Coal Desulfurization by Solvent Leaching Methods

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ABSTRACT

Coal desulfurization prior to usage is a preprocessing in order to achieve clean fuel and reduce environmental impacts such as acid rain. Desulfurization of Lakhra (Pakistan) coal was conducted with different solvents. Coal was leached with different solvents like hot water, H_2O_2/H_2SO_4 and HNO_3. It was found that the effects of the leaching temperature, agitation time and particle size on the removal of different forms of sulfur are very significant. Sulfur recovery increases with agitation time, temperature and mesh number up to a certain optimum value and then have a different trend.

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Introduction

Coal is the most important nonrenewable energy source of fossil origin. It is also the most common fuel in thermal power plants [1].

In recent years, with the rising prices of crude oil and natural gas and shortage of oil and gas resources, worldwide energy industries have been focusing on accelerating the development of coal chemical industry [1]. The coal chemical industry can make a significant contribution in the sustainable development of some countries' energy resources in the next twenty years, and will thereby reduce environmental pollution caused by coal burning. It will also reduce dependency on oil and gas as energy sources.

Coal usually contains significant quantities (normally more than 10%) of different impurities such as sulfur, silicates, carbonates etc., [2]. Harmful effects on agricultural products, corrosion of metal structures and respiratory problems of humans and animals are undesirable effects of sulfur [1] and its compounds in coal. Therefore, it is essential to reduce sulfur and mineral matter (ash) from coal prior to usage in many applications.

Pakistan has emerged as one of the leading country - seventh in the list of top 20 countries of the world after the discovery of huge lignite coal resources in Sindh [3]. Economists say that the energy demand over the next 5 years is expected to grow at a rate of 7.4 % per annum [3]. It may be noted that in India the share of coal is as high as 54.5% in the total energy mix [3]. To meet the future requirements of the country with indigenous resources, domestic exploration would have to be intensified to increase the share of coal from 5 to 25% by 2020 [3].

Having so much large reserves of coal, Pakistan is facing energy crisis because coal is not being utilized. The main reason is that during coal incineration in power plants, high sulfur content of coal poses serious environmental problems owing to sulfur dioxide emission. Combustion of fossil fuels such as coal in thermal power plants releases SO_2, which is formed by oxidation of sulfur present in coal. Oxides of sulfur undergo photochemical oxidation in the atmosphere, to be eventually converted into sulfuric acid. The acids when washed by rain make the rainwater acidic [1]. Total worldwide SO_2 emissions from coal utilization are 90 million ton/year [4].

Negative effects of 'S' present in coal:

Combustion of coal produces Pollutants (SOx and NOx) in addition to particulate matter. It causes acid rain which has harmful effects on lakes and vegetation, and cause corrosion. 'S' reduces heating value of coal. SOx reduce adiabatic flame temperature

Need for 'S' removal:

Sulfur is removed to sell coal to customers whether they have installed pollution control measures or not, to reduce transportation and combustion cost, and also to reduce load on flue gas scrubber.

Methods for removing 'S':

Demineralization and desulfurization of coal may be achieved by both physical and chemical methods. Some demineralization can be achieved by simple physical processes based on the differences in the physical properties of the mineral and carbonaceous parts of the coal [6].

Physical processes are cost effective methods but not effective in separation of the finely dispersed minerals and those bound to the coal structure. However, chemical method is known as being the solution for obtaining clean demineralized and desulfurized coal, which involves solubilization of inorganic constituents in various solvents [6].

The sulfur present in coal appears in pyritic, organic and sulfate forms [7]. The organic and pyritic sulfur contents are almost equally partitioned in many coals and the sulfate form is usually very small [7]. Pyritic sulfur refers to ferrous disulfide and is usually removed by physical separation methods such as froth flotation and gravity separation. Up to 50% of inorganic sulfur can be removed by the froth flotation process [7].

Organic sulfur is fixed in the chemical structure of coal and often much more difficult to remove than inorganic sulfur. Organic sulfur is partially removed by breaking its chemical bonds using chemical methods [7] and [8]. Meyers has summarized the structure of the organic sulfur in the coal which includes mercaptanes (RSH), disulfides (RS-S-R′), sulfides (R-S-R′) and thiophenes [7] and [9]. R and R′ represent hydrocarbon groups and for mercaptanes, R denotes aliphatic groups.

