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Pyrolysis of High Sulfur Indian Coals

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Pyrolysis experiments under laboratory conditions for five numbers of high sulfur coal samples from the states of Meghalaya and Nagaland, India, were carried out at temperatures of 450, 600, 850, and 1000 °C, respectively. The yield of products and thermal release of sulfur from these coals are investigated. The distribution of sulfur in the pyrolyzed products, i.e., char/coke, gas, and tar, is also reported. Hydrocarbon and sulfurous gases released at different temperatures were analyzed by a gas chromatograph (GC) with an FID (flame ionized detector) and an FPD (flame photometric detector), respectively. H₂S evolution during coal pyrolysis was found to be a function of temperature up to 850 °C. The low concentration of SO₂ detected for some of the samples is due to decomposition of inorganic sulphates present. Evolution of methane for the coals tested increases with the increase of temperature. Maximum sulfur release was found in the range of 600–850 °C and has a decreasing tendency from 850–1000 °C, which might be due to the incorporation of sulfur released into the coal matrix. Activation energies for sulfur release were found in the range of 38–228 KJ mol⁻¹, which were higher than the reported activation energies for lignites and bituminous coals mainly due to highly stable organic sulfur functionalities.

Introduction

Coal is a heterogeneous mixture of organic and inorganic matters. Pyrolysis is an important intermediate stage in coal gasification, combustion, and liquefaction, and it is also considered as a simple and effective method for coal desulfurization. Pyrolysis, as a process technology, is a simple and an effective method for a clean conversion of coal.^{1–3} The organic and inorganic constituents of coal, including organic and inorganic sulfur, undergo significant changes during the pyrolysis process. The level of these changes depends on many variables, which can be grouped in two classes: the initial condition, i.e., coal properties (rank of coal, topographic conditions, mineral matter content, sulfur content, and its forms) and the pyrolysis conditions of coal (temperature, heating rate, reaction time, pressure, size distribution of pyrolyzed coal, and velocity of carrying gas). Among all the reaction parameters, temperature is the most important factor affecting the transformation of sulfur during coal pyrolysis. The basic chemistry of sulfur transformation during pyrolysis is important for process design and optimization in gainful utilization of high sulfur coals. With the stringent environmental regulations, sulfur reduction is essential prior to use.

Sulfur in coal exists both as inorganic and organic forms. Inorganic sulfur exists mostly as pyrite and marcasite with small amounts of sulphate sulfur. The organic sulfur exists in aromatic rings as well as aliphatic functional groups. The functionality and distribution of organic sulfur varies from coal to coal.

Extensive studies on sulfur transformation during pyrolysis have been made and many useful results have been reported and reviewed in detail.^{4–7} During pyrolysis, pyrite transforms into sulfide

and nascent sulfur at temperatures above 350 °C. The nascent sulfur is very active, and it captures hydrogen from coal to form H₂S that converts to gas and/or is captured by an organic matrix to form organic sulfur that remains in char/coke or tar^{8–13} and/or is fixed by mineral matters in coal, mainly calcium, sodium, or iron compounds, to form sulfides that remains in char/coke.^{8–19} The behaviour of organic sulfur depends mainly on the functional group of organic sulfur in coal.^{20–24} The removal of organic and inorganic sulfur during pyrolysis depends upon pyrolysis conditions, mineral matter, and char/coke characteristics of sulfur groupings in the parent coal.

In India, a good deposit of high sulfur coals is found in the northeastern (NE) region. These low rank coals have different physicochemical attributes in comparison to other Indian coals. The general char/coke characteristics, which restrict their usage in the domestic as well as industrial sectors, are that the coal is high in sulfur, high in volatile matter, and mostly caking and

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Table 1. Physicochemical Characteristics of Coals (As Received Basis)^a

char/coke characteristics	MM	MS	MK	MB	NA
thickness of seam (m)	0.63	1.50	0.63	0.65	
nature of sample	ROM	ROM	ROM	ROM	outcrop
		Proximate Analysis (wt %)			
moisture	2.7	2.9	3.1	1.5	3.4
ash	11.5	20.0	11.5	11.5	11.9
VM	34.6	35.6	41.4	40.5	37.2
FC	51.2	41.5	44	46.5	47.5
		Ultimate Analysis (wt %)			
carbon	66.4 (77.2)	59.7 (77.5)	56.7 (67.5)	66.25 (76.1)	60.0 (70.8)
hydrogen	5.4 (7.0)	6.0 (7.8)	4.6 (5.7)	5.37 (6.9)	4.0 (4.7)
nitrogen	1.0 (1.3)	0.9 (1.2)	1.2 (1.4)	1.0 (1.1)	0.9 (1.1)
oxygen by difference	(14.5)	(13.5)	(25.4)	(15.9)	(23.4)
		Sulfur Distribution (%)			
total sulfur	3.0	2.9	3.98	4.46	4.0
organic sulfur	2.6	2.5	3.5	3.5	3.28
pyritic sulfur	0.33	0.15	0.24	0.26	0.08

