Desulfurization of Thar Lignite by Oxidative Alkali Leaching Under Pressure

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Abstract

Pakistan is the world largest lignite bearing country in the world due to the Thar coal reserves. Sulfur contained in this coal need to be removed prior to combustion. Oxidative alkali leaching in dissolved oxygen technique was used to remove the sulfur from Thar coal. This method removed enough all three types of sulfur; about 90% pyretic sulfur, 78% organic sulfur and 50% sulfate sulfur and more than 82S% of total sulfur removal was achieved. Effect of various reaction parameters were observed, it was investigated that reaction time and partial pressure of oxygen has positive effect on the desulfurization, higher the reaction time and oxygen partial pressure higher the degree of desulfurization, also the desulfurization increased with increase in reaction temperature and alkali concentration till some optimum value and then decreases with further increase in value of temperature and concentration of alkali, although desulfurization was observed maximum with minimum particle size. Coal was also characterized with Thermogravimetric Analysis (TGA) and Testo smoke number to investigate the combustion behavior of processed coal. It was observed that combustion properties of processed coal were improved and black smoke in processed coal was reduced.

1. Introduction

Coal is highly abundant fossil fuel on the earth surface and has been used since long, it is about 70% of total known fossil fuel resources in the world(Franco and Diaz 2009), even it is reported that the coal reserves are more than other fossil fuel like oil and gas, that are more than enough to face the present energy requirement (Rehman et al. 2018), and still it is fulfilling the requirement of the energy generation. About more than 40% of electric power plants are utilizing the coal fuel (Meshram et al. 2015). Pakistan is the 7th largest country in coal reserves, about 186 billion tons sedimentary rock fossil fuel (coal) is present in Pakistan and mostly 97% is lignite coal (Malkani 2012), hence Pakistan becomes the top lignite coal bearing country in the world .Thar is largest coal mine in the country, about 175,506 million tons of coal is estimated . Thar coal field spreads over 9000 km² and has 20 maximum coal seams, ultimate and proximate composition of the coal varies with block to block and with different depth (Malkani and Malik 2018).Before the discovery of Thar coal field Pakistan was not appeared in the list of coal rich countries (Munir et al. 2018). As Thar lignite coal contains the variable amount of sulfur with respect to block and depth the presence of sulfur in coal may enhance the calorific value of coal, but it causes the serious destruction to ecological system as production of SO_x and hydrogen sulfide during combustion. Therefore it is needed to remove or reduce the Sulphur amount from coal (S. Mukherjee and Borthakur 2001).

Sulfur in coal is present in different forms, like inorganic Sulfur (mostly in the form of pyrite), organic Sulfur (mostly present in trace amounts). Organic Sulphur in coal is present as thiol, sulfide, thiophenol, and disulfide; however, almost 95% of the organic Sulfur is in the form of thiophenes and sulfate sulfur present in different ranges (Kozłowski, Wachowska, and Yperman 2003). Coal desulfurization prior to combustion is an important technology to avoid air pollution (Prasassarakich and Thaweessri 1996).Sulphur is covalently bonded with carbon (C-S bond) in these compounds, this bond is difficult to

breakdown by any physical process, hence it requires chemical processing for cleaving of the bond for Sulphur removal.

Chemical leaching is an effective way for desulfurization and demineralization. Chemical leaching has ability to remove the minerals that strongly bound to the coal, and that cannot be removed easily with physical method (Samit Mukherjee and Borthakur 2003). Repetition of chemical leaching process causes reduction in the organic sulfur content due to the breakage of C-S bonds, which tends to decrease or even eliminate sulfur from the coal (Kozłowski, Wachowska, and Yperman 2003). Samit has observed that alkali leaching is highly effective for pyritic sulfur removal, he leached the Indian coal with KOH 16% solution followed by acid treatment at 150°C, about 90% inorganic sulfur and 11% organic sulfur could be removed. He stated that demineralization of Indian coal was not found as high as with NaOH, because KOH treatment needs acid treatment followed by the alkali treatment, only potassium hydroxide could not remove that sufficient amount of pyrite, also potassium aluminosilicate is formed, and traces of potassium remains with coal (Samit Mukherjee and Borthakur 2003). The similar phenomenon was observed by the Sharma (Sharma and Gihar 1991). The pyrite removal by NaOH leaching was also observed by Li and Cho, it was found that more than 70% of pyritic sulfur in Pittsburgh No. 8 coal was removed at the conditions of 0.4 M hypochlorite, 0.4 M NaOH, and 90 °C, 37.8% of organic sulfur in Illinois No. 6 coal was removed at the conditions of 0.4 M hypochlorite with room temperature, followed by hydrolysis at 0.3 M NaOH and at 90 °C (Xia and Xie 2017). Mursito performed leaching under pressure (hydrothermal treatment) of Banten Indonesian high sulfur coal. The total sulfur was reduced up to 70% by hydrothermal processing without the addition of NaOH during the desulfurization process. However, after the addition of 0.025 mol/g concentration of NaOH, the total sulfur content was reduced from 3.1 to 0.3 %, which showed a 90% reduction in the total sulfur content (Mursito, Hirajima, and Sasaki 2011).

