Ash and Total Sulphur Study of Coal by Various Beneficiation Techniques

Asmat Ayoub [(1*)], Romaisa Amin [(2)], Mauzzmah Shahid [(3)], Rimsha Raees [(4)] Faseeha Ashraf [(5)], Huma Shahid [(6)]

[1]: Department of Chemistry, University of Engineering and Technology, Lahore-54890

2. Department of Chemistry, University of Engineering and Technology, Lahore-54890

3. Department of Chemistry, University of Engineering and Technology, Lahore-54890

4. Department of Physics, Riphah Institute of Computing and Applied Sciences, (RICAS) Riphah International University, Lahore-54000

5. Department of Physics, University of Lahore.

6. Department of Physics, Riphah Institute of Computing and Applied Sciences, (RICAS) Riphah International University, Lahore-54000

Abstract:

During present experimental investigation different physical techniques such as sieving, tabling and flotation were applied and change in ash and total sulphur were compared to the original coal sample. Scanning electron microscopy (SEM) was used to access the morphology of the fractions obtained from different techniques. It was found that sieving is helpful in selecting proper fraction to be used as base for other beneficiation techniques. Concentrated fraction obtained from tabling process show 13% less amount of ash and 11 % less total sulphur than original sample. Middling fraction show 21% less amount of ash and 14% less total sulphur than the original one. The concentration fraction obtained from froth flotation showed 26 % less amount of ash and 9 % less amount of sulfur. From this investigation it is concluded that Concentration and middling fractions obtained from tabling and flotation techniques may be used independently for different energy applications and are more environmentally friendly than the original stock.

Key words: Coal upgradation, Ash content, Total sulfur, Sieving, Beneficiation Techniques, SEM technology

Corresponding Author:

[(3*)]Mauzzmah Shahid

Department of Chemistry, University of Engineering and Technology

Lahore:

Introduction

Coal is the cheapest source of energy and its consumption rate is increasing day by day. It is used in many power generation plants for the production of electricity. However it is the most polluting source of energy and constantly threatening the environment [1]. It emits CH_4, CO_2, SO_2 and NO_2 that deplete the ozone layer and damage the environment. Moreover, it is carbon intensive compound and creates a potential danger to environmental quality due to its excessive use [2]. Minerals present in coal are mainly iron, aluminum, sulfur, oxygen and calcium. Their sizes vary from submicroscopic level to a couple of inches [3]. When the coal is ignited most of mineral matter and trace element generally form ash and some minerals are converted into gaseous compounds. Pyrite, for instance, breaks down into individual elements iron and sulfur. Every component at that point consolidates with oxygen to turn out to be, separately, iron oxide and sulfur oxide. Some trace elements detach from their organic host when coal is burned and follow distinct tracks. A few of volatile elements such as selenium and mercury might be transmitted as flue gas [4].

Coalification is a process that determines the coal rank. The coal rank is determined by the percentage of fixed carbon, moisture, calorific value and volatile matter after the removal of sulfur and mineral matter content [5]. Coal is classified into peat, lignite, bituminous coal, anthracite coal [6]. Due to environmental concerns many methods have been developed for the removal of sulfur from coal. It can be removed by passing dry chlorine from it. Particle size, chlorination time and temperature has great importance. Both organic and inorganic sulfur can be removed by this method. Desulfurization increases by increasing the particle size. Total sulfur, pyritic sulfur, sulfate sulfur and organic sulfur with 67.7%, 93.05, 65.6% and 61.65 can be removed with this method [7]. Nano sized titanium oxide (TiO_2) powder by sol-gel process is effective for desulfurization. It increases the calorific value and melting temperature effectively [8].

Fe doped Mn based sorbents has a good capacity of adsorption and durable stability for H_2S removal. They were prepared from industrial water glass so the method is cheap and easily available [9]. Ultra sonication is an efficient technique for the desulfurization process through mixed alkali media. The method is helpful for both the removal of ash and the different forms of sulfur including total sulfur, pyritic sulfur and sulfate sulfur. When the solution is exposed to ultrasonic waves, it experiences mechanical vibration and causes cavitation. The cavity helps to

Proceed the chemical reaction by cracking the surface. Surface cracking helps the reagent reach to the interior particle by capillary action [10]. Moreover, gas-vibro fluidized bed with active pulsing gas is also an effective method for the desulfurization and de-ashing of fine coal. The method was helpful for the removal of inorganic sulfur such as pyritic and sulfate sulfur [11].