^a The figures in parentheses indicate daf basis.

friable in nature. The sulfur content in these coals is in the range of 2–8% in general, and the majority of the sulfur is in an organic matrix (70–95%), which is not easily removable. However, cokes from these coals are found to be suitable in cement industries, ferro-alloys, etc.^{25–31} The present study aims to investigate the effect of temperature, sulfur types, and transformation during pyrolysis, which has not been studied so far. The pyrolysis temperatures selected were 450, 600, 850, and 1000 °C corresponding to primary coal carbonization, semicoke formation, secondary coal carbonization, and coke formation, respectively. Here, char is referred to as the product of the primary carbonization temperature (450 °C) and coke above this temperature for all the coal samples.

Experimental

Coal Samples. The freshly mined coal samples from Mondiatia (MM), Sutanga (MS), Khlieriat (MK), and Bapung (MB) of Jaintia Hills, Meghalaya (91°58′–92°50′ E longitude and 25°02′–25°45′ N latitude) and Akhunushaba (94°14′–94°40′ E longitude and 26°14′–26°45′ N latitude) of Nagaland (NA), India, were used in this study. The air-dried samples are ground to 0.211mm before use. The proximate analysis and forms of sulfur of all the samples were done by standard methods.³⁵ The carbon, hydrogen, and nitrogen were determined by using a Perkin-Elmer (model 2400) elemental analyzer and total sulfur by Leco S 144 DR sulfur determinator (accuracy ±0.02). Physicochemical characteristics of these coals are summarized in Table 1.

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Table 2. Operating Conditions of Gas Chromatograph

operating conditions	H ₂ S and SO ₂	CH ₄
oven temperature	50 °C at 0 min, with ramp 6 °C/min, hold 80 °C for 5 min	40 °C at 2 min, with ramp 6 °C/min, hold 80 °C for 5 min
injector temperature (°C)	60	125
run time (min)	10	8.4
detector	FPD (flame photometric detector)	FID (flame ionized detector)
detector temperature (°C)	200	150
column	Porapak Q-S teflon, 6 ft	Mol. Sieve 5A SS, 6 ft
carrier gas flow of	He	He
carrier gas (mL/min)	20	20
retention time (min)	2.3 and 5.6	2.3

Pyrolysis Apparatus and Procedure. Pyrolysis experiments were carried out in a quartz fixed-bed reactor (19 mm i.d.) with a temperature programming system in an inert atmosphere. In each run, about 20 g of air-dried coal sample was taken into the retort, and the free space of the retort was filled with quartz wool and ceramic granules. The retort with coal samples was inserted into the furnace heated up to the desired temperatures. The final temperatures of 450, 600, 850, and 1000 °C were attained in 15, 25, 35 and 60 min, respectively, and were kept constant for 1 h for complete evolution of gas. The retort was cooled, and the coke/char was weighed. The pyrolysis products, including gas, tar, and liquor (aqueous portion) were collected and measured.³⁵

Gas Chromatograph Analysis. The gas samples collected into tedlar bags were analyzed by gas chromatography (Chemito GC 8610). The details of GC method are given in Table 2. H₂S, SO₂, and CH₄ were analyzed from the gaseous samples.

Calibration standards (gaseous) of sulfurous gases (SO₂, H₂S) and CH₄ were used to calibrate FPD and FID, respectively. The responses of the detector with the mass of gases were found to be in good agreement (correlation coefficients were 0.9993 for H₂S, 0.998 for SO₂, and 0.999 for CH₄, respectively). The gas chromatograms of H₂S and SO₂ for one of the coal samples (MS) are shown in Figure 1.

Results and discussion

Products of pyrolysis. The yield of pyrolysis products (char/coke, tar, liquor or aqueous portion, and gas) for all the coal

