Desulfurization of Oxidized Indian Coals with Solvent Extraction and Alkali Treatment
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The north eastern region (NER) of India has a substantial deposit of high sulfur (2–8%) coals with low ash and high volatile matter contents. Assam, one of the coal producing states of the region, has coal deposits with 75–90% of organic sulfur functionalities affixed to the coal structure and difficult to remove. The present investigation reports desulfurization of oxidized Assam coals by solvent extraction and alkali treatment separately. The two coal samples are selected to represent two categories: one with high organic sulfur and low ash (Baragolai) and the other with low organic sulfur and high ash (Ledo) coals of the region. The desulfurization techniques widely used are classified as physical, chemical, thermal, radiolytic, or biochemical, which are known to have desulfurization effects up to a limited extent. Chemicals employed for desulfurization are either oxidizing agents such as ferric sulfate, ferric chloride, ferricyanide, potassium dichromate, potassium permanganate, cupric chloride, sodium hypochlorite, peroxycetic acid, perchloric acid, performic acid, oxygen, sodium hypochlorite, and sodium hydroxide.

In view of stringent environmental regulations, utilization of high sulfur coals has severe limitations for emission of sulfur dioxide and the development of clean coal technologies for sulfur removal is gaining importance worldwide. The precombustion desulfurization techniques widely used are classified as physical, chemical, thermal, radiolytic, or biochemical, which are known to have desulfurization effects up to a limited extent. Chemicals employed for desulfurization are either oxidizing agents such as ferric sulfate, ferric chloride, hydrogen peroxide, potassium dichromate, potassium permanganate, cupric chloride, sodium hypochlorite, peroxycetic acid, perchloric acid, performic acid, oxygen, sodium hypochlorite, and chlorinolysis.
sodium hydroxide followed by HCl treatment,32 hydrogen peroxide in the presence of dilute sulfuric acid43 for desulfurization of Assam coal, etc. or alkaline solutions such as sodium carbonate,34–36 sodium hydroxide,47–49 calcium hydroxide,4 etc. These processes have been suggested to reduce ash and sulfur contents in coal. Besides these processes, hydrogenation30 has also been effective in sulfur removal from northeast Indian coals.

A number of other clean coal processes45 have also been developed removing a majority of pyritic sulfur with acceptable recovery of the heating value. Some of them are also capable of removing organic sulfur content. These processes at bench scale levels have demonstrated 95–99% removal of pyritic sulfur and up to 40% removal of organic sulfur from US coals.45 Some of the major processes developed which remove pyritic sulfur only are Magnex, Syracuse, TRW, and Ledgemont. The other processes are ERDA, GE, Battelle, JPL, IGT, KVB, and ARCO which claim to remove most of pyritic and varying amounts of organic sulfur. However, with deep coal cleaning, loss of carbon values takes place.

Among the processes that remove both organic and pyritic sulfur, the KVB process appears to have low capital investment as it is a partially dry process. However, the process has limitations in oxygen concentration requirements in the treat gas exceeding the explosion limits of coal dusts, which may be hazardous and nitrogen uptake by coal structure, which may also increase NOx emissions from combustion of clean product.

High sulfur coals of the northeastern region of India are of recent origin (60–80 million years) with high volatile matter, mostly caking, low ash and high sulfur contents. The total sulfur of these coals is in the range of 2–8% with about 75–90% of them being in organic form46 unlike other high sulfur coals of the world where the majority of sulfur is in a pyritic form. The organic sulfur present in coals47 is generally aliphatic or aromatic thiols, aliphatic or mixed sulfides, aliphatic or aromatic disulfides, heterocyclic compounds of the thiophenic types, etc.58–50 The presence of five types of organic sulfur functional groups in the Assam coal namely disulfide, thiols, sulfides, thiophenic, and thioketoic has been reported51 which are difficult to remove from the coal matrix, unless the chemical bonds that hold it are broken. Various chemical methods are attempted by different workers for desulfurizations of these coals. Baruah et al.30 reported up to 31% removal of organic sulfur by mild hydrogenation using tetralin as solvent, but the product coal is generally obtained as depolymerised viscous material with high degree of dissolution. Mukherjee and Borthakur32 observed complete removal of inorganic sulfur and 10% organic sulfur from these coals by treatment with aqueous sodium hydroxide followed by acid. Mukherjee et al.32 reported removal of 5% organic sulfur and up to 78% inorganic sulfur by treatment with hydrogen peroxide in the presence of sulfuric acids. Chlorinolysis50 of NER coals in aqueous medium has also been found to remove up to 50% organic sulfur.

