

## Disposition Pattern of Sulphur Functional Groups in High Sulphur Ledo Coals of Assam

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**Abstract:** Studies for determination of sulphur functional groups present in Ledo 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 Ledo coal. Six numbers of hydrogen sulphide evolutions from Ledo coal were observed in the temperature range of 190 – 220<sup>o</sup>C, 260 – 290<sup>o</sup>C, 360 - 390<sup>o</sup>C, 460 – 490<sup>o</sup>C, 510 – 540<sup>o</sup> C and 590 – 620<sup>o</sup>C corresponding to mercaptan/ disulphide (0.30), Thiol (1.70), Aromatic Thioether (0.50), Thiophene (0.90), pyrite + part of complex thiophene (0.60), part of complex thiophene (0.30), The thioketonic sulphur in Ledo coal is estimated to be 1.59 using controlled nitric acid oxidation experiments.

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

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### 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. sulphate sulphur 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 thiobacillus Ferro oxidans was observed.

It 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 sulphur assam coal as a blend (5-10%) for coke making in steel industry as well as thermal power stations with lesser SO<sub>2</sub> evolution, a knowledge of all the sulphur functional groups present in coal is a must. Temperature Programmed Reduction method have been reported by Attar and Dupuis[3],Majchrowicz [4] in the past and recently by E.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<sub>2</sub>S 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 Ledo coal was essential and have been done. Studies on optimization of reaction conditions for total evolution of hydrogen sulphide from each and every sulphur functional groups is also a must in order to remove ambiguity Thus the present paper is an attempt to fill the gap in the above mentioned studies carried by

earlier workers, and comprises of all the various studies mentioned above to know the distribution of sulphur (mainly organic form).

## **II. Experimental**

Temperature Programmed Reduction studies (TPR) on Ledo 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 thermometer 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 solution. The 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<sup>3</sup> per minute. The mixture was heated at 10<sup>0</sup>C per minute heating rate until evolution of H<sub>2</sub>S commenced at a particular temperature and that point temperature was maintained constant until evolution of H<sub>2</sub>S 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<sub>2</sub>S was completed, the temperature was further raised at the same rate until the second evolution of H<sub>2</sub>S started and later ceased as before. The gradual heating and consequent evolution of H<sub>2</sub>S was continued until the temperature of 620<sup>0</sup>C was reached. The H<sub>2</sub>S 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<sup>0</sup>C 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 coal particle size used was ~8,-212µm. The Ledo 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 (Leco Corporation, USA). These have been given in Table – I in on as received basis.

The determination of thioketonic sulphur has been given in our study “Estimation of thioketonic sulphur in high sulphur assam coals by nitric acid oxidation. [18 ]

## **III. Results And Discussion**

Table I summarises the data on Proximate and Ultimate analyses, calorific value and sulphur distribution figures of Ledo coal on as received basis and Table II 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<sub>pyr</sub> = Pyrite Sulphur and S<sub>sulph.</sub> = Sulphate sulphur.

### **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<sub>2</sub>S/SO<sub>2</sub>. 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<sub>2</sub>S 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<sup>0</sup>C temp., several pyrolytic reactions occur and one form of the sulphur functionality may change to another resulting in different temperature of H<sub>2</sub>S evolution. Thus our approach involves the immediate and continuous flushing out of H<sub>2</sub>S formed as soon as it is formed in the TPR study.

### **3.2 Temperature Programmed Reduction studies on Model sulphur compounds**

Model sulphur 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

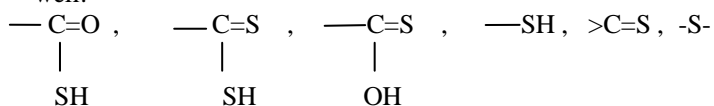
optimum reaction condition i.e. 10<sup>0</sup>C/minute rate of heating and 70m<sup>3</sup> flow of hydrogen. H<sub>2</sub>S gas was evolved at different temperature ranges. The same has been presented in Table- III for different model sulphur compounds along with the assignment of sulphur functional groups .