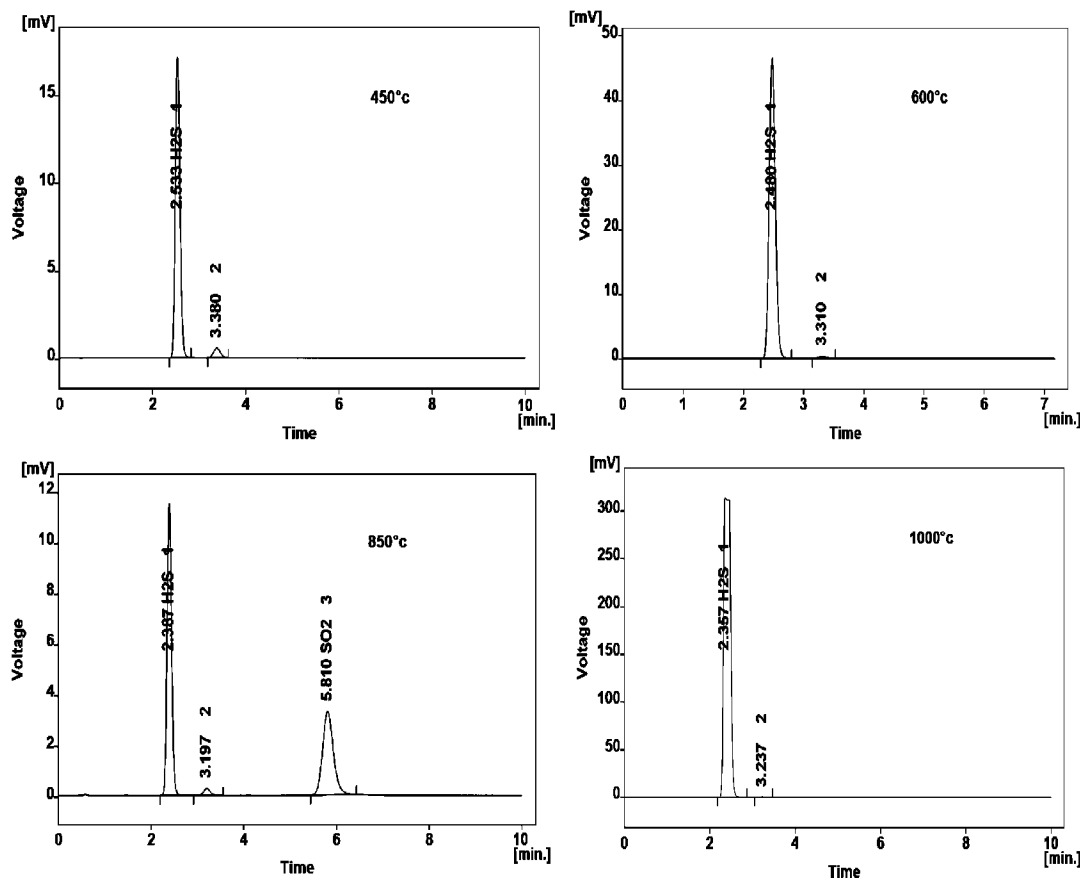


Figure 1. Gas chromatogram of H₂S and SO₂ for the MS coal sample at various temperatures.

Table 3. Yield of Pyrolysis Products (percent) at Different Temperatures (Dry Basis)

sample sites	temperature (°C)	char/coke (%)	tar + liquor (%)	gas (%)
NA	450	73.4	18.1	8.4
	600	68.1	24.8	7.1
	850	64.6	25.5	9.9
	1000	57.3	16.7	26.0
MS	450	83.3	10.6	6.1
	600	73.7	15.2	11.1
	850	70.1	10.4	19.5
	1000	60.2	15.2	24.6
MM	450	73.4	18.1	8.4
	600	72.4	17.6	10.1
	850	71.9	13.3	14.8
	1000	47.2	22.7	30.1
MK	450	75.0	9.6	15.4
	600	68.0	12.2	19.8
	850	66.8	13.2	20.0
	1000	46.9	17.6	35.4
MB	450	73.5	14.2	12.3
	600	69.9	14.1	16.0
	850	65.4	11.9	22.7
	1000	40.8	25.2	34.0

samples at different temperatures (450, 600, 850, and 1000 °C) is summarized in Table 3. The maximum weight loss at 1000 °C for the coal samples was found in the range of 40–60%, out of which 50–80% is contributed by liquor and gas. Earlier studies also reported that in sub-bituminous coals, water and CO₂ contribute up to 60% of total weight loss and 20–40%³⁶ for tar only.

Effect of Coal Properties. The relations between pyrolysis products and the H/C atomic ratio of the coals are shown in

Figure 2. Marginal increase in yield of char/coke is seen, while gaseous product does not have a clear trend with the H/C ratio. Increase in the H/C atomic ratio is indicative of more dehydrogenation and coalescence of higher molecular weight substances³⁷ which may account for the slight increase of char/coke. The yield of tar shows a slight decreasing trend till 850 °C. Pyrolysis products and the H/C ratio show no relation at 1000 °C.

Distribution of Sulfur

In Coals. The coals used for this study do not differ much in their total sulfur content. The total sulfur content in the coals ranges from 2.9 to 4.5% with a maximum in MB coal and a minimum in MS coal. Organic sulfur (2.5–3.3%) is dominant over inorganic forms (0.08–0.33%). Organic sulfur functionalities present in these high sulfur coals may be in the form of mercaptan/disulphide, thiols, aromatic sulphides, and thiophenes,³⁸ which are not easily removable.

