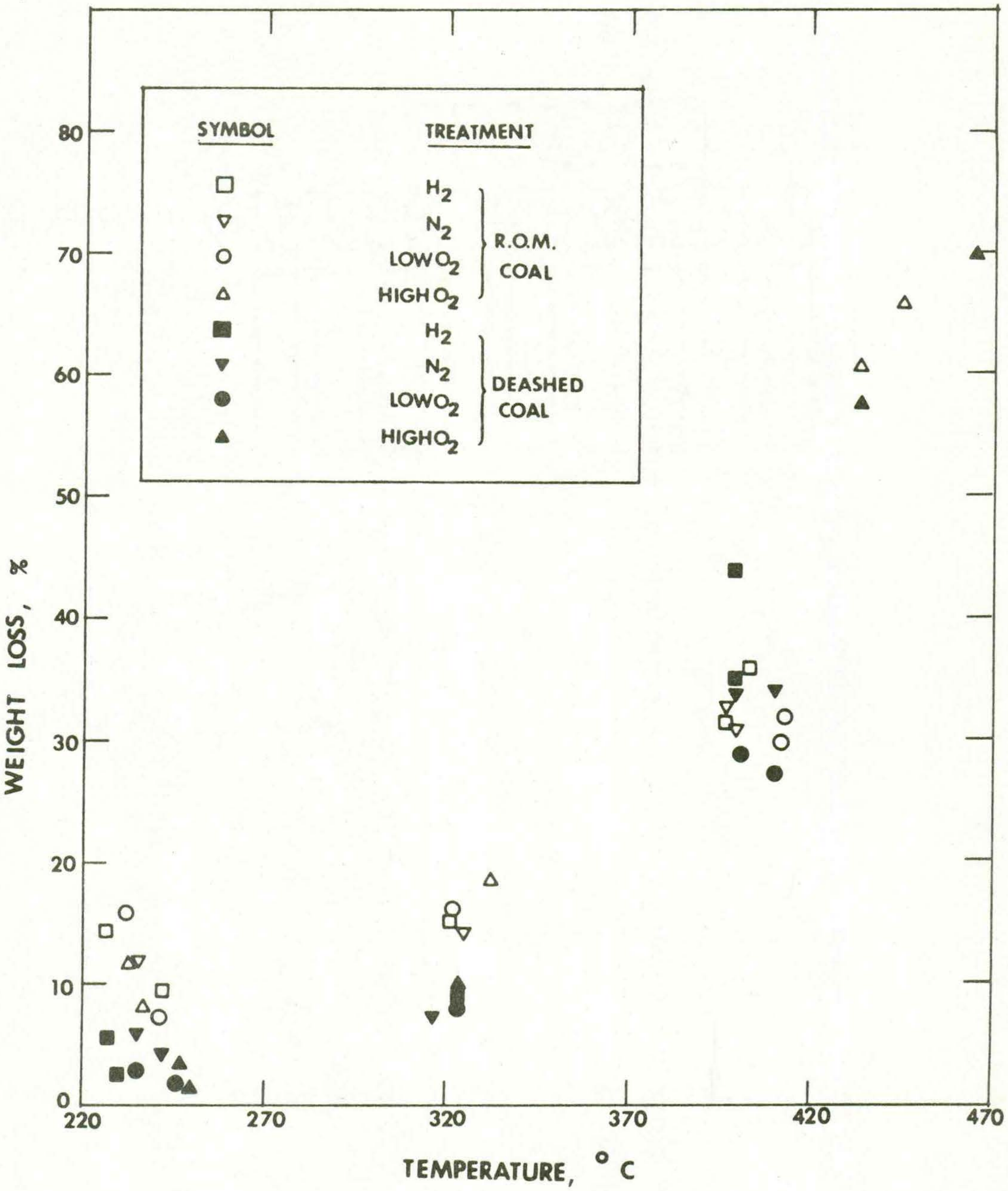

Figure 8. Variation of coal weight loss with reaction temperature

high temperature level the weight loss appeared to be independent of the type of coal. This is in conflict with the inference drawn from Scheffé's statistical test which showed no significant contrasts. However this does not detract from the validity of the statistical analysis. Scheffé's test, in general, tends to give conservative estimates. It is entirely possible that if the factorial design of experiments had included more replications the differences in the observations for the two types of coal would become significant in a statistical test.

In order to study the effect of temperature on weight loss a temperature dependency function for the fractional weight loss (W) was chosen and its significance was tested by the "t-test".

The model used for this purpose was the following first order kinetic rate equation proposed by Wiser et al. (51)

$$\frac{dW}{dt} = k(1-W) \qquad (20)$$

where W = fractional weight loss at any time

k = assumed reaction rate constant

Wiser et al. assumed an Arrhenius type exponential relation for k. Substituting this relation for k in equation 20, and integrating between the time limits o and τ (duration of the run) the following relation is obtained:

$$-\ell n(1-W_f) = k_1 e^{-k_2/T}\tau \tag{21}$$

where W_f = fractional weight loss at $t=\tau$

k_1, k_2 = constants

T = reaction temperature, °K

Taking the logarithm of both sides of equation 21 reduces it to

$$\ell n[-\ell n(1-W_f)] = \ell n k_1 + \ell n \tau - \frac{k_2}{T} \tag{22}$$

The weight loss was correlated with the reaction temperature using equation 22. A linear regression yielded the following equation.

$$\ell n[-\ell n(1-W_f)] = 4.37 - \frac{3.67\times10^3}{T} \tag{23}$$

At 90 percent confidence, a t-test showed that the temperature coefficient in equation 23 was significantly different from zero. This established that the weight loss is a sensitive function of reaction temperature.

<u>Volatile matter loss</u> The percent loss of volatile matter was estimated by equation 24.

$$\%\text{ volatile matter loss} = 100\left[\frac{\text{wt. of vol. matter in feed} - \text{wt. of vol. matter in residue}}{\text{wt. of vol. matter in feed}}\right] \tag{24}$$

The volatile matter content of the feed coal and the residue was obtained from the proximate analysis. The variation of percent volatile matter loss with reaction temperature is shown in Figure 9.

The statistical analysis was similar to that done for weight loss. Table 8 gives the mean values of the observed volatile matter loss for all the blocks of the design. The overall variance was estimated to be 17.3 and the critical value for Scheffé's test was 20.3. The total number of blocks available for contrasts was 12.

On using Scheffé's test for comparing treatment means, it was found that a level of significance of 0.1, there were no significant effects due to treatment gas or type of coal. However, on examining Table 8 it is possible to detect differences between the treatment blocks. At the low and intermediate temperature levels, for both types of coal, the volatile matter loss depends on the treatment gas. Thus in the order of increasing volatile matter loss the gases are hydrogen, nitrogen, low oxygen and high oxygen. Moreover, at these temperature levels R.O.M. coal tends to lose more volatile matter than Deashed coal. At the high temperature level, for both types of coal, the volatile matter loss for low oxygen was the least for all gases. Further at this temperature level, Deashed coal loses more volatile matter than R.O.M. coal when nitrogen or hydrogen is used

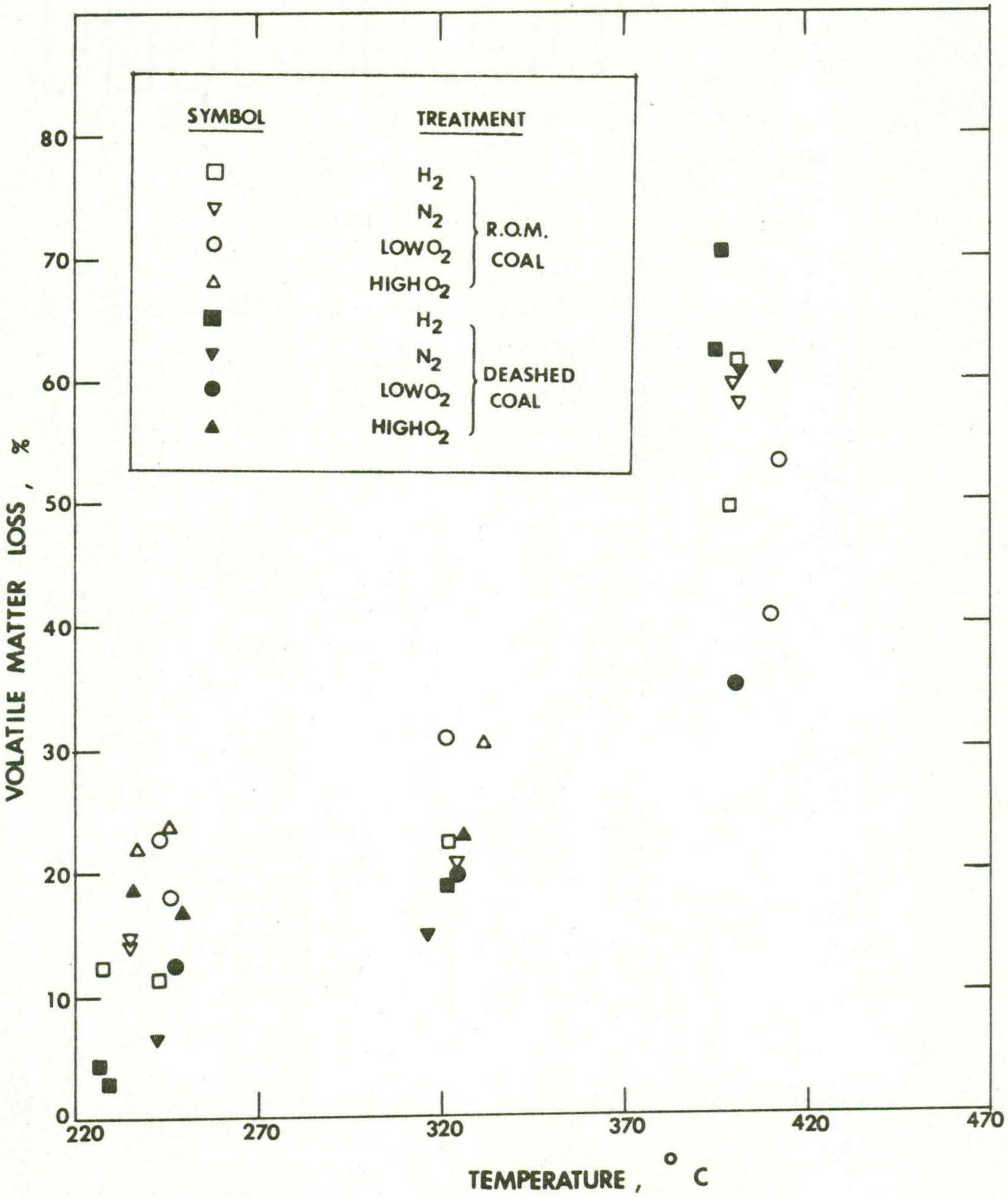

Figure 9. Variation of volatile matter loss with temperature

Table 8. Mean volatile matter loss (%) for different treatments, Series I

Temp. level	Treatment gas N_2	 H_2	 low O_2	 high O_2
		R.O.M. coal		
Low	14.4	11.9	20.3	23.0
Intermediate	20.7[a]	22.4[a]	30.8[a]	30.1[a]
High	58.7	55.4	46.8	--
		Deashed coal		
Low	6.4[a]	3.4	13.5	17.6
Intermediate	14.6[a]	18.6[a]	20.2[a]	22.6[a]
High	61.5	66.2	34.8[a]	--

[a] Blocks containing only one observation.

for the treatment.

In order to test for the effect of temperature a model was used to fit the experimental data. The loss of volatile matter can be described by a first order kinetic equation as proposed by Stone et al. (48).

$$\frac{dV}{dt} = k(1-V) \qquad (25)$$

where V = fractional loss of volatile matter at any time k = assumed reaction rate constant

By going through the algebraic manipulations shown for the weight loss model, one can obtain the following functional relationship for the volatile matter loss.

$$\ell n[-\ell n(1-V_f)] = \ell nK_1 + \ell n\tau - \frac{K2}{T} \qquad (26)$$

where V_f = final fractional volatile matter loss

T = reaction temperature, °K

K_1, K_2 = constants

The volatile matter loss data was correlated with the reaction temperature using equation 26. Linear regression gave the following equation.

$$\ell n[-\ell n(1-V_f)] = 4.99 - \frac{3.61\times 10^3}{T} \qquad (27)$$

At 90 percent level of confidence, the application of a t-test showed that the temperature coefficient in equation 27 is significantly different from zero. Hence, this indicated that the loss of volatile matter is a sensitive function of temperature.

<u>Pyritic sulfur removal</u> The percent pyritic sulfur removal was defined as:

$$\text{\% pyritic sulfur removed} = 100\left[\frac{\text{Wt. of pyr. S. in feed} - \text{Wt. of pyr. S. in residue}}{\text{Wt. of pyr. S. in feed}}\right] \qquad (28)$$

The pyritic sulfur contents of the feed coal and residue was obtained from the sulfur distribution analysis.

In order to do a factorial analysis of the pyritic sulfur removal one had to take into consideration the fact that whereas R.O.M. coal contained 2.4 percent pyritic sulfur, Deashed coal had only 0.6 percent of this sulfur species. Hence, the accuracy of the pyritic sulfur determination for Deashed coal was not comparable with that for R.O.M. coal. In order to do a meaningful analysis of the removal of pyritic sulfur, this statistical study was restricted to R.O.M. coal only.

Table 9 shows the mean values obtained for the percent pyritic sulfur removed from R.O.M. coal. The overall variance for this set of observations was 6.9. The critical value for Scheffé's test was 11.4, and the total number of blocks available for contrasts was 7.

The removal of pyritic sulfur was seen to be independent of the type of gas used at the low and intermediate temperature levels. However, at the high temperature level the pyritic sulfur removed by using either hydrogen or low oxygen was significantly greater than that removed by using nitrogen. The effectiveness of low oxygen was greater than that of hydrogen.

The effect of temperature on the removal of pyritic sulfur was studied by correlating the percent sulfur removed

Table 9. Mean values of pyritic sulfur removed (%) from R.O.M. coal, Series I

Temp. level	Treatment gas N_2	 H_2	 low O_2	 high O_2
Low	9.2	7.1	8.2	7.9
Intermediate	7.8[a]	7.7[a]	12.9[a]	8.6[a]
High	7.4	29.2	41.2	---

[a] Blocks containing single observations.

with the reaction temperature using an assumed relationship of the form:

$$X_{FeS_2} = A + BT \tag{29}$$

where X_{FeS_2} = percent removal of pyritic sulfur

A,B = constants

T = reaction temperature, °C

The observations in the low oxygen and the hydrogen blocks were pooled together and correlated using equation 29. A t-test showed that the desulfurizing action of either hydrogen or oxygen is temperature sensitive.

A similar analysis with nitrogen showed that the removal of pyrite using this gas is insensitive to temperature.

The overall conclusion drawn was that the removal of pyritic sulfur with any gas at low and intermediate temperatures is governed entirely by pyrolytic reactions. A reducing gas or an oxidizing gas is particularly effective only at high temperature levels.

Organic sulfur removal The percent organic sulfur removed was defined as:

$$\text{\% organic sulfur removed} = 100\left[\frac{\text{Wt. of Org. S. in feed} - \text{Wt. of Org. S. in residue}}{\text{Wt. of Org. S. in feed}}\right] \qquad (30)$$

The organic sulfur content of the feed coal and the residue was obtained from the sulfur distribution analysis. In some of the runs, the organic sulfur in the final residue was more than the amount in the original coal. Thus negative values for the percent organic sulfur removal were obtained.

Table 10 gives the mean value of organic sulfur removed for each of the treatment blocks. The overall variance of the observations was 68.6 and the critical value for Scheffé's test was 42.7. There were 14 blocks available for comparison.

On performing the test for significant contrasts it was found that the organic sulfur removal is not significantly affected by the type of coal or the type of treatment gas. Although the statistical test fails to show any significant contrasts, it is possible to detect some differences in the treatment means reported in Table 12. It can be seen that in

Table 10. Mean values of organic sulfur removal (%), Series I

Temp. level	Treatment gas N_2	 H_2	 low O_2	 high O_2
			R.O.M. coal	
Low	10.7	7.0	12.2	18.4
Intermediate	3.2[a]	12.3[a]	25.3[a]	22.7[a]
High	49.1	35.4	46.4	--
			Deashed coal	
Low	-11.6	0.6	-13.4	-6.7
Intermediate	-18.8[a]	1.4[a]	-8.5[a]	12.6
High	37.7	34.7	24.1	--

[a] Blocks containing single observations.

low and intermediate temperature level treatment of Deashed coal, there is a gain in the weight of organic sulfur. This is particularly true when nitrogen gas or low oxygen gas is used for the treatment. This would indicate that a part of the inorganic sulfur which is removed by the treatment gas is readsorbed in the carbon matrix to form organic sulfur. However, this phenomenon is not evidenced in the treatment of R.O.M. coal.