Bottom ash facilitates the reduction of SO_2 from a coal fire power plant. It acts as a sorbent. Removal efficiency is 3.7- 4.7%. The method is economic and environmentally friendly too as it saves energy consumption by 4.0-5.0% [12]. Mineral components and pyritic sulfur are the major concern in the replacement of coal as an effective fuel. Froth Flotation is another technique for the removal of these components [13]. Organic sulfur is difficult to remove from coal by physical method. However, chemical leaching or biological treatments are helpful for the removal of organic sulfur. But these methods require high treatment time and huge investment. Conversely iron powder can remove with low coast. It yields 65.5% clean coal [14].

Magnetic properties of coal can be improved by providing microwave energy. It creates high magnetic separation [15]. 80% of thiophene sulfur, mercaptane, sulfoether can be removed by using potassium tert butoxide/ hydoxilane system [16]. Ionic liquids combined with 30% H_2O_2 is helpful to proceed oxidative desulfurization [17]. High sulfur and high ash coal is real threat to world as the combustion of such coal is responsible for smog formation so microwave desulfurization with NaOH is a good beneficiation technique [18]. NaOH and HCl both are good reagents for the desulfurization of coal [19].Indian coal is quite challenging due to its low grade and physicochemical process is hard to apply due to its oxidized nature and presence of complex ash forming mineral matter. So chemical beneficiation is an alternate method [20].

Molten casting leaching technique can reduce ash up to 85% and sulfur up to 40% [21]. Concentration of alkali has a great effect on the desulfurization [22]. Similarly particle size also has a great effect on desulfurization properties. Finer particles are highly reactive [23]. Low temperature is effective for desulfurization [24]. Diesel is the best frothing agent for desulfurization [25].kerosene oil and palm oil contribute effectively for the desulfurization of coal [26].

Here some physical methods have been applied for de-sulfurization and de-ashing of coal. Based on the proximate analysis of sample and its mesh size different techniques i.e. flotation technique

And tabling technique were applied to investigate the decrease in sulphur and ash from the originalsample. All the methods used in this study are environmentally friendly.

Materials and Methods

Sampling and proximate analysis

Indigenous coal sample was arranged from coal testing section of PCSIR, Laboratories complex Lahore, Pakistan. Sample preparation was made as per ASTM method of sample preparation. After crushing and grinding the representative sample was stored in air tight bags for further analysis. Ash and total Sulphur were determined by ASTM, D: 3174-12 and D: 3177-07 respectively.

Techniques used for up gradation of coal

Sieving

Eight coal fractions were prepared by sieving method for ash and sulphur content estimation. Different sieves of 250mesh, 200mesh, 150 mesh, 120 mesh, 100 mesh, 80 mesh, 52 mesh and 16 mesh were used Fig 1).

Fig. 1: Sieve fractions of different mesh size

Tabling

2 kg coal indigenous coal sample was taken. After grinding it was sieved up to 100 mesh. Sieved sample was dipped in water for 2 hrs. Then it was run on Wilfley table. Three fractions were obtained that are known as Concentrate, Middling and Tailing. (Fig 2, 3, 4, 5). After drying in oven the ash content and total sulfur in each fraction were calculated.

Fig 2: Crushing of coal.

Fig 3: Sieving of coal

Fig 4: Concentrate and Tailing. **Fig 5: Middling**

Froth Flotation

250 g of coal sample was taken after grinding and crushing sample was sieved up to 100 mesh. After that it was proceeded in flotation tank. Some drops of kerosene oil were added into it. Two fractions were obtained, tailing and concentrate. Concentrate was bubbled out as shown in (Fig 6). While tailing remained at the bottom. After drying the fractions, ash and total sulfur was calculated.