Waugh (Waugh Aand Bowing 1984) used the method of pressure leaching on the coal with 2.5 molarity of NaOH solution at 200°C with particle size of 200µm for 40 minutes, he achieved 90% demineralization. Michael has worked on the mechanism of organic sulfur removal from coal by sodium hydroxide NaOH, he observed that alkali metal cation are more effective to decompose the thiophenes and furan of organic sulfur present in the coal, hence the alkali hydroxide has ability to remove not only pyritic sulfur but also organic sulfur (Nowak et al. 1989). Oxidative desulfurization is promising technology for removing sulfur from coal at lower temperature and in economical way (Saikia, Khound, and Baruah 2014). Oxidative desulfurization is an effective way to remove most of the pyritic sulfur as well as organic sulfur (Taylor, n.d.),

The reaction of pyritic desulfurization is given by the equation 1 and 2. In first step pyrite reacts with dissolved oxygen and forms the precipitate layer of hematite and sulfuric acid, then sulfuric acid immediately neutralizes with alkali (NaOH) and produces sodium sulfate and water. The sodium sulfate is soluble in water and hematite forms precipitate in the solution.

Pyrite is naturally effective to react with water and oxygen (Chiri and Schlegel 2017). Chuang (Taylor, n.d.) reported that rate controlling step is the diffusion of oxygen through the product hematite (Fe_2O_3) layer at temperature from 120°C to 180°C and partial pressure of oxygen from 0.41MPa to 1.04MPa.

It was also observed by J.E Andersen (Andersen, Halpern, and Samis 1953) while he was leaching the galena with sodium hydroxide he concluded the kinetics of chemical reaction that, reaction of metallic sulfide (PbS) with Oxygen is in first step, while neutralization with alkali sodium has secondary effect on kinetics of reaction arising from its influence on the solubility and transport of oxygen with in the solution, and also hydrate (water) is the product of the reaction due to the neutralization. He calculated the activation energy for the reaction to be 6300 calory per mole.

K C(Chuang, Markuszewski, and Wheelock 1983) Chuang leached the American coal in oxygen and in air by oxidation in alkaline (NaOH) solution. He observed that rate of reaction (oxidation reaction) was proportional to the oxygen partial pressure, hence he decided that in first step pyrite reacts with oxygen forms hematite and sulfuric acid and then immediately this acid is to be neutralized with alkali, the reaction was first order reaction. Tao has performed the reaction between pyrite and dissolved oxygen in water and calculated the , the activation energy was 12.2Kcal/mole (Tao, Graves, and Wheelock 1977) for chemical reaction between the dissolved oxygen and pyrite. Same observations were found by C Y Tai, he leached the coal with sodium carbonate in dissolved oxygen. He also observed that oxygen reacts with pyrite in first step and then alkali neutralized the sulfuric acid produced with pyrite and oxygen reaction. Mketo (Mketo, Nomngongo, and Ngila 2017) performed the leaching of South Africa coal with sodium hydroxide and hydrogen peroxide (as oxidative agent) and found that it could reduce the sulfur of raw coal up to 55% .

JB Joshi (Стрыков and Леванюк 1983) has observed that pyrite oxidation reaction is the intrinsic chemical reaction between the dissolved oxygen and pyrite, he calculated the activation energy as 35×10^3 KJ/mole. He observed that the fine particle size requires less reaction time for the conversion of pyrite as compared to coarse particle size. The desulfurization of coal with oxidative method highly reduces its corrosive effects (Ahmad et al. 2019)

Organic sulfur

Although the alkali leaching either alone or with dissolved oxygen is very effective for pyritic sulfur removal, yet it can also remove the organic sulfur, in this work about 78% organic sulfur could be removed (at alkali concentration of 0.25 molarity, partial pressure of oxygen of 200 psi, reaction time of 4 hours, at temperature 120°C, and with particle size of 40µm).. Ca Michael (Nowak et al. 1989) worked on the mechanism of organic sulfur removal from coal by sodium hydroxide NaOH, he observed that alkali

hydroxide containing large alkali metal cation are more effective in decomposition of thiophenes and furan of organic sulfur present in the coal. B.R Utz (Utz, Friedman, and Soboczenski 1986) found the chemistry of molten alkali hydroxide for organic species in the coal. He used the mixture of NaOH and KOH to study the organic sulfur species in the coal, he selected benzothiophene and dibenzothiophene as model compounds that simulated the organosulfur compounds in the coal. He analyzed, the mechanism of desulfurization involves thiophene ring opening to form an aromatic thiol that produces desulfurization process, desulfurization was accrued by sodium thiophenolate or potassium thiophenolate although water has minimum or no role in the organic sulfur removal.