The effect of temperature on the removal of organic sulfur was tested by fitting the data to an assumed function of the form:

$$X_{Org.S.} = A + BT \tag{31}$$

where $X_{Org.S.}$ = percent removal of organic sulfur

A, B = constants

T = reaction temperature, °C

After obtaining the values of the regression coefficients, A and B, a t-test was performed to test the significance of B. This showed that the removal of organic sulfur is strongly influenced by the temperature of the treatment.

Some interesting conclusions may be drawn from this analysis. The data indicated that neither oxygen nor hydrogen significantly react with organic sulfur. This suggests that this sulfur species can be removed only by the pyrolysis reactions. Furthermore, the removal of organic sulfur was seen to be temperature sensitive like weight loss and volatile matter loss. Hence, this further supports the argument that pyrolysis and devolatilization are responsible for the removal of organic sulfur from coal.

Sulfur transformation Figures 10-13 show the sulfur distribution at various reaction temperatures for both types of coal treated with nitrogen, hydrogen, low oxygen, and high oxygen, respectively. In these diagrams the data are presented as cumulative percentages, as in a phase diagram.

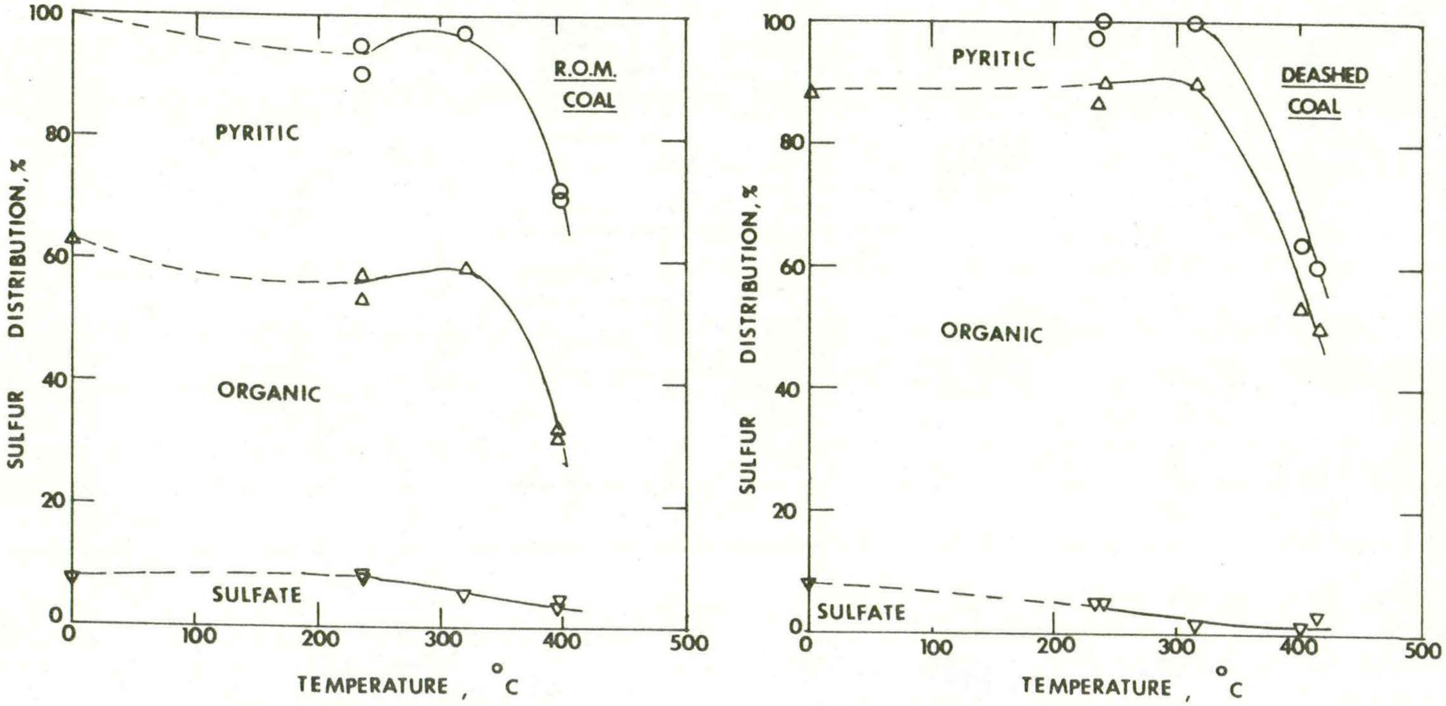

Figure 10. Sulfur distribution diagrams for coal treated with nitrogen

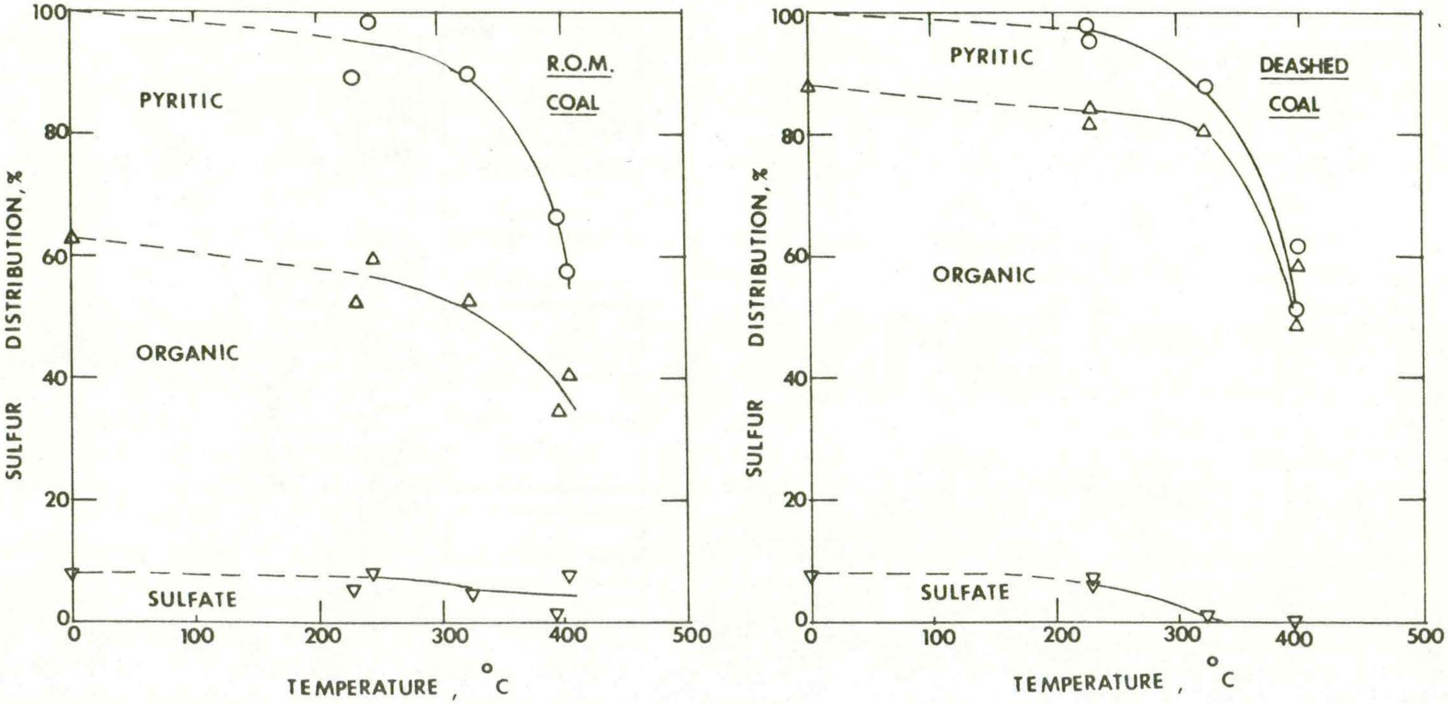

Figure 11. Sulfur distribution diagrams for coal treated with hydrogen.

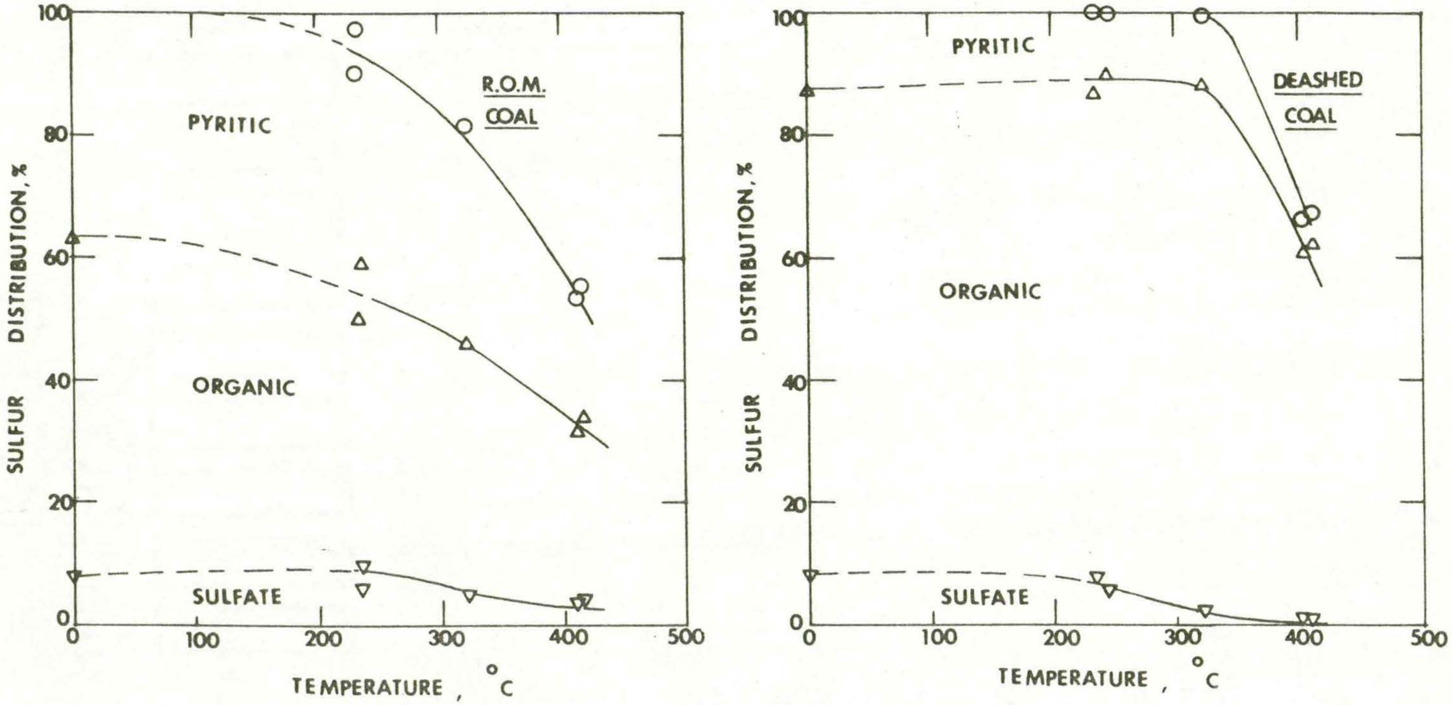

Figure 12. Sulfur distribution diagrams for coal treated with low oxygen

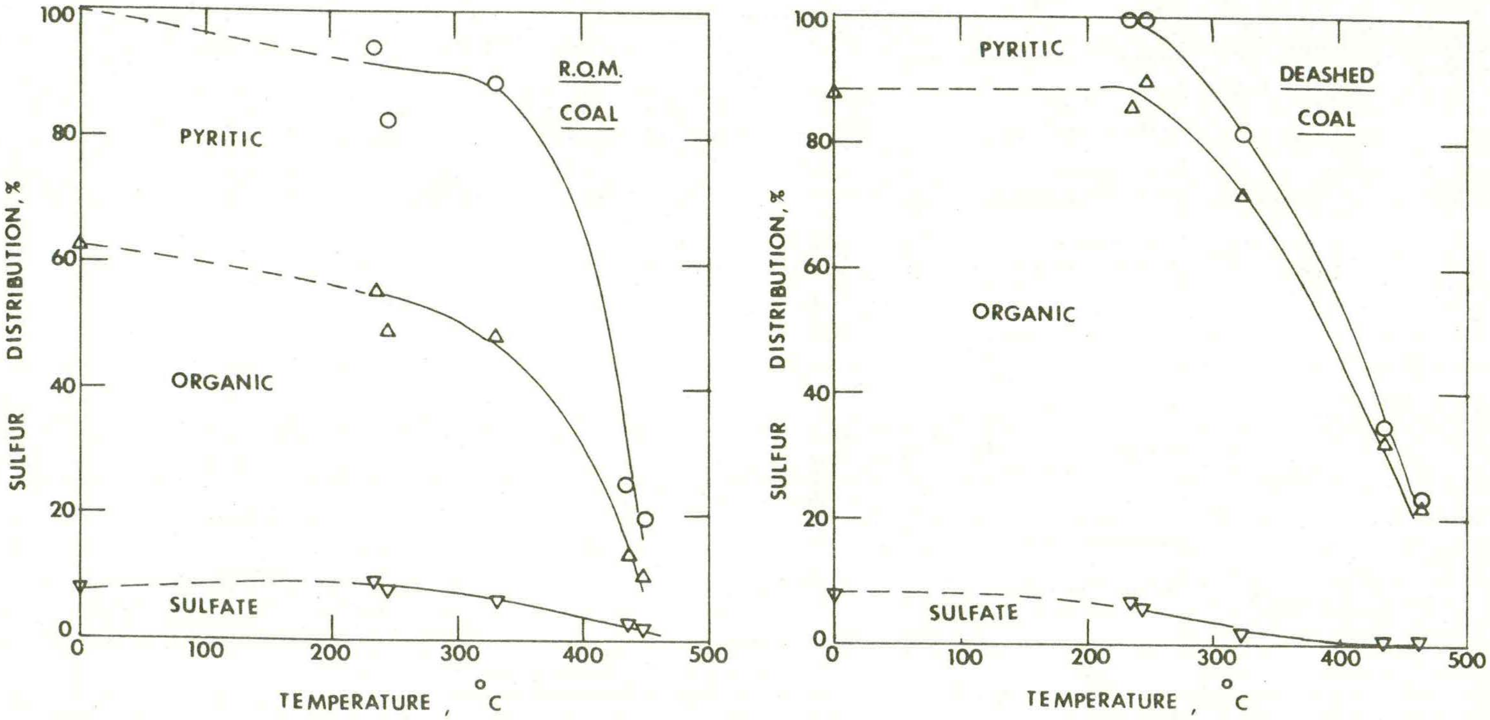

Figure 13. Sulfur distribution diagrams for coal treated with high oxygen

The percentage of a sulfur species was expressed as

$$\left.\begin{matrix}\text{\% of sulfur}\\ \text{species}\end{matrix}\right] = 100\left[\frac{\text{Wt. of sulfur species in residue}}{\text{Wt. of total sulfur in feed}}\right] \quad (32)$$

The percentage of any given form of sulfur can be found from the difference between the intercepts of a vertical line with the boundaries of the corresponding domain for that form. This type of presentation was chosen to show more clearly the interconversion of the different species of sulfur.

By examining the diagrams for the behavior of organic sulfur it is possible to detect slight gains in this species compared to the amount in the untreated coal. This is particularly true for the treatment of Deashed coal by hydrogen, nitrogen and low oxygen in the temperature range 200°-325°C. The feature common to all diagrams is the dramatic decrease in the organic sulfur content at temperatures greater than 325°C. This reinforces the observation that the removal of organic sulfur is temperature sensitive and that the conversion of this species becomes appreciable at temperatures above 300°C.

The pyritic sulfur content in the residue also decreases appreciably at temperatures greater than 300°C. For all gases this drop is greater in Deashed coal than in R.O.M. coal. However, since the initial content of pyritic sulfur in Deashed coal is small this decrease does not substantially lower the total sulfur content. In the case of R.O.M. coal the decrease in the pyritic sulfur is greatest when high oxygen gas is used for the treatment. The least change in the pyritic sulfur content is noticed when nitrogen is used as the treatment gas.