Organic sulfur compounds, like mercaptans (thiols), sulfides, disulfides, and thiophenes, are also reported in crude oil and synfuels. Conventionally, the hydrodesulfurization (HDS) method is adopted for removal of these sulfur groups. However, HDS is not effective for removing sulfur compounds such as dibenzothiophene and its derivatives especially 4,6-dibenzo- thiophene (4,6-DMDT). Therefore, oxidative desulfurization (ODS) has been given much attention as an alternative technology for deep desulfurization. Various oxidative desulfurization techniques for removal of sulfur from light gas oil, vacuum gas oil, fuel, etc. have also been reported50 and have been found to be alternative methods to HDS. ODS is basically a two-stage process, oxidation followed by extraction. The sulfur containing compounds are oxidized first to sulfoxides and sulfones and, then, are extracted due to their relative increase in polarity.53–56 The reactivity of sulfur compounds increases with the increase of electron density on sulfur atoms,57 which could be removed by the extraction57–63 with solvents. Recently, ODS techniques have also been tried for desulfurization of coals. Potassium hydroxide treatment or high temperature thermal treatment

(36) Yang, R. T.; Subho, K.D.; Tsai, M.C. Fuel 1985, 64, 735–742.
(38) Given, P. H.; Jones, J. R. Fuel 1966, 45, 151.
(48) Bhatnagar, S. S.; Dutta N. L. Report, Board of Scientific and Industrial Research; Department of Commerce, Govt. of India, 1940; Vol. 41, pp 16–17.
(56) Babich, I. V.; Moulijn, J. A. Fuel 2003, 82, 607.
achieved 43% desulfurization of the oxidized sulfur compounds. Oxidative desulfurization of sulfur-rich Ukrainian coal was carried out in the temperature range of 623–723 K by an air–steam mixture in the fluidized bed reactor.

All the processes reported so far could succeed in the removal of organic sulfur to a certain extent only, which may be due to the steric hindrance of the dibenzo thiophenes (DBT) and alkylated thiophenes present in fuels. The oxidation of dibenzo thiophenes in a hydrogen peroxide and formic acid medium has been reported by Aida et al. The divalent sulfur of DBT can be oxidized by the electrophilic addition reaction of oxygen atoms to the hexavalent sulfur of DBT sulfone. Hence, the reactivity of oxidation becomes higher for a sulfur atom oxidized by formic acid and hydrogen peroxide. Hydrogen peroxide was added drop by drop to the mixture of coal and formic acid for oxidation.

Table 1. Physicochemical Analysis of the Coal Samples of Different Sizes (weight percent)*

<table>
<thead>
<tr>
<th>coal sample size (mm)</th>
<th>Baragolai</th>
<th>Ledo</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>ash</td>
</tr>
<tr>
<td>0.211</td>
<td>2.40</td>
<td>5.70</td>
</tr>
<tr>
<td>0.152</td>
<td>3.40</td>
<td>7.20</td>
</tr>
<tr>
<td>0.076</td>
<td>3.20</td>
<td>7.50</td>
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<tr>
<td>0.211</td>
<td>3.07</td>
<td>10.35</td>
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<tr>
<td>0.152</td>
<td>2.70</td>
<td>11.35</td>
</tr>
<tr>
<td>0.076</td>
<td>2.70</td>
<td>12.35</td>
</tr>
</tbody>
</table>

* M, moisture; VM, volatile matter; FC, fixed carbon; PS, pyritic sulfur; SS, sulfate sulfur; OS, organic sulfur; TS, total sulfur.

As five types of organic sulfur functionalities are present in Assam coals, new oxidative desulfurization routes have been proposed for these coals. The present investigation reports effectiveness in removal of sulfur by oxidation in H_2O_2–HCOOH mixture, extraction of oxidized sulfur functionalities with solvent of high polarity (dimethylformamide, DMF), and treatment with alkali separately.

**Experimental**

**Chemicals.** Hydrogen peroxide (30%), formic acid (85%), sodium hydroxide of AR grade, and HPLC grade N,N′-dimethylformamide (DMF) purchased commercially were used in the experiments. Concentrations of H_2O_2 and NaOH were determined volumetrically.