In Products. The pyrolysis of coal leads to distribution of sulfur compounds in char/coke, tar, and gas. Distribution of sulfur in char/coke, gases, and tar during the pyrolysis of the coal samples is given in the Table 4. From the chromatograms obtained, three peaks were identified for all the coal samples. The peaks for H₂S and SO₂ are quantified whereas third small peak may be due to CS₂/COS.³⁹ The sulfur concentration in the gas is the sum of the H₂S and SO₂ released with the gas. The effect of temperature on sulfur concentration is quite

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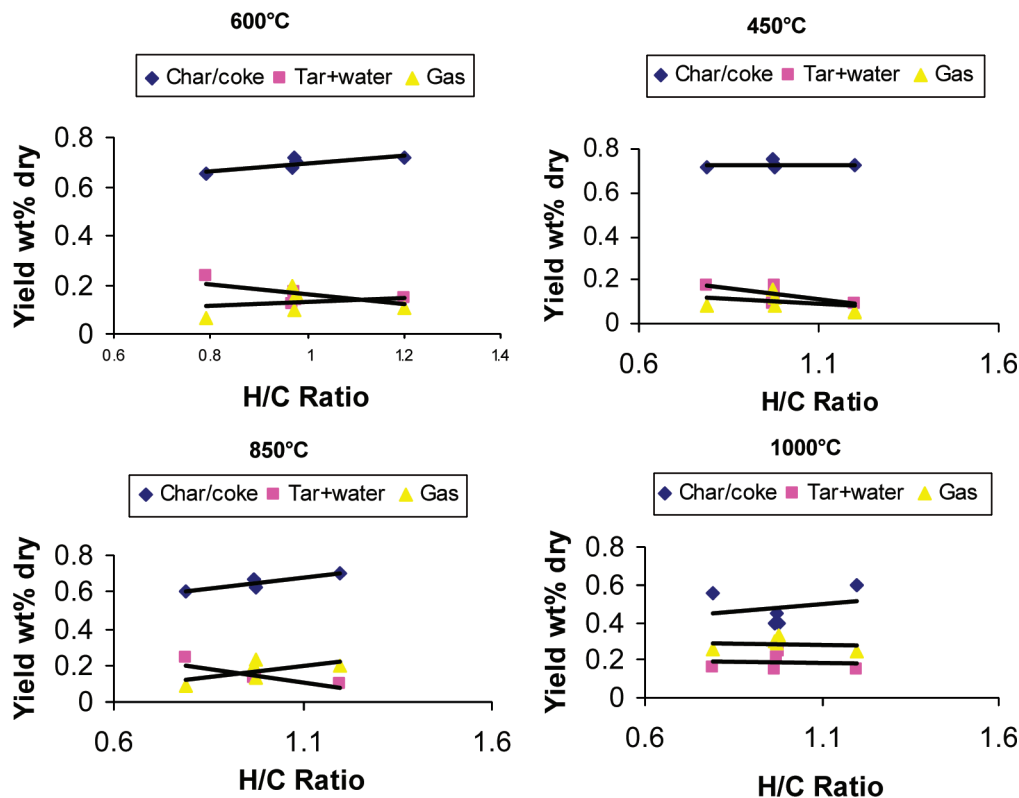


Figure 2. Yield of pyrolysis products vs H/C atomic ratio of coals at different temperatures.

Table 4. Sulfur Concentration in Coal and Pyrolyzed Products

sample	temperature (°C)	S in char/coal (ppm)	S in coke (ppm)	S in gases (ppm)	S in tar ^a (ppm)
NA	450	40350	30700	0.13	17939
	600		31330	247	19165
	850		25710	4004	23242
	1000		16210	3887	30099
MS	450	29290	26560	0.5	7245
	600		21720	208	13194
	850		20910	2415	14170
	1000		19850	2121	16849
MM	450	30020	28670	0.5	9091
	600		28310	245	9612
	850		25920	3919	10769
	1000		23810	3386	17814
MK	450	39800	31220	5	16384
	600		31110	209	18604
	850		30330	3989	18681
	1000		28540	3926	24996
MB	450	44610	28550	6	23489
	600		24430	215	27474
	850		21050	2212	30426
	1000		18540	2440	36179

^a Sulfur in tar = (ppm of sulfur in coal – (ppm of sulfur in char/coke × yield of char/coke) – (ppm of sulfur in gas × yield of gas)). It may also account for some low concentrations of unidentified gases like COS/CS₂.

predictable. An increase in temperature is accompanied by a decrease of the sulfur content in char/coke. The sulfur in char/coke is always lower than the original coals due to the devolatilization of sulfur. However, the amount of sulfur released varies with the coals examined, probably due to the different amounts of inorganic and organic forms of sulfur. In the temperatures studied, the distribution of sulfur was 40–96% in char/coke, 0.003–13.05% in gas, and the rest may be in tar. The high concentration of sulfur in char/coke may be due to the insufficient H₂ environment during pyrolysis and in situ reaction of sulfur with active sites of the organic matrix in coal to form new organic sulfur compounds. The nascent sulfur