Some insight can also be gained about the interconversion of pyritic sulfur and sulfate sulfur. It must be pointed out that the chemical analysis of sulfate sulfur also includes any pyrrhotite (Fe_7S_8) or ferrous sulfide (FeS). Hence, a reduction of pyritic sulfur to ferrous sulfide or pyrrhotite could lead to an increase in the apparent sulfate sulfur. Figures 10 and 11, which show the results for the nitrogen gas and hydrogen gas treatments, amply demonstrate this phenomenon. In these diagrams there is a slight increase in the sulfate sulfur content of R.O.M. coal at temperatures between 200° and 250°C. However, the sulfate sulfur in Deashed coal decreases from its initial value at all reaction temperatures. This is true because the initial concentration of pyritic sulfur in Deashed coal is small and, hence, the decrease of sulfate sulfur is not unduly offset by the formation of ferrous sulfide which shows up in the analysis as "sulfate".

The oxidation of pyritic sulfur could proceed by several steps. Some of the thermodynamically feasible reactions yield ferrous sulfate as a byproduct, others yield various oxides of iron. In Figures 12 and 13 which illustrate the results of the oxygen gas treatments, the sulfate sulfur in R.O.M. coal shows a slight increase from its initial value when treated at a temperature of 240°C. But at higher temperatures the sulfate content decreases. This suggests that at temperatures greater than 250°C the pyritic sulfur is preferentially oxidized to oxides rather than to sulfates.

Loss in heating value It was shown that the treatment of coal at various temperatures by gases leads to a partial removal of the sulfur species in the coal with an attendant loss of volatile matter and fixed carbon due to devolatilization and combustion. This loss was responsible for reducing the heating value of the solid residue from all the runs.

Hence, the effectiveness of a particular treatment gas for coal desulfurization was judged from two standpoints, namely, the amount of sulfur which was removed from the coal and, the loss in heating value of the product.

A convenient parameter incorporating these two factors is the specific sulfur content or the ratio of the mass of sulfur in the residue to the heating value of the residue. This ratio (lb.S./MM Btu) was determined for the residue from each run in this series and plotted for both types of coal in Figure 14.

From the diagrams of Figure 14 it is clear that for both types of coal the specific sulfur content for the treated

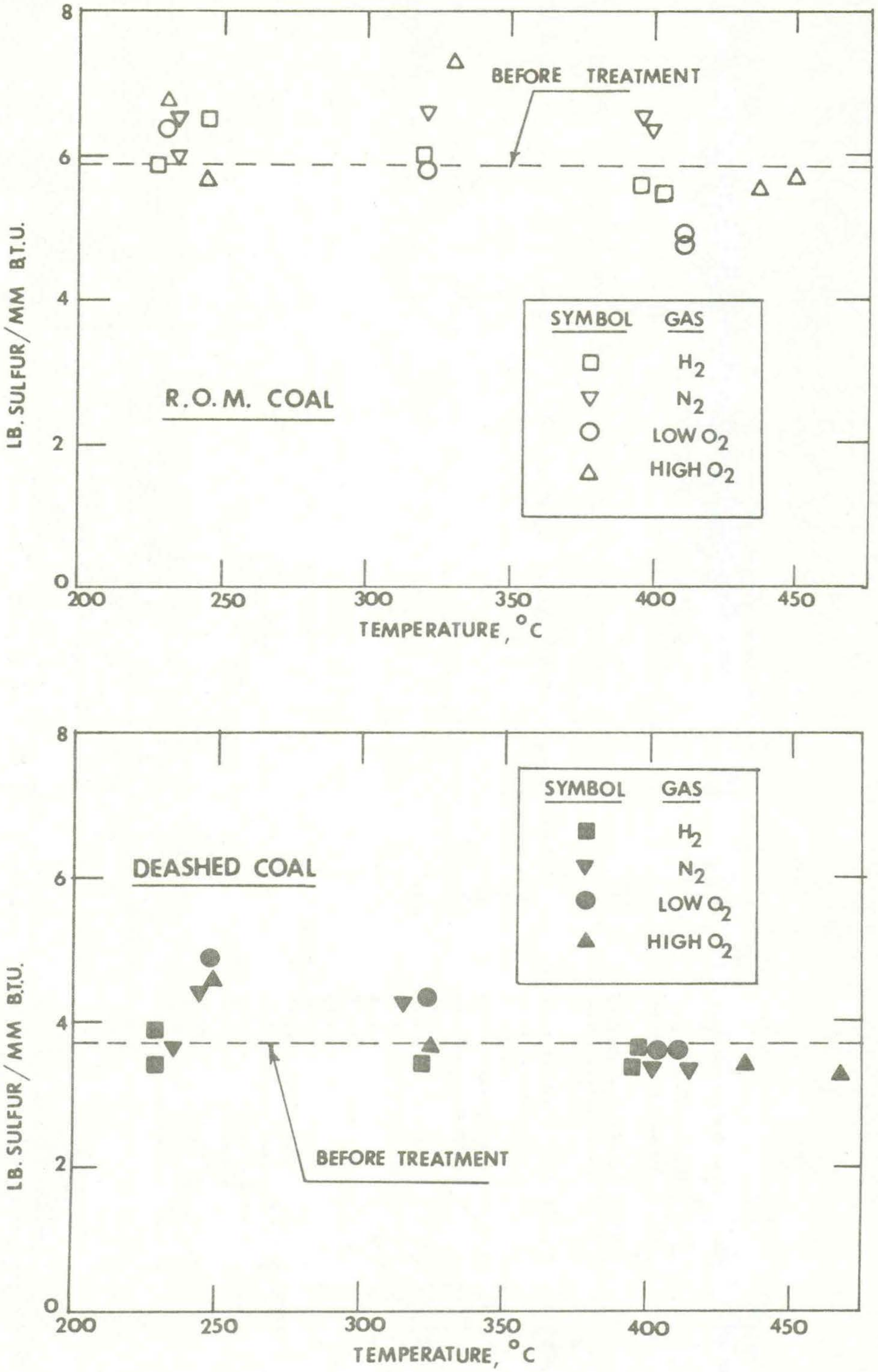

Figure 14. Variation of the specific sulfur content of the residue with temperature, Series I

coal is not substantially less than that for the untreated coal (shown by the dotted lines). In fact, at low and intermediate temperatures, the specific sulfur content of some of the treated coal samples was greater than that for the untreated coal. This suggests that at these temperatures the loss in heating value outweighed the advantage gained by sulfur removal. If the gas formed due to devolatilization and partial combustion of coal is desulfurized and used as a fuel in combination with the residual coal char, the specific sulfur content of the two fuels could possibly be less than the value of the coal char alone.

Series II Experiments

This series of runs was performed to identify and estimate the concentration of the gaseous products produced when coal was treated at elevated temperatures with different gases in a fluidized bed reactor. The concentration of several species in the reactor off gas was monitored with the mass spectrometer and the data were used to determine the heating value of the off gas and to elucidate the kinetics of desulfurization.

Operating conditions

The set of experiments consisted of four runs which were performed using nitrogen as the treatment gas, three runs with hydrogen (concentration of 85 percent) and four with oxygen (concentration of 9.5 percent). The reaction temperature for all these runs ranged between 318° and 400°C.

The materials used for the reactor feedstock were R.O.M. Jude coal and Deashed Jude coal. The chemical analysis, method of preparation, and the procedure used to obtain a representative sample of coal for each run were reported above.

For each run 200 g. of coal were injected into a preheated bed containing 250 g. of sand. The sand to coal mass ratio was therefore 1.25. A larger ratio would have been desirable for better thermal characteristics but was not employed for the following reasons. The reactor was designed to hold 500 g. of granular solids in the -20+50 mesh size range. Preliminary runs carried out using 50 g. of coal and 400 g. of sand showed that the mole concentrations of gaseous species evolved from the coal were too small to be estimated accurately with the mass spectrometer. In order to obtain an accurate gas analysis, a larger quantity of feedstock (200 g. coal) had to be used. Therefore the maximum amount of sand which could be accommodated in the reactor was 250 g.

In spite of the small sand to coal mass ratio, the method of injecting coal into the preheated bed of sand provided nearly isothermal conditions. Figure 15 shows the time variant temperature profile for some typical runs. The thermal behavior of the reactor and other operating conditions are presented in Table 11.

Analysis of experimental data

Samples of the reactor off gas were withdrawn at discrete time intervals during a run and were analyzed with the mass spectrometer. The cumulative yields of each gaseous species in the off gas were obtained by numerical integration of the discrete gas composition data using the trapezoidal rule. Assuming ideal gas behavior, it was then possible to estimate the volume yield of each component per unit mass of coal. For the runs employing hydrogen as the treatment gas it was not possible with the mass spectrometer to determine the yield of hydrogen from the volatile matter in the coal.

The heating value of the reactor off gas was estimated by summing the heats of combustion for hydrogen, carbon monoxide, methane, ethane and propane. This calculation assumed that the gases were at 25°C and, hence, neglected their sensible heat.

For each run an overall material balance was performed on all entering and exiting streams. The inlet mass flow

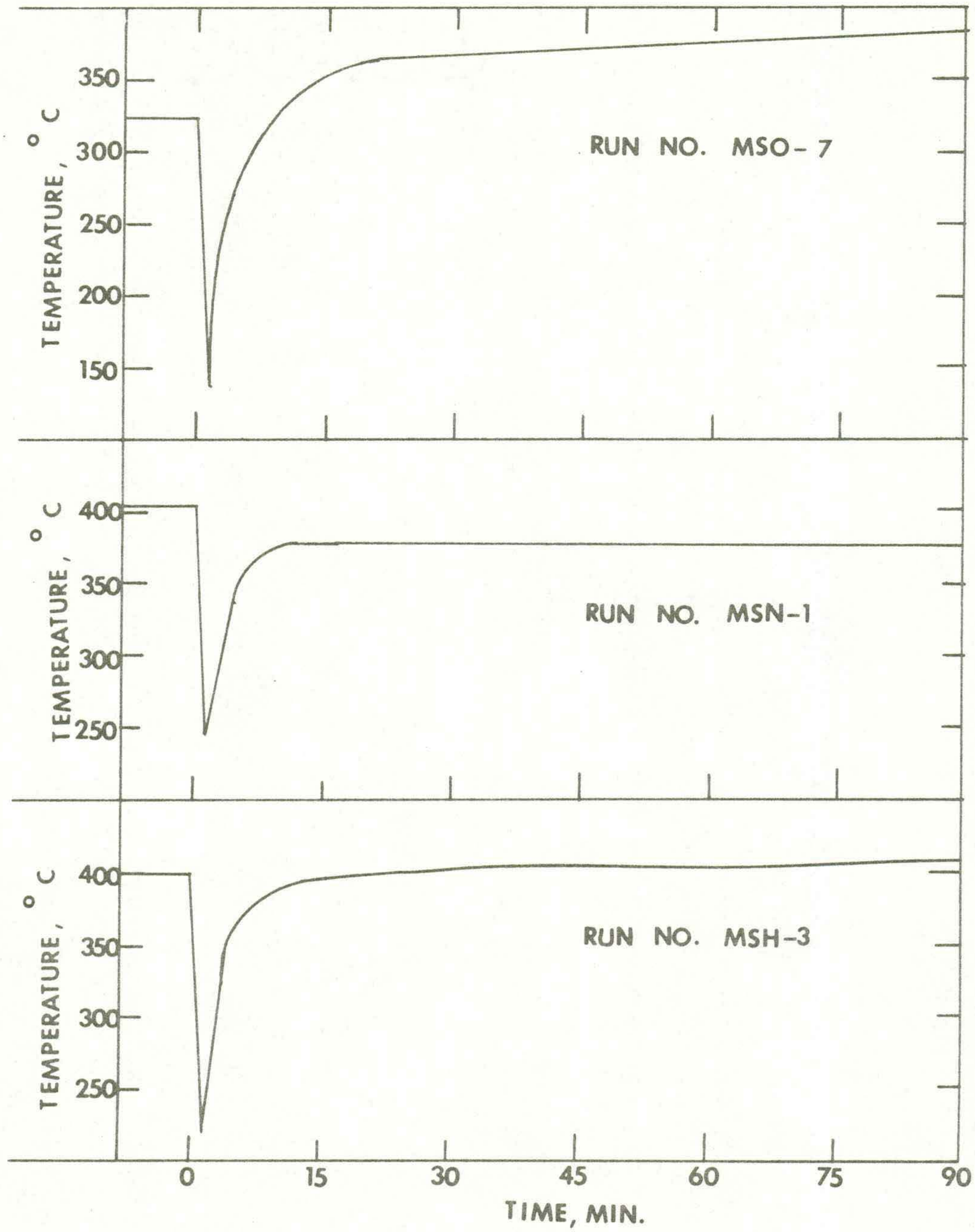

Figure 15. Typical time variant temperature profiles in the reactor, Series II

Table 11. Operating conditions for runs in Series II[a,b]

Run no.	Wt. of coal treated,[c] g.	Type of coal	Concen. of treatment gas	Run length min.
MSN-1	191.0	R.O.M.	100% N_2	60
MSN-4	200.0	Deashed	100% N_2	60
MSN-5	199.3	R.O.M.	100% N_2	60
MSN-6	199.7	Deashed	100% N_2	60
MSH-1	199.3	R.O.M.	86.5% H_2	60
MSH-3	198.5	Deashed	84.3% H_2	90
MSH-4	197.1	R.O.M.	86.3% H_2	90
MSO-2	196.4	R.O.M.	9.4% O_2	60
MSO-3	193.0	R.O.M.	9.4% O_2	60
MSO-7	194.9	R.O.M.	9.5% O_2	90
MSO-8	197.0	Deashed	9.9% O_2	90

[a] Sand to coal mass ratio = 1.25.

[b] Particle size of sand: -40+50 mesh.

[c] Particle size of coal: -20+40 mesh.

[d] Calculated at the temperature of the feed gas.

Thermal behavior			
Temp. drop on coal injection, °C	Coal preheat time, min.	Av. temp. during run, °C	Superficial gas velocity,[d] cm./sec.
138	9	377	43.6
127	9	393	25.9
154	15	318	33.1
138	9	321	23.6
127	9	396	47.8
166	15	401	32.2
168	12	366	39.5
141	15	371	40.4
143	12	371	32.7
171	12	374	33.5
116	15	371	25.7

of the gases was known from the rotameter indication and the mass yield of different species in the off gas was known from the numerical integration of discrete gas composition data. A nitrogen balance was assumed between the inlet and outlet gas streams. The weight of coal carried over to the cyclone and the tar condensed in the tar trap were also accounted for in the balance.

The weight loss, yield of tar, the heating value and the average composition of the product gas are summarized in Table 12.

The sulfur distribution in the residue from each experiment was determined. The analytical results are reported on a moisture and ash free basis in Table 13.

The reliability of the mass spectrometer data for the quantity of various sulfur species in the off gas (H_2S, SO_2 and COS) was checked against the amount of sulfur collected by the gas absorber during a run. The data from both of these sources were in reasonable agreement as can be seen from Table 14.

The total amount of sulfur removed from the coal was also determined from the chemical analysis of the untreated coal and solid residue. These results are also reported in Table 14. A wide discrepancy is seen between the values of sulfur removal obtained from the gas analysis and those determined from the solids analysis. Hence, it is inferred

Table 12. Summary of results of runs in Series II

Run no.	Treatment gas	Weight loss %	Liquid yield[a] g./g. coal	Product gas yield[b,c] cc./g. coal	Average heating value of gas[f], Btu./scf.	Overall material balance[e], %
MSN-1	N_2	32.8	0.14	127.4	521.7	99.5
MSN-4	N_2	23.5	0.14	93.2	524.0	99.3
MSN-5	N_2	12.6	0.08	91.6	495.3	100.2
MSN-6	N_2	10.0	0.06	79.5	425.2	99.8
MSH-1	H_2	29.8	0.17	60.5[d]	780.1	97.7
MSH-3	H_2	22.4	0.15	59.7[d]	911.6	99.6
MSH-4	H_2	24.2	0.13	50.7[d]	1115.4	98.3
MSO-2	O_2	27.6	0.18	399.1	417.8	96.0
MSO-3	O_2	29.6	0.13	442.0	394.0	93.9
MSO-7	O_2	37.4	0.10	812.8	432.0	99.9
MSO-8	O_2	30.1	0.12	454.5	378.7	97.5

[a] Tar and water condensing in the tar trap.

[b] Volume calculated at 0°C and 1 atm. pressure.

[c] Dry basis, free of nitrogen.

[d] Excludes hydrogen evolved from coal.

[e] Calculated as 100 x (output/input).

[f] Averaged over run length.