**Coal samples.** The freshly mined coal samples were collected from the Ledo and Baragolai coalfields of the Makum coalfield (27°0’18” N, 95°0’51” E) of North Eastern Coalfields, Margherita, Assam. The samples ground to ~0.211, ~0.152, and ~0.076 mm fractions were analyzed. The proximate and ultimate analysis of all the size fractions of coal samples were done by Indian standard methods [IS 1350]. The carbon, hydrogen, and nitrogen were estimated by using a Perkin-Elmer (model 2400) elemental analyzer, and total sulfur is estimated (±0.02 accuracy) by following Eschka methods [ASTM D 3177]. The forms, pyritic sulfur (accuracy of ±0.01), and sulfite sulfur (accuracy of ±0.01), were determined by a standard method [ASTM D 2492]. The percent of organic sulfur was calculated by difference. The calorific values were determined by using a bomb calorimeter [ASTM D 2313]. All analyses were done in quadruplicate, and the mean is reported. The Fourier transform infrared (FTIR) analyses of the coals and treated samples were recorded by a Perkin-Elmer system 2000, model 640B (wavelength 400–4000 cm⁻¹, with an accuracy of ±0.3) using a KBr pellet with same weight of dried coal samples and KBr.

**Oxidation of Coal Samples.** The Baragolai and Ledo coal samples of sizes ~0.211, ~0.152, and ~0.076 mm, respectively, were oxidized by formic acid and hydrogen peroxide. Hydrogen peroxide was added drop by drop to the mixture of coal and formic acid for in-situ formation of permisic acid. The experiment is carried out by refluxing 100 g of each coal with 250 mL of 20% H_2O_2 and 44 mL of 20% formic acid (pH < 2) for 1 h at atmospheric pressure. The oxidized coal samples were filtered and washed until the pH of the filtrate became neutral. The oven dried samples were kept for subsequent experiments.

**Solvent Extraction of Oxidized Coal Samples.** DMF, a polar solvent, is more effective for the extraction of oxidized organosulfur compounds in comparison to other solvents like methanol, DMSO, and sulfolane. Here, the extraction of all the size fractions of oxidized coal samples was carried out by refluxing 30 g each with 100 mL of DMF (30% v/v) for 1 h at atmospheric pressure. The extracted coal samples were filtered, washed, and oven dried up to 100 °C.

**Alkali Treatment of the Oxidized Coal Samples.** A 30 g portion of each of the oxidized coal fractions was mixed with 100 mL of NaOH (1 N) and refluxed for 1 h at atmospheric pressure. Finally, the mixture was cooled, filtered, and washed with dilute HCl (1 N) solution until the pH of the filtrate became neutral. The washed coal samples were dried and preserved for subsequent analysis.

**Results and Discussion**

Baragolai and Ledo coals of Assam belong to the tertiary formation. Their physicochemical attributes are low ash, high volatile matter, and high sulfur having high heat values (Table 1). These two samples were selected for desulfurization to represent two categories: Baragolai with high organic sulfur (4.1%) and low ash (~6–7%) and Ledo with low organic sulfur (2.5%) and high ash (10–12%) coals of the region. However, the sulfur assay of these coals showed about 78% of total sulfur to be in the organic form.

The atomic S/C ratio for raw and treated coals (0.211 mm) is shown in Figure 1. Atomic S/C ratios for Baragolai and Ledo...
coals are 0.026 and 0.018, respectively. Ratios are found to decrease after oxidation with \( \text{H}_2\text{O}_2 = \text{HCOOH} \) (0.016 and 0.012 in respective oxidized samples) and marginal reduction in alkali treated and solvent extracted samples.

**Sulfur Removal**

**Oxidation.** The probable reactions taking place during the oxidation of coal are the following.

1. Formation of performic acid
   \[
   \text{HCOOH} + \text{H}_2\text{O}_2 \rightarrow \text{HCO}_2\text{H} + \text{H}_2\text{O}
   \] (1)

2. Oxidation of pyrites by performic acid to form hematite iron and sulfuric acid
   \[
   \text{FeS}_2 + 15\text{O}_2 + 8\text{H}_2\text{O} \rightarrow 4\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{SO}_4
   \] (2)

3. Oxidation of organic sulfur compounds to sulfoxides, sulfonic acid, and sulfones by an electrophilic addition mechanism\(^{72}\)
   \[
   \text{S} + \text{OH} \rightarrow \text{SO} \rightarrow \text{SO}_2\text{O} \rightarrow \text{SO}_3\text{H}
   \] (3)

**Figure 1.** Atomic S/C ratio of raw and oxidized coals.

![Figure 1](image)