Fig 6: Concentrate obtained from flotation tank

Results and Discussions

Sieving technique

Ash values differ among varying size fractions. A number of possible assumptions can be made in this regard. It may be due to different composition of minerals and different quantity of minerals among sizes. Large particles may have more minerals than small particles due to which they exhibit different physical properties like hardness, toughness and friability. Mathews et al also found in their study that the ash content vary with size **[27**]. This trend can also be observed in this study with mesh of 250 having highest ash content and 100 mesh with lowest ash content as shown in table 1.

It was also observed that by decreasing the particle size the sulfur removal decreased and then increased again as shown in the table 1. The reason is the difference in surface area among different fractions [28]. The maximum sulfur content was observed at the particle size of 100 mesh.

Mesh Size	Ash	Total Sulfur
250 Mesh	17.9 %	4.9 %
200 Mesh	16.7 %	4.7 %
150 Mesh	15.8 %	4.6 %
120 Mesh	15.5 %	3.8 %
100 Mesh	15.3 %	3.3 %
80 Mesh	15.5 %	4.1 %
52 Mesh	15.7 %	4.3 %
16 Mesh	15.9 %	4.5 %

Table 1: Study of sieving on ash and total sulphur

Tabling Technique

Three different fractions obtained from the tabling technique show variation in results. Tailing shows 34 % high amount of ash content which clearly means it contains impurities hence it is

noted on the basis of studies that Tailing is not good enough to be used. Concentration and Middling fraction show low amount of ash and can be used as they are economically viable and are environmentally friendly. Concentration fraction shows 13% less amount of ash than the original one and Middling fraction shows 21% less amount of ash as compared to the original sample. Similarly Tailing shows 27 % increase in total sulphur, Concentrating shows 11% and middling shows 14 % less amount of total sulfur than the original sample**.** So all three are environmental friendly and safe to use separately.

Sample	**Original**	**Tailing**	**Concentrate**	**Middling**
Ash	15.3%	20.5 %	13.3%	12.1%
Sulfur	3.3%	4.2 %	2.9%	2.8%

Table 2: Results obtained from Tabling technique

Flotation Technique

Result show 74 % and 91 % increase in ash and total sulphur in the tailings and 26 % and 9% decrease in concentrate than the original sample after flotation procedure. This can be attributed to the hydrophobic surface of coal because coal is mainly non polar hydrocarbon. Since water is a polar substance while oil is non polar so it has a little tendency to wet nonpolar material. On the other hand oil have strong tendency for non-polar surfaces and wet them easily. Some ash, mineral such as clays and silicates are composed of strongly polar compounds therefore water wets them but oil do not [30]. The basic difference in structure is then responsible for the ease of cleaning coal by froth flotation process.

Sample	**Original**	**Tailing**	**Concentrate**
Ash	15.3%	26.6 %	11.3%
Sulfur	3.3 %	6.3%	3.0 %

Table 3: Results obtained from flotation technique

SEM Analysis

SEM analysis was performed to understand the nature of changes occurring in the morphology of original sample after going through tabling and flotation procedures. It is clearly shown how the surface topology changed before and after applying beneficiation techniques. The overview SEM image of the original sample shows a micro bead type aggregating, agglomerated with each other forming a sheet like structure. Enlarged SEM image shows that these collections having size from nano to few micron range and can be seen individually. Furthermore, the distinct pores can be observed among combinations. The overview of SEM image of tabling concentrate shows micro structures having mesopores among them. Enlarged images shows that these structures are nano sized and are spherical to pseudo spherical shape. SEM image obtained from the flotation concentrate shows a flake like morphological features. Enlarged images shows these flakes are heterogeneous in shape and size are random in distribution. More enlarged view shows flake are smooth in appearance.