### 3.3 Assignment of Various Sulphur Functionalities Present in Ledo coal:

An attempt has been made in the present paper to correlate the various sulphur evolution from Ledo coal 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<sub>2</sub>S 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<sub>2</sub>S 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 thiobascillus ferro oxidans ,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[18] In Assam coal. "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 Ledo coal as well:



These sulphur groups would react in presence of hydrogen to give H<sub>2</sub>S corresponding to different C-S bond strengths at different temperature ranges.

(g) >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<sub>2</sub>S may come out above 500<sup>0</sup>C.

Thus, keeping in view of the above facts the assignments made for Ledo coal are provided In Table-V.

IR spectra of Ledo coal has been given in fig. I, II, III, IV for four different conditions of Ledo coal.

Coal-viz. (i) Raw Ledo (ii) Ledo coal treated upto 220<sup>0</sup>C in presence of resorcinol (iii) Residue coal treated upto 620<sup>0</sup> in presence of resorcinol (iv) Nitric acid treated coal for thioketonic sulphur determination. The IR spectra of raw coal gives a broad absorption band at 3440 cm<sup>-1</sup> in 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<sup>-1</sup> appear to be for those associated with clay minerals. The aromatic hydrogen band at 3040 cm<sup>-1</sup> is absent in the coal indicating its highly substituted and condensed nature. The peak at 2920 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> appearing as sharp peaks of medium intensity, may be assigned to aliphatic and alicyclic CH<sub>3</sub>, CH<sub>2</sub> and CH groups although the major contribution is expected to be due to CH<sub>2</sub> groups. The intensity of peak at 2920 cm<sup>-1</sup> is greater than the peak 2850 cm<sup>-1</sup> indicating the presence of long aliphatic chains in the coal. The peak at 1699 cm<sup>-1</sup> appears to indicate the presence of carbonyl (C=O) content. The peak around 1600 cm<sup>-1</sup> in 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<sup>-1</sup> in the coal was observed. This is mainly due to CH<sub>3</sub> asymmetric deformation and CH<sub>2</sub> 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<sup>-1</sup> is mainly due to CH<sub>3</sub> symmetric deformation while -CH<sub>3</sub> and -CH<sub>2</sub> in cyclic structures may also partly contribute to this band. Intensity of this peak is much lower than the peak at 1436 cm<sup>-1</sup> indicating that the methylene as long side chains. The band between 880 cm<sup>-1</sup> and 750 cm<sup>-1</sup> has been assigned to aromatic structures. The weak band at 690 cm<sup>-1</sup> observed 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<sup>-1</sup> in the coal suggesting the presence of disulphide i.e., -S-S- group [19]. No substantial information on organic sulphur functionalities is obtained from the IR spectra of (i) raw Ledo coal and that from (ii) Ledo coal treated upto 220<sup>0</sup>C in presence of resorcinol (iii) Residue coal treated upto 620<sup>0</sup> in presence of resorcinol. On comparison of IR spectra of the raw Ledo 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<sup>-1</sup> for C=O of acid, & (iii) 1540 cm<sup>-1</sup> for C-O-H bending, which is slightly upshift, in

addition, there is a characteristic spectral band at 1340-1345 cm<sup>-1</sup> which is very very weak and seems like noise and hence can not substantiate the presence of S=O group from sulphonic acid and sulphones in the IR spectra of nitric acid treated coal. There are no bands in the range 2800-2900 cm<sup>-1</sup> corresponding to alicyclic CH<sub>3</sub>, CH<sub>2</sub>, CH groups in nitric acid treated coal. This is perhaps due to destruction of coal moiety due to acid oxidation. It can be observed from the values given in the Table-V 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<sub>2</sub>S. The IR spectra of the raw coal has spectral bands in the region 1050-1100 cm<sup>-1</sup> supports the presence of C=S functional group Hence this form of sulphur has been estimated as thioketonic sulphur.