Most of the oxygen that reacts with the organic matrix remains attached as hydroperoxides and their decomposition products. Lui(Liu et al. 2008) achieved the removal of 73% organic sulfur, and 83% pyritic sulfur by alkali leaching of Yangzhou (Eastern China) in dissolved oxygen and then further treated with acid reflux. He stated that loss of organic sulfur may be occurred due to removal of thiols compounds present in the coal that are very attractive to oxidation, they are easily converted to the disulfides under basic condition. He observed that mostly organic sulfur compounds on oxidation produces sulfoxides, sulfones, sulfonic acids, sulfonic acid and sulfenic acid depending upon the nature of organic compound and oxidizing agent and conditions, although S=O group is common in the oxidized products. M. Kozloski(Kozłowski, Wachowska, and Yperman 2003) observed that C-S breaks and aliphatic thiols forms as precipitation in the solution (but these aliphatic thiols are different from the thiols that are present in organic sulfur) further these aliphatic thiols are to be converted into the soluble sulfides. He concluded and practically proved that coal do not contains the non-volatile aliphatic thiols. He worked on the Spanish coal Maquinna and American coal Illinois No.6, and leached the coal with potassium liquid ammonia solution. A detail mechanism of oxidation of organic disulfides was investigated by the Rois Benassi(Benassi, Fiandri, and Taddei 1997) he stated that oxidation of organic disulfides proceeds via steps of intermediates leading to sulfonic acid as final product, also desulfurization of coal thiols carried out in similar manner. Oxidative leaching is effect for removing the all types sulfur up to higher percentage.

2. Materials And Method

Coal was collected from the site of Thar coal, lumps were crushed in jaw crusher, the crushed coal was dried in an oven at 110°C and then ground in ball mill to get pulverized coal. The pulverized coal was screened through standard sieving process to get different particle size from 30µm-40µm to 200µm-400µm. A basic solution of NaOH was prepared in distilled water with different concentrations from 0.1Molarity to 1Molarity for different runs of the experiment.

Raw coal was characterized by ultimate and proximate analysis and heating values to study the coal. The sulfur was determined by D2492, proximate analysis by D7582, Ultimate analysis by D3176, and gross calorific value of coal by D5868, that was 3624.55(Kcal/Kg). At the end raw coal and products were characterized with thermogravimetric analysis, and Testo smoke number to study the combustion behavior of coal.

An isothermal hot jacketed tank reactor was used to perform this reaction, manufactured by Edibon International. The total capacity of the reactor was about 3 lit. The tank was jacketed with hot paraffin oil circulation to achieve and maintain the required temperature. The hot paraffin oil was circulated by centrifugal pump fixed at the base unit and was heated by immersed electrical heater in hot oil tank. A three-stage agitator was immersed into the reactor tank to agitate the solution, powered by a motor with speed regulator. Reactor tank has different valves for Oxygen, for reactant inlet, for product outlet and for sampling. In this experiment the solution and raw coal were fed manually. The temperature of circulating oil and reacting solution were taken with thermocouple and their reading was displayed on attached computer. The flow rate of oxygen was measured by rotameter installed in equipment.

Pulverized coal and prepared basic solution were poured into the reactor manually from the top of the reactor tank. The heater was kept on heating circulating oil until the reaction temperature was achieved and oxygen flow was started. The reaction time for the process was different for each run. As soon as the reaction was achieved, circulation of hot oil, gas flow and agitator all were turned off and solution was cooled at room temperature and product was withdrawn from the reactor. The solution was filtered with grade 1 filter paper to separate filtrate liquid and coal cake. Coal was washed with distilled water and air-dried for 24 hours and then oven dried at 110°C and then characterized in laboratory.