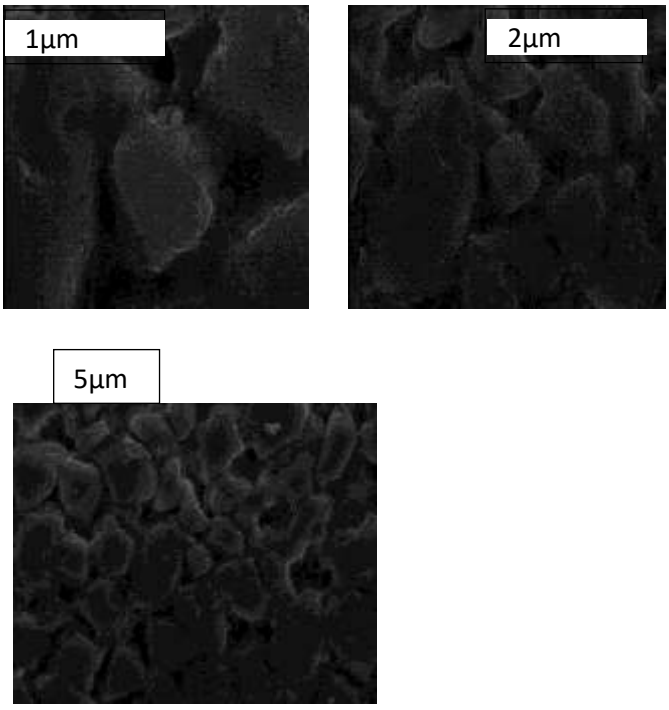

Fig 7 a, b, c: SEM images before applying techniques.