**TABLE - I**  
**CHARACTERISATION OF LEDO COAL**  
**(ON AS RECEIVED BASIS)**

<b>1. Proximate Analysis ( % )</b>	
Ash	18.2
Moisture	3.3
Volatile Matter	35.3
Fixed Carbon	43.2
<b>2. Calorific Value ( K Cal/ Kg )</b>	
	5950
<b>3. Ultimate Analysis ( % )</b>	
C	59.06
H	4.44
N	0.97
S	6.10
O (by difference)	7.93
<b>4. Sulphur Distribution ( % )</b>	
Pyritic	0.76
Sulphate	0.35
Organic	4.99
Total 'S'	6.10

**TABLE-II**  
**CHARACTERISATION OF LEDO COAL**  
**ON DRY MINERAL MATTER FREE BASIS**

<b>1. Proximate Analysis ( % )</b>	
Volatile Matter	45.0
Fixed Carbon	55.0
<b>2. Ultimate Analysis ( % )</b>	
C	78.50
H	5.90
N	1.30
S	6.60
O (by difference)	7.70

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

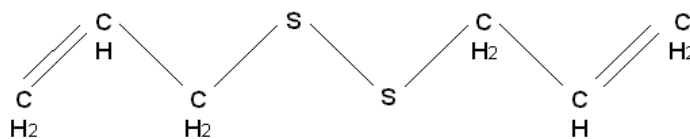
**TABLE - III**  
**TPR STUDY ON MODEL SULPHUR COMPOUNDS**

Model Compounds	Temp. Ranges of H <sub>2</sub> S evolution	'S' Functional Group Present
Synthetic Rubber	210 – 220 <sup>0</sup> C	Disulphide
	360 – 370 <sup>0</sup> C	Sulphide
Thiokol	220 – 240 <sup>0</sup> C	Polysulphide
	310 – 330 <sup>0</sup> C	Thiol
	410 – 430 <sup>0</sup> C	Thioether
	520 – 530 <sup>0</sup> C	Thiophene
	600- 620 <sup>0</sup> C	Condensed Thiophene
Thianthrene	360 – 390 <sup>0</sup> C	Aromatic Sulphide
Dibenzothiophene	480 – 490 <sup>0</sup> C	Thiophenic Sulphur
Thioplast	260 – 270 <sup>0</sup> C	Thiol
Cysteine	210 – 220 <sup>0</sup> C	Mercaptan
Pyrite	530 – 540 <sup>0</sup> C	Pyrite
Garlic ( Dried)	Approx. same as Thiokol *	same as from Thiokol #

\*Garlic contains allicin and when allicin degrades it produces various diallyl sulphides, the most common of which is diallyl disulphide: Allicin degrades very easily when temp. increases or garlic is crushed. The similarity in H<sub>2</sub>S 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 Diallyl Disulphide



Structure of Thiokol [ CH<sub>2</sub>-CH<sub>2</sub>-S-S-CH<sub>2</sub>-CH<sub>2</sub> ]

TABLE – IV  
ESTIMATION OF THIO-KETONIC SULPHUR

Sulphur Value Heads	% ‘S’ in Ledo Coal ( before and after estimation )
Total Sulphur in Original Coal ( A )	6.10
Total Sulphur in Oxidised Coal ( B )	3.20
Pyritic + Sulphate Sulphur in Original Coal ( C )	1.10
( A ) – ( B ) – ( C ) i.e., Thio- Ketonic Sulphur	1.80

TABLE – V  
SULPHUR EVOLUTIONS AT DIFFERENT TEMPERATURE RANGES FROM LEDO COAL AND  
ASSIGNMENT OF SULPHUR FUNCTIONAL GROUPS.

