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Distribution of Sulphur Functional Groups in High Sulphur Bapung Coals of Assam

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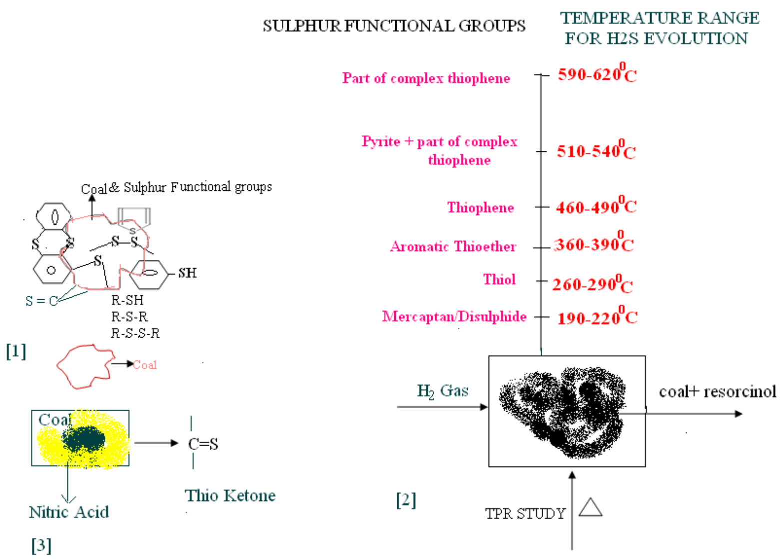


***Abstract**: Studies for determination of sulphur functional groups present in Bapung coal of Assam State of North Eastern Region of India were carried out using Temperature Programmed Reduction (TPR) method. TPR studies were carried out in presence of Resorcinol and hydrogen gas to arrive at the final result. TPR studies on model sulphur compounds viz. L-Cysteine, synthetic rubber, Thiokol, having hydroxyl terminal groups, thioplast, pyrite with sand, and Garlic were carried out in order to assign various sulphur functional groups present in Bapung coal. Six numbers of hydrogen sulphide evolutions from Bapung coal were observed in the temperature range of 190 – 220^{0}C, 260 – 290^{0}C, 360 - 390^{0}C, 460 – 490^{0}C, 510 – 540^0 C and 590 – 620^{0}C corresponding to mercaptan/ disulphide (0.20), Thiol (1.20), AromaticThioether (0.50), Thiophene (0.40), pyrite + part of complex thiophene (1.10), part of complex thiophene (0.30), The thioketonicsulphur in Bapung coal is estimated to be 0.30using controlled nitric acid oxidation experiments.*

***Keywords**:Bapung coal, Assam coal, high sulphur coal, model sulphur compounds, TPR, desulphurization, hydro desulphurization, disulphide, Thiol, Thioether, Thiophene, Thioketone.*

I. Introduction

India is blessed with very high ash coals. The only source of low ash coal is north eastern region of India. But these coals have high sulphur content. In general it contains 3 to 6% sulphur out of which 75 – 90% is in organic(1,2) form while rest is in inorganic form viz. sulphatesulphur and pyritic sulphur. Since pyritic sulphur is highly disseminated in the organic matrix of coal, it can not be physically separated using specific gravity principle. When these coals are chemically treated with oxidizing agents or reducing agents or auto oxidized, the desulphurization does not occur quantitatively. The iron sulphate can be removed easily by washing with water. The pyrite is converted into iron sulphate which is soluble in water. Physical separation processes can not remove organic sulphur while Microbial method can remove only to a small extent of organic sulphur but 90% pyrite removal with thiobascillus Ferro oxidans was observed.