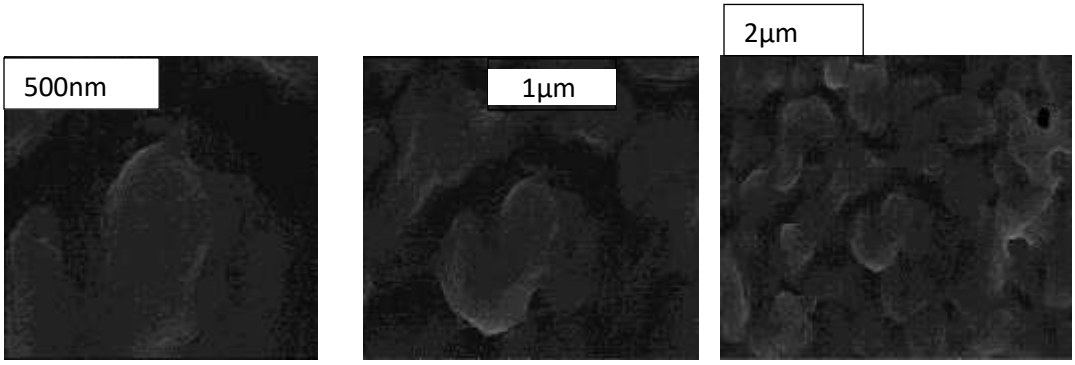

Fig 8 a, b, c: SEM images of tabling concentrate

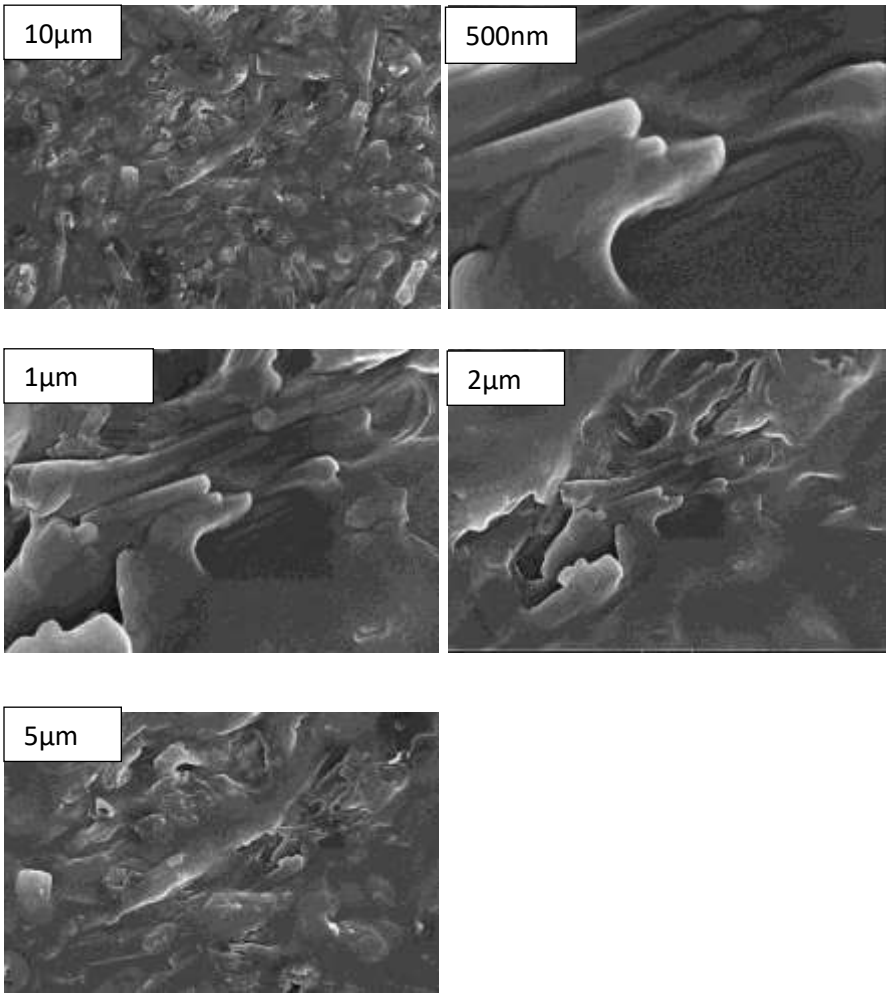

Fig 9 a, b, c: SEM images of flotation concentrate

Conclusion

Coal is widely used in many industries and Pakistan is rich in this natural resource but the environmental consequences of coal limits its use. The present study reveals that sieving and gravitational methods are one of the most promising and sustainable techniques for improving coal quality. These techniques are also environmental friendly and cost effective**.** Hence indigenous coal can be used if preparation methods such as de-ashing and de- sulfurization are used to increase to increase the potential use.

Acknowledgement

I am very grateful to my research supervisor, **Dr. Arjumand Iqbal Durrani** for her support and patience at all times. I owe my deepest gratitude to my co-supervisor **Zahid Mahmood** in MPRC, PCSIR, Lahore. Without his continuous optimism concerning this work, enthusiasm, couragement and support this study would hardly have been completed. I also express my warmest gratitude to **Dr. Asma Sheikh**, whose guidance in laboratory analysis have been essential during this work. I am indebted to my fellows; **Mauzzmah Shahid** for her constant support.

References

[1] Bilgen, S. (2016). The environmental effects of coal-related activities. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 38(22), 3283-3289.

[2] Galli, A., Kitzes, J., Niccolucci, V., Wackernagel, M., Wada, Y., & Marchettini, N. (2012). Assessing the global environmental consequences of economic growth through the ecological footprint: a focus on China and India. Ecological Indicators, 17, 99-107.

[3] Berkowitz, N. (2012). An introduction to coal technology. Elsevier.

[4] Riaza, J., Mason, P., Jones, J. M., Gibbins, J., & Chalmers, H. (2019). High temperature volatile yield and nitrogen partitioning during pyrolysis of coal and biomass fuels. Fuel, 248, 215-220.

[5] Flores, R. M. (2013). Coal and coalbed gas: fueling the future. Newnes.

[6] Hower, J., Granite, E., Mayfield, D., Lewis, A., & Finkelman, R. (2016). Notes on contributions to the science of rare earth element enrichment in coal and coal combustion byproducts. Minerals, 6(2), 32.

[7] Shen, S., He, J., Pan, M., Zhou, Z., Feng, C., & Liang, G. (2012). Effective removal of sulfur from high-sulfur coal prior to use by dry chlorination at low temperature. Journal of hazardous materials, 217, 116-122.

[8] Zhao, Y., Wang, S., Shen, Y., & Lu, X. (2013). Effects of nano-TiO2 on combustion and desulfurization. Energy, 56, 25-30.

[9] .Zhang, Y., Liu, B. S., Zhang, F. M., & Zhang, Z. F. (2013). Formation of (FexMn2− x) O3 solid solution and high sulfur capacity properties of Mn-based/M41 sorbents for hot coal gas desulfurization. Journal of hazardous materials, 248, 81-88

[10] Saikia, B. K., Dutta, A. M., Saikia, L., Ahmed, S., & Baruah, B. P. (2014). Ultrasonic assisted cleaning of high sulphur Indian coals in water and mixed alkali. Fuel Processing Technology, 123, 107-113.