Composition of reactor off gas,[f] mole %										
N_2	O_2	CO_2	CO	H_2	CH_4	C_2H_6	C_3H_8	H_2S	SO_2	COS
97.84	0.02	0.16	1.24	0.22	0.33	0.02	0.03	0.11	0.03	0.00
97.02	0.71	0.06	0.44	1.11	0.36	0.02	0.05	0.18	0.00	0.00
98.39	0.02	0.04	0.37	0.87	0.23	0.01	0.02	0.06	0.00	0.00
98.00	0.00	0.05	0.20	1.46	0.19	0.00	0.01	0.05	0.01	0.00
12.92	0.01	0.05	0.34	86.19	0.26	0.01	0.03	0.15	0.02	0.00
15.78	0.17	0.04	0.18	83.33	0.27	0.02	0.03	0.13	0.00	0.00
15.09	0.00	0.03	0.06	84.28	0.32	0.01	0.04	0.18	0.00	0.00
98.22	3.18	2.53	3.18	0.67	0.16	0.07	0.05	0.03	0.22	0.03
89.87	2.51	2.78	3.27	1.07	0.17	0.04	0.03	0.14	0.11	0.02
87.11	3.72	2.80	3.07	2.49	0.42	0.08	0.06	0.09	0.11	0.01
89.51	2.28	3.19	2.84	0.88	0.03	0.07	0.03	0.04	0.09	0.02

Table 13. Sulfur distribution and heating value of residue from runs in Series II[a]

Run no.	Total sulfur, %	Pyritic sulfur, %	Organic sulfur, %	Sulfate sulfur, %	Heating value, Btu./lb.
MSN-1	9.34	5.35	3.55	0.44	13692
MSN-4	5.02	0.64	4.35	0.02	14169
MSN-5	10.44	4.62	5.40	0.42	13716
MSN-6	6.03	0.59	5.39	0.05	14092
MSH-1	8.10	2.51	5.22	0.37	13735
MSH-3	5.75	0.25	5.47	0.03	14149
MSO-2	8.00	4.14	3.26	0.59	12484
MSO-3	8.60	4.67	2.97	0.96	12404
MSO-8	5.52	0.30	5.10	0.13	13080

[a] Estimated on a moisture and ash free basis.

Table 14. Percent sulfur removed from coal during runs in Series II

Run no.	Based on gas analysis		Based on solids analyses
	Mass spec.	Absorption	
MSN-1	14.9	13.7	39.1
MSN-4	16.5	18.1	41.8
MSN-5	6.2	5.0	5.7
MSN-6	5.5	5.5	17.3
MSH-1	19.9	21.8	44.1
MSH-3	25.4	27.0	32.3
MSH-4	25.8	19.0	--
MSH-2	28.4	25.3	42.6
MSO-3	27.6	28.3	45.5
MSO-7	35.0	33.1	48.7
MSO-8	17.0	19.5	41.7

that some sulfur from the coal was evolved in association with aromatic compounds which condensed along with the tar in the tar trap. Since the tar was not analyzed, it was not possible to verify this.

Presentation of results

The time variant behavior of the desulfurization, devolatilization and combustion processes leading to the formation of various gaseous species was studied. The results obtained for each type of treatment gas are presented below.

Nitrogen runs The volume of different gaseous species produced by the nitrogen gas treatment of R.O.M. and Deashed coals is shown in Figures 16 and 17 respectively. The temperatures during the treatment were 393°C for the Deashed coal and 377°C for the R.O.M. coal.

It is seen that in spite of a slightly lower reaction temperature, the total volume of gas produced from R.O.M. coal is more than that produced from Deashed coal. Secondly, the relative proportions of carbon monoxide and hydrogen changed with temperature. At a higher pyrolysis temperature more hydrogen was released than carbon monoxide. The temperature did not appear to affect the release of the hydrocarbons.

The percent desulfurization was defined as

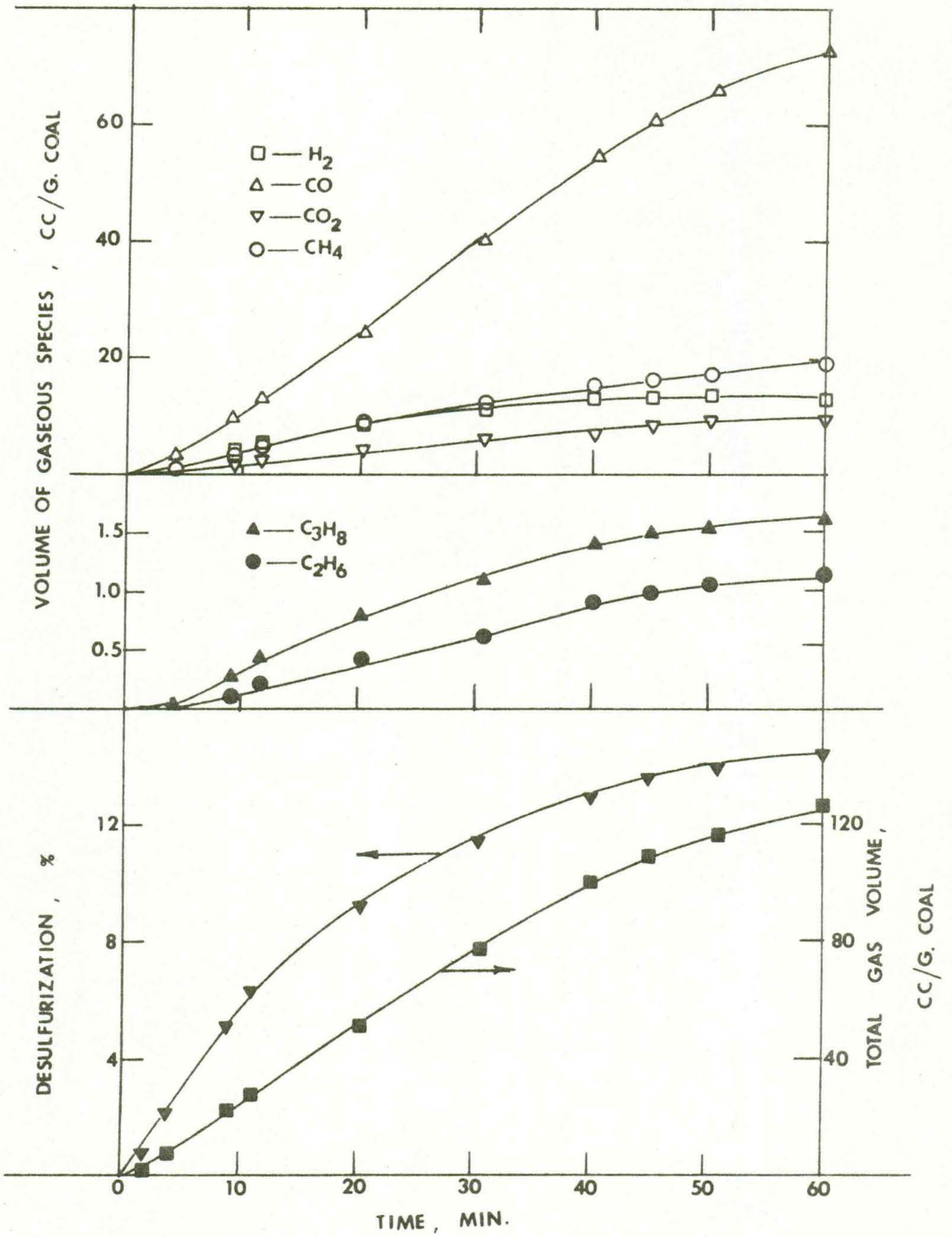

Figure 16. Volume of gaseous species produced during nitrogen treatment of R.O.M. coal in run no. MSN-1

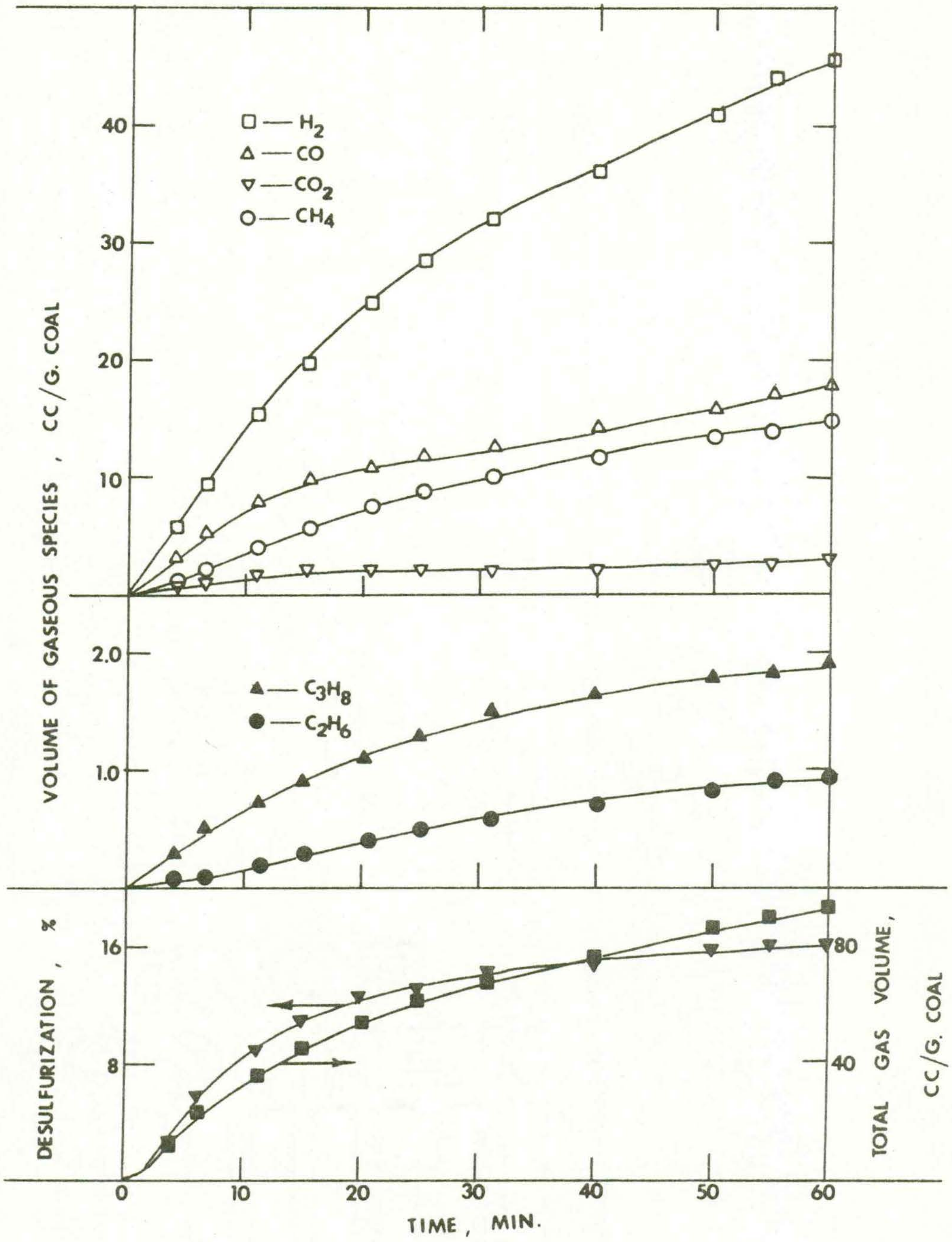

Figure 17. Volume of gaseous species produced during nitrogen treatment of Deashed coal in run no. MSN-4

$$\% \text{ desulfurization} = 100\left[\frac{\text{Wt. of sulfur in off gas as } H_2S, SO_2 \text{ and } COS}{\text{Wt. of total sulfur in feed coal}}\right] \qquad (33)$$

On examining Figures 16 and 17 it is seen that the percent desulfurization tended to increase with the reaction temperature. But in both instances the desulfurization reached a constant limiting value at 60 minutes.

Hydrogen runs Figures 18 and 19 represent the results of the hydrogen gas treatment of R.O.M. coal and Deashed coal at 366° and 401°C respectively. From these figures it is seen that the volume of total gas evolved from the Deashed coal is slightly higher than that from the R.O.M. coal. This difference could be attributed to the higher reaction temperature in the case of the Deashed coal run. The amounts of carbon monoxide, carbon dioxide, propane and ethane were similar to those obtained with the nitrogen treatments. However, the amount of methane was about twice the amount produced by pyrolysis. This suggests that hydrogenation of fixed carbon took place by the following reaction to yield the additional amount of methane.

$$C + 2H_2 = CH_4 \qquad (34)$$

Oxygen runs Figures 20 and 21 show the distribution of gases evolved during oxygen treatment of R.O.M. and

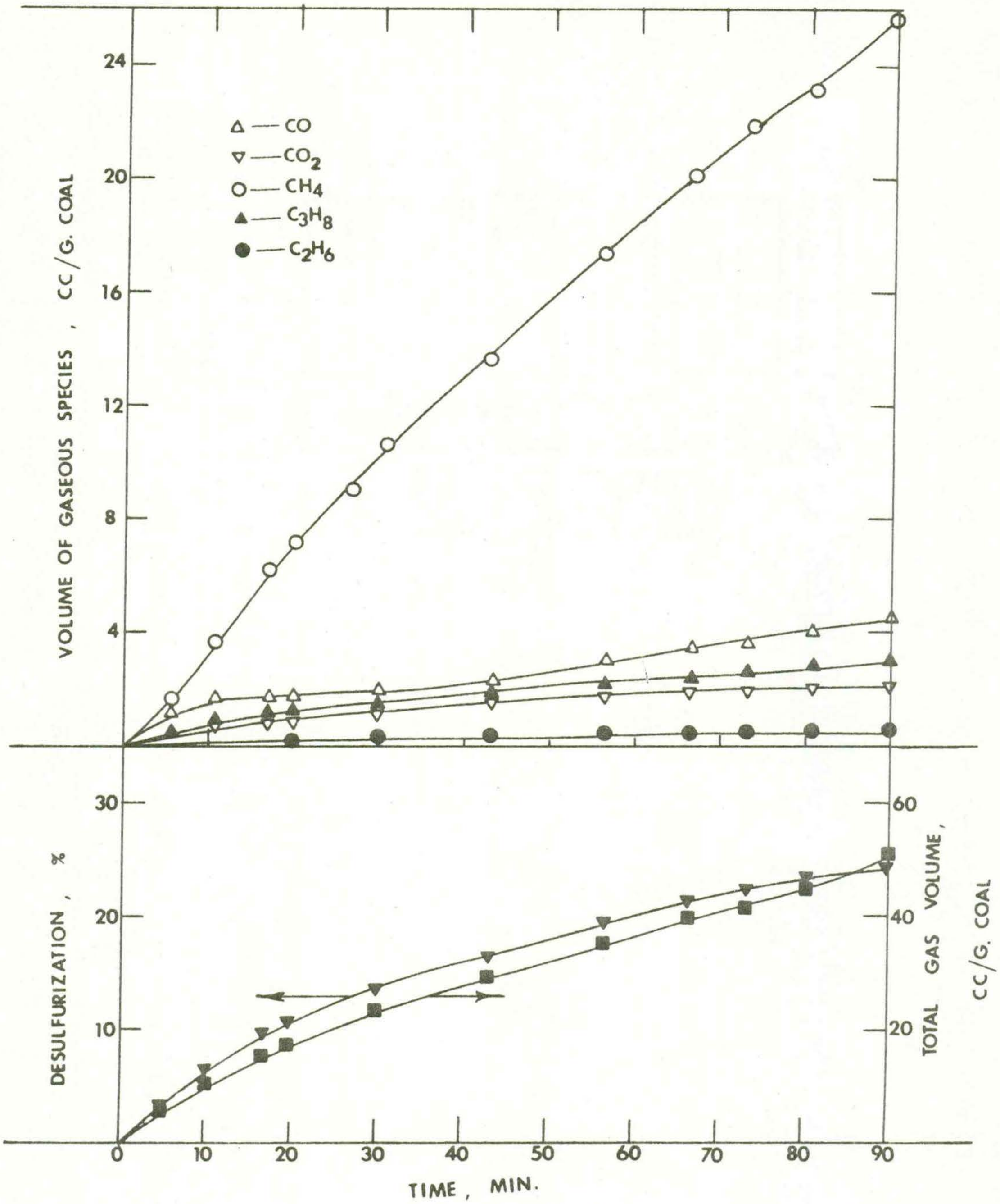

Figure 18. Volume of gaseous species produced during hydrogen treatment of R.O.M. coal in run no. MSH-4