This lead us to think that organic sulphur is present in these coals in more than one or two forms. Thus in order to have effective chemical desulphurization of NE region coals of India and also to utilize high sulphurassam coal as a blend (5-10%) for coke making in steel industry as well as thermal power stations with lesser SO_2 evolution, a knowledge of all the sulphur functional groups present in coal is a must. Temperature Programmed Reduction method have been reported by Attarand Dupuis(3),Majchrowicz(4) in the past and recently byE.Jorjani et al (5) for this purpose.Juntgen and Juntgen[6]and Van Heek(7)proposed a thermokinetic method involving linear temperature time program for measuring the rate and amount of sulphur evolution as a function of temperature for evaluating various sulphur functional groups **.**The capability for direct speciation and approximate quantification ($\pm$10%) of organic sulphur forms has also been demonstrated using XANES and XPS(8-11).XPS and XANES have also been used to establish the trend of increasing aromatic sulphur content with increasing rank (12).These studies basically establish the potential connections between the reactions of sulphur during coal metamorphism and laboratory pyrolysis as were examined by Kelemen(13) while studying the thermal reactivity of sulphur forms in coal using XANES,TPD and XPS.Thus these suggests that sulphur forms are transformed during the study by these methods and hence can not give an estimate of sulphur functional group unambiguously.Moreover,a comparison of reductive method with X-ray based instrumental techniques –XANES,XPS etc .reported by William H. Calkins(14)showed comparable trends in organic sulphur forms in coal.However, complete assignment of sulphur functional group could not be done owing to certain draw backs most importantly due to ambiguity about complete sulphur evolution from each functional group in the form of H_2S as found in the earlier work of Juntgen and Juntgen(6), VanHeek(7), Dupuis(3),&Majchrowicz(4)and as per the work reported by Srivastava SK et al (15,16,17).

For assigning the sulphur functional groups in high sulphur coal, TPR studies- both on model sulphur compounds and on Bapung coal have been done.Resultsforstudies on optimization of reaction conditions for total evolution of hydrogen sulphide from each and every sulphur functional groups would be similar to that of Tipong coal[18]. Thus the present paper is an attempt to know the distribution of sulphur (organic form) in Bapung coals.

II. Material And Methods

2.1 Analysis of Bapungcoal: The coal particle size used was ~8,-212um.The Bapung coal was analysed for ash(A),moisture(M),volatile matter(VM),fixed carbon (FC),C,H,N and oxygen contents,calorific value and sulphur distribution as per the Bureau of Indian Standard methods specified in the literature.The total sulphur in the coal was determined using a Leco model SC-132 (LecoCorporation,USA)sulphurdeterminator.

2.2Temperature Programmed Reduction studies(TPR): Temperature Programmed Reduction studies(TPR) on Bapung coal was carried out with X72 B.S.Mesh sized coal particles.A glass/quartz tubular reactor was fabricated having I.D.;4.0 cms and height 16.5 cms. with three openings at the top.Through the first opening hydrogen gas was passed continuously (which acted as a flushing gas also) and through second opening a thermometre cap was inserted.The third opening was used as outlet for gaseous products of reaction taking place inside the reactor along with residual hydrogen and it was passed through a series of bubblers containing cadmium acetate solutionThe outlet of reactor was separated from a series of bubblers by an ice cooled tar catch pot..The TPR study was carried out inside a tubular furnace with 5.0 cms I.D. and 34 cms. height. The glass /quartz reactor with specified size of coal sample and resorcinol was placed inside the reactor and thereafter controlled flow of hydrogen gas was switched on.For measurement of the temperature of the reaction zone ,both thermometer (inside the reactor) and thermocouple (outside the reactor and inside the furnace) were used to monitor and cross check the temperature.Heating rate was controlled through Sunvic energy regulator.

The coal and resorcinol(hydrogen-donating compound) mixture was heated in the aforementioned reactor in the presence of hydrogen gas flowing very close to the reaction mixture at the rate of 70 m^3 per minute. Hydrogen gas flow very close to reaction mixture facilitated the flushing out of H_2S gas completely thus inhibiting the re-fixation of sulphur in coal matrix in some other form.The mixture was heated at 10^0C per minute heating rate until evolution of H_2Scommenced at a particular temperature and that temperature was maintained constant until evolution of H_2S gas ceased.This was checked by passing the product gas to bubblers filled with cadmium acetate solution when no more yellow precipitate of cadmium sulphide is obtained.After the first evolution of H_2S was completed,the temperature was further raised at the same rate until the second evolution of H_2S started and later ceased as before.The gradual heating and consequent evolution of H_2S was continued until the temperature of 620^0C was reached.The H_2S evolved within different temperature ranges was absorbed in cadmium acetate solution to estimate sulphur gravimetrically as yellow cadmium sulphide for each temperature range.The yellow cadmium sulphide was filtered,washed with hot distilled water and dried in an air oven at 110^0C till constant weight.One blank filter paper was also washed and dried in similar way in order to subtract the weight of blank filter paper.The determination of thioketonicsulphur has beendoneand is presented in “Estimation of thioketonicsulphur in high sulphurassam coals by nitric acid oxidation”.[19]