The effect of hydrogen peroxide on desulfurization in the presence of formic acid for all the different size fractions of the coal samples is shown in Table 2. Total sulfur removal from different size fractions varies from 34.5 to 39.2% and 33.1 to 36.7% for Baragolai and Ledo coals, respectively. The amount of pyritic sulfur removed was 82–83.6% and 79–84% for Baragolai and Ledo coal samples, respectively. The remaining pyrites may be of finer size, deeply embedded into the coal matrix, and not affected by the oxidative mixture in the leaching time and temperature considered. The removal of sulfate sulfur for Baragolai and Ledo coals has been found to be 72–77% and 72–77.8%, respectively, for different size fractions. Organic sulfur removal for the Baragolai and Ledo coal samples has been found to be 22.8–28% and 16–18.5%, respectively. For the low rank Assam coal samples, it is anticipated that mainly thiols, simple unstable disulfides, and sulfides are being oxidized to sulfonic acids and sulfoxides/sulfones. The greater level of desulfurization in Baragolai coal indicates that simple unstable disulfides and disulfides are more as compared to that in Ledo coals.

Ford et al.\(^{73}\) also reported that the rate of oxidation of thiophenic compounds is lower than that of sulfides. The oxidation of sulfur compounds depends upon the availability of the lone pair of electrons in sulfur atoms and steric strain in the reaction products.\(^{57}\) The minimum value for electron density to cause the oxidation is 5.72.\(^{57}\)

The degree of desulfurization depends upon the solubility of oxidized sulfur compounds in the reaction mixture.\(^{74}\) Oxidation of nonthiophenic organic sulfur groups such as sulfides, disulfides, thiols, etc. may produce soluble sulfoxides, sulfonic acids, and sulfones.\(^{52,75–78}\) However, butane thiols and thiophenols can be removed almost completely in accordance with the high solubility in the aqueous phase of produced sulfonic acids. Sulfones of benzo thiophenes and dibenzo thiophenes have a low degree of solubility. After oxidation, they may remain in the coal matrix. Therefore, extraction of these groups with solvent/alkali may be more effective. Minor alterations on the surface of coal samples may also occur during oxidation in the \( \text{H}_2\text{O}_2 = \text{HCOOH} \) mixture.\(^{79}\)

**Solvent Extraction.** Sulfoxides and sulfones which have been formed during oxidation can be removed by solvent extraction. Gogoi et al.\(^{80}\) has reported that DMF was an effective solvent for extraction of oxidized sulfur compounds from coal due to its high electron donating nature. Otsuki et al.\(^{57}\) also found it to be more effective for the extraction of sulfur compounds from vacuum gas oil (VGO). Sulfur removal (90%) from fuel could be achieved by using acetone, DMF, and other solvents after oxidation.\(^{71}\) Desulfurization increases with the increasing electron donating capacity of the solvent and electron density on the sulfur atoms. The order of electron density of some sulfur compounds is butane thiols > thiophenol > dephenyl sulfide > debenzo thiophenes.\(^{74}\)

DMF extraction of oxidized Assam coals showed removal of 41–43% and 40–42% of total sulfur from Baragolai and Ledo coal samples, respectively (Table 3). Inorganic sulfur removal was found to be about 90%. Organic sulfur removal was found to be 28–30.5% and 20–23% for Baragolai and Ledo coal samples, respectively. As DMF is a polar solvent, extraction of low molecular weight sulfur compounds is more. The remaining sulfur compounds after extraction of oxidized samples appear to be sulfones.

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with high molecular weight with lower polarity. The partial removal of organic sulfur compounds may not be due to insufficient oxidation but due to the extraction efficiencies of DMF. The solvents with higher polarity may be more effective in sulfur removal.

**Alkali Treatment.** The alkali has been found to be more effective in removal of all the forms of sulfur. It reacts with pyritic sulfur forming soluble sulfates.\(^8\)

\[
2\text{NaOH} + \text{FeS}_2 \rightarrow \text{Na}_2\text{S} + \text{Fe(OH)}_2 + \text{S}
\]