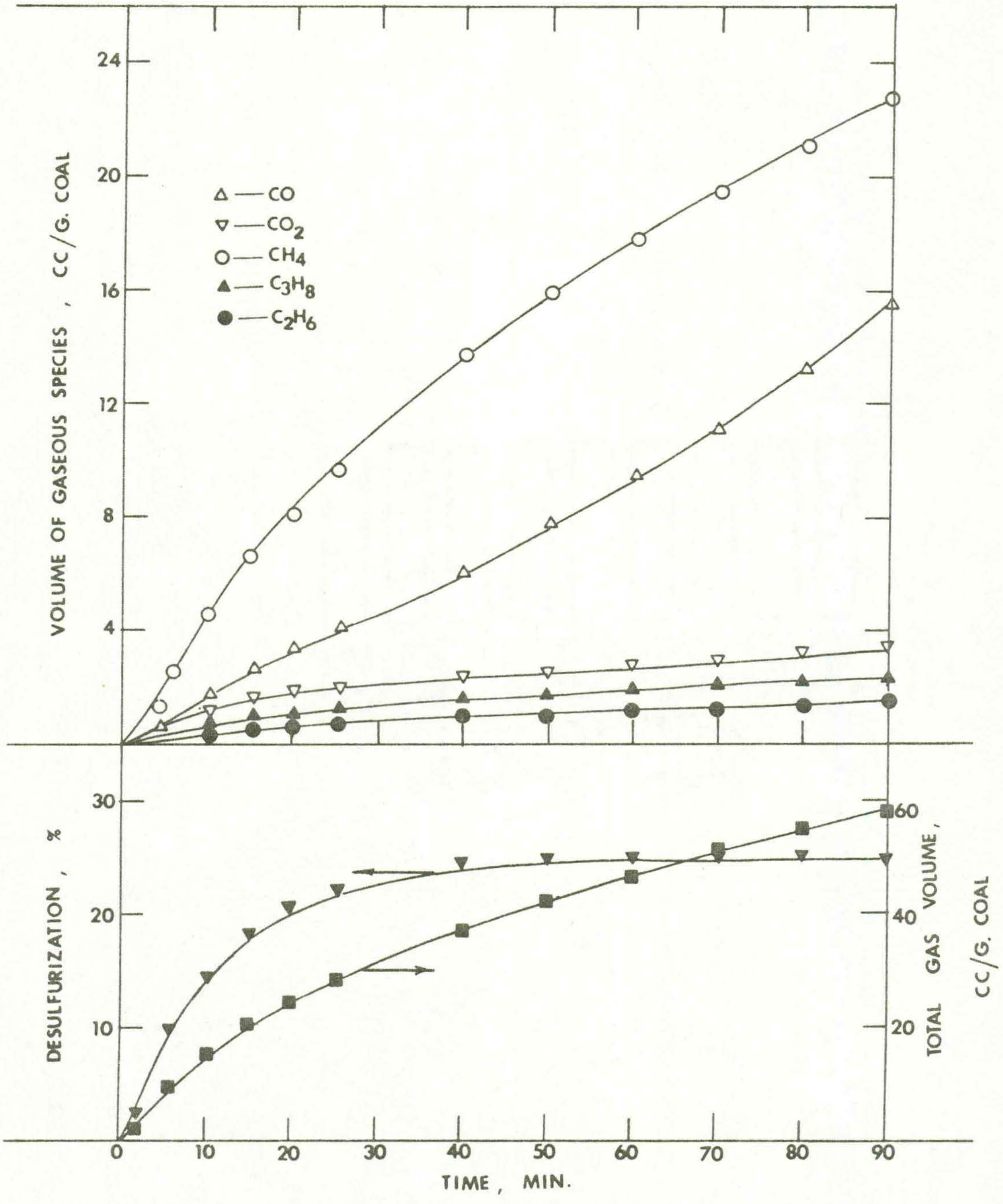

Figure 19. Volume of gaseous species produced during hydrogen treatment of Deashed coal in run no. MSH-3

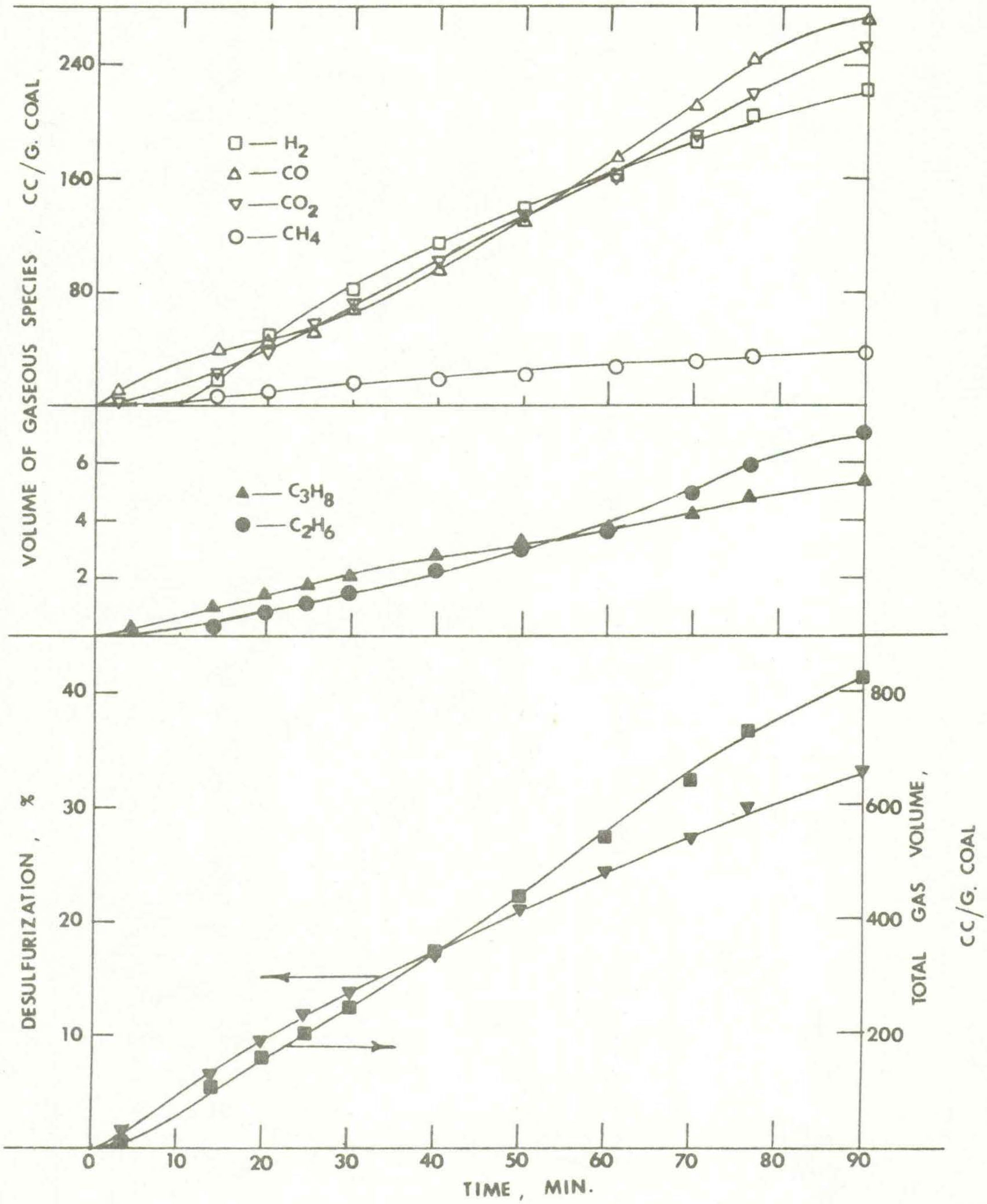

Figure 20. Volume of gaseous species produced during oxygen treatment of R.O.M. coal in run no. MSO-7

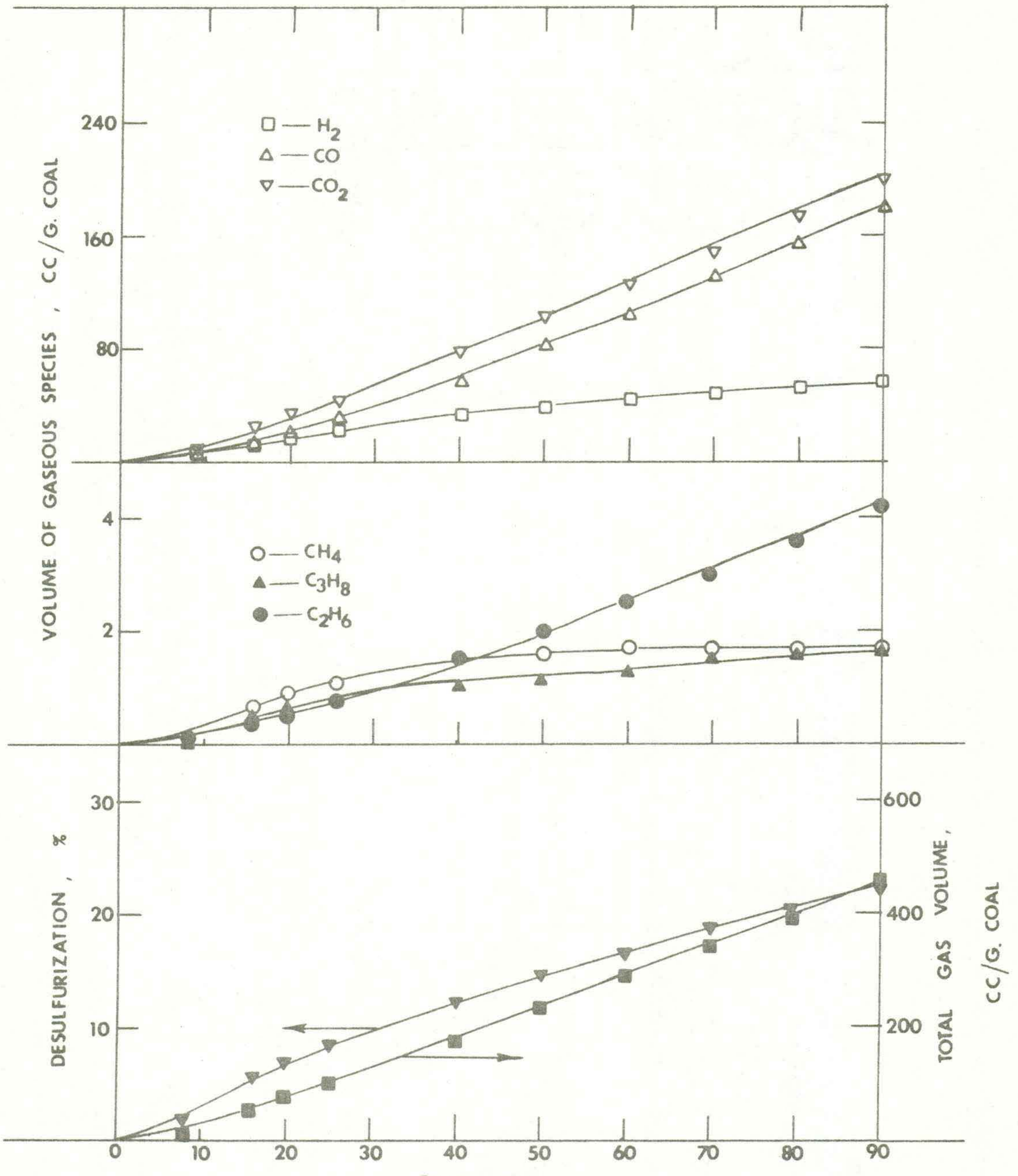

Figure 21. Volume of gaseous species produced during oxygen treatment of Deashed coal in run no. MSO-8

Deashed coals respectively. The reaction temperature was identical for the two runs and, hence, any observed differences in the volumes of gases produced could be attributed to some intrinsic property of the coal.

The combustion reactions lead to substantial formation of carbon monoxide and carbon dioxide. On examining these diagrams it is evident that combustion of R.O.M. coal proceeds more readily than combustion of Deashed coal. A plausible explanation for this can be given. Combustion of coal is known to be inhibited by the presence of chlorinated compounds (43). It may be recalled that a mixture of tetrachloroethylene and hexane was used as a floating agent for the preparation of Deashed coal. It is entirely possible that there was some inhibition of combustion of Deashed coal due to the presence of residual traces of tetrachloroethylene. Consequently the oxygen preferentially oxidized the volatile hydrocarbons thereby reducing their yields from Deashed coal.

Another explanation for the larger burnoff of carbon from R.O.M. coal could be that the mineral matter in the coal served as a catalyst in the combustion process.

The percent desulfurization of Deashed coal was less than that of R.O.M. coal. This result is not unexpected because Deashed coal contained mainly organic sulfur and it was shown in the series I experiments that oxygen did not react with this sulfur species.

Kinetic modeling

From the gas analysis data it was possible to estimate the rate of evolution of various sulfurous gases. The rate data were used for fitting a theoretical model to the desulfurization reactions taking place in coal treated with nitrogen or hydrogen.

In the case of oxygen treatment, the system was more complicated. Hence, no model fitting was attempted. The rate data is presented graphically and some qualitative arguments are given in support of a possible mechanism.

Hydrodesulfurization reactions   Figures 22 and 23 present the rate data for the evolution of hydrogen sulfide in nitrogen and hydrogen gas treatments respectively. The trends in both of these figures are similar. The rate of formation of hydrogen sulfide appears to increase to a peak and then monotonically decrease towards zero as conversion proceeds. The initial rise in the rate probably took place during the preheating period immediately after the coal was injected into the sand bed.

Another interesting feature common to nitrogen and hydrogen treatments is the difference between the rate curves for R.O.M. coal and Deashed coal. The data for Deashed coal show an almost linear relationship between the hydrogen sulfide formation rate and the total sulfur conversion. In the case of R.O.M. coal it is seen that the data is nonlinear