2.3 IR Spectroscopy: Coal and Potassium bromide (KBr) mixed pellets were used to analyze coal samples by double beam IR spectrophotometer(model-883 from M/S Perkin Elmer). 2 mgCoal (X72 MESH) was thoroughly mixed with dry spectroscopic gradeKBr and pellets were made under vacuum.IR spectra were recorded thereafter.

III. Results And Discussion

Table 1summarises the data on Proximate and Ultimate analyses,calorific value and sulphur distribution figures of Bapung coal on as received basis and Table 2 on dry mineral matter free (dmmf) basis.The values on dmmf basis was calculated using the equation:

$MM – 1.11A + 0.5S_{pyr} + 2.5S_{sulph.}$

Where MM = mineral matter , A = Ash , S_{pyr} = Pyrite Sulphur and $S_{sulph.}$ = Sulphatesulphur.

3.1 Approach Towards the Problem:Coal desulphurization involves cleavage of carbon-sulphur (C-S) bonds present in coal and taking out the sulphur mainly as H_2S/SO_2.If sulphur is present in coal in more than one form then depending, upon the sulphur functionality and the environment of the C-S bond,the strength of the different C – S bonds would vary.if the coal is heated at a certain rate,the weakest C-S bond would break first and the strongest C-S bond would break last.If the sulphur is taken out as H_2S and is quantified at each level of evolution,the number of sulphur functionalities along with their quantitative values can be determined.By using model sulphur compounds (some of which are polymeric in nature), containing known sulphur functionalities in TPR studies,comparison of the results of sulphur evolution with that obtained from coal would identify sulphur functional group present in coal matrix.While assigning the sulphur functionalities present in coal it should be borne in mind that above 300^0C temp.,severalpyrolytic reactions occur and one form of the sulphur functionality may change to another resulting in different temperature of H_2S evolution.Thus our approach involves the immediate and continuous flushing out of H_2S formed as soon as it is formed in the TPR study.

3.2 Role of Resorcinol: When coal was subjected to TPR study alone the evolution of sulphur in the temperature ranges 190-220^0C and 260-290^0 C (even in hydrogen atmosphere) was small.When resorcinol was added to coal for carrying out TPR experiments ,per cent sulphur evolution enhanced to great extent in comparison to corresponding blank experiments at two different temperature ranges (190-220^0C and 260-290^0 C).It is important to mention here that the flash point of resorcinol is 277^0C.This indicates that resorcinol has definite role to play in the reaction process.

The mechanism of hydrogen donation to coal by resorcinol in all probability suggests ionic mechanism considering (i) the copious evolution of H_2S and exothermic nature of reaction below 300^0C and in the temperature range of 190-220^0C which is certainly a lower temperature for sulphur evolution, especially considering the presence of sulphur in complex structural environment of coal;(ii) resorcinol recovered, by solubilising residue coal obtained after TPR study upto 220^0C in water ,filtering and evaporating the filterate, was up to the extent of 97%. A general mechanism of hydrogen donation by resorcinol in removal of mercaptan, thiol, disulfide sulfur from coal is given in fig.I. ,II, III& IV &V .