After DMF Extraction

<table>
<thead>
<tr>
<th>coal sample size (mm)</th>
<th>M</th>
<th>ash</th>
<th>VM</th>
<th>CV (kcal/kg)</th>
<th>sulfur distribution (wt %)</th>
<th>total desulfurization</th>
<th>total demineralisation</th>
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<tbody>
<tr>
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<td>4.62</td>
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<td>0.12</td>
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<th>coal sample size (mm)</th>
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<th>ash</th>
<th>VM</th>
<th>CV (kcal/kg)</th>
<th>sulfur distribution (wt %)</th>
<th>total desulfurization</th>
<th>total demineralisation</th>
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<th>ash</th>
<th>VM</th>
<th>CV (kcal/kg)</th>
<th>sulfur distribution (wt %)</th>
<th>total desulfurization</th>
<th>total demineralisation</th>
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**Demineralization.** The reduction in ash by the oxidative mixture was found to be 19–37% and 28–33% for Baragolai and Ledo coals, respectively, while DMF extraction of oxidized coals showed about 21–39% and 25–37% removal, respectively. During alkali extraction, a marginal increase in ash content from oxidized coals is observed due to the formation of sodium alumino silicates. Alkali dissolves alumina and silica from clay and other silica and alumina bearing materials present in the coal, forming soluble sodium silicate and sodium aluminate. The sodium alumino silicate precipitates out in the form of a gel when the concentration of the silicate and aluminate ions in the alkaline solution exceeds the solubility product of alumino silicate. The possible reaction is represented as

\[
\text{NaOH(aq)} + \text{NaAl(OH)}_3\text{(aq)} + \text{Na}_2\text{SiO}_3\text{(aq)} \rightarrow [\text{Na}_4(\text{AlO}_2)_6(\text{SiO}_2)_6\cdot\text{NaOH}\cdot\text{H}_2\text{O}]
\]

Treatment of oxidized samples with alkali (1 N) removed up to 47% of total sulfur. Complete removal of pyritic sulfur and 98% of sulfate sulfur was observed for both the coals, while 28–33% and 23–26% of organic sulfur were removed from the Baragolai and Ledo coals, respectively. The concentration of alkali, extent of oxidation, and C–S bond energies are the governing factors for the removal of sulfur from oxidized coals. As aromatic compounds, e.g., thiophene and benzo(b)thiophenes have high C–S bond energies, for cleavage of these bonds from their oxidized compounds requires high strength of alkali.

\[
\text{RCH}_2\text{SCH}_2\text{R} + 2\text{NaOH} \rightarrow \text{RCH}_2\text{OH} + \text{R'}\text{CH}_2\text{O} + \text{Na}_2\text{S} + \text{H}_2\text{O}
\]

\[
2\text{RSSR} + 4\text{OH}^- \rightarrow 3\text{RS}^- + \text{RSO}_2\cdot\text{H}_2\text{O}
\]

\[
\text{RSH} + 2\text{NaOH} \rightarrow \text{Na}_2\text{S} + 2\text{H}_2\text{O} + \text{R'}\text{CH} \equiv \text{CH}_2\text{O}
\]

Alkalai may also react with sulfoxides and sulfones formed during oxidation.\(^7\)

[Image: chemical structure]

such as sodalite, nosalite, etc. depending on alkali concentrations.\footnote{Breck, D. W. \textit{Zeolite Molecular Sieves}; Wiley: New York, 1973; p 250} The formation of hydroxy sodalite \([\text{Na}_6 (\text{AlO}_2)_6 (\text{SiO}_2)_6 \cdot x\text{NaOH} \cdot (8 - 2x)\text{H}_2\text{O}]\) is also reported on treatment of Kaolinite and illite type clays with NaOH solution.\footnote{Baruah, B. P.; Saikia, B. K.; Kotoky, P.; Rao, P. G. \textit{Energy Fuels} 2006, 20, 1550–1555.  
(84) Borah, D.; Baruah, M. K.; Haque, I. \textit{Fuel} 2001, 80, 1475–1488.}

\textbf{Particle Size.} The efficiency of the chemical desulfurization processes depends upon the particle sizes of the coals.\footnote{Borah, D.; Baruah, M. K.; Haque, I. \textit{Fuel} 2001, 80, 1475–1488.} The ash content of the raw coals of Baragolai and Ledo used for desulfurization also varies with the particle size and decreases with an increase in particle size. With the decrease of particle sizes, desulfurization (Figures 2–4) and demineralization increase in the oxidized coals. However, slight variation in desulfurization is observed after extraction of the oxidized coal samples by DMF and alkali.

\textbf{Calorific Values.} Calorific values (CVs) of raw and treated samples do not show much variation with the size. In the oxidized samples, the CV increases by 335 to 1079 kcal/kg in comparison to raw coals due to reduction in ash contents. However, the decrease of 2–5\% in calorific value during the oxidation of Mae Moh coal has also been reported.\footnote{Borah, D.; Baruah, M. K.; Haque, I. \textit{Fuel} 2001, 80, 1475–1488.} Values of CV in DMF treated samples decrease in comparison to oxidized samples, which may be due to the slight solubility of the oxidized coal samples in the solvent (about 10\%). However, alkali treated samples show marginal variation with oxidized samples (Figure 5).