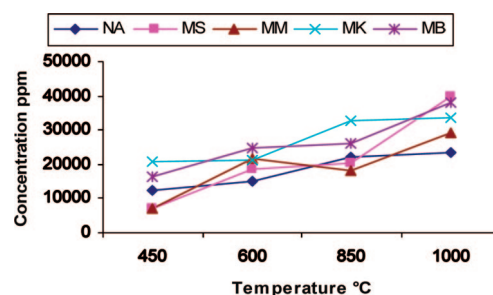


Figure 3. Release of CH₄ during pyrolysis at different temperatures.

released during the pyrolysis captures hydrogen from coal to form H₂S. Maximum sulfur removal takes place in the range of 600–850 °C and has a decreasing tendency beyond that. In the experiment conducted, it was found that sulfur evolution starts rapidly from 450 °C onwards. Above 500 °C, sulfur containing compounds in the bulk of coal begin to produce more HS[•] radicals.⁴⁰ Some of these radicals either react with indigenous hydrogen in coal or form H₂S or other sulfur containing gases. The rest of the radicals react with char/coke and still remain in char/coke and/or a part of them conglomerate on char/coke surface and increase the evolution of H₂S with temperature rise. The sulfur removal obtained at the temperatures studied was 23–59% for NA, 9–32% for MS, 5–20% for MM, 21–28% for MK, and 36–58% for MB, respectively. Observed variations in sulfur removal in these coals may be due to the presence of different sulfur groups and their properties.

Gaseous Components of Pyrolysis

CH₄ Concentration. The concentration of CH₄ varies between 7012.6 and 20757 ppm at 450 °C, 14995 to 24216 ppm at 600 °C, 17952 to 32769 ppm at 850 °C, and 23565 to 38040 ppm

Table 5. Concentration of SO₂ and H₂S at Various Temperatures

sample sites	temperature (°C)	SO ₂ (ppm)	H ₂ S (ppm)
NA	450	nd ^a	0.13
	600	15	232.2
	850	nd	3990
	1000	nd	3887
MS	450	0.4	0.12
	600	nd	202
	850	6	2415
	1000	nd	2121
MM	450	0.4	0.12
	600	3.0	241.5
	850	nd	3919
	1000	nd	3386
MK	450	nd	5
	600	nd	209
	850	nd	3989
	1000	nd	3928
MB	450	nd	6
	600	nd	215
	850	nd	2212
	1000	nd	2440

^a nd = not detected.

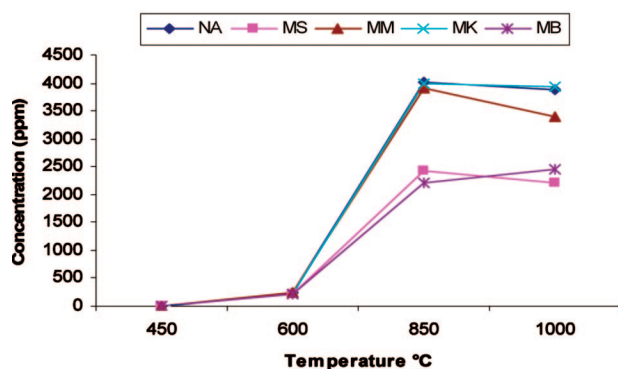


Figure 4. Release of H₂S at various pyrolysis temperatures.

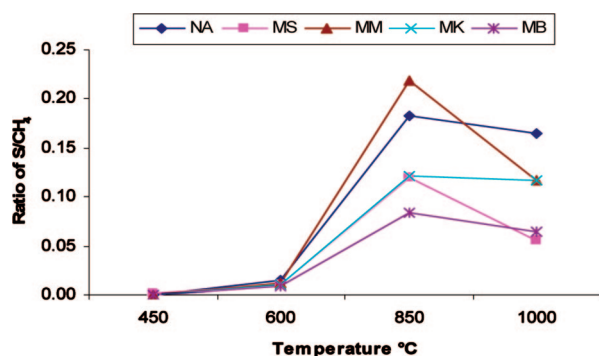


Figure 5. Thermal desulfurization of coal.

at 1000 °C, respectively. Methane concentrations for these coals increase with the increase in temperature (Figure 3). At lower temperatures, the loss of weight in coal is due to a loss of water and hydrocarbons, including aromatic hydrocarbons. The volatiles obtained at low temperatures have been evaporated from the coal matrix rather than being formed by the thermal breakdown of coal.⁴¹ Hence, the low yield of methane is due to its release from volatiles only. The increase at higher temperatures may be due to the thermal breakdown of coal.

Sulfurous gases. The concentration of H₂S and SO₂ for each sample quantified is given in Table 5.

