Desulfurization of Tabas Coals Using Chemical Reagents

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ABSTRACT: *Large reserves of coal in Tabas region of Iran are characterized by low ash and high caking index, suitable for use in metallurgy as coking coal. However, these coals cannot be gainfully utilized because of their high sulfur content. In this work, studies on desulfurization of Tabas coals were carried out in a batch reactor using various reagents. The most effective reagents,* $Fe_2(SO_4)_3$, $FeCl_3$, *NaOH,* CH_3OH, HNO_3, *and* H_2O_2 , *were used to remove sulfur and ash from Tabas coals under reasonable pressure and temperature. Results obtained from coal desulfurization experiments using these reagents are presented in this paper. It was found that ferric sulphate is one of the suitable chemical reagent for desulfurization of Tabas coal which could be used to remove most of the fine distributed pyritic sulfur content.*

KEY WORDS: *Desulfurization, Coal, Sulfur, Chemical reagents, Caustic, Nitric acid, Ferric sulphate, Ferric chloride, Hydrogen peroxide, Methanol.*

INTRODUCTION

Desulfurization of coal is necessary, not only for minimizing the air pollution caused by emission of sulfur oxides during combustion, but also for increasing the coal quality for coke making. In steel making industry, the sulfur content of coke, sediments on the iron crystal surface make steel more brittle and decreases its plasticity property.

The effective precombustion desulfurization methods can be divided into; the physical, the chemical and the microbial. Physical treatment concentrates on the inorganic sulfur, while microbial processes are characterized by a relatively slow bacterial action, able to reduce organic sulfur. However, the chemical method, depends on the nature of coal involves the removal of inorganic and various types of organic forms of sulfur simultaneously.

Meyers proposed the following six types of reaction by which organic sulfur may be chemically removed from coal prior to combustion [1]:

1. Solvent partitioning
2. Thermal decomposition
3. Acid-base neutralization
4. Sulfur reduction
5. Sulfur oxidation
6. Nucleophilic displacement

In practice, the most successful processes developed to date for removal of organic sulfur from coal utilize oxidation or displacement reaction [2].

Chemical processes can also be used to convert pyritic sulfur into soluble forms. This is of particular value for pyrite which is too finely distributed to be removed by physical separation. The possible chemical

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1021-9986/06/2/59 8/$/2.08

reactions of pyrite are numerous, and include the following reactions:

1. Displacement reactions
2. Acid-base neutralization
3. Oxidation reactions
4. Reduction reactions

Oxidation reactions are primarily effective for pyritic sulfur removal. Oxidation based processes need to be selective for sulfur to be practical, as otherwise oxidation of the coal results in losses of heating value.

Both pyritic and organic sulfur can be removed by treatment with a strong base, either aqueous or molten. While reactions with a strong base are known to work well, the mechanisms and products of the reaction are complex and not well characterized [2]. Only the molten alkali method can remove both pyritic and organic sulfur virtually completely [3]. Molten caustic leaching (MCL) is one of the most effective methods for coal desulfurization, which uses a strong base in the absence of water at high temperature [4]. MCL removes almost all of the pyritic and sulfidic sulfur and about 90% of the thiophenic organic sulfur, while producing small amounts of elemental and sulfatic sulfur [5]. However, the MCL treatment is a harsh process, and results in a partial conversion of the coal to volatile and produce changes in the coal structure [6]. This process required high temperature and pressure, making the desulfurization process uneconomic for industrial uses. Therefore, the aqueous caustic process with lower operating conditions, which will have practical value, should be considered. Demineralization and desulfurization of high sulfur Indian coal was investigated by Mukherjee and Borthakur [7] using aqueous solution of sodium hydroxide followed by hydrochloric acid treatment, resulted in significant removal of mineral and sulfur from the coal. However, Chriswell, et al. [8] stated that during caustic wash unwanted carbonate by-products are formed which result in the loss of coal carbon, significant consumption of expensive caustic solution, and subsequent filtration problems during the reprocessing of spent caustic solutions.