\textbf{Activated Complex Theory of Desulfurization.} To understand the kinetics and thermodynamics of desulfurization, the activated complex theory (ACT) is applied.

For effective organic sulfur removal, C–S bonds must be cleaved. Assuming that desulfurization proceeds with the interaction of organic sulfur (coal–OS) and oxidants with the initial formation of an intermediate complex (I*), which is in equilibrium with the reactants, a certain fraction of which decomposes resulting in sulfur loss (eq 12),
coal–OS + D_A ⇌ coal–OS·D_A → sulfur loss

(12)

where D_A = oxidizing agent/DMF/alkali.

The formation of I* is the slowest and also the rate-determining step for the sulfur loss. The earlier work shows that the formation of I* is a pseudo-first-order kinetics for pyrite,63 and organic sulfur removal.84

Considering the thermodynamic aspects of desulfurization, which could provide a better insight into the reaction, a semiquantitative approach has been considered essential. The Gibbs free energy of activation (ΔG*) for the formation of the activated complex is determined by applying the reaction isotherm85 (eq 13).

\[ \Delta G^* = -RT \ln K_c^* \]  

where \( K_c^* \) is the equilibrium constant, \( R \) is the universal gas constant, and \( T \) is the reaction temperature in kelvin. \( K_c^* \) is expressed in terms of soluble sulfur to total coal organic sulfur.

The change in the entropy of activation (ΔS*) for the formation of activated complexes at equilibrium is calculated by modifying the derivation used for evaluating the entropy of mixing, given by (eq 14).

\[ \Delta S^* = -nR \ln n \]  

where \( n \) is the molar number of soluble sulfur species. The heat content or enthalpy of activation (ΔH*) for the formation of the activation complex at equilibrium is evaluated by using the well-known Gibbs–Helmholtz equation (eq 15).

\[ \Delta G^* = \Delta H^* - T \Delta S^* \]  

Application of the activation complex theory86 enables us to evaluate the activation energy (\( E_a \)) for the desulfurization reaction.

\[ E_a = \Delta H^* + RT \]  

The calculated value of the Gibbs free energy of activation (ΔG*), enthalpy of activation (ΔH*), entropy of activation (ΔS*), and activation energy (\( E_a \)) for the desulfurization reaction are presented in Table 4.

**Thermodynamics.** The positive values of the Gibbs free energy (ΔG*) of activation for the formation of the activated complex represent the nonspontaneous nature66 of the desulfurization reaction. This may be substantiated by the presence of aromatic sulfur compounds in the coal matrix. Therefore, desulfurization is mainly due to the cleavage of C–S bonds in aliphatic sulfur compounds because of their low bond dissociation energies.84 The enthalpy of activation was found to be positive which indicates that the desulfurization reaction proceeds with the absorption of heat (endothermic nature).

The positive values of the entropy of activation in the system indicate that the desulfurization reaction is thermodynamically favorable. The low values of ΔS* are responsible for the nonspontaneous nature of the sulfur loss reaction to a certain extent. A loosely bound activated complex has a higher entropy of activation than tightly bound ones.85 Low values of the entropy of activation indicate that the activated complexes formed are tightly bound resulting from arrest of degrees of freedom of the constitutents, other than they should have in the bulk system. These tightly bound activated complexes would only be possible with low molecular weight aliphatic sulfur compounds of coal. With condensed aromatic sulfur compounds, oxidants cannot form tightly bound activated complexes because of crowding; the steric effect offered by large aromatic rings would be more prominent. Thus, bulky organic sulfur compounds, even if some of them could form activated complexes, because of loose attracting forces responsible for binding, may dissociate into reactants rather than transforming into products.

**Activation Energy.** Activation energies for organic sulfur removal are given in Table 4. Activation energies of H\(_2\)O\(_2\)–HCOOH oxidation reactions vary between 6.4 and 6.9 and 7.8–8.2 for Baragolai and Ledo coals. Low activation energies for Baragolai coal are due to the presence of simple C–S bonds in sulfides and disulfides, which are easily oxidized and removed. The chemistry involved in the desulfurization of organic sulfur from coal is primarily governed by the cleavage of C–S as well as S–S bonds. Borah et al.84 studied the oxidation of pure compound methionine (commonly occurring in meat) and dibenzothiophene (aromatic compound). It was observed that methionine oxidized due to susceptibility of aliphatic sulfur for desulfurization under an oxic system. Dibenzothiophene gave negative results due to the high stability of dibenzothiophene toward cleavage of the C–S bond. The activation energies for solvent extraction and alkali treatment of oxidized samples of 0.152 and 0.076 mm size fractions of both the coals and the 0.211 mm fraction of Ledo coal have slight variations. In comparison, for the 0.211 mm size fraction, the decrease in \( E_a \) is observed, showing better desulfurization in DMF.