[11] Dong, L., Zhang, Y., Zhao, Y., Wang, H., Wang, Y., Luo, Z., & Zhang, B. (2015). Deash and desulfurization of fine coal using a gas-vibro fluidized bed. Fuel, 155, 55-62.

[12] Rathnayake, M., Julnipitawong, P., Tangtermsirikul, S., & Toochinda, P. (2018). Utilization of coal fly ash and bottom ash as solid sorbents for sulfur dioxide reduction from coal fired power plant: Life cycle assessment and applications. Journal of cleaner production, 202, 934-945.

[13] Saleemi, H. A., & Ullah, M. S. (2017). Desulfurization and Parametric Study of Bituminous Coal via Froth Flotation Technique. INTERNATIONAL JOURNAL OF ADVANCED BIOTECHNOLOGY AND RESEARCH, 8(4), 237-245

[14] Xia, W., Li, Y., He, W., & Peng, Y. (2018). Desulfurization of low rank coal co-pyrolysis with reduced iron powder followed by dry magnetic separation. Journal of cleaner production, 204, 525-531.

[15] Zhang, B., Zhu, G., Lv, B., Dong, L., Yan, G., Zhu, X., & Luo, Z. (2018). A novel high-sulfur fine coal clean desulfurization pretreatment: Microwave magnetic separation, high-gradient effect and magnetic strengthen. Journal of cleaner production, 202, 697-709.

[16] Tang, L., Wang, S., Zhu, X., Guan, Y., Chen, S., Tao, X., & He, H. (2018). Feasibility study of reduction removal of thiophene sulfur in coal. Fuel, 234, 1367-1372

[17] Wang, L., Jin, G., & Xu, Y. (2019). Desulfurization of coal using four ionic liquids with [HSO4] −. Fuel, 236, 1181-1190.

[18] Yu, X., Luo, Z., & Gan, D. (2019). Desulfurization of high sulfur fine coal using a novel combined beneficiation process. Fuel, 254, 115603.

[19] Singh, J. P., Kumar, S., & Mohapatra, S. K. (2018). Chemical treatment of low-grade coal using Taguchi approach. Particulate Science and Technology, 1-8.

[20] Deb Barma, S., Baskey, P. K., & Biswal, S. K. (2018). Chemical beneficiation of high-ash indian noncoking coal by alkali leaching under low-frequency ultrasonication. Energy & fuels, 32(2), 1309-1319.

[21] Wahab, A., Nawaz, S., Shahzad, K., Akhtar, J., Kanwal, S., Munir, S., & Sheikh, N. (2015). Desulfurization and demineralization of Lakhra coal by molten caustic leaching. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 37(11), 1219-1223.

[22] Rehman, F., Ahmad, S. W., Zafar, M. S., Ahmad, S., & Zia-Ul-Haq, M. (2018). Parametric optimization of coal desulfurization through alkaline leaching. Polish Journal of Chemical Technology, 20(3), 103-109.

[23] Yu, D., Xu, M., Sui, J., Liu, X., Yu, Y., & Cao, Q. (2005). Effect of coal particle size on the proximate composition and combustion properties. Thermochimica Acta, 439(1-2), 103-109.

[24] Zaidi, S. A. H. (1993). Ultrasonically enhanced coal desulphurization. Fuel processing technology, 33(2), 95-100.

[25] Shafeeq, A., Ashraf, M., Muhammad, A., & Shahid, S. A. (2015). Application of Froth Flotation Technique to Reduce Sulfur from Lakhra Coal Using Froth Flotation. In International Conference on Advances in Environment Research (Vol. 87).

[26] Ehsani, M. R., & Eghbali, F. (2007). Reduction of sulfur and ash from Tabas coal by froth flotation. Iranian Journal of Chemistry and Chemical Engineering (IJCCE), 26(2), 35-40.

[27] Rehman, F., Ahmad, S. W., Zafar, M. S., Ahmad, S., & Zia-Ul-Haq, M. (2018). Parametric optimization of coal desulfurization through alkaline leaching. Polish Journal of Chemical Technology, 20(3), 103-109.

[28] Yu, D., Xu, M., Sui, J., Liu, X., Yu, Y., & Cao, Q. (2005). Effect of coal particle size on the proximate composition and combustion properties. Thermochimica Acta, 439(1-2), 103-109.