Many different reagents have been used to attempt to selectively oxidize the sulfur in coal without excessively oxidizing the coal. Oxygen can be used but requires high temperature and pressure to obtain significant conversions. Other oxidizing reactants such as metallic salts, chlorine gas, nitrogen or sulfide dioxides, peroxides, organic peroxyacids, ozone or potassium permanganate can be used in milder conditions. But, these agents are more expensive than oxygen, and their consumption by the process is a major operating expense. Various chemical processes are presently being developed employing agents such as nitric acid [1], hydrogen peroxide [9], ozone [10], oxygen [11], chlorine [12], potassium dichromate [13], ferric salts [14], and cupric salts [15] for the extraction of pyrite. Potassium permanganate can reduce both organic and pyritic sulfur levels in coal as expressed by Attia and Fung [16]. They used the modified procedure in which acid washing with 16% HCl after each step, and 15 minutes of ultrasonic treatment during the third step to help break up the oxidation product layer were applied.

Alvarez Rodriguez, et al. [17] used nitric acid for desulfurization of Spanish coal, concluded that nitric leaching at atmospheric pressure is a good media of desulfurization for intermediate-rank coal, especially with reference to inorganic sulfur.

Supercritical fluids such as methanol and ethanol have previously been reported as good media for organic sulfur removal of coal [18]. They have capability to enhance the solubility of organic compounds. Meffe, et al. [19] reported that the coal desulfurization by methanol was high at low solvent density and high temperature. The supercritical process required a high temperature and pressure, making the desulfurization process uneconomic. In an investigation, Ratanakandilok, et al. [20], using methanol/water and methanol/KOH, studied the desulfurization of coal at medium temperature and pressure. They obtained the reduction ranged from 36 to 74% in pyritic sulfur, 20 to 42% in organic sulfur and 33 to 62% in total sulfur.

Since Iran is rich in oil, coal is used mainly for coke making for steel industries. Large reserves of coal in Tabas region of Iran are characterized by low ash and high caking index, suitable for use in metallurgy as coking coal. However, these coals cannot be gainfully utilized because of their high sulfur content. It is the objective of the extensive work undergoing to find a suitable desulfurization method or combination methods to reduce the sulfur content of high sulfur Tabas coals, in order that the clean obtained coal could be used either separately or as a blending material for coke making for the steel industry. In this paper, results obtained using various chemical reactants are presented in order to find suitable chemical reagents for the desulfurization of Tabas coal at reasonable temperature and pressure. The effect of reaction variables on the desulfurization of the coal was evaluated by measuring the sulfur content, the ash content, the clean coal yield and the coke number.

EXPERIMENTAL

Apparatus

The desulfurization reactions with various agents except nitric acid were carried out using a reactor with 7.0 liters capacity. The reactor is equipped with a thermocouple, pressure gauge and an agitator.

The desulfurization reaction with nitric acid was carried out in a sealed glass flask of one liter volume equipped with an agitator. The reaction flask provided with backflow cooling, stirring system, gas outlet, thermometric tube and coal inlet. The flask was submerged in a thermostatic bath, and the gas exhaust, under slight suction, led the gases through a series of wash-bottles containing water to dissolve the nitrogen oxides released during attack on the coal.

Experimental procedure

About 70% of total reactor volume was filled by feed and solution and the rest was left empty. At each experiment, 1 kg of the air-dried coal samples were mixed with leaching solution with stirring for various periods of time. The heater was turned on to certain temperature and pressure depending on the reagent condition required. For all these experiments, the reaction time was started after the reaction mixture reached the required reaction temperature. At the end of each experiment, the heater was withdrawn and the reactor was cooled down to room temperature.