**FTIR Study of the Coal Samples.** FTIR studies of raw and oxidized coal samples indicate the removal of sulfur and mineral matter (Figure 6a and b). A sharp band at 475 cm\(^{-1}\) is observed for the coal and treated samples due to stretching vibration of S–S bonds; however, the peak intensity (peak height) is reduced for treated coal samples. The peak heights (intensity) of the absorbance calculated85 are 0.4, 0.07, and 0.08 for oxidized, DMF extracted, and alkali treated coals, respectively. The bands at 536, 658, 694, and 1103–1101 cm\(^{-1}\) are assigned to mineral matter present in these coals. Hematite iron shows absorption peaks at 1101–1103 cm\(^{-1}\) and 1167–1165 cm\(^{-1}\). The peak observed at 1166 cm\(^{-1}\) belongs to the hematite formed, and the intensity of these peaks increases after oxidation of the coal samples due to conversion of pyritic iron into hematite.

Absorption bands close to 520, 610, and 640 cm\(^{-1}\) are due to stretching vibration of S–S bonds of sulfides and C–S bonds in primary and secondary thiols.73 The intensity of these bands in the spectra of coals is low because the IR bands of organic sulfur groups are very weak and not very prominent even in the case of high organic sulfur coals. However, a slight decrease in the intensity of these bands in treated coal samples indicates the elimination of these groups.

FTIR spectra have shown that organically bound sulfur has been converted to sulfoxides (S=O) and sulfones (–SO\(_2\)). All the oxidized sulfur compounds have the common S=O linkage. Absorbance bands for organic sulfates occur in the region of 1415–1380 and 1200–1185 cm\(^{-1}\).87 Prominent IR bands are observed in the region of 1432–1383 cm\(^{-1}\) for oxidized, DMF and alkali treated samples. The intensities of the bands for all treated coals are in the following order: oxidized samples > DMF treated samples > alkali treated samples > raw coals.

The stretching vibration in sulfoxides generally occurs in the range 1070–1030 cm\(^{-1}\). The broad band appearing in the region

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(86) Moore, W. J. Basic physical Chemistry; Prentice Hall: New Delhi, 1989.

1041–1020 cm\(^{-1}\) has been assigned to the symmetrical stretching vibration of S\(\text{d}O\). The presence of S\(\text{d}O\) bands for the untreated sample may also be due to SO\(_4\) which might have contributed to some extent to the appearance of the band in that region. In Baragolai coal samples, it disappears completely after alkali extraction, while in Ledo coal samples a decrease in intensity of the band is observed. This also supports the assumption that Baragolai coal has more sulfides and disulfides, oxides of which can be removed easily. In oxidized samples, peak intensities of these bands are increased. In DMF treated, oxidized samples, the peak intensities were found to be the same as in the case of oxidized samples due to the low solubility of high molecular weight sulfones. However, it does not appear in the alkali treated samples due to elimination of these groups.

The absorption band for \(-\text{SO}_2\) in sulfones occurs at 1350–1300 cm\(^{-1}\) for asymmetrical vibration and at 1160–1120 cm\(^{-1}\) for symmetrical vibrations.\(^{87}\) Peaks appearing at 1368 and 1090 cm\(^{-1}\) in oxidized coals belong to \(-\text{SO}_2\) vibration.

A qualitative attempt has been made to understand the extent to which oxidized sulfur species of coal are removed. The absorbance range for the S\(\text{d}O\) stretch (for sulfoxide, sulfone, sulfonic acid, and sulfenic acid) was evaluated. The peak intensity (peak height) of each raw and treated coal sample is shown (Figure 7a and b). It is clearly indicated in the figures that after oxidation there is an increase in the formation of oxidized sulfur species which declines after alkali treatment. The difference of absorbance between the S\(\text{d}O\) and S\(\text{O}_2\) stretches could give the magnitude of sulfoxide and sulfonic acid formation.\(^{88}\) In oxidized samples, intensities of these bands increase and decline in the alkali treated samples. The decrease is more pronounced in the S\(\text{d}O\) stretch band as compared to the S\(\text{O}_2\) absorption band.