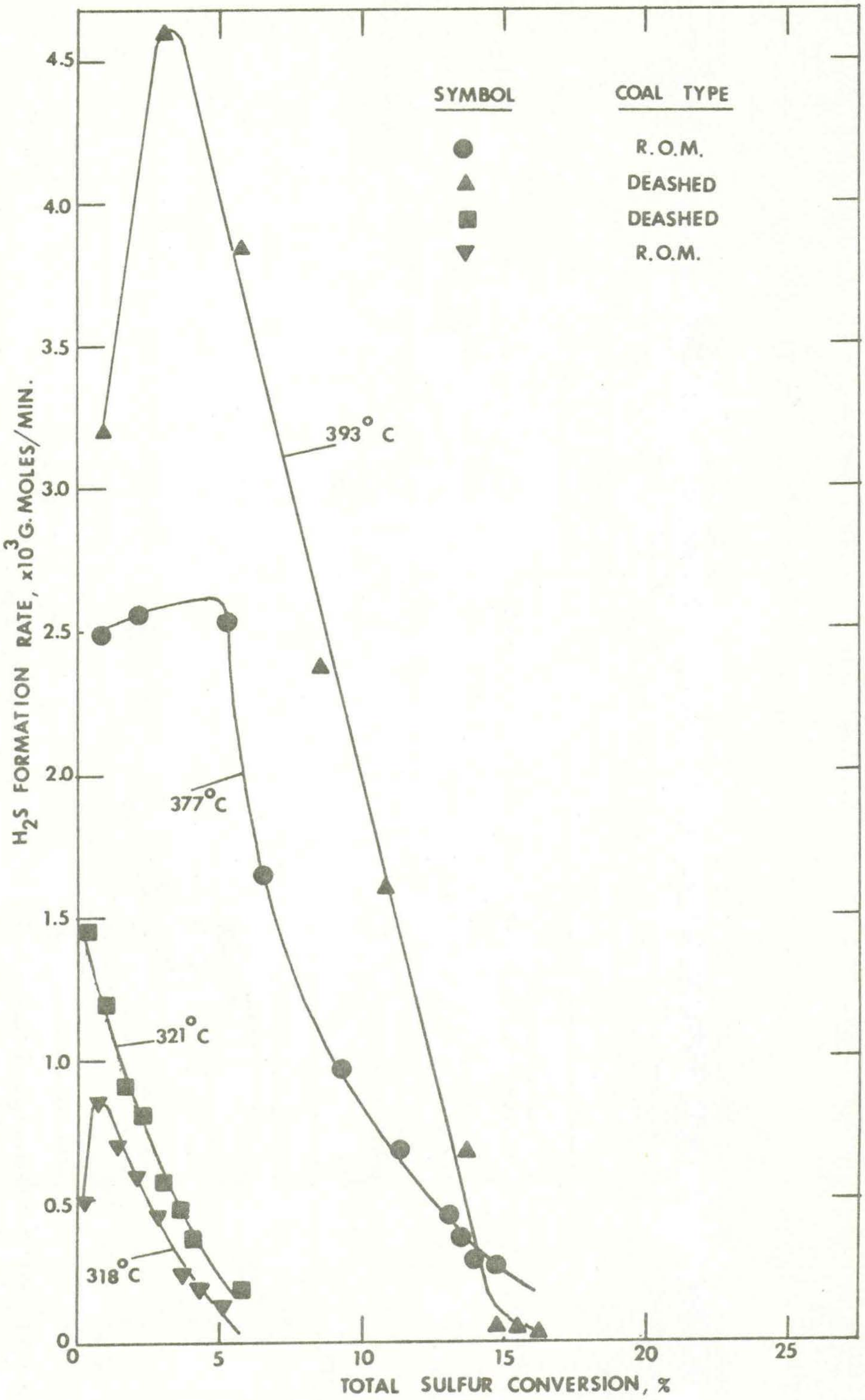

Figure 22. Rate of desulfurization during coal pyrolysis in nitrogen, Series II

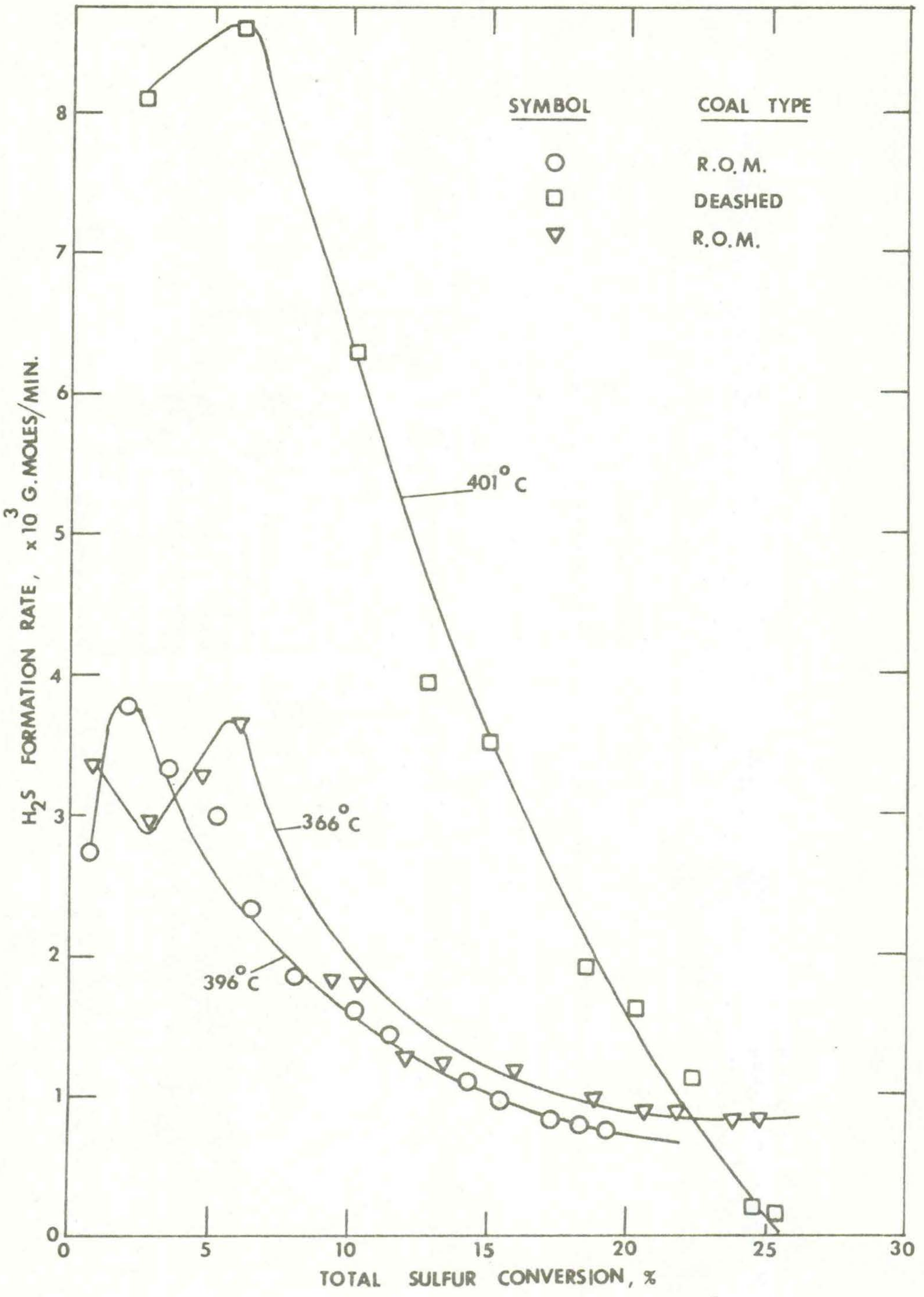

Figure 23. Rate of desulfurization during the hydrogen treatment of coal, Series II

and at higher conversions of sulfur, the rate of formation of hydrogen sulfide approaches a plateau. This is probably due to the fact that R.O.M. coal contains appreciable quantities of both pyritic and organic sulfur. Hence, the rate of formation of hydrogen sulfide is governed by the superposition of two reactions, namely, the reduction of pyritic sulfur and that of organic sulfur.

With these arguments in mind, it was hypothesized that the evolution of hydrogen sulfide during the treatment of Deashed coal is derived entirely from the organic sulfur. A model proposed by Yergey et al. (52) was then fitted to the data from the Deashed coal runs to obtain kinetic parameters.

The pyrolytic decomposition of organic sulfur (Org. S), in coal occurs due to the rearrangement of the coal lamallae leading to the formation of hydrogen sulfide (H_2S), and residual sulfur linked to the organic structure in the devolatilized coal (B). The overall reaction is represented by equation 35.

$$(\text{Org. S})_{\text{solid}} \rightarrow (H_2S)_{\text{gas}} + (B)_{\text{solid}} \qquad (35)$$

This equation is first order with respect to the organic sulfur species, and the rate may be written as:

$$\frac{-d[\text{Org.S}]}{dt} = k[\text{Org.S}] \qquad (36)$$

where k = first order reaction rate constant

[Org.S] = concentration of reaction sites of this species.

The concentration of reaction sites of organic sulfur may be expressed in terms of the moles of the evolved gas (M) by equation 37.

$$[\text{Org.S}] = \alpha(M_o - M) \tag{37}$$

where M = moles of hydrogen sulfide evolved up to time t,

M_o = total moles of hydrogen sulfide evolved when the rate vanishes,

α = proportionality factor.

Making these substitutions the rate equation becomes

$$\frac{dM}{dt} = k(M_o - M) \tag{38}$$

A similar rate equation can be developed for the desulfurization reaction in an atmosphere of hydrogen. This reaction is represented by

$$(\text{Org.S})_{\text{solid}} + (H_2)_{\text{gas}} \rightarrow (H_2S)_{\text{gas}} + (B)_{\text{solid}} \tag{39}$$

The following rate equation is written for this reaction

$$\frac{d[\text{Org.S}]}{dt} = -k[H_2][\text{Org.S}] \tag{40}$$

where $[H_2]$ = concentration of hydrogen in the gas stream.

Since the concentration of the hydrogen in the inlet gas stream was held constant during a run, the concentration term in equation 40 could be absorbed in the constant k. Hence equation 40 reduces to a form similar to equation 38.

The rate data for Runs MSH-3, MSN-4 and MSN-6, all of which were performed on Deashed coal, were fitted to the kinetic model using linear regression. Estimates were obtained for the parameters M_o and k in equation 38. From the values of M_o and the initial moles of organic sulfur in the coal, it was possible to obtain a value for the limiting organic sulfur conversion (X_o). These parameters are reported in Table 15. Figure 24 shows a plot of the rate of evolution of hydrogen sulfide $(\frac{dM}{dt})$ against moles of hydrogen sulfide formed (M).

The parameters X_o and k are possibly functions of temperature. Since only three runs were available for the present work this analysis could not be extended to a study of the temperature dependency.

The foregoing analysis indicates that the desulfurization reactions of organic sulfur are first order with respect to the sulfur species. Also for any reaction temperature, there

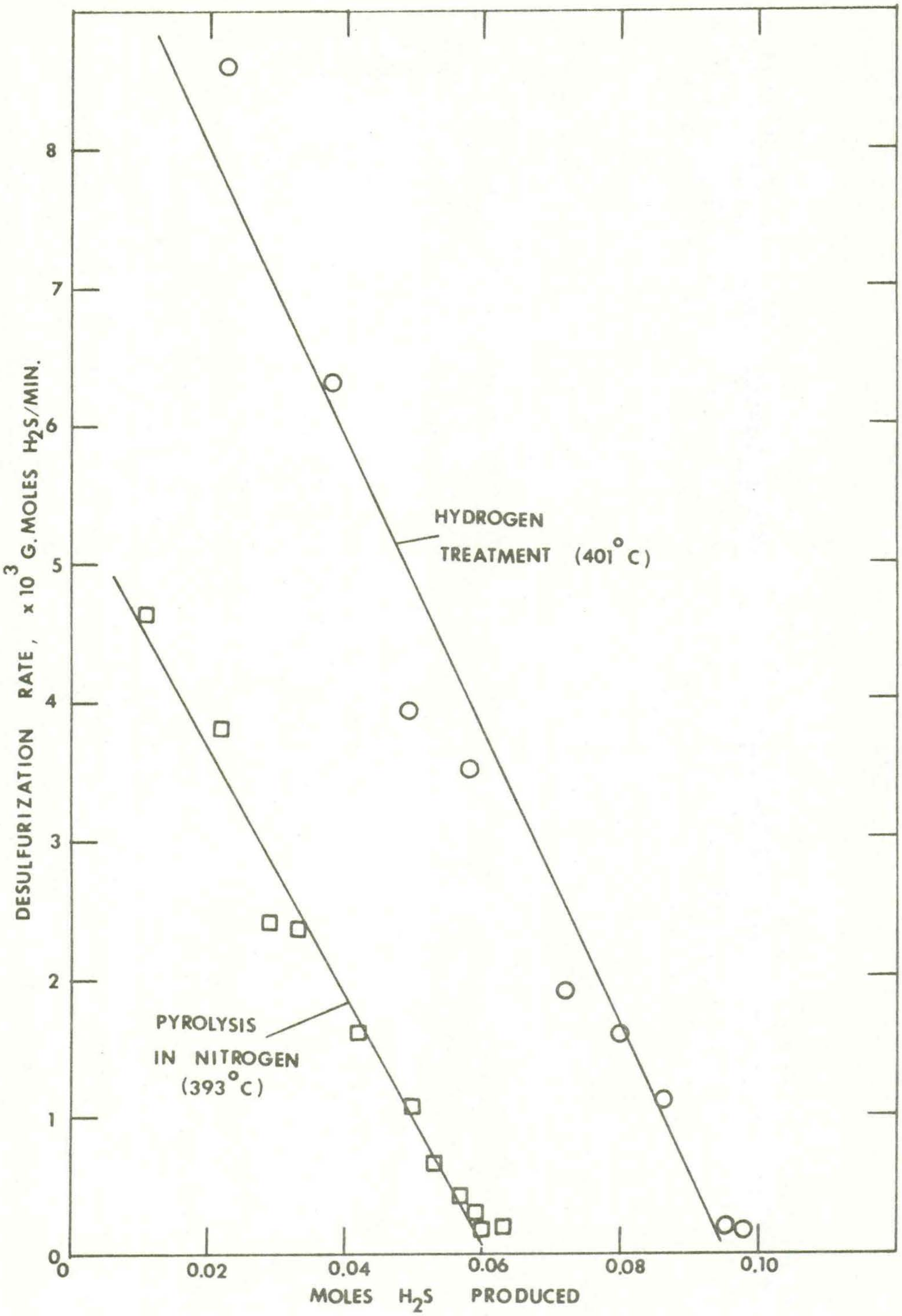

Figure 24. Correlation of the rate of desulfurization with the kinetic model

Table 15. Kinetic parameters for the reactions of organic sulfur

Run no.	Treatment gas	Reaction temp., °C	Rate constant k, min^{-1}	Limiting conversion X_o, %	Correlation coefficient
MSH-3	Hydrogen	401	0.105	28.8	-0.98
MSN-4	Nitrogen	393	0.089	18.2	-0.99
MSN-6	Nitrogen	321	0.047	5.5	-0.97

is a maximum attainable conversion of organic sulfur. Once this has been achieved, no further removal of organic sulfur is possible.

Oxidizing reactions   Figure 25 presents the rate data for the removal of sulfur from coal treated with an oxygen containing gas. Curves are shown for runs made on both types of coal. Three species of sulfur were observed in the off gases from these runs namely, sulfur dioxide, hydrogen sulfide and carbonoxysulfide. However sulfur dioxide was the major component.

The analysis of this reaction system is complicated by the large number of reactions which are thermodynamically feasible. The pyritic sulfur could react with oxygen by reactions 7 through 12 to yield sulfur dioxide and various

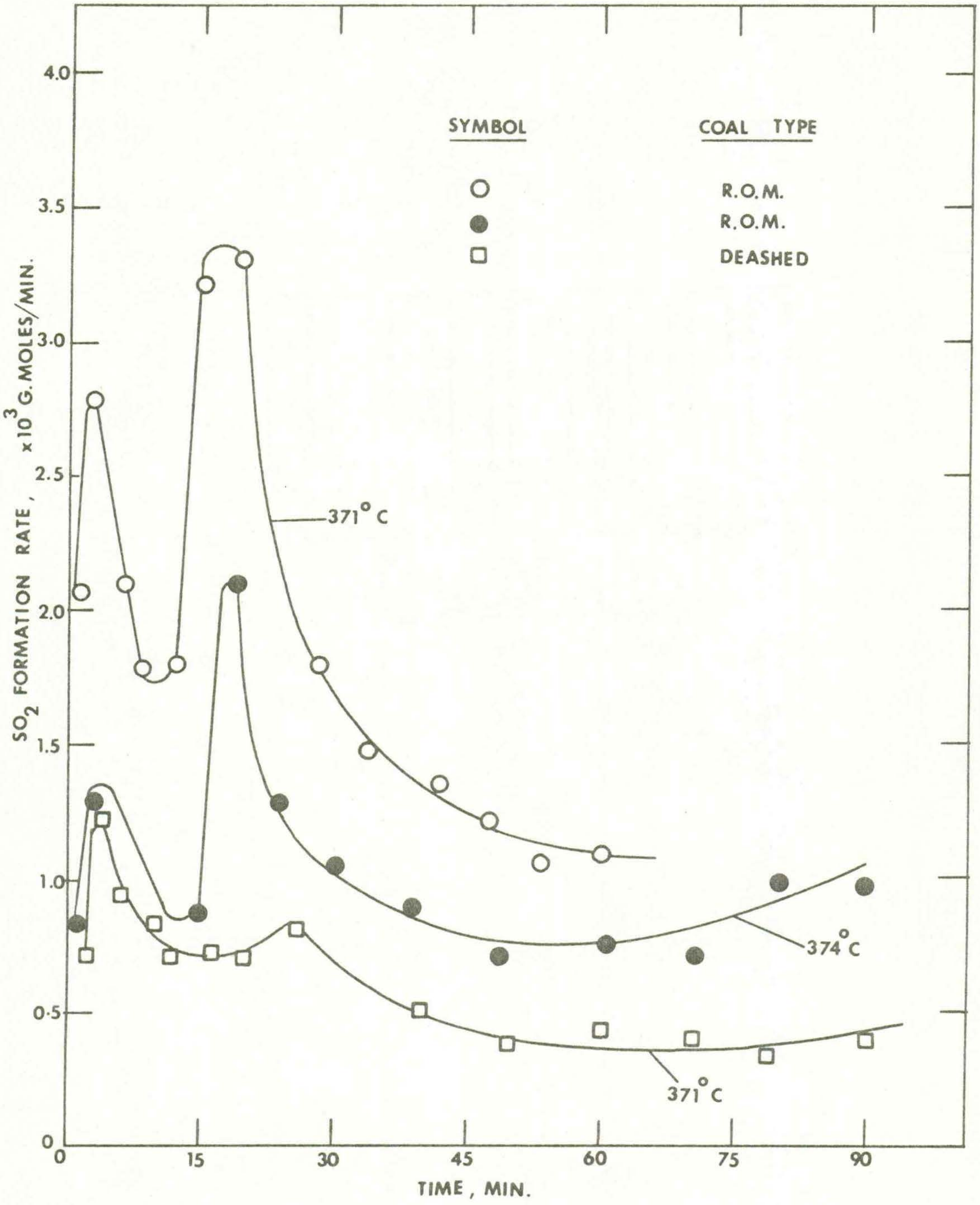

Figure 25. Rate of formation of sulfur dioxide during the oxygen treatment of coal, Series II

oxides and sulfates of iron.