The leached coal was recovered by filtration, then washed through with water and dried for 3 hrs in an oven at 90 to 110 ºC. The raw and leached coal were analyzed for pyritic sulfur and total sulfur using ASTM methods D2492 and D3177 [21]. Organic sulfur was determined by difference. The percentage changes in ash and sulfur in comparison to the original values were calculated as follows:

$$\text{Coal yield} = 100(m_2/m_1) \quad (1)$$

$$\text{Sulfur reduction} = 100[x_1 - x_2(m_2/m_1)]/x_1 \quad (2)$$

Table 1: Chemical analysis of original Tabas coal samples.

Ash	16.8%
Volatile matte in ash and sulfur	22.5%
Total sulfur	3.1%
Pyritic sulfur	2.5%
Organic sulfur	0.6%
Coke number	5

$$\text{Ash reduction} = 100[y_1 - y_2(m_2/m_1)]/y_1 \quad (3)$$

where m_1 is the original amount of dry coal sample, m_2 the amount of leached dry coal sample, x_1 the sulfur percent in the original coal, x_2 the sulfur percent in leached coal, y_1 and y_2 the ash percents in original and leached coals respectively.

Chemicals

The coal samples used in this study was collected from Tabas mine of Iran. The coal samples ground to 0.5 to 2.8 mm, as is needed for coke making in Isfahan Steel Company, were used in all experiments.

A series of experiments was carried out to determine the effects of system parameters and various reagents on the reduction of sulfur content of the coal samples. The properties of the feed coals based on dry-basis are given in table 1.

No elemental sulfur was found in the original Tabas coal. The pyritic sulfur is more dominant form of sulfur in this coal. This coal is characterized by low ash content and high coke number and is suitable for use in coke making industries.

RESULTS AND DISCUSSION

In order to investigate the possible reduction of sulfur content in Tabas coals by chemical methods, various reactants are used in this work. As the pyritic sulfur is the dominant form of sulfur in this coal, those chemical reagents effective in desulfurization of pyritic sulfur, are selected.

Large coal sizes necessary for coke production in Isfahan Steel Cooperation in the range of 0.5 to 2.8 mm were used in these experiments. In general, it is expected to obtain low sulfur removal with such large coal sizes used since; desulfurization is enhanced with small coal sizes. The experimental results obtained are as follows;

Ferric chloride

Results obtained using ferric chloride, $FeCl_3$ are presented in table 2. Desulfurization reacts with $FeCl_3$ was carried out at 94 °C the maximum temperature could be achieved at atmospheric pressure using aqueous solutions of ferric chloride. Results in this table indicate that when coal samples were oxidized with three different chloride solutions, the pyritic sulfur reductions increased with time and concentrations. The significant reductions obtained in total sulfur content of Tabas coal samples are due to the strong effect of this reactant on pyritic sulfur content. Tabas coal with 15% $FeCl_3$ solution could remove 71.2% and 53.4% of the pyritic sulfur and total sulfur content respectively.

Ersahan, et al [22] using Turkish coal samples have found reduction in pyritic content of coal up to 60% during leaching by ferric chloride depending on the concentration of ferric chloride, the particle size of the sample, the temperature and the rate of stirring.

Ferric sulphate

Studies on pyritic sulfur removal from Tabas coals were carried out using aqueous ferric sulphate. Desulfurization results obtained at different concentration of $Fe_2(SO_4)_3$ and reaction time are presented in table 3. Results indicate that sulfur reductions increase with time and ferric sulphate concentration. A maximum reduction in pyritic sulfur of Tabas coal of 45.8% was obtained at concentration of 38% and reaction time of 1 hr. In fact pyritic sulfur in Tabas coal are fine distributed in organic matrix of coal which cannot be removed easily by physical processes. Ferric sulphate solution is one of the suitable chemical method which could be used to recover most of the fine distributed pyritic sulfur in some value-added product. Pyrite reacts with an aqueous ferric sulphate solution at moderate temperatures ranging from 90 to 130 °C, resulting in ferrous sulphate, sulphuric acid and elemental sulfur. Applying the method for desulfurization of very high sulfur coals of India by Srivastava [23] led to reduction of up to 90% of pyritic sulfur of very fine coal particles.