Leaching is one of the most common methods employed for coal desulfurization. Coal is mixed with acid or alkali and its sulfur is extracted while being heated or stirred. The type of reagent depends upon the type of sulfur in coal [2] and [10].

Various chemical processes are presently being developed employing agents such as hydrochloric acid [6] and [10], nitric acid [6], [10] and [2], sodium hypochlorite [7], hydrofluoric acid [11] and [12], potassium hydroxide [8] and [13] and sodium hydroxide [11] for the extraction of sulfur from coal.

The Meyers process uses P-cresol as a chemical solvent to reduce organic sulfur [14]. It used 3 h leaching with P-cresol at 100 °C to achieve 47% (average) organic sulfur removal for Indiana No.5 coal. Alvarez et al observed that using nitric acid led to rapid reduction of inorganic sulfur [15]. They reported that at high temperatures the oxidization capacity of coal increased and the oxygen of nitrate group appeared as carbonyl group in molecular structure of coal, indicating that the desirable characteristics and appearance of coal could be altered when leaching with nitric acid.

Bolet et al. studied the chemical demineralization of Turkish coal using different acids alone and 0.5N aqueous NaOH in combination with one or two of the acids [2]. At optimum approach for chemical cleaning of the coal (extraction with 0.5N NaOH followed by leaching with 10% HCl), the maximum degree of demineralization obtained being 46.8% [2].

The effect of mineral acids at different concentrations on desulfurization and demineralization of Indian coal has been investigated by Mukherjee et al. at ambient temperature and at 95 °C [16]. The results showed that HNO_3 leads to maximum (40.1%) and H_2SO_4 leads to minimum desulfurization of the coal samples. S.Karaca has undertaken leaching with nitric acid on a coal sample from Askal coal mine. In this experiment, the coal samples were dissolved in nitric acid and stirred at 25–103 °C for 0–3 h [15]. The highest sulfur reduction was observed at 25% HNO_3 concentration and at 103 °C (the boiling point of acid) [17]. Steel et al. investigated the leaching behavior of the mineral matter in coal toward aqueous HCl and HF [18]. They reported that HCl can dissolve simple compounds such as phosphates and carbonates, yet it cannot completely

dissolve the clays. HF reacts with almost every mineral in the mineral matter except pyrite and most of the reaction products are water-soluble [18].

Experimental work:

As discussed above, there are a lot of methods to remove sulfur from coal, but we selected pre-combustion desulfurization by solvent leaching method (see figure-1).

Sample: Lakhra (Pakistan) Coal

Table 1: Proximate Analysis

Moisture	7±0.5%
Volatile Matter	36±1%
Ash	37±1%
Fixed Carbon	20±2%

Table 2: Form of sulfur in coal

Form of Sulphur	Percentage in Coal
Total	37.5
Elemental	4.5
Pyrite	12
Sulphate	13
Organic	8

Calorific value= 4200cal/g coal

Characteristics of Solvent:

Solvent must be economical, readily available, efficient and easily recoverable for recycling.

General process scheme:
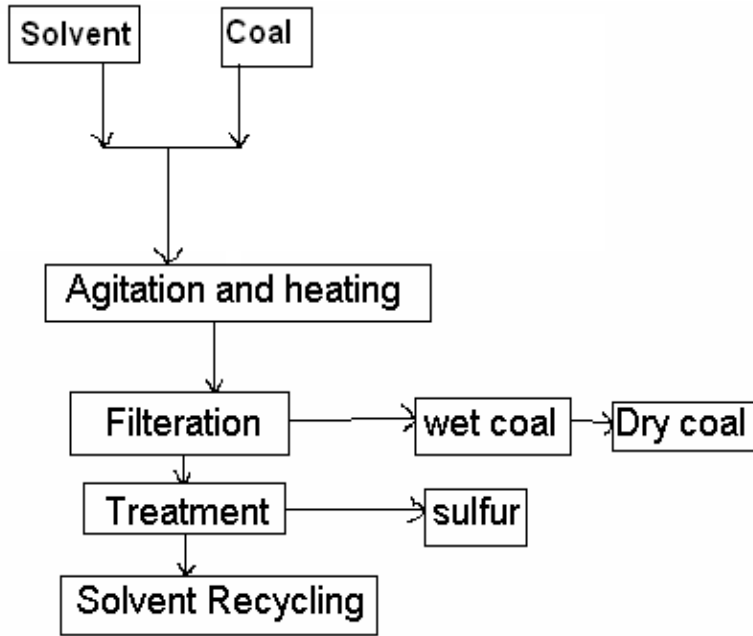
Figure 1: Block diagram of ´S´ recovery from coal by solvent leaching

Solvent used for Leaching of coal:

For leaching, hot water, H_2O_2/H_2SO_4 and HNO_3 were used according to their characteristics as discussed above.