Table 1 Ultimate and proximate analysis of Thar raw coal

Proximate Analysis				Ultimate Analysis							
M	C	V	A	C	N	H	O	Sp	Ss	So	St
16.84	33.13	24.53	18.19	55.59	0.84	2.05	33.86	1.78	0.1	0.3	2.17

Moisture is on air dried basis, and C, N, H, and O are on dry and ash free basis

3. Results And Discussion

3.1. Effect of alkali concentration

A series of runs were conducted to observe the effect of alkali concentration on desulfurization of Thar coal. The pulverized coal of particle size 40µm was treated with the different concentrations of NaOH taken from 0.1Molarity to 0.4Molarity. Temperature was kept constant at 120°C while reaction time was maintained for 1.5 hour, the dissolved oxygen partial pressure was 50 psi and 100 psi respectively. It was observed that pyritic sulfur reduction while treating only with distilled water was 34%. The maximum pyrite removal was about 67% at 0.25M and 50 psi partial pressure of oxygen. Furthermore, at 100 psi pyritic removal was about 70.3% and total sulfur removal was improved from 51% to 55.5%. Organic sulfur reduction was 32% at 50 psi and 0.25M and increased up to 35% sulfur reduction at 100 psi and at 0.25M. The maximum sulfate sulfur reduction was 35% at 100psi and 0.25 Molarity as shown in figure 2(a) and figure 2(b). Maximum sulfur reduction was occurred at 0.25 molarity of NaOH and further

increase in molarity of NaOH showed decrease in sulfur reduction. Hence the 0.25 Molarity of NaOH was found as optimum value for alkali concentration for this reaction.

It was observed that rate of coal desulfurization was increased with increase in concentration of alkali solution till optimum value of 2.5 Molarity of NaOH, and at higher concentration of alkali, the sulfur content in coal starts to increase, means the desulfurization tends to reduce as shown in figure 3(a) and figure 3(b). Similar behavior was observed by the Mukherjee (S. Mukherjee and Borthakur 2001), while leaching the Makum (Assam India) coal with different concentrations of NaOH, he found demineralization of coal was increased with increase in alkali concentration, till optimum value and then it tends to reduce due to formation of $[\text{Na}_a(\text{AlO}_2)_b(\text{SiO}_2)_c \text{NaOH} \cdot \text{H}_2\text{O}]$ sodium aluminosilicate precipitates. E. Andersen reported the decrease in demineralization degree due to increase in alkali concentration after optimum values owing to less solubility of oxygen at higher concentration of alkali (Andersen, Halpern, and Samis 1953). He performed the oxidative sodium hydroxide leaching on galena crystal from ViolaMac mines Sardon and observed that solubility of oxygen reduced at higher concentration of NaOH. TD Wheelock performed leaching of US coal in dissolved oxygen, and observed that desulfurization increases with increase in alkali concentration till optimum value (0.35 Molarity of sodium carbonate), and then at higher value of alkali concentration it tends to reduce rapidly (Wheelock 1981).

Mukherjee had reacted the Boragolai and Ledo (Indian) coal with sodium hydroxide, he observed that the desulfurization of coal increases with increase in alkali concentration from 2% to 8% NaOH solution, while at 16% it starts to decrease in Boragolai coal. He also noted that NaOH was more effective for pyritic sulfur removal as compared to organic and sulfate sulfur removal (Samit Mukherjee and Borthakur 2004).

3.2. Effect of reaction time

A series of different experiments were performed to study the effect of oxidative leaching time on Thar coal desulfurization. During reaction (leaching), coal particle size was 40 μm , molarity of NaOH was 0.25, the temperature was 120°C. While oxygen pressure was fixed at 50psi and 100psi for each run respectively. And reaction time was from half hour to 4 hours, eight experiments were conducted with difference of 30 minutes to study the behavior of reaction time on desulfurization. It was observed that influence of time on sulfur removal was uniform, i.e. with increase in reaction time, desulfurization was also increased. Although the rate of desulfurization in pyrite was higher than that of organic and sulfate sulfur reduction as shown in figure 4(a) and figure 4(b).

At maximum time of 4 hours, around 72.6% pyrite was reduced at 50psi, and 74% pyrite was removed at 100psi. Maximum organic sulfur reduction was 48% and sulfate sulfur reduction was 50%. And total sulfur reduction was achieved up to 62.8% as shown in figure 5(a) and figure 5(b).

The behavior of higher sulfur reduction due to higher reaction time was also investigated by Mukherjee and Borthakur (Samit Mukherjee and Borthakur 2004). He noted that rate of desulfurization was increased with increase in leaching time. Rehman and Waqar (Rehman et al. 2018) observed the similar

effect in leaching the Chola Saidan Shah coal, they used the Quadratic module response (ANOVA) to analyze their experimental data. They observed that increasing the reaction time increases the degree of desulphurization, he concluded his results that when coal particle remained within the hot alkali solution for longer time the more sulfur removal occurred. Husein Kara (Kara and Ceylan 1988) treated four Turkey coals (Beysehir, Dadagi, Ermenek and Ilgin) with NaOH. He observed that Dadagi coal and Beysehir coal showed increase in desulfurization of coal with increase in treatment time.