Hydrogen Peroxide

Table 4, indicates the results obtained using H_2O_2 with concentration of 10 and 20% at room temperature for 1 hr. It was found that as the H_2O_2 concentration was increased the extent of desulfurization increased from 21.94 to 30.96% and ash removal increased from 21.42% to 45.24%. Therefore this oxidant is effective for desulfurization and simultaneous demineralization of Tabas coal. Ali et al. [24] comparing the results obtained using different reagents, concluded that H_2O_2 (30%) was the most suitable reagent for various kind of coals and depending upon the various forms of sulfur present in the coal structure, the extent of desulfurization varied, being higher for low organic sulfur coals.

Nitric acid

Nitric acid causes rapid pyritic sulfur reduction even under mild attack conditions, but it has no effect on organic sulfur removal. To obtain an effective reduction of sulfur in partcle sizes larger than those required in certain physical processes under mild conditions, experimental tests were carried out using nitric acid. The desulfurization results are presented in table 5 at various reaction times and with different coal size ranges. The reaction temperature was fixed to about 40ºC and the nitric acid concentrations of 22% were used in all experiments.

The results in table 5 indicate that in general, the desulfurization is quite rapid in the early stages of the reaction up to 1 to 2hrs, but slows toward the latter stages. Therefore the most practical and economical reaction time could be 1hr. The removal of total sulfur increased with reducing the coal particle sizes due to increase in surface area. This implies that the reaction takes places at the surfaces of the particles. This conclusion is in agreement with the microscopic structure of pyrite, which is generally nonporous. Alvarez, et al. [25] have found a reduction of 92% in total sulfur of coal using nitric acid and very small coal sizes.

Sodium hydroxide

The temperature is the most important parameters affecting the coal desulfurization using NaOH solution. This effect is studied in the experiments at higher temperature which the concentration of caustic was fixed to 20% and the reaction time was kept to 1 hr. The desulfurization results are presented in table 6. Both pyritic and organic sulfur reductions are increased with temperature in this process. Although using high temperature and pressure, the desulfurization rate

Table 2: Effect of reaction time and concentration on desulfurization of Tabas coal using ferric chloride.

Reaction time (min)	$FeCl_3$ concentration (wt%)	Pyritic sulfur reduction (%)	Total sulfur reduction (%)
20	8	52.3	39.2
	12	55.2	41.4
	15	56.8	42.6
40	8	54.4	40.9
	12	59.8	44.8
	15	62.1	46.6
60	8	58.3	43.7
	12	65.1	48.8
	15	71.2	53.4

Table 3: Effect of reaction time and concentration on desulfurization of Tabas coal using ferric sulphate.

$Fe_2(SO_4)_3$ concentration (wt%)	Reaction time (min)	Pyritic sulfur reduction (%)	Total sulfur reduction (%)
12	15	20	15
	30	26.1	19.6
	45	31.1	23.3
	60	35	26.35
22	15	23.1	17.3
	30	32	24
	45	36	27
	60	38.9	29.2
38	15	28.1	21.1
	30	38.4	28.8
	45	40	30
	60	45.8	34.3

Table 4: Results on desulfurization of Tabas coal using hydrogen peroxide.

H_2O_2 concentration (wt%)	Organic sulfur content (%)	Pyritic sulfur content (%)	Total sulfur content (%)	Ash content (%)	Coke number	Organic sulfur reduction (%)	Pyritic sulfur reduction (%)	Total sulfur reduction (%)	Ash removal (%)	Coal yield
20	0.6	1.54	2.14	9.2	6	0	38.4	30.96	45.24	92
10	0.6	1.82	2.42	13.2	5	0	27.2	21.94	21.42	93

Table 5: Effect of particle size and reaction time on desulfurization of Tabas coal using nitric acid.