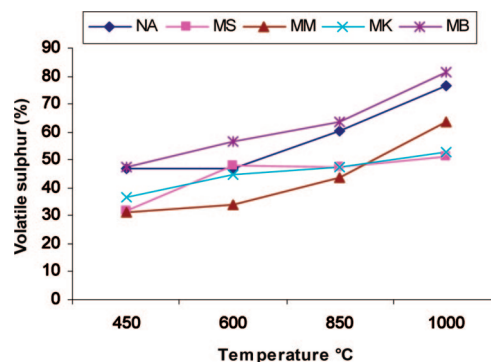
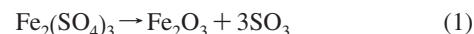
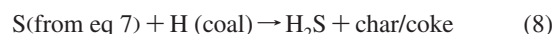


Figure 6. Volatile sulfur at different pyrolysis temperatures.

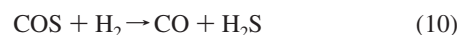
SO₂ Concentration. As the pyrolysis of the coal samples was carried out in absence of oxygen, the SO₂ released during pyrolysis for the coal samples was found to be inconsistent. The SO₂ concentration was detected in the samples, however, and ranged between 0.4 and 15 ppm at different temperatures. The SO₂ released at 450–850 °C may also be due to sulphate decomposition resulting in sulfur oxide formation with sulfides and/or oxides. Iron sulfates usually decompose at lower temperature (<500 °C) and form SO₂.^{10,42} The decomposition of calcium sulphate occurs at higher temperature (<850 °C).^{43,44} The probable reactions taking place during pyrolysis are



H₂S Concentration. H₂S evolution during coal pyrolysis is a function of temperature (Figure 4). At 450 °C, the emission of H₂S is quite low. At this temperature, thiols and dimethyl sulphides began to decompose to form H₂S. The second possible reaction is of pyrite decomposition to H₂S.⁴⁵ At this temperature, the H₂S concentration varies from 0.12 to 0.13 ppm for the coals studied. The reactions (5–8) indicate the thermal release of H₂S.



At 600 °C, the H₂S concentration ranges between 202 and 242 ppm. Alkyl and aryl sulfides lose H₂S between the 440 and 630 °C temperature ranges. H₂S emission between 600 and 850 °C was highest as shown in Figure 4. Benzyl sulphide, mercaptans and sulphides lose S as H₂S in this temperature range. Above 650 °C, CH₄ promotes H₂S evolution for all coals by decomposition of CH₄ to form H₂. This may be caused by the following reactions during coal pyrolysis:³⁹



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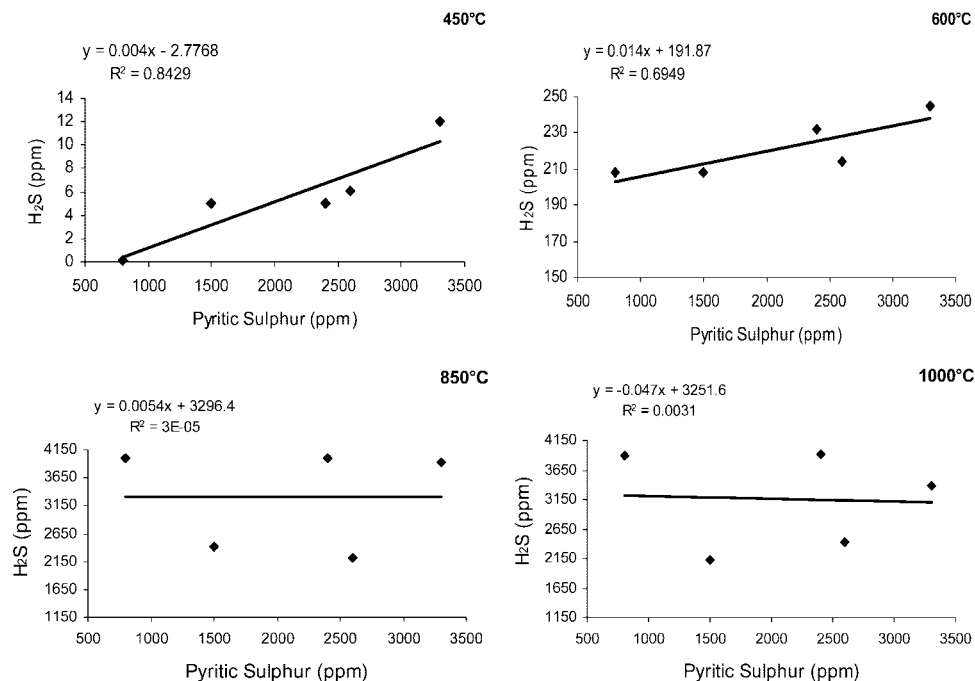


Figure 7. Yield of sulfur-containing gas as H_2S vs pyritic sulfur in coal.