The organic sulfur does not react with oxygen, as shown by the results of Series I runs. However, hydrogen sulfide released by the pyrolytic decomposition of organic sulfur could be oxidized by the following reaction.

$$H_2S + O_2 \rightarrow H_2O + SO_2 \qquad (41)$$

Thus Figure 25 shows the rate of evolution of sulfur dioxide which was formed by a superposition of the reactions of pyritic sulfur and reaction 41. The rate curve shows two unmistakable peaks for sulfur dioxide, and they occur at the same points in time for all the runs. The first peak is possibly due to the oxidation of hydrogen sulfide by reaction 41. In the first fifteen min. of a run the coal particles are probably engulfed in a film of hydrogen sulfide and other gases evolved during pyrolysis. Hence, the oxygen cannot effectively contact the pyritic sulfur and reacts instead with the hydrogen sulfide. Once the degassing effects have subsided the oxygen can penetrate to the pyritic sulfur to initiate the oxidation reactions. The second peak would then correspond to a point in time when the oxidation of pyritic sulfur becomes a process limited by the diffusion of oxygen through the product layer of oxides and sulfates. As this layer builds up the diffusion resistance increases and the rate drops.

Series III Experiments

This series of runs was performed to study the kinetics of the oxidizing and reducing reactions of iron pyrites. The objective was to obtain a kinetic model for these reactions and to determine whether it was applicable to the reactions of pyritic sulfur in coal. The treatment gases used in these runs and the operating conditions were similar to those employed in Series II. The course of the desulfurizing reactions of iron pyrites was followed by monitoring the concentration of the sulfurous species in the reactor off gas.

Operating conditions

The set of experiments consisted of three runs which were performed using an oxygen mixture as the treatment gas and two runs where a hydrogen mixture was employed. The materials used for the reactor feedstock were two particle size fractions of iron pyrites, namely, -40+60 mesh and -80+100 mesh.

For each run 200 g. of iron pyrites were injected into a preheated bed containing 250 g. of sand. The sand to coal mass ratio was therefore 1.25. The operating conditions during these runs are reported in Table 16.

Figure 26 shows the thermal behavior for typical runs using both types of treatment gases. It can be seen that for

Table 16. Operating conditions for runs in Series III[a]

Run no.	Wt. of pyrites treated, g.	Particle size of pyrites, U.S. mesh	Particle size of sand,[b] U.S. mesh	Superficial gas velocity,[c] cm./sec.
PH-1	196.8	-40+60	-20+30	32.8
PH-2	199.7	-80+100	-60+80	12.6
PO-2	199.2	-40+60	-20+30	26.8
PO-3	200.0	-80+100	-60+80	7.8
PO-4	199.2	-40+60	-20+30	26.6

[a] All runs were conducted for a duration of 90 min.

[b] Sand to pyrites mass ratio = 1.25.

[c] Gas velocity is computed at the temperature of the feed gas.

Concen. of treatment gas	Thermal behavior of reactor		
	Temp. drop on pyrites injection, °C	Preheat time min.	Av. temp. during run, °C
80.0% H_2	60	9	374
78.6% H_2	76	9	374
9.8% O_2	54	3	410
9.4% O_2	60	12	379
9.8% O_2	45	3	406

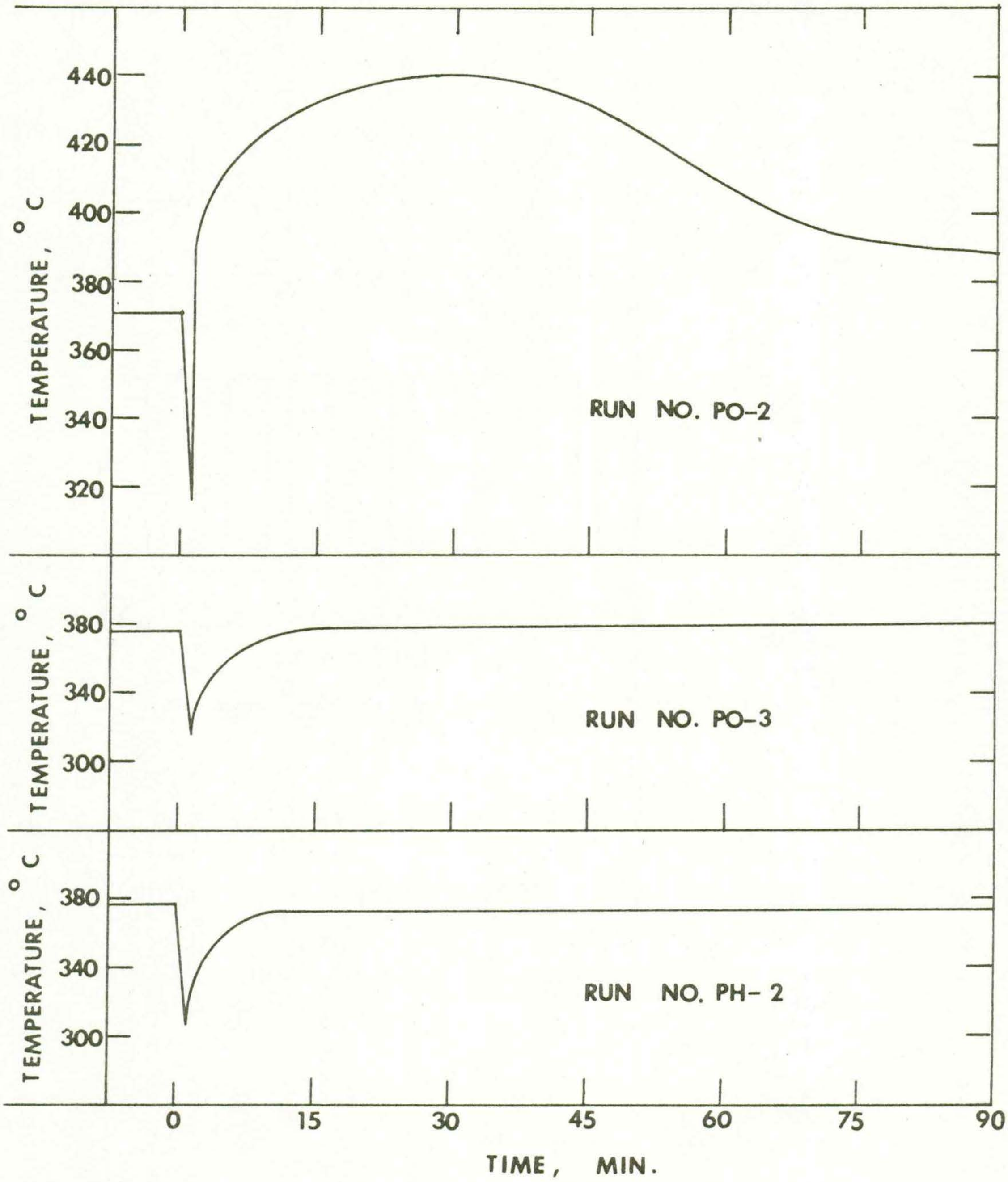

Figure 26. Time variant temperature profiles in the reactor, Series III

Runs PH-2 and PO-3, the conditions within the reactor were nearly isothermal. However, for Run PO-2 the time variant temperature profile in the reactor indicated a nonisothermal behavior. As can be seen from Figure 26, the temperature in the reactor rose 70°C above the initial temperature of the sand. This rise was probably caused by the large exothermic heat of reaction evolved due to the oxidation of iron pyrites. Run PO-4 was a duplicate of Run PO-3 and here also an identical temperature rise was observed. In both these runs the temperature rose to a peak and then decreased as the reaction approached completion.

Experimental results

Samples of the reactor off gas were withdrawn at discrete time intervals during a run and analyzed with the mass spectrometer to determine the concentration of hydrogen sulfide, hydrogen, oxygen, sulfur dioxide and nitrogen. The cumulative yield of each sulfurous gas was obtained by numerical integration of the discrete gas composition data. The percent sulfur removed from the iron pyrites was then estimated by equation 42.

$$\text{\% sulfur removed} = 100\left[\frac{\text{Total moles of } H_2S \text{ or } SO_2 \text{ in off gas}}{\text{Initial moles of S in pyrites}}\right] \qquad (42)$$

An overall material balance was performed on all entering and exiting streams. The values of percent sulfur removed from the iron pyrites, the average concentration of the sulfurous species in the off gas and the results of the material balance are reported in Table 17.

Table 17. Summary of results of runs in Series III

Run no.	Avg. concen. of sulfurous gas, %	Sulfur removed, %	Total material balance,[a] %
PH-1	1.4	24.8	99.6
PH-2	4.9	33.1	101.1
PO-2	4.0	59.9	99.5
PO-3	5.4	24.1	99.9
PO-4	3.9	58.3	99.4

[a] Calculated as 100 x (output/input).

The total amount of sulfur removed from the pyrites was also estimated by titration of the ammoniacal hydrogen peroxide solution in the gas absorber. However, the results of this estimation were found to be unreliable. This was because the off gas contained a fairly concentrated stream of hydrogen sulfide or sulfur dioxide. When this stream contacted the hydrogen peroxide a sulfuric acid mist was formed which was carried away by the gases. Hence a wide discrepancy was noticed between the values of sulfur removal obtained from the mass spectral analysis and those obtained by titration of the absorbent solution. As can be seen from Table 17, a close material balance was achieved for all the runs. This attested to the accuracy of the gas analysis.

Kinetic modeling

Oxidation of pyrites From the gas analysis data it was possible to determine the rate of evolution of sulfur dioxide. The rate data for the oxygen runs are plotted against time in Figure 27. In the case of the -60+80 mesh size pyrites it can be seen that the rate increased rapidly in the first ten minutes and thereafter remained steady. The total sulfur removed at the end of the run was 24 percent. The runs performed on -40+60 mesh pyrites showed an altogether different behavior. The rate increased to a peak in 12 minutes and then steadily decreased to zero towards the end of the run. The total removal of sulfur in these runs was 59 percent. Since the rate of evolution of sulfur dioxide became small, the maximum attainable conversion in these runs was 59 percent.

The oxidation of iron pyrites could proceed by several steps. The equilibrium constants of the feasible reactions were plotted in Figure 2. From the standpoint of

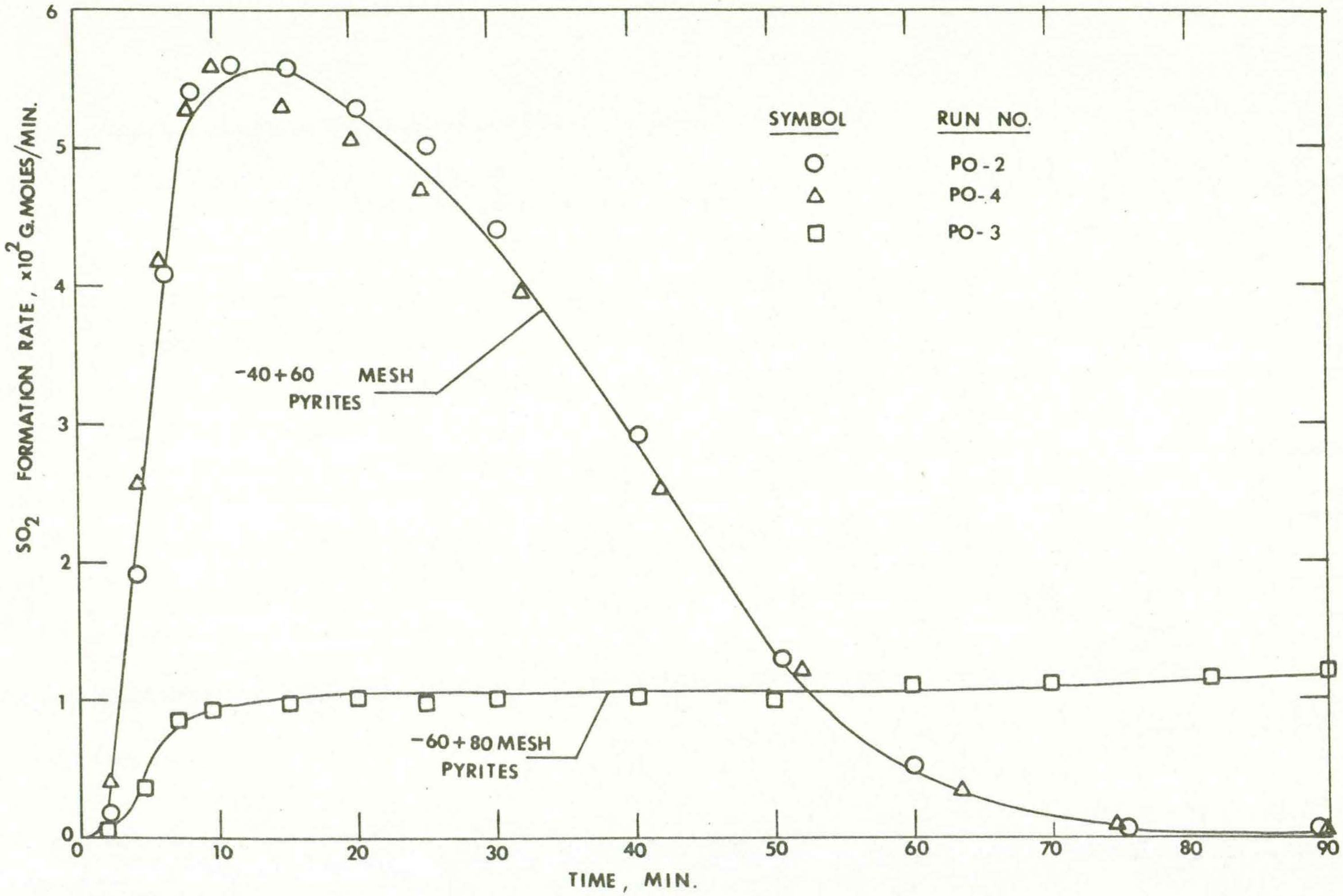

Figure 27. Rate of oxidation for different particle size fractions of iron pyrites

thermodynamic feasibility, the two most predominant reactions would be:

$$FeS_2 + 3O_2 = FeSO_4 + SO_2 \qquad (7)$$

$$FeS_2 + \frac{11}{4}O_2 = \frac{1}{2}Fe_2O_3 + 2SO_2 \qquad (8)$$

Reactions 7 and 8 are highly exothermic in nature and their heats of reaction are, respectively, -253.6 and -202.5 kcal. per g. mole of iron pyrites. If the heat released by the reactions is not dissipated, the temperature of the pyrite particle increases as the conversion increases. This fact is clear on comparing Figures 26 and 27. Thus, in the oxygen treatment of -40+60 mesh pyrites, the temperature increased with the rate of reaction. Thereafter, as the rate dropped, the temperature also decreased to the original temperature of the sand. This behavior was not evidenced in the treatment of -60+80 mesh pyrites. In this case, the thermal behavior of the reactor was nearly isothermal and the rate of reaction remained steady after the initial preheating period. It is possible that the smaller particle size of pyrite improved the rate of heat transfer and the heat was rapidly dissipated from the reaction surface. Hence, in spite of the exothermic nature of the reaction the temperature of the reactor remained constant and no runaway instability occurred.

A kinetic model to describe the oxidation of pyrites is complicated by the number of feasible reactions and the complex interrelationship between the inherent diffusion processes. Since very little data was obtained in the present study, it was not possible to do any mathematical modeling for these reactions.

Reduction of pyrites The reduction of iron pyrites by hydrogen proceeds by reaction 3.

$$FeS_2 + H_2 = H_2S + FeS \qquad (3)$$

Further reduction of ferrous sulfide is precluded by thermodynamic considerations.

Runs were performed on two particle sizes of iron pyrites at a temperature of 374°C. The reaction rate of iron pyrites was monitored by analyzing the concentration of hydrogen sulfide in the off gas from the reactor. The pyrite conversion was defined as:

$$\text{\% conversion of pyrites} = 100\left[\frac{\text{g. moles of } H_2S \text{ in off gas}}{\text{g. moles of } FeS_2 \text{ in feed}}\right] \qquad (43)$$

Shen and Smith (42) studied the kinetics of reaction 3 and found that a shrinking core model effectively described the reduction of iron pyrites by hydrogen. The following assumptions were implicit in the model:

(a) The pyrite particle is perfectly spherical.

(b) The gas stream has a constant composition and temperature.

(c) The reaction at the surface of the pyrite is first order with respect to the concentration of hydrogen.

(d) The system is at quasi-steady state.

(e) The reacted and unreacted regions are separated by a sharp interface.

The kinetics could be controlled by three rate controlling mechanisms. If the rate of reaction is controlled by the diffusion of hydrogen through the film of gas surrounding the pyrites particle, the fractional conversion, X_B, could be expressed as a function of time, t, by the equation:

$$\frac{t}{\tau} = X_B \tag{44}$$

where τ = time required for the complete conversion of the pyrite particle.

