ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY (AAiT)

SCHOOL OF CHEMICAL AND BIO ENGINEERING

Characterization and Energy Enhancement of Dawuro Coal Using Froth Flotation and Alkali/Acid Leaching

A Thesis

Submitted to Addis Ababa University, Addis Ababa Institute of Technology, in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemical Engineering (Process Stream)

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Advisor
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Addis Ababa, Ethiopia

Declaration

I, Leager Minwuyelet Meleak, declare that the thesis, entitled "*Characterization and Energy Enhancement of Dawuro Coal Using Froth Flotation and Alkali/Acid Leaching*", is the result of my own work and all the sources and materials used have been duly acknowledged. I confidently declare that this thesis report has not been submitted in part or in whole to any other institution anywhere for the award of any academic qualification.

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This is to certify that the thesis prepared by **Leager Minwuyelet Meleak**, entitled "*Characterization and Energy Enhancement of Dawuro Coal Using Froth Flotation and Alkali/Acid Leaching*", and submitted to AAU, AAiT (Addis Ababa Institute of Technology) in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering (Process-Stream) compiles with the University's regulations and meets the accepted standards with respect to its originality and quality.

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Abstract

Ethiopia has huge deposits of low-rank coal, which is characterized by calorific-value (an average 4,500 kcal/kg), high ash content (up to 50%), high moisture content (up to 35%) and high volatile matter. Thus, the country is still dependent on partial import of better quality coal, and so, significant amount of money in foreign-exchange is spent to meet the demand. Therefore, this study was carried out on domestic coal beneficiation by applying the froth-flotation and alkali-acid leaching, sequentially, for enhancing the quality of Dawuro Coal, in Southwestern Region of Ethiopia. The Design-Expert (version-13) software was used for the experimental design and the RSM with BBD were applied for modeling the influence of some factors on the performance of flotation and alkali-acid leaching experiments. Flotation experiments were conducted by considering particle size, collector and frother dosages as independent variables, and then, alkali- and acid-leaching experiments were carried out, sequentially, both by using leaching concentration, temperature and time as independent variables. For each, ash-reduction was defined as process-response (dependent variable). The test results revealed that the resulted ash-reduction models were found to be statistically significant and also the predicted values were in good agreement with the experimental results – with R^2 value of 0.9801, 0.9858, and 0.9711 for ash-reduction in flotation, alkali and acid-leaching, respectively. Results revealed that particle-size for flotation and leaching concentration followed by temperature for both alkali and acid leaching play important role in ash-reduction. The maximum ash reduction of 73.84%, 71.88% and 49.40% were obtained at the working conditions: (125-63 μm particle-size, 55 g/ton diesel-oil/collector, and 370 g/ton n-octanol/frother), (1 mol/dm^3 NaOH, 220 ^{o}C and 60 minutes), and (1 mol/dm^3 HCl, 80 ^{o}C and 3 hours) for flotation, alkali and acid leaching, respectively. The result from proximate analysis shows that the raw samples of coal contain 10.67% moisture, 33.73% ash, 30.34% volatile matter, 25.26% fixed-carbon, and 0.67% sulfur with 3,643.08 kcal/kg calorific value. The results for the treated coal sample show that the ash content was 8.92%, 2.51% and 1.27%; and sulfur percentage was 0.45%, 0.38% and 0.37% with 4,996.20 kcal/kg, 6,195.29 kcal/kg and 7,124.58 kcal/kg of calorific values for flotation-concentrate, alkali-leached and acid-leached coal samples, respectively. The results of this study confirm that the treated samples of coal resulted in higher heating-values and fixed-carbon, and lower ash and sulfur contents as compared to the raw sample. Hence, with the determined optimum conditions, applying froth-flotation followed by sequential alkali/acid leaching is effective to increase the heating-values and upgrade the energy/quality of the sample coal, being as suitable energy source for industries like cement and steel.

Keywords: *Froth flotation, Alkali-acid leaching, Box–Behnken design, Response surface methodology*

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Acronyms and Abbreviations

AAiT	Addis Ababa institute of Technology
AASTU	Addis Ababa Science and Technology University
AFC	Ash-Free Coal
ASTM	American Society for Testing and Materials
BBD	Box-Behnken Design
CV	Calorific Value
dmmf	dry, mineral-matter-free
EIGS	Ethiopian Institute of Geological Survey
FC	Fixed Carbon
H_2SO_4	Sulfuric Acid
HF	Hydrogen Fluoride
HCl	Hydrochloric Acid
HNO_3	Nitric Acid
IEA	International Energy Agency
ITC	International Trade Center
Kcal/kg	Kilo calorie per Kilogram
MC	Moisture Content
MJ/Kg	Mega Joule per kilogram
mmmf	moist, mineral-matter-free
NaOH	Caustic Soda
NOx	Nitrogen oxides
rpm	Revolution per minutes
RSM	Response Surface Methodology
SOx	Sulfur oxides
WCA	World Coal Association
UCC	Ultra Clean Coal
USA	United States of America
USD	United States Dollar
VM	Volatile Matter

CHAPTER ONE

1 INTRODUCTION

1.1 Background

Studies show that coal is the most available solid-structured fossil-fuel resource, existing as an organic sedimentary-rock that gives energy. Two-third of the world's resources of fossil-fuel are existing as coal and due to its cheapness, the rate of its consumption is increasing day-by-day. Coal is used as a main and important source of heat and energy in different industries, and its usefulness is also well-understood as it is used in many electricity generation plants [1, 2, 3].