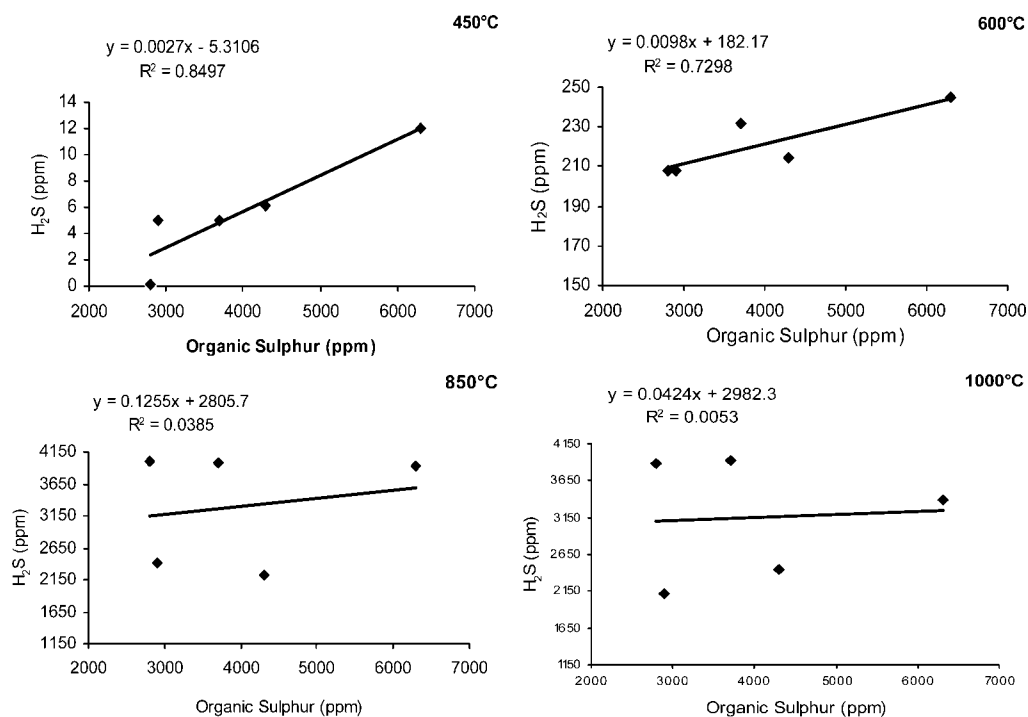
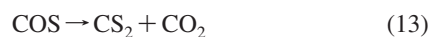
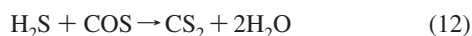
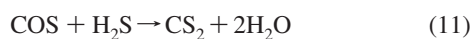


Figure 8. Yield of sulfur-containing gas H_2S vs organic sulfur in coal.

Or CS_2 may be formed as a product of secondary reactions of COS and H_2S .



H_2S evolution also increases by decomposition of CH_4 to form H_2 , which promotes the decomposition of pyrrhotite and/or thiophenes present in the coal to form H_2S .³⁹ At 1000 °C, the concentration of H_2S was not found to have any significant variation in comparison to 850 °C. Earlier studies also reported

similar results that H_2S concentrations remain the same up to 900–1000 °C.⁴⁶

The ratio of gaseous sulfur to hydrocarbon release (S/CH_4) in each temperature may be used to evaluate the thermal release of sulfur. The ratio reaches a maximum at 850 °C due to the higher release of sulfur (Figure 5). However, the decreasing trend of S/CH_4 ratio at 1000 °C indicates that breaking of the C–C bond or cracking is higher in comparison to cleavage of the C–S bond. Maximum sulfur is released between 600 and 850 °C temperatures and is either in a decreasing trend or constant up to 1000 °C which may be due to capture of H_2S by

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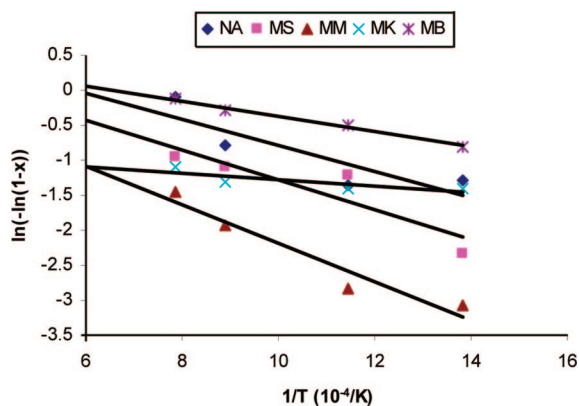


Figure 9. Arrhenius plot for total sulfur removal during pyrolysis of coal according to eq 18.