Temp. Range ( °C )	Sulphur Evolved ( % )	Sulphur Functionality Assigned
190-220	0.30	Mercaptan/ Disulphide
260-290	1.70	Thiol
360-390	0.50	Aromatic sulphide
460-490	0.90	Simple Thiophene
510-540	0.60	Pyritic + Part of complex thiophene
590-620	0.30	Part of complex thiophene

TABLE-VI  
COMPLETE ASSIGNMENT OF SULPHUR FUNCTIONAL GROUPS PRESENT IN LEDO 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							
Ledo Coal	0.30	1.70	0.50	0.90	0.76	0.35	1.59

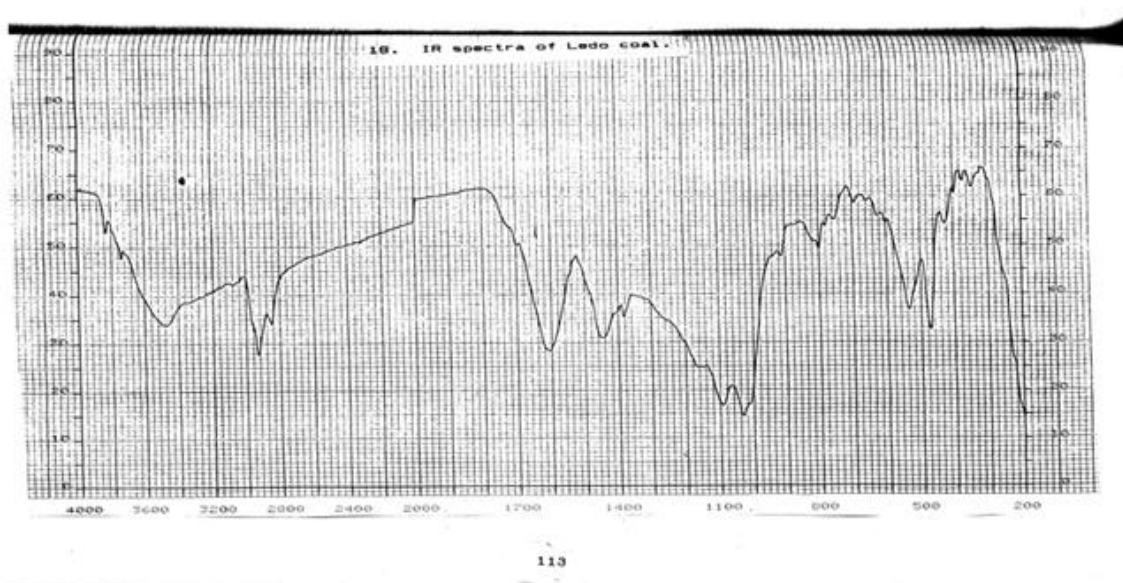


Fig-I IR spectra of raw Ledo coal

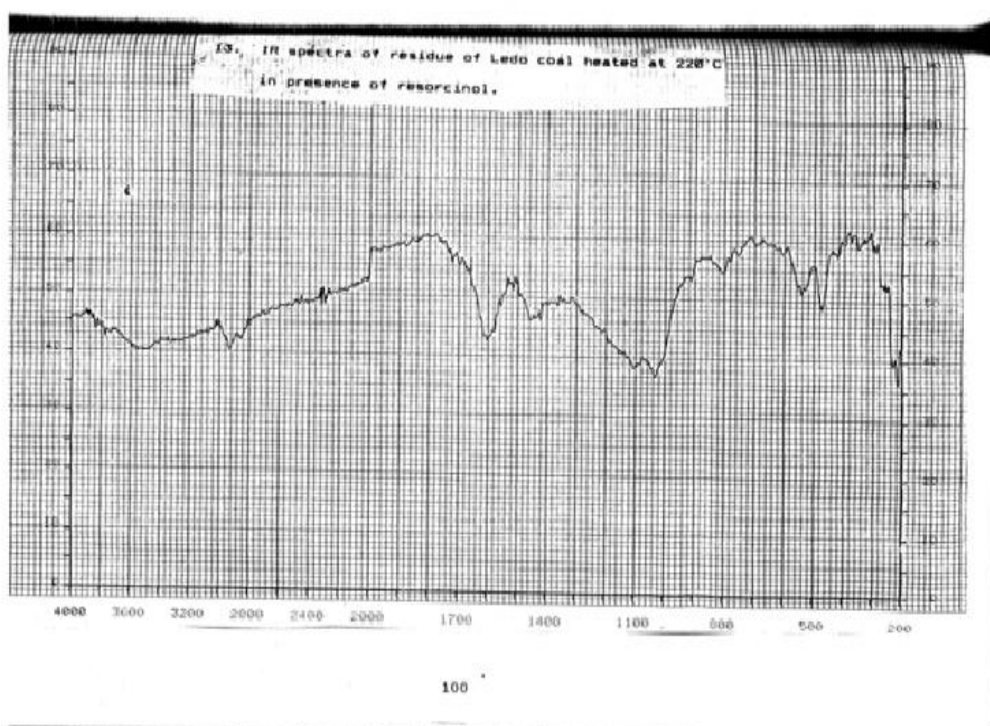


Fig-II IR spectra of Ledo coal treated upto 220°C in presence of resorcinol

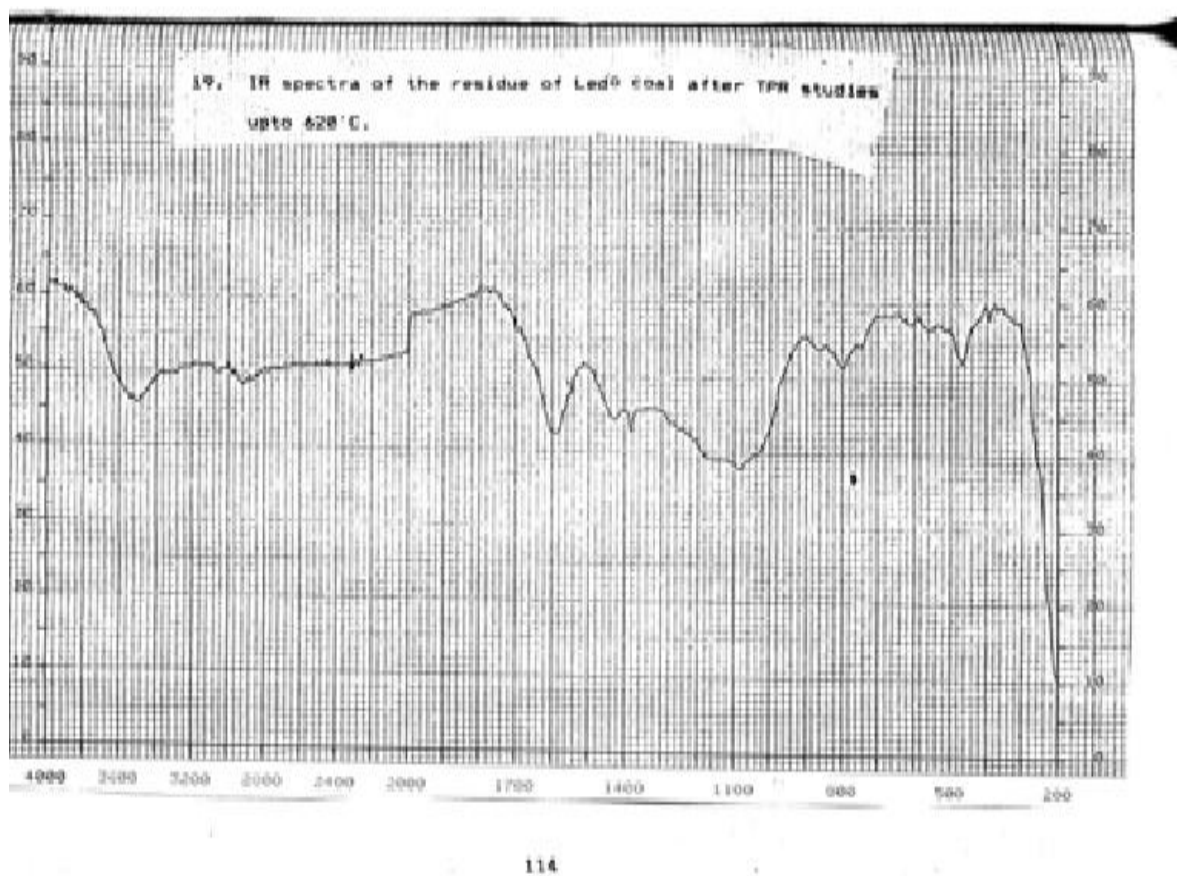


Fig-III IR spectra of Ledo coal treated (TPR) upto 620°C in presence of resorcinol