M. Guru (Ahmad et al. 2019) leached the Turkey Askale coal with nitric acid as oxidant agent and he observed that desulfurization increased with increase in leaching time, concentration of nitric acid was 65% the optimum leaching time was 16 minutes and he removed about 40% sulfur from Askale coal.

3.3. Effect of particle size

Four experiments were conducted to observe the effect of particle size on desulfurization. Different particle size for each experiment were selected ranging from 40 μ m to 400 μ m and all other parameters were kept constant. The partial pressure was 100 psi, treatment time was 2 hours, NaOH concentration was 0.25 Molarity, and temperature was 120°C. It was observed that desulfurization decreased with increase in Thar coal particle size, or in other words at smaller particle size, the rate of desulfurization was higher. The amount of sulfur content with respect to the particle size is shown in figure 6.

Joshi observed that the fine particle size requires less reaction time for the conversion of pyrite to ferric oxide as compared to coarse particle size (Струков and Леванюк 1983). Faraz Anwar (Anwar et al. 2020) leached the coal (from Jehlum district) with potassium hydroxide with different particle size from 60 to 220 meshes, he observed that when particle size was decreased the rate of desulfurization was increased, he removed as maximum as 75% of total sulfur. Pattarapan (Prasassarakich and Thaweessri 1996) treated the Mae Moh coal (from Lampang Thailand) with sodium Benz oxide, he also observed that amount of desulfurization increases with decrease in particle size, he used the particle size from 250 μ m to 850 μ m, temperature from 190 °C to 250°C. He was able to remove sulfate and pyritic sulfur from 65% to 85%. However organic sulfur removal was up to 30%. He concluded that rate of reaction was inversely proportional to the coal particle size, he also observed that mass transfer rate was inversely proportional to square root of coal particle size, however an optimum particle size should be decided for desulfurization, because a sufficient amount of energy is required for grinding and weighing of coal during size reduction. Chuang (Chuang, Markuszewski, and Wheelock 1983) observed that Time for complete conversion of FeS₂ to hematite depend up on the square root of particle size. Guru(Gürü, Sariöz, and Çakanyildirim 2008) performed the leaching of Turkey coal with H₂O₂ as oxidative agent, he observed that rate of desulfurization was decreased with increase in particle size, the minimum particle size in his experiment was 0.25mm and larger was 0.45mm and the reaction time was 12 hours.

3.4. Effect of temperature

The effect of temperature on desulfurization of Thar coal by oxidative alkali treatment is shown in figure 7(a) and 7(b), different experiments were conducted to investigate the effect of temperature on

desulfurization. It was observed that degree of desulfurization was increased with increase in temperature till an optimum value, then it tends to reduce. The optimum value for temperature was 120°C and other parameters were; particle size 40µm, time was 1.5 hour and 3 hours, partial pressure of oxygen was 100 psi and agitation speed was 700rpm, flow rate of oxygen was 1.2 liters per minute, the ratio of Thar coal to alkali solution was 50 grams of coal in 500 ml of alkali solution, the maximum sulfur reduction was observed at temperature of 120°C.

At 1.5hour pyrite sulfur reduction was about 70.3%, organic sulfur reduction was 44%, sulfate sulfur was 35% while total sulfur reduction was achieved about 57%. Although at 3 hour time and at 120°C temperature the pyritic sulfur reduction was improved up to 80.6%, organic sulfur reduction up to 66% and sulfate sulfur up to 45%, while total sulfur was reduced up to 70% as shown in figure 8 (a) and 8 (b). The decrease in desulfurization at higher temperature (more than 120°C) may be due to the lower solubility of oxygen at higher temperature as reported by T.D Wheelock (Wheelock 1981). The similar effect was observed by Waqas Ahmed (Ahmad et al. 2019) that desulfurization of coal was increased till an optimum value and then it tends to reduce, he selected the Lakhra coal for his study, he treated the Lakhra coal with three different alkali compounds sodium hydroxide, sodium carbonate, and potassium hydroxide at different concentrations, time and temperatures. He investigated that its optimum temperature was 40°C and about 50% sulfur was removed at that temperature, although at higher temperature desulfurization tends to reduce. This behavior of temperature was also observed by Semra Karaca (Karaca and Akyu 2003), he leached the Askale Turkish coal with nitric acid as an oxidative agent at different temperatures and observed that desulfurization was increased with increase in temperature and it was started to reduce at higher temperature. He found that the optimum temperature was 103°C at 25% solution of nitric acid. He investigated that at higher temperature the leaching agent starts to destroy. At initial stage an increment in desulfurization with increase in temperature was observed and then an equilibrate was observed by Zhiling Li (Li, Sun, and Jia 2010).