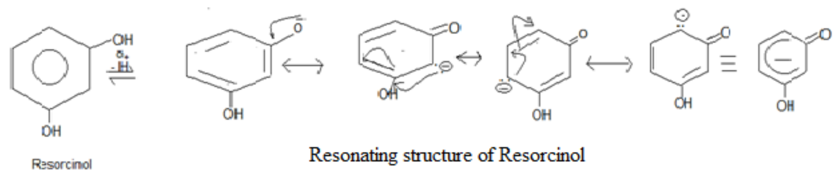


fig-I

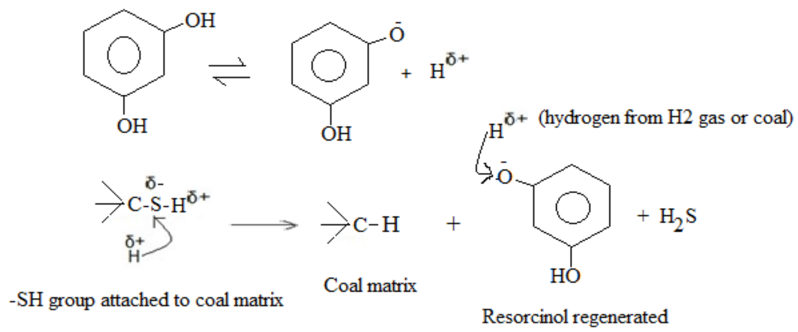


fig.-II

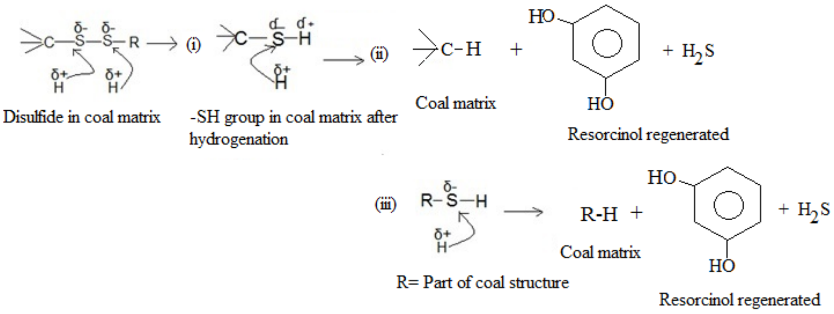


fig.-III

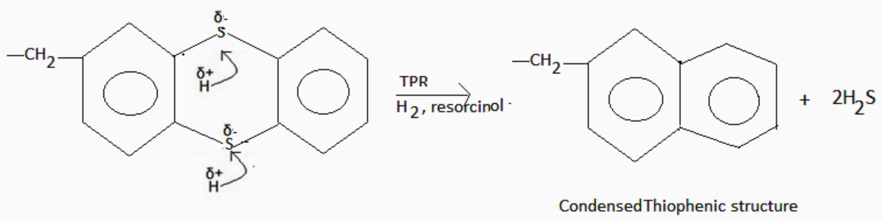


fig.IV

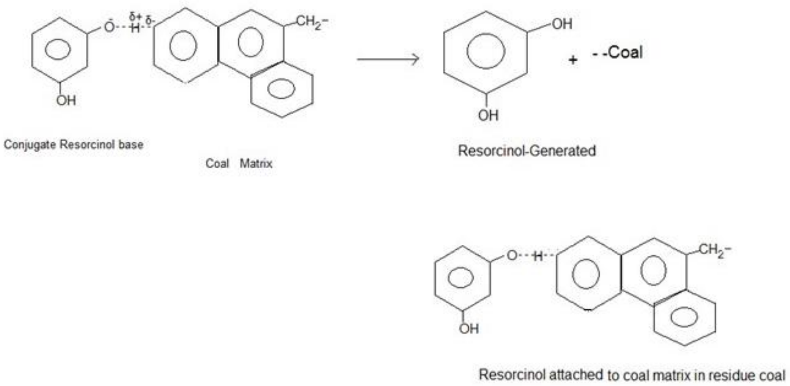
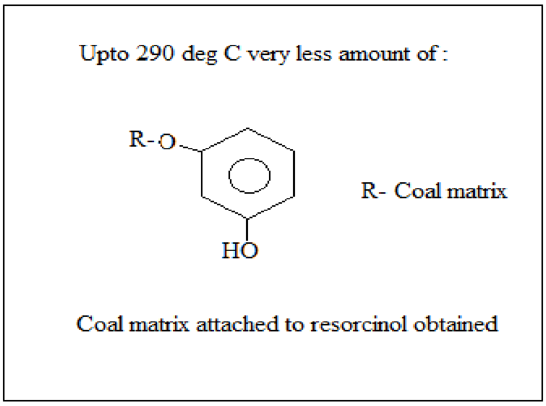
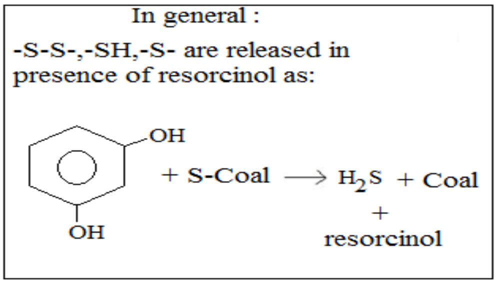
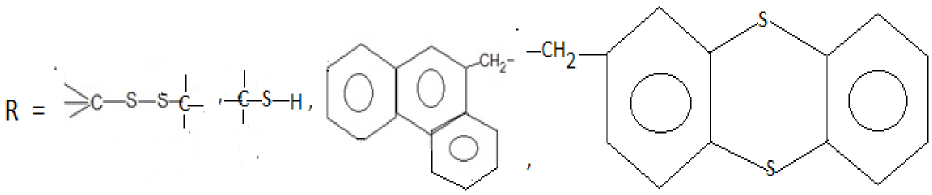