Table 6. Kinetic Parameters for Sulfur Release during the Pyrolysis of Coal

coal	NA	MS	MM	MK	MB
activation energy (E) (KJ mol^{-1}) in the temperature range from 723 to 1273 K	156	177	228	38	90

the organic matrix to form organic sulfur functionalities that remain in char/coke or tar.

Volatile Sulfur. The total volatile sulfur released during pyrolysis⁴⁷ is the difference between the total sulfur and nonvolatile sulfur in coal. The nonvolatile sulfur content of the original coal can be calculated by multiplying the sulfur content in char/coke and the mass fraction of char/coke in the coal. Using the same formula, volatile sulfur was calculated for each pyrolysis temperature (Figure 6). Volatile sulfur shows increasing trends with the temperature. Volatile sulfur ranges from 46 to 77% for NA, 32 to 51% for MS, 31 to 66% for MM, 36 to 52% for MK, and 48 to 81% for MB coals, respectively. The high volatility of sulfur in MB coal may be due to the association of sulfur with inorganic and volatile organic matter. The low volatile sulfur in MS at 1000 °C may partly be due to the in-situ formation of a thermally stable form of sulfur during pyrolysis or incorporation of released sulfur in active sites of carbon.

Relation of Sulfur Release with Pyritic and Organic Sulfur in Coal. Regression analysis (Figures 7 and 8) shows a linear relation of H_2S with pyrite and organic sulfur in coal at 450 and 600 °C, which may be due to release of more aliphatic sulfur compounds and pyrites present in these coals. No significant relation was found at higher temperatures (850–1000 °C), because of formation of stable sulfur compounds and/or fixation of sulfur by mineral matter.

Reaction Kinetics. The kinetic data available in the literature for sulfur release from coal in various processes are limited. Yergey et al.⁴⁸ have determined kinetic data for the reactions of sulfur compounds in coal hydrolysis by nonisothermal methods in detail. Other workers have used similar approaches to study the kinetics of sulfur evolution in fluidized bed gasifiers⁴⁹ and evaluation of H_2S in pyrolysis reactions.⁵⁰

Sulfur functionalities in coal have different decomposition temperatures. So, it is necessary to use a distributed activation

energy model⁴⁸ to describe the transformation of sulfur in such process reactions for coal. It is, however, difficult to apply the kinetic data of the literature to the processes occurring in this study since the activation energy distribution is strongly dependent upon coal type.⁵¹ Thus, a pseudo-first-order rate equation is assumed for the removal of sulfur from these coals during pyrolysis.^{52,51}

$$dX/dt = A \exp(-E/RT) \quad (14)$$

where X is the extent of sulfur removal at time t and E and T are activation energy and temperature (K), respectively.

Integration of eq (14)⁵²

$$\ln X_- = \ln(A - E/RT) \quad (15)$$

where

$$X_- = \ln(1-x) \{ [1 - 2RT/E] RT^2/EM + t_h \}^{-1} \quad (16)$$

Here, M is the heating rate and t_h is the holding time at the reaction temperature.

Considering the reaction conditions used and the range of possible activation energies, it is possible to conclude that⁵²

$$[1 - 2RT/E] RT^2/EM \ll t_h \quad (17)$$

Thus, eq (15) is simplified as

$$\ln(-\ln(1-X)) = \ln(At_h) - E/RT \quad (18)$$

The extent of total sulfur removal is plotted against the reciprocal temperature according to eq 18 (Figure 9). The values of the activation energy (E) are obtained from the slopes of the straight lines in the figures and listed in the Table 6. Activation energies for total sulfur removal from Meghalaya and Nagaland coals range from 38 to 228 KJ mol^{-1} . The reported values⁵² for lignites and bituminous coals is in the range of 150–300 KJ mol^{-1} . The values for NA, MS, and MM coals were found in the range of 150–300 KJ mol^{-1} , while those for MK and MB samples were found below this range.

All of these coals have high organic sulfur content in the range of 78–88% of total sulfur. The extent of sulfur removal or activation energy depends upon the presence of different organic sulfur functionalities. The aliphatic C–S structures decompose at lower temperatures while aromatic ones are thermally stable leading to higher activation energies. NA, MS, and MM coal samples probably contain more thiophenic and aromatic groups leading to high activation energies as compared to MK and MB samples.

Conclusion

Pyrolysis of high sulfur NE Indian coals shows removal of sulfur up to 60%. H_2S is the major sulfurous gas released during pyrolysis. Release of sulfur depends upon the temperature; however, other processes like incorporation of sulfur into the coal matrix, in-situ formation of organic sulfur, and fixation of sulfur by mineral matter also affect sulfur removal during pyrolysis. The extent of sulfur removal and activation energies depends upon the presence of different organic sulfur functionalities in the coals.

The study of sulfur transformation during pyrolytic reactions at 450, 600, 850, and 1000 °C for high sulfur NE coals will be useful in actual commercial practices.

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