3.5. Effect of partial pressure of oxygen

The partial pressure shows a great influence on the desulfurization, a sufficient reduction in all pyritic, sulfate and organic sulfur was observed at higher value of partial pressure of oxygen. About 5 different experiments were conducted to study the behavior of oxygen partial pressure. The pressure of oxygen was from 25 psi to 200 psi, while other parameters were constant as; temperature was 120°C, concentration of NaOH was 0.25Molariy, particle size was 40µm, reaction time was 3 hours, oxygen flow was from 1liter per min to 2.5 liter per min (different for each value of oxygen pressure), agitation speed was 700 rpm, and Thar lignite coal to solution ratio was 50 grams of coal to 500ml of NaOH solution.

It was investigated that the higher the value of oxygen partial pressure, lower the value of sulfur in processed coal (higher rate of desulfurization). Although the pyritic sulfur reduction was higher than that of organic sulfur and sulfate sulfur. The behavior of sulfur reduction with respect to the oxygen partial pressure was uniform as shown in figure 10. About 88% pyritic sulfur was removed at 200psi partial

pressure of oxygen, organic sulfur reduction was achieved up to 74%, while sulfate sulfur removal was about 50% and around 79.8% of total sulfur was removed at that pressure as shown in figure 9.

The related behavior was observed by Chaung (Taylor, n.d.), that when the oxygen partial pressure was raised the conversion rate of pyrite to hematite was also increased. He leached the iron pyrite (of Lova state) with sodium carbonate in dissolved oxygen (and also with water and dissolved oxygen) he found more than 75% sulfur from pyrite was removed. He concluded that the rate of desulfurization of pyrite depends up on the overall rate of diffusion of dissolved oxygen. This study also showed temperature effect at two different oxygen partial pressures indicated that more organic sulfur was removed at the higher oxygen partial pressure than that at the lower oxygen partial pressure. These results suggested that oxygen partial pressure has an important effect on the removal of both organic and inorganic sulfur.

The agitation speed has also great influence on the desulfurization. To study the effect of agitation speed Thar coal was leached with 0.25 Molarity of NaOH, leaching time was 3 hours and oxygen partial pressure was 100 psi, the oxygen flow rate was 1.2 liters per minute, leaching temperature was 120°C, ratio of raw Thar coal to NaOH was 50grams in 500 ml of solution and particle size was 40 µm, the speed of agitation was different for each experiment ranged from 150 rpm to 2000 rpm. At 2000 rpm the pyritic sulfur reduction was achieved about 78.8% and sulfate sulfur reduction was about 60% while organic sulfur reduction was observed as 58% and total sulfur reduction was achieved up to 70% as shown in figure 12.

It was observed that with increase in agitation speed from 150 rpm to 1500 rpm the rate of desulfurization was also increased and above 1500 rpm it became constant and did not change as shown in figure 11. Hence 1500rpm was found to be an optimum speed of agitation. Sulfur reduced slightly in organic as well as in sulfate sulfur, while in pyritic sulfur, great sulfur reduction was observed. Ali Ahmed (Ahmed et al. 2008) leached the Lakhra coal with Hydrogen peroxide (H_2O_2) and nitric acid was used as Oxidative agents for desulfurization of coal, he investigated that desulfurization of coal was increased with increase in rate of agitation. K Chuang (Chuang, Markuszewski, and Wheelock 1983) treated the American coal with dilute sodium carbonate solution in dissolved oxygen under pressure, he studied the effect of agitation on desulfurization rate, he observed that coal desulfurization was increased rapidly with increase in agitation.

Optimize Reaction

After getting the optimum value of each factor an optimize reaction was performed to get the practical optimized value of sulfur removal from Thar coal, in this reaction the temperature was 120°C, partial pressure of oxygen was 200 psi, reaction time was 4 hours, particle size was 4µm and agitation speed was 1500 rpm. After lab analysis of product coal, pyrite sulfur reduction was achieved up to 90.3% (0.17% pyrite was left in processed coal), and organic sulfur was removed up to 78% (0.11% organic sulfur left in processed coal) and sulfate sulfur removal was up to 50%, while total sulfur removal was achieved up to 82%, and the processed coal contained only 0.83% total sulfur. This data shows that

oxidative alkali leaching is very effective for the pyritic sulfur removal as well as for organic sulfur removal and amount of sulfate sulfur was also reduced to half.