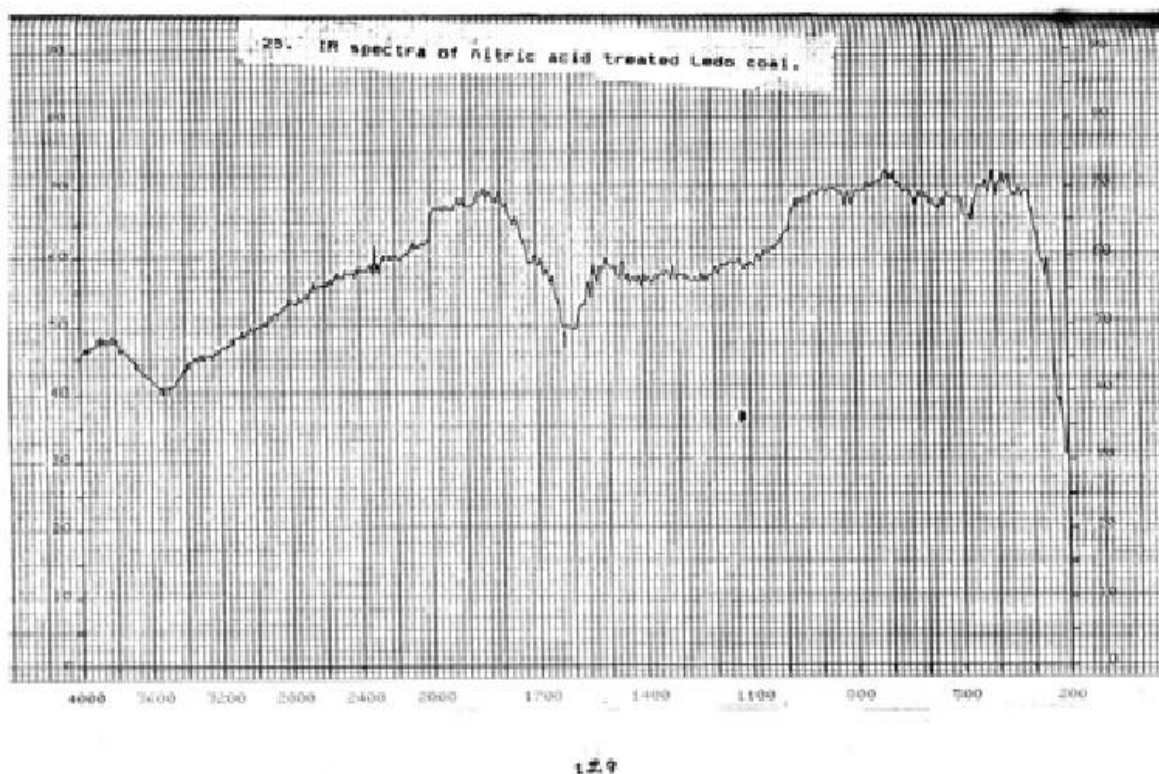


Fig-IV IR spectra of nitric acid treated Ledo coal

#### IV. Conclusion and Summary :

A systematic optimization study using Temperature programmed reduction study along with nitric acid oxidation on Ledo 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°C are due to mercaptan, disulphide/thiol, thioether, thiophene, pyrite and complex thiophene groups. The thioketonic group is also present as determined from nitric acid oxidation. IR studies showed that resorcinol was not destroyed up to 300°C. On heating coal upto 600°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 Ledo coal are in the forms: mercaptan, disulphide/thiol, thioether, thiophene, pyrite, sulphate and thioketone. These forms are shown in Table VI.

Thus TPR study in combination with nitric acid oxidation 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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