Table 4. Thermodynamic Parameters for Organic Sulfur Removal\(^a\)

<table>
<thead>
<tr>
<th>size (mm)</th>
<th>(\Delta G^*)</th>
<th>(\Delta H^*)</th>
<th>(\Delta S^*)</th>
<th>(E_a)</th>
<th>(\Delta G^*)</th>
<th>(\Delta H^*)</th>
<th>(\Delta S^*)</th>
<th>(E_a)</th>
<th>(\Delta G^*)</th>
<th>(\Delta H^*)</th>
<th>(\Delta S^*)</th>
<th>(E_a)</th>
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<td>4.6</td>
<td>3.9</td>
<td>1.91</td>
<td>6.9</td>
<td>7.1</td>
<td>6.7</td>
<td>0.41</td>
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<td>0.51</td>
<td>9.2</td>
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<td>6.9</td>
<td>6.8</td>
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<tr>
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<td>3.3</td>
<td>1.84</td>
<td>6.4</td>
<td>9.9</td>
<td>9.9</td>
<td>0.19</td>
<td>12.9</td>
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<td>5.5</td>
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</table>

\(\Delta G^*\), Gibbs free energy of activation (in kilojoules per mole); \(\Delta H^*\), enthalpy of activation (in kilojoules per mole); \(\Delta S^*\), entropy of activation (in joules per kelvin per mole); \(E_a\), activation energy (in kilojoules per mole).


\(89\) IS 1350: Methods of Test for Coal and Coke—Proximate Analysis, Total Sulphur and Calorific Value; Indian Standard, 1984; part 1.

\(90\) ASTM D 3177-02: Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke. In ASTM Book of Standards; ASTM: West Conshohocken, PA, 2006; Vol. 05.06.

\(91\) ASTM D 2492-02: Test Method for Forms of Sulfur in Coal. In ASTM Book of Standards; ASTM: West Conshohocken, PA, 2006; Vol. 05.06.

\(92\) ASTM D 3286-91a: Test method for Gross Calorific Value of Coal and Coke by the Isoperibol Bomb Calorimeter. In ASTM Book of Standards; ASTM: West Conshohocken, PA, 2006; Vol. 05.06.
Conclusion

The high organic sulfur Indian coals can be conveniently desulphurised and demineralized by solvent extraction and alkali treatment of the H$_2$O$_2$–HCOOH oxidized coal samples. The alkali treatment of the oxidized coals shows complete removal of inorganic and a maximum of 32.8 and 26.4% organic sulfur for Baragolai and Ledo coals, respectively. The finding that the remaining organic sulfur could not be removed by alkali and DMF may be due to the much stronger C–S bonds in organic sulfur functionalities. The C–S bonds in these compounds are resistant to oxidation followed by extraction and also account for about 50% of the organic sulfur groups. Alkali treatment after oxidation is much more effective than DMF treatment for the removal of inorganic as well as organic sulfur. Demineralization is also achieved during oxidation, solvent extraction, and alkali treatment of these coals. The results show alternative routes for chemical desulfurization of high sulfur coals along with reduction in ash content; however, better desulfurization may be possible with increase of the strength of alkali and time of extraction. Decrease in the atomic S/C ratio suggests the effective desulfurization. Calorific values increase after oxidation of coal samples due to demineralization. Slight variation in calorific values was observed after the alkali treatment of oxidized samples. A decrease in calorific values was observed in DMF treated samples. FTIR spectra of the desulphurized coal showed the conversion of organically bound sulfur to their oxides after oxidation with H$_2$O$_2$–HCOOH and removal of these oxides after treatment with solvent and alkali. FTIR spectra also show the prominent peaks of organic sulfates. The intensities of these peaks have been found to reduce during the process steps. These results strengthen the assumption that C–S bonds have been broken due to the weakening of the bonds during pretreatment oxidation (H$_2$O$_2$–HCOOH) by the formation of sulfones, sulfoxides, or sulfonic acid from the divalent sulfur present in the coal. Desulfurization and demineralization increase with the decrease of particle sizes. The positive value of the enthalpy of activation shows the endothermic nature of desulfurization. Computation of the Gibbs free energy of activation suggests the nonspontaneous nature of the desulfurization reaction and is also attributed to the involvement of aromatic sulfur compounds in the formation of an activated complex. Low positive values of the entropy of activation represent the fact that the activated complexes formed are tightly bound and are only possible with aliphatic sulfur compounds of low molecular weight. Oxidative desulfurization methods could be useful for the precombustion desulfurization of high sulfur coals.

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