TGA of raw coal and processed coal

Desulfurization of coal effects on the combustion behavior of coal (Ken et al. 2018), thermogravimetric test is well known technique to identify the various important changes in combustion of coal owing to coal desulfurization (Gundogar and Kok 2014), TGA gives the mass of fuel changes during combustion as a function of time, to study this variation the raw coal and processed samples were characterized by TGA test as shown in figure 13.

A raw coal and three processed samples were selected for this study. Sample 1 was coal that was treated at optimum temperature 120°C for three hours, having the composition as; pyrite sulfur 0.34%, sulfate sulfur 0.14%, organic sulfur 0.17%, and total sulfur 0.65%. Sample 2 was processed coal that was treated at optimum pressure of 200psi, its composition was; pyrite sulfur 0.21%, sulfate sulfur 0.1%, organic sulfur 0.13% while total sulfur was 0.44%. And sample 3 was the processed coal that was treated under optimized conditions with composition as; pyrite 0.17%, sulfate sulfur 0.1%, organic sulfur 0.11% and total sulfur 0.38 %.

It was observed that in raw Thar lignite coal a little amount of mass loss was observed up to the temperature of 150°C, this mass loss was due to the decomposition of light volatile matters, as observed by Kulnil (Cong et al. 2019) and then shows the static behavior (no slope in TGA graph) of coal till the temperature reached 400°C, that showed the thermal stability (Sikarwar et al. 2018)(Marinov et al. 2010) of Thar lignite till 380°C. After 380°C mass of coal was rapidly reduced, about 75% coal mass lost as the temperature was further raised about 300°C (up to 680°C), this was owing to rapid combustion of coal between 380°C to 680°C, this mass loss was due to release of volatile matter and burning of coal and this demonstrate coal combustion region or primary reaction region in TGA test as reported by Kok (Ozbas, Kök, and Hicyilmaz 2002). Hence the peak combustion temperature of Thar lignite was 380°C, after that temperature the Thar coal started to degrade. While in processed coal loss of mass with rise in temperature was smooth as compared to raw coal. Kok and Hicyilmaz observed that coal leaching showed the significant effect on the coal combustion, they studied the raw and cleaned coal by TGA characterization and found that the coal leaching reduced the peak combustion temperature and showed the smooth mass reduction with the temperature increase. The similar behavior was observed by Bhupendra (Ken et al. 2018) while examining the TGA analysis of raw Indian coal and processed coal with KOH of various concentrations, he observed that coal mass was rapidly lost from temperature 330°C to 520°C, while coal samples that were processed with KOH for longer time showed some uniformity of mass loss per temperature rise.

Testo smoke number

The raw coal and treated coal were characterized with testo smoke number to study the difference in combustion smoke of raw coal and two samples of treated coal. Sample 1 was treated at optimum pressure of 200psi with composition as; pyrite sulfur 0.21%, sulfate sulfur 0.1%, organic sulfur 0.13% and total sulfur 0.44%. And sample 2 was treated under optimum condition, its composition was; pyrite 0.17%, sulfate sulfur 0.1%, organic sulfur 0.11% and total sulfur 0.38 %.

The Thar coal was characterized with testo smoke number. Initially the smoke number of raw Thar coal was 2, but after 5 minutes it became 6, and after 10 minutes smoke of raw coal was totally black and was measured as 9 on testo smoke number, hence it reached the highest number of coal smoke. Similarly, the testo smoke number of processed coals was also observed, initially the testo smoke number of sample was 1 after five minutes the smoke number became 4 and after ten minutes the smoke number was reduced to 3 and the sample was very clean than that of raw Thar coal. Sample 2 also showed similar results initially but after five minutes the smoke number was 5 and then after ten minutes it became 3. So the testo smoke number showed that smoke property of processed coal was enhanced and the coal become environmental friendly.

4. Conclusion

Desulfurization of coal by alkali oxidative leaching under pressure was found to be very effective, about 90.3% pyritic sulfur was removed and other sulfur contaminations types present in coal as organic sulfur was removed up to 78% and sulfate sulfur was removed 50% and total sulfur removal was up to 82.5%. Hence a sufficient amount of sulfur reduction was achieved.

As the reaction starts pyrite reacts with water and oxygen to form the hematite and sulfuric acid, this sulfuric acid immediately neutralizes with sodium hydroxide (NaOH) and forms sodium sulfate precipitate (noncombustible sulfur) and water molecules. Oxygen plays an important role in chemical reaction, and is responsible to convert the pyrite to hematite, owing to this maximum amount of pyritic sulfur and total sulfur was removed at higher amount of oxygen partial pressure. While studying the effect of various factors individually, almost in every case pyritic sulfur was removed in greater amount than that of sulfate or organic sulfur.