Coal size (mm)	Total sulfur reduction (wt%)					Ash removal (%)
	1 hr	2 hrs	3 hrs	6 hrs	48 hrs	
0-2	30	45	52	58	62	6
0-2.5	25	28	42	53	58	6.5
0-3	25	30	37	48	55	6.5
0-5	20	22	28	35	48	8.3
0.5-2.8	15	18	25	33	42	9.5
0.5-5	15	18	22	31	38	9.5

Table 6: Effect of temperature on desulfurization of Tabas coal using 20% NaOH solution.

Temperature (ºC)	Pyritic sulfur reduction (%wt)	Organic sulfur reduction (%wt)	Total sulfur reduction (%wt)	Coal yield (%wt)
150	16.8	6.67	14.84	70
180	21.2	8.33	18.71	60
210	70.8	16.67	60.32	45

Table 7: Results on desulfurization of Tabas coal using methanol reagent.

CH_3OH concentration (wt%)	Organic sulfur content (%)	Pyritic sulfur content (%)	Total sulfur content (%)	Ash content (%)	Coke number	Organic sulfur reduction (%)	Pyritic sulfur reduction (%)	Total sulfur reduction (%)	Ash removal (%)	Coal yield
5	.52	2.07	2.59	16.1	5	13.33	17.2	16.5	4	95
10	0.5	2.05	2.55	17.7	6	16.67	18	17.75	5.4	93
20	0.48	1.93	2.41	14.25	6	20	22.8	22.3	15.25	91

increases considerably, but it makes the process uneconomic for industrial purposes. Moreover, the temperature strongly affects the coal yield resulted in low yield at high reaction temperatures.

More results obtained using sodium hydroxide at different concentration and temperatures can be found in previous work [26].

Methanol

It is shown in table 7 that treating Tabas coal with 20 wt% methanol solution at fixed temperature of 150 °C and the reaction time of 60 min could remove 20% of organic sulfur and 22.8% of pyritic sulfur, resulted in reduction of 22.26% of the total sulfur in the coal. Methanol is effective reagent in desulfurization of both forms of sulfur in coal. Although the coal desulfurization with methanol under supercritical condition used by some workers could be more effective for sulfur removal but require higher operating cost and equipment cost and so are not commercially acceptable.

CONCLUSIONS

Studies on desulfurization of Tabas coals using various reagents appear that some chemical reagents are effective in reducing the sulfur in the coal. At high temperatures of above 200 ºC, NaOH could remove both organic and pyritic forms of sulfur in coal. Nitric acid causes rapid pyritic sulfur reduction even under mild attack conditions of 40 ºC and ambient pressure. The total sulfur reduction of Tabas coal was obtained of about 50%

using nitric acid with concentration of 20%. This reduction increases with time.

Ferric chloride was found to be the most effective reagent in reduction of pyritic sulfur of Tabas coal. However this reagent can affect on the coal structure as a result of formation of HCl.

In order to have an economically viable process for the chemical removal of pyrite from coal, it would be necessary to utilize an aqueous oxidizing agent that has the following characteristics;

(a) highly selective to pyrite
(b) regenerable
(c) does not react with the organic coal matrix
(d) highly soluble in both oxidized and reduced forms
(e) cheap

Ferric sulphate almost fulfill the above criteria and was found to be the most effective. However, techno-economic feasibility studies need to be done for this process.

One drawback in using the oxidative reagents for chemical desulfurization is destruction of the caking property of the coal especially at high temperatures necessary for reaction of most chemical reagents. Studies on desulfurization of Tabas coal using physical and biodesulfurization methods are undergoing by author in order to find the most suitable and economical desulfurization and demineralization method which can be used for industrial purposes.

Acknowledgement

This research project has been supported by grant of National Research Projects and with the support of National Research Council of Islamic Republic of Iran, as well as Isfahan Steel Cooperation. The author wishes to thank for supporting this project.

Received : 20th December 2004 ; Accepted : 8th January 2006

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