Leaching with hot water:

Only 1% 'S' removed and it has no effect on calorific value of coal.

Leaching with H_2O_2/H_2SO_4:

H_2O_2/H_2SO_4 is for removal of any form of 'S' in coal. It acts as aqua regia (because this solvent dissolves all types of sulfur present in coal) for this case.
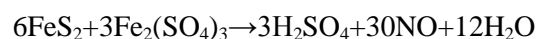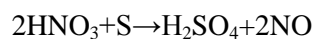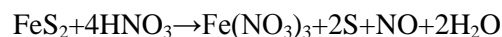
Experimental Scheme:

50 g coal was taken in beaker and it was leached with 25 ml H2O2 and 60 ml H2SO4 solvents. The system was agitated and heated for different intervals. After agitation and heating it was filtered and from where wet coal was separated. Wet coal was dried and same analysis was done.

Leaching with HNO_3:

HNO_3 is mainly for Pyrite 'S' and it has no significant effect on Calorific value.

<u>Reactions</u>:

$$FeS_2+4HNO_3 \rightarrow Fe(NO_3)_3+2S+NO+2H_2O$$

$$2HNO_3+S \rightarrow H_2SO_4+2NO$$

$$6FeS_2+3Fe_2(SO_4)_3 \rightarrow 3H_2SO_4+30NO+12H_2O$$

Results and Discussions:

With H_2O_2/H_2SO_4:

Effect of particle size:

To study the effect of particle size on sulfur removal from coal samples of the various particle sizes (+20, +40, +70, +100 and +200 mesh numbers) were leached at 80 °C for 1 h. Rate of extraction is proportional to the decrease in particle size.
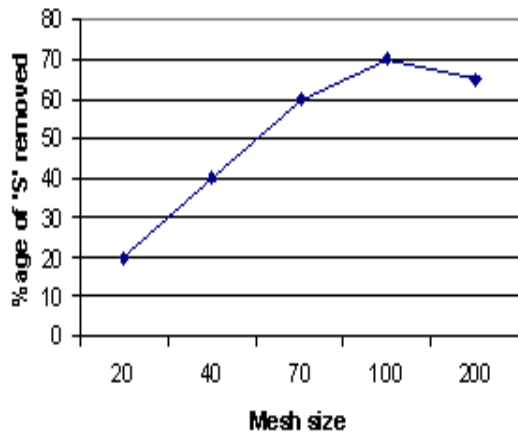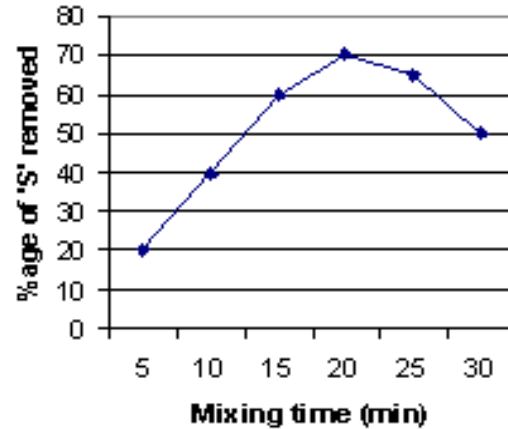

Figure 2: Effect of mesh size on %age of sulphur

From graph, It is clear that rate of extraction increases as mesh size increases but after specific mesh size, rate of leaching decreases. Particle size influences the extraction rate in a number of ways. The smaller the size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded, and separation of the particles from the liquid and drainage of the solid residue are made more difficult. It is generally desirable that the range of particle size should be small so that each particle requires approximately the same time for extraction and, in particular, the production of a large amount of fine material should be avoided as this may wedge in the interstices of the larger particles and impede the flow of the solvent.