Desulfurization was maximum at higher values of reaction time, partial pressure of oxygen and agitation speed. The value for partial pressure for maximum desulfurization was found to be 200psi, reaction time 4 hours at agitation speed of 1500rpm. Although desulfurization was observed to be greater with smaller particle size. Optimum value for NaOH concentration was 0.25Molarity and that of temperature was 120°C.

Thermogravimetric and smoke properties of processed coal were also improved.

Declarations

Conflict of interest

Authors declare that there is no conflict of interest with editor and with the reviewer.

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Figures

Figure 1

Flow diagram of alkali oxidative leaching of Thar coal

Figure 2

(a) Sulfur removal % from Thar lignite coal at 2.5 Molarity of NaOH, temperature at 120°C, Oxygen partial pressure 50psi, leaching time 1.5 hours (b) Sulfur removal % from Thar lignite coal at 2.5 Molarity of NaOH, at 120°C, Oxygen partial pressure 100psi, leaching time 1.5 hours

Figure 3

(a) Effect of concentration on Sulfur removal at partial pressure of oxygen 50psi, temperature 120°C, particle size 40µm (b) Effect of concentration on sulfur removal at partial pressure of oxygen 100psi, temperature 120°C, particle size 40µm

Figure 4

(a) Effect of reaction time on desulfurization, at partial pressure of oxygen 50psi, particle size 40 μ , NaOH concentration 0.25Molarity, temperature 120°C and at 500grams in 50ml solution of NaOH (b) Effect of reaction time on desulfurization, at partial pressure of oxygen 100psi, particle size 40 μ , NaOH concentration 0.25Molarity, temperature 120°C and at 500grams in 50ml solution of NaOH.

Figure 5

(a) Sulfur removal % at maximum reaction time 4-hour, partial pressure of oxygen 100psi, particle size 40 μ , NaOH concentration 0.25Molarity, temperature 120oC. (b) Sulfur removal % at maximum reaction time 4-hour, partial pressure of oxygen 50psi, particle size 40 μ m, NaOH concentration 0.25Molarity, temperature 120oC.

Figure 6

Effect of particle size on desulfurization of Thar coal at partial pressure of oxygen 100psi, NaOH concentration 0.2Molarity, temperature 120oC and coal to solution ratio 50grams in 500ml solution of NaOH, reaction time was 2 hours

Figure 7

(a) Effect of temperature on desulfurization of Thar coal at partial pressure of oxygen 100psi, NaOH concentration of 0.2Molarity, agitation speed 700 rpm, flow rate of oxygen 1.2 liter per minute, particle size 4 μ m, coal to solution ratio was 500grams in 50ml of solution of NaOH, reaction time was 1.5 hours.

(b) Effect of temperature on desulfurization of Thar coal at partial pressure of oxygen 100psi, NaOH concentration of 0.2Molarity, agitation speed 700 rpm, particle size 4 μ m, reaction time was 3 hours.

Figure 8

(a) Sulfur removal % at optimum reaction temperature of 120°C, partial pressure of oxygen 100psi, particle size 40 μ m, NaOH concentration 0.2Molarity and reaction time 1.5 hours.

(b) Sulfur removal % at optimum reaction temperature of 120°C, partial pressure of oxygen 100psi, particle size 40 μ m, NaOH concentration 0.2Molarity and reaction time 3hours.

Figure 9

Sulfur removal % at maximum partial pressure of oxygen of 200psi, particle size 40 μ m, NaOH concentration 0.25 Molarity and reaction time 3hours, temperature of 120oC, reaction time 3 hours

Figure 10

Effect of oxygen partial pressure with NaOH concentration 0.2Molarity, particle size 4 μ m, reaction time 3 hours, reaction temperature 120oC

Figure 11

Effect of agitation speed on desulfurization of Thar coal at NaOH concentration 0.2Molarity, particle size $4\mu\text{m}$, coal to solution ratio 50 grams in 500ml solution of NaOH, reaction time 3 hours, leaching temperature 120°C

Figure 12

Sulfur removal % at maximum agitation speed 1500 rpm, oxygen partial pressure of 100psi, particle size 40 μ m, NaOH concentration 0.25 Molarity, reaction time 4hours, reaction temperature 120oC,

Figure 13

Sulfur removal % by optimized reaction at maximum agitation speed 2000 rpm, partial pressure of oxygen of 200psi, particle size 40 μ m, NaOH concentration 0.25 Molarity, reaction time 3hours, reaction temperature of 120oC.

Figure 14

Thermogravimetric analysis of raw Thar coal and processed coal

Figure 15

Testo Smoke number of raw Thar coal and processed coal