fig. V







R= Coal matrix containing sulphur functional group and thiphenic rings

3.3 Temperature Progammed Reduction studies on Model sulphurcompounds:Modelsulphur compounds e.g,synthetic rubber, Thiokol, Thianthrene, Dibenzothiophene, Thioplast ,Cysteine , Pyrite and garlic were mixed with resorcinol thoroughly and TPR studies were carried out under optimum reaction condition i.e.10^0C/minute rate of heating and $70m^3$ flow of hydrogen.H_2S gas was evolved at different temperature ranges.The same has been presented in Table- 3 for different model sulphur compounds along with the assignment of sulphur functional groups

3.4 Assignment of Various Sulphur Functionalities Present in Bapungcoal:An attempt has been made in the present paper to correlate the various sulphur evolution fromBapungcoal to different organic sulphur forms based on temperature programmed reduction studies of model organic sulphur compounds under exactly similar reaction conditions to that of coal in addition to the facts obtained from literature-which corroborates the assignment made.TPR studies on the model organic sulphur compounds gave a clear cut temperature range at which H_2S evolution took place corresponding to different functionalities.However, these evolutions cannot match exactly with those evolving from coal for different steric, electronic environmental (around C-S bond) reasons.Considering the structural complexity of coal , H_2S evolution will take place at slightly different temperatures than the above stated evolutions for model sulphur compounds.

During the formation of Assam coals,sulphur has probably interchanged with oxygen atom owing to the presence of microorganism thiobascillusferrooxidans ,and also considering the marine bed present in the area in the past,sulphur is also present in Heteroatomic rings as well as in linking units(20) in Bapungcoal."O" containing functional groups normally present in coal are –COOH, -OH, >C=O, and –O–, hence by replacing 'O' atom by 'S', the following forms of sulphur would be present in assam coals and it is true for Bapung coal as well:

, C=S—SH ,>CS , -S-

SH

These sulphur groups would react in presence of hydrogen to give H_2S corresponding to different C-S bond strengths at different temperature ranges.>C=S form,if present would react with aliphatic chains present in the coal under pyrolytic conditions to present condensed thiophenic form which is very difficult to break small amounts of H_2S may come out above 500^0C.Thus,keping in view of the above facts the assignments made for Bapung coal are provided In Table-5.