Effect of mixing time:

To study the effect of mixing time on sulfur removal from coal samples of +70 mesh size (optimum size) were leached at 80 °C for 5min, 10min, 15min, 20min and 25min. Rate of extraction is proportional to the mixing time.
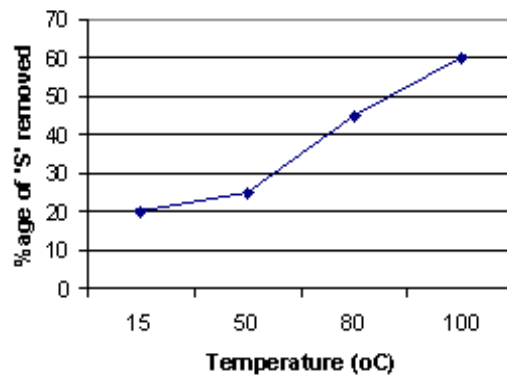
Figure 3: Effect on mixing time on %age of 'S' removed

From graph, It is clear that rate of extraction increases as mixing time increases but after specific mixing time, rate of leaching decreases. As agitation time increases, size of particles decreases due to collision of impeller of agitator with particles, since, rate of leaching increases. But after optimum mixing time, particles get smaller size as mixing time increases, since cause same effect as discussed above, so rate of leaching decreases.

Effect of Temperature:

To study the effect of temperature on sulfur removal from coal samples of +70 mesh size (optimum size) were leached for 20 minutes at (15, 50, 80 and 100)°C. Rate of extraction is proportional to the temperature.

As the temperature of the system increases, rate of leaching increases due to more easy diffusion of solvent into coal particles to extract sulfur from coal.

Figure 4: Effect of temperature on %age of 'S' removed

So, at optimum temperature (80°C), mixing time (20min) and mesh size (+70); results carried out are as follows:

Table 4: Percentage of sulfur removed

Form of Sulphur	Percentage of Sulphur removed
Total	65.2
Elemental	90
Pyrite	50
Sulphate	43.44
Organic	5

Calorific Value:

Before Treatment: 4200 cal/g coal

After Treatment: 3688 cal/g coal

This method is quite effective for removal of 'S' from coal but this cause reduce in calorific value of as shown above and also not favourable for pyrite 'S' removal. There are some areas where pyrite 'S' is in large amount. Since this solvent is not suitable for that coal. So, other alternative solvents are used to remove 'S' from coal, having no affect on calorific value of coal.

With HNO_3:

Approximately same effect of different factors as discussed above, on percentage of 'S' removed.

After treatment,

Calorific value: 4000cal/g coal

Table 5: Percentage of sulfur removed

Form of Sulphur	Percentage of Sulphur removed
Total	57.33
Elemental	44.44
Pyrite	83.33
Sulphate	55.38
Organic	21.25

This solvent has not much effect on calorific value of coal as well as much favourable to remove pyrite 'S' present in coal. Its also favourable for other types of 'S' but it is also not used to remove organic 'S' rich coal.

Conclusions:

The rate of sulfur recovery increased with increasing temperature, mesh number (decrease in particle size) and agitation time.

Table 6: Comparison of sulfur recovery by different solvents

Form of Sulphur	Percentage of Sulphur removed by hot water	Percentage of Sulphur removed by H_2O_2/H_2SO_4	Percentage of Sulphur removed by HNO_3
Total	1	65.2	57.33
Elemental	--	90	44.44
Pyrite	--	50	83.33
Sulphate	--	43.44	55.38
Organic	--	5	21.25

Coal was leached with different solvents like hot water, H_2O_2/H_2SO_4 and HNO_3. It was found that the effects of the leaching temperature, agitation time and particle size on the removal of different forms of sulfur are very significant. Sulfur recovery increases with agitation time, temperature and mesh number up to a certain optimum value and then have a different trend.

Particle size influences the extraction rate in a number of ways. The smaller the size, the greater is the interfacial area between the solid and liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid as already indicated. On the other hand, the surface may not be so effectively used with a very fine material if circulation of the liquid is impeded, and separation of the particles from the liquid and drainage of the solid residue are made more difficult.

As agitation time increases, size of particles decreases due to collision of impeller of agitator with particles, since, rate of leaching increases. But after optimum mixing time, particles get smaller size as mixing time increases, since cause same effect as discussed above, so rate of leaching decreases.

As the temperature of the system increases, rate of leaching increases due to more easy diffusion of solvent into coal particles to extract sulfur from coal

According to the experimental results obtained, more suitable solvent is HNO_3 as discussed above. For organic 'S', microbial methods may be employed because we have used inorganic solvents which are more efficient for inorganic forms of sulfur.

Acknowledgement:

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