In the event that the product layer of ferrous sulfide constitutes a major resistance, the conversion is described by:

$$\frac{t}{\tau} = 1-3(1-X_B)^{2/3} + 2(1-X_B) \tag{45}$$

If the product layer or the film of gas around the pyrites particle has no effect on the conversion rate, the rate may be controlled by the rate of chemical reaction at the core interface. In this case the following equation would apply:

$$\frac{t}{\tau} = 1 - (1-X_B)^{1/3} \tag{46}$$

The results of Shen and Smith indicated that at temperatures less than 450°C, reaction 3 is controlled by the resistance to chemical reaction for an average particle radius of 0.035 mm. In the present study the particle sizes of pyrites used in runs PH-1 and PH-2 were 0.030 mm. and 0.016 mm. respectively. Since the particle size of pyrites in run PH-1 was close to that used by Shen and Smith, the data from this run was correlated using equation 46. A least squares linear regression yielded an estimated value of 456.7 min. for τ, the time required for complete conversion. The regression curve for run PH-1 is drawn in Figure 28 and this shows very good agreement with the data. This suggests that the reduction of pyrites in run PH-1 was chemical reaction rate controlled.

The data from run PH-2, which was performed on -80+100 mesh pyrites, did not fit the model used above. On examining Figure 28, it is seen that for times greater than 30 min. the data points for this run fall on a straight line. This suggests that there is a linear relationship between time, t,

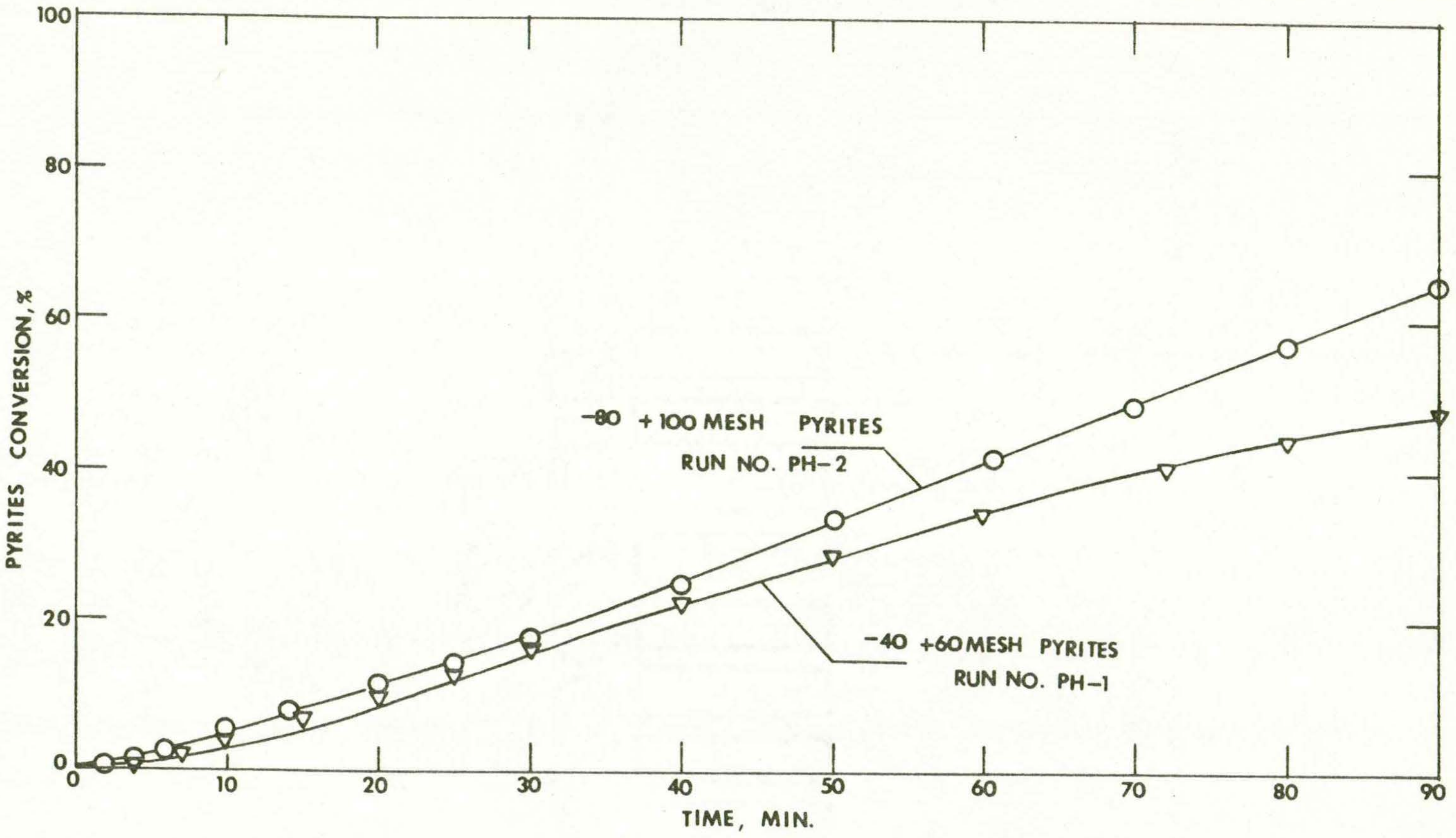

Figure 28. Conversion of iron pyrites to hydrogen sulfide, Series III

and conversion, X_B. Hence, this indicates a gas-film diffusion controlling mechanism as described by equation 44.

Although there is no substantive experimental evidence, the difference in the rate determining mechanisms can be explained qualitatively. The concentration of hydrogen in the feed gas in both the runs was similar. However, the superficial gas velocity for the two runs were different. The velocities in runs PH-1 and PH-2 were 32.8 and 12.6 cm./sec. respectively. A lower gas velocity and a smaller particle diameter would lower the Reynolds number and thereby increase the thickness of the gas-film around the particle. Secondly, a lower gas velocity would reduce the rate at which the product gas, hydrogen sulfide, is swept away from the reactor. Hence, the driving force for the diffusion of hydrogen through the gas-film would be lower. Thus the rate controlling mechanism in run PH-2 was probably the diffusion of hydrogen through the gas-film around the pyrites particles.

The reduction of iron pyrites by hydrogen in a fluidized bed reactor is therefore adequately described by the shrinking core model. The rate controlling mechanism would however depend on the reaction temperature, particle size of pyrites, and the superficial gas velocity.

Discussion and Evaluation of Results

Reactions of coal sulfur

The results from the three series of experiments helped to give a better understanding of the reactions occurring between the sulfur species in coal and the treatment gases. Although the experiments were performed in a batch set-up, the method of injecting the feed into a preheated bed of sand served to simulate the conditions obtained in a continuous reactor. Thus, most experiments were carried out under nearly isothermal conditions, with a reasonably small transient period for preheating the coal.

The statistical method of analysis used in series I was necessitated by the complexity of the reaction system. The microscopic heterogeneity of the raw material and the complex behavior of the solid and gas species in the fluidized bed reactor were responsible for the large random error in all the observations. The effectiveness of some of the statistical tests could have been improved by more replications of runs. Nevertheless, the use of a factorial design of experiments made it possible to systematically assess the effects of treatment gas, type of coal and reaction temperature on various parameters of devolatilization and sulfur removal.

The removal of organic sulfur was shown to be sensitive to the reaction temperature employed but was independent of the type of treatment gas. Substantial amounts of this sulfur species were removed by treating coal at 400°C. The runs in Series II also demonstrated that the rate of reaction of organic sulfur decreases linearly as conversion increases and vanishes at a limiting conversion, X_o. It is likely that the value of X_o depends on the reaction temperature. Hence, further work could be directed towards establishing the functional relationship between temperature and limiting conversion.

The reactions of pyritic sulfur in coal were also shown to be dependent on the reaction temperature. However, unlike the behavior of organic sulfur, this sulfur species did react with the treatment gas. At 410°C it was found that a low oxygen concentration, namely 3.8 percent, was more effective than hydrogen as a treatment gas. Thus, 41 percent of the pyritic sulfur could be removed from R.O.M. coal treated at 410°C for 30 min.

From the Series II experiments, it was seen that the rate of oxidation of iron pyrites to sulfur dioxide becomes appreciable after the initial degassing of coal subsided. This is in accord with the observations made by earlier investigators (8,9,10,23) who reported that the period of chemical attack, comprising a chemical reaction between pyritic sulfur and oxygen follows the period of devolatilization.

The desulfurization of coal was not adversely affected by the ash content. This observation was not in accordance with the findings of Cernic-Simic (44) who reported that ash acts as a sulfur acceptor and adsorbs the sulfurous gases evolved during the coal treatment. The present study however showed that at all reaction temperatures, more organic sulfur was converted to gases in R.O.M. Jude coal than in Deashed coal. In fact, at these temperatures a gain in the organic sulfur content was noticed when oxygen was used to treat Deashed coal. This could mean that the ash present in R.O.M. coal was not sufficiently calcareous in nature to adsorb sulfurous gases. It would be instructive to chemically analyze the ash in this coal for oxides of iron, aluminum and calcium. It is possible that some of the higher metal oxides present in ash act as mild catalysts in the desulfurization reactions.

Kinetic studies

The kinetics of the desulfurization reactions were studied in the Series II and III experiments. In general, it was found that the reducing reactions of organic and pyritic sulfur are simple to characterize and hence amenable to mathematical modeling. The oxidizing reactions are far more complex and hence no modeling was attempted.

In Series II runs, an empirical model was used for the hydrodesulfurization of organic sulfur. This model did not purport to explain the reaction mechanism as it was based on the overall macro process of desulfurization. The model was fitted to the rate data from the experiments with Deashed coal. The underlying assumption was that the sulfur in Deashed coal was organic in nature. The model fitted the data adequately and kinetic parameters could be obtained. It would be interesting to extend this work in order to obtain the values of these parameters for a range of temperatures.

In Series III, the reduction of iron pyrites to ferrous sulfide was seen to follow a shrinking core model. The rate controlling step could either be the resistance to the diffusion of hydrogen through the gas-film around a pyrites particle, or the chemical reaction occurring on the solid surface. Since very little data was obtained for the pyrites runs in Series III, it was not possible to study the parameters of the kinetic model in detail. Further work needs to be done to quantitatively determine the effect of the particle size of pyrites and the superficial gas velocity on the reaction rate. The hydrodesulfurization model for organic sulfur and the shrinking core model for the reactions of iron pyrites could then be jointly tested with the rate data from the desulfurization of R.O.M. coal.

The oxidation of iron pyrites needs to be studied in more detail. In the present study no rate data could be obtained for the oxidation reactions conducted in isothermal conditions. The large temperature rise noticed in the runs performed on -40+60 mesh pyrites could be avoided by maintaining a larger sand to pyrites mass ratio in the bed. A larger mass of sand could act as a heat sink for the heat released during the oxidation of pyrites.

A mathematical model for the oxidation of pyrites is complicated by the large number of reactions which are possible. In one sense, this set of reactions is similar in complexity to those encountered in the desulfurization of organic sulfur. These modeling problems could be circumvented by assuming the following generalized reaction for the oxidation of iron pyrites.

$$FeS_2 + aO_2 \rightarrow bSO_2 + cFe_2O_3 + dFeSO_4 \qquad (47)$$

where a,b,c,d = stoichiometric coefficients.

A number of experiments could then be conducted on various particle sizes of iron pyrites using different concentrations of oxygen and reaction temperatures. The data could then be correlated using an empirical kinetic model which could be used to predict pyritic sulfur conversions in coal.

Feasibility of desulfurization process

The feasibility of a coal desulfurization process utilizing a treatment gas will have to be judged from the standpoint of the environmental acceptability of the product fuels.

In Series I it was shown that although about 30 to 50 percent of the coal sulfur is removed by treating with hydrogen or oxygen gas mixtures, the specific sulfur content of the coal char (lb.S/MM Btu.) is not significantly reduced. This is because of the loss of volatile matter and fixed carbon which lowered the heating value of the char. From the results of the runs in series II, it was clear that the off gas from the reactor contained significant quantities of hydrocarbons, hydrogen and carbon monoxide which could be used as a low Btu. fuel gas. The criterion for judging the feasibility would be the specific sulfur content of the overall product. This parameter was estimated for all the runs performed in Series II. It was assumed that there were no material losses in the process and that the only combustible gaseous species evolving from the coal were carbon monoxide, hydrogen, methane, ethane and propane. The specific sulfur content, and the heating values of the char and fuel gas are reported in Table 18.

On examining Table 18 it is obvious that this process cannot comply with the 1975 EPA standard of 0.6 lb. S/MM Btu.

Table 18. Specific sulfur content of products from experiments, Series II

			Heating value		Specific sulfur content	
Run no.	Type of coal[a]	Treatment gas	Char[b] Btu./lb.	Fuel gas Btu./scf.[c]	Char lbs./MM Btu.	Char+fuel gas lbs./MM Btu.
MSN-1	R.O.M.	Nitrogen	13692	522	6.82	6.05
MSN-4	Deashed	Nitrogen	14169	542	3.54	3.32
MSN-5	R.O.M.	Nitrogen	13716	495	7.61	7.13
MSN-6	Deashed	Nitrogen	14092	425	4.28	4.11
MSH-1	R.O.M.	Hydrogen	13735	780	5.90	5.50
MSH-3	Deashed	Hydrogen	14149	912	4.06	3.84
MSO-2	R.O.M.	Oxygen	12484	418	6.41	5.26
MSO-3	R.O.M.	Oxygen	12762	394	6.17	5.00
MSO-7	R.O.M.	Oxygen	12404	432	6.93	4.46
MSO-8	Deashed	Oxygen	13080	379	4.22	3.62

[a] Specific sulfur content of feed was 7.42, 4.89 lb.S/MM Btu. for R.O.M. and Deashed coal respectively.

[b] On a moisture, ash free basis.

[c] Excludes volume of CO_2, H_2S, SO_2 and N_2.

for large power plants. However, the proposed emission standards for the State of Iowa would limit the specific sulfur content of the fuel used by existing power plants to 4 lb. S/MM Btu. Thus the fuel products obtained from runs MSH-4, MSH-3, and MSO-8 could yield an overall specific sulfur content which complies with the proposed Iowa standard.

It must be pointed out that in conventional coal fired power plants the particle size of the feed coal is usually -200 mesh. In the experiments conducted in the present study, the particle size of the coal was restricted to -20+40 mesh. A smaller particle size of coal of the order of -200 mesh could very likely increase the percent removal of sulfur in a gaseous desulfurization process.

The removal of organic sulfur was shown to be limited by the temperature of the gaseous treatment. The reaction temperature in the present work was restricted to the range 200° to 410°C because, at higher temperatures, the coal agglomerated thereby adversely affecting the performance of the fluidized bed. In order to improve the removal of organic sulfur it would be desirable to render the coal nonagglomerating so that it can then be treated at temperatures greater than 410°C in a fluidized bed. Methods of pretreating the coal by mild surface oxidation should be studied to determine ways to reduce the agglomerating tendencies of coal at high temperatures.

SUMMARY OF CONCLUSIONS

Conclusions drawn from the results of this experimental project are summarized below.

1. Desulfurization of coal by oxidizing and reducing reactions was demonstrated in a fluidized bed reactor. The effectiveness of the gaseous treatment was shown to improve considerably as the reaction temperature was increased.
2. The reactions of organic sulfur were seen to be temperature sensitive like those of coal pyrolysis. Oxygen or hydrogen did not significantly react with this sulfur species. The presence of ash probably catalyzed the reactions of organic sulfur.
3. The reactions of pyritic sulfur in coal are also temperature sensitive. Unlike organic sulfur, the presence of oxygen in the treatment gas significantly enhanced the removal of pyritic sulfur. The percent removal obtained using hydrogen for the treatment was less than that for oxygen.
4. An empirical model was seen to adequately fit the rate data for the reducing and pyrolytic reactions of organic sulfur. Thus, the rate was first order with respect to the sulfur species.
5. A shrinking-core model was seen to be a good representation for the reducing reaction of iron

pyrites. The rate controlling step is either the chemical reaction rate or gas-film diffusion.

6. The composition of the gases evolved due to coal devolatilization, combustion and desulfurization were determined. The heating value of the off gas from the reactor was seen to vary between 400 and 900 Btu./scf. on a carbon dioxide, nitrogen and sulfurous gas free basis.
7. The specific sulfur content of the char is not significantly reduced from that in the feed coal. However, if the desulfurized fuel gas is used in combination with the char, the specific sulfur content of the overall product can be appreciably reduced.

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