3.5 IR spectra: IR spectraBapung coal has been given in fig.VI,VII,&VIII,for three different conditions of Bapungcoal.Coal-viz. (i) Raw Bapung(ii)Residue coal treated upto 620^0 in presence of resorcinol (iii) Nitric acid treated coal for thioketonicsulphur determination. The IR spectra of raw coal gives a broad absorption band at 3440 cm−1in the coal, which appears to be mainly due to N–H and O–H groups. The peaks for O–H groups at 3600–3800 cm−1appear to be for those associated with clay minerals. The aromatic hydrogen band at 3040 cm−1is absent in the coal indicating its highly substituted and condensed nature. The peak at 2920 cm−1and 2850 cm−1appearing as sharp peaks of medium intensity, may be assigned to aliphatic and alicyclic CH3, CH2 and CH groups although the major contribution is expected to be due to CH2 groups. The intensity of peak at 2920 cm−1is greater than the peak 2850 cm−1indicating the presence of long aliphatic chains in the coal. The peak at 1699 cm−1appears to indicate the presence of carbonyl (C=O) content. The peak around 1600 cm−1in the coal is observed due to aromatic C=C, vinylic C=C and possibly due to other O-containing functional groups. The oxygen containing functional groups found in coal specifically include phenols and alcohols, ethers, carboxylic acid and carbonyls. In view of the diversity of decomposed plant matter, finding any systematic variation in the distribution of these functional groups in coal seems unlikely. Several authors have reviewed quantitative determination of these various oxygen functional groups.A strong band at 1436 cm−1in the coal was observed. This is mainly due to CH3 asymmetric deformation and CH2 group in bridges but may also be partly due to aromatic C=C and strongly hydrogen bonded O–H groups. The band at 1372 cm−1is mainly due to CH3 symmetric deformation while –CH3 and –CH2 in cyclic structures may also partly contribute to this band.Intensity of this peak is much lower than the peak at 1436 cm−1indicating that the methylene as long side chains. The band between 880 cm−1and 750 cm−1has been assigned to aromatic structures.The weak band at 690 cm−1observed in the coal could possibly be due to C–S bond. These absorptions are most useful in determining the aromatic ring structure of a coal.Vibrational IR frequency is also observed at 485 cm^{-1} in the coal suggesting the presence of disulphide i.e., -S-S- group (21).No substantial information on organic sulphur functionalities is obtained from the IR spectra of (i) raw Bapung coal and that from (ii) Residue coal treated upto 620^0 in presence of resorcinol.On comparison of IR spectra of the raw Bapung coal with that of nitric acid treated coal,it is observed that the number of –COOH functional groups have enhanced in the nitric acid treated coal as a result of oxidation.It is further substantiated by the presence of overlapping C-H (str.) band,(i) 1705-1720 cm^{-1} for C=O of acid ,& (iii) 1540 cm^{-1} for C-O-H bending ,which is slightly upshift ,in addition,there is a characteristic spectral band at1340-1345 cm^{-1} which is very sharpbut weak and hence can substantiate the presence of S=O groupofsulphonic acid and sulphones in the IR spectra of nitric acid treated coal and indicates the presence of thioketonicgroup.There are weak bands in the range 2800-2900 cm^{-1} corresponding to alicyclic CH_3,CH_2,CH groups in nitric acid treated coal. This is perhaps due to partial oxidation of the alkyl groups on coal moiety due to controlled acid oxidation. It can be observed from the values given in the Table-5 that some amount of sulphur is still left in the residual coal which is probably due to thioketonic (>C=S)form of sulphur which has converted into condensed thiophene, within the structure of coal under pyrolytic conditions and which is very difficult to break in order to evolve as H_2S. The IR spectra of the raw coal has spectral bands in the region 1010-1050 cm^{-1} which is slightly downshift ,supports the presence of C=S functional group Hence this form of sulphur has been estimated as thioketonicsulphur.The IR spectras have been taken from the thesis of one of the author submitted for the fulfilmentof the requirement of award of PhD.

TABLE - 1Charecterisation Of Bapung Coal(ON AS RECEIVED BASIS)

1. Proximate Analysis (%)	
Ash	12.40
Moisture	1.10
Volatile Matter	42.00
Fixed Carbon	44.50
2. Calorific Value (K Cal/ Kg)	7060
3. Ultimate Analysis (%)	
C	69.79
H	5.07
N	0.89
S	4.65
O (by difference)	19.6
4. Sulphur Distribution (%)	
Pyritic	2.00
Sulphate	0.25
Organic	2.40
Total ‘S’	4.65

Table-2 Charecterisation Of BapungCoal (On Dry Mineral Matter Free Basis)

1. Proximate Analysis (%)	
Volatile Matter	48.6
Fixed Carbon	51.4
2. Ultimate Analysis (%)	
C	82.9
H	6.20
N	1.10
S	3.70
O (by difference)	6.10

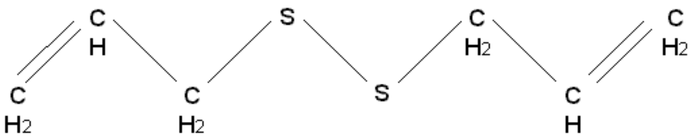
$$MM = 1.11A + 0.5\ S_{pyr} + 2.5\ S_{Sulphate}$$

Table – 3 TPRStudy On Model Sulphur Compounds

Model Compounds	Temp. Ranges of H_2S evolution	'S' Functional Group Present
Synthetic Rubber	210 – 220^{0}C	Disulphide
	360 – 370^{0}C	Sulphide
Thiokol	220 – 240^{0}C	Polysulphide
	310 – 330^{0}C	Thiol
	410 – 430^{0}C	Thioether
	520 – 530^{0}C	Thiophene
	600- 620^{0}C	Condensed Thiophene
Thianthrene	360 – 390^{0}C	Aromatic Sulphide
Dibenzothiophene	480 – 490^{0}C	ThiophenicSulphur
Thioplast	260 – 270^{0}C	Thiol
Cysteine	210 – 220^{0}C	Mercaptan
Pyrite	530 – 540^{0}C	Pyrite
Garlic (Dried)	Approx. same as Thiokol *	same as fromThiokol #

*Garlic contains allicin and when allicin degrades it produces various diallylsulphides, the most common of which is diallyldishulphide:Allicin degrades very easily when temp. increases or garlic is crushed.The similarity in H_2S evolutions for both Thiokol and garlic is mainly due to similarity in poly sulphide structure. # Given in table no.III for Thiokol polymer.

Structure of DiallylDisulphide



Structure of Thiokol[CH_2- CH_2-S-S- CH_2- CH_2]

Table 4 Estimation OfThio-KetonicSulphur

Sulphur Value Heads	% 'S' in Bapung Coal (before and after estimation)
Total Sulphur in Original Coal (A)	4.65
Total Sulphur in Oxidised Coal (B)	2.10
Pyritic + SulphateSulphur in Original Coal (C)	2.25
(A) – (B) – (C) i.e., Thio- KetonicSulphur	0.30

Table – 5 Sulphur Evolutions At Different Temperature Ranges From Bapung Coal And Assignment Of Sulphur Functional Groups.

Temp. Range (^{0}C)	Sulphur Evolved (%)	Sulphur Functionality Assigned
190-220	0.20	Mercaptan/ Disulphide
260-290	1.20	Thiol
360-390	0.50	Aromatic sulphide
460-490	0.40	Simple Thiophene
510-540	1.10	Pyritic + Part of complex thiophene
590-620	0.30	Part of complex thiophene

Table-6,Complete Assignment Of Sulphur Functional Groups Present In Bapung Coal.

Temperature Range Code	I	II	III	IV	V	V	VI
Sulphur Functionality	Mercaptan	Disulphide/Thiol	Thio-Ether	Thiophene	Pyrite	Sulphate	Thio-Ketone
Coal Sample							
Bapung Coal	0.20	1.20	0.50	0.40	2.00	0.25	0.10

IV. Conclusion And Summary

A systematic optimization study usingTemperature programmed reduction study along with nitric acid oxidation on Bapung coal has been carried out .After carrying out TPR study on model sulphur compounds it was found that hydrogen sulphide evolutions in the temperature ranges 190-220, 260-290,, 360-390, 460-490, 510-540, 590-620^{0}C are due to mercaptan, disulphide/thiol, thioether, thiophene, pyrite and complex thiophenegroupsThethioketonic group is also present as determined from nitric acid oxidation.Table 4 represents the results obtained for thioketonic form of sulphur(19).IR studies showed that resorcinol was not destroyed up to 300^{0}C.On heating coal upto 600^{0}C,the various functional groups present in coal are devolatilised and on nitric acid treatment, the coal was oxidized leading to enhancement in –COOH functional group.Thus based on above studies,it was concluded **that sulphur present in Bapung coal** are in the **forms:mercaptan, disulphide/thiol, thioether, thiophene, pyrite, sulphate and thioketone .**Theseformsare shown in Table 6.

Thus TPR study in combination with nitric acid oxidation as well as supporting evidence by IR spectroscopy can effectively be used for determining the organic sulphur functional groups in any high sulphur coal of the world.The data generated would enable chemical methods of desulphurization to be selected/devised and also prior knowledge of the extent to which coal can be desulphurised.

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