Ethiopia has different useful and valuable natural resources with great potential, among which is coal. Due to the expanding of industrial-development and country's high population-growth and, there is a highly increasing demand of energy from time to time, where the supply of energy is limited and not counterbalanced with the existing demand [4, 5, 6]. Based on the report by [7], the deposits and occurrences of coal resource of the country estimated at 600 million metric tons. The majority of the deposit is found in the south-western part of the country including areas such as Yayo-Wittete, Achibo-Sombo, Moye, and Delbi. In Dawuro zone of South-Western Region of Ethiopian, a huge amount of coal-deposit has also been explored and additional exploration (and mining-activity) has started in Benshangul Gumuz region [5, 4, 8]. However, the existing coal resource of the country is characterized by existence of high impurity (or low-grade), and hence, doesn't fulfill the quality and requirements for the intended/desired applications. Low-grade coals, containing high amount of ash and sulfur contents and low carbon content, are characterized with low calorific values.

Coal is still the world's most plentiful and widely distributed resources of fossil fuel, which is 64% globally recoverable fossil resources compared to oil (19%) and natural gas (17%) [9]. In general, coal is classified based on its quality and application as low-rank (poor) coal and hard coal. Considering percentage of the coal types with respect to their reserve worldwide, lignite (17%) and subbituminous (30%) are categorized under low-rank coal. Bituminous (52%) and Anthracite (1%) are grouped under hard coal. Despite the abundance of its reserve, Ethiopian coal's quality falls in the category of lignite to subbituminous classification described by: low heating-value, higher ash-content (up to 50%), high

moisture content (up to 35%), high volatile-matter, and low to medium sulfur-content (1.5 – 3%).

Coal-based industries, which have played important roles in the modern world development, are expected to play a critical and dominant roles for a long-time to come –specifically, in the case of developing countries. Globally, the primary application of coal for source of energy shows [10]: for cement-production (over 90%), iron and steel-production (70%), electricity-generation (41%), transportation fuels, feedstock to produce chemicals, industrial-process heating, and household-heating and cooking.

According to [11], with the combined annual production of 6.35 billion tons coal, countries such as China, India, Indonesia, USA and Australia were considered as the top five coal (includes all grades) producing countries and ranked in the order they are listed, respectively. China, which produced about 3.94 billion tons, accounts for about 50.8 percent of the total production of the world. On the other hand, five countries mainly Australia, Indonesia, Russia, USA, and South Africa are identified as the biggest five exporters of coal to the global markets, for instance, these five mentioned countries shipped 84.5 percent of the total values sold at the international markets during the year 2021.

In Ethiopia, coal has been used as sources of energy in different industries (such as metallurgical and cement factories) that are currently expanding in the country. Coal is used in cement industries for burning the raw-materials and metallurgical industries (like: iron and steel) for melting of iron with high temperature. Due to the high-impurity and low quality of domestic coal, these factories are forced to use and depend more on imported coal by spending high foreign exchange-rate to satisfy the growing demands of their industries [4, 8]. To solve such problems related with the existing high impurities of coal and enhance its quality for the desired applications, several researchers have been trying to develop different upgrading technologies of highly impure coal to minimize its impurities and fit with its desired applications [3, 2, 12, 1, 13]. The recent techniques that have been developed and used for upgrading low-grade coal are mainly categorized as physical and chemical beneficiations. These techniques are used to increase the utility and cost-effectiveness of high ash and high sulfur-containing coal [14, 15].

Both chemical and physical purification methods are more selective for the separation of minerals, and need attention to reduce the challenges due to their high economic cost and low efficiency. Besides the expensiveness and cost, chemical-reagents that are used in

applying these techniques for the purification of coal are dangerous, which need to be purified and treated before discharging [13, 14, 15]. The use and application of alkalis, acids, oxidants, leachants and different combinations of alkalis/acids are proved to be an effective and attractive options for demineralization or desulfurization of different low-ranked coals. However, incurred costs and expensiveness of these chemicals still remain a concern for using them commercially for the purpose of cleaning coal [16, 17]. Hence, work needs to be done to reduce/minimize the consumption of those chemicals or apply the combination of physical treatment with the chemical means, further, to minimize their consumption for cleaning of coal and its efficient utilization. Therefore, the current study was aimed at beneficiation of low quality domestic coal by using the forth-flotation technique followed by the sequential alkali-acid leaching experiments to separate and remove impurities, and hence, to upgrade quality of domestic coal collected from Dawuro area of Southwest Region of Ethiopia.

1.2 Statement of the Problem

The high cost of heat and energy such as heavy fuel oil for industrial application had forced some cement factories either to change their existing equipment fit for cheaper energy such as coal or to install appropriate new technology at their initial investment period here in Ethiopia. As a result the country was a net importer of foreign coal for the cement plants as a source of cheap energy. It was only five years ago that the practice of using domestic coal in small quantity has begun and now reached to a considerable amount. Ethiopian Revenue and Customs Authority information shows that for the last five years import of 2,944,907 metric tons of coal, Ethiopia had to pay USD 375,886,000 for those industries, typically cement factories requiring the product for their energy source. The necessity of such an import is highly related with the quality of domestic coal.

Even though the country is known by the high availability of coal resources, its quality is characterized as very poor due to the higher ash and sulfur contents, which identified with lower content of fixed carbon and very low heating value. Thus, energy demand of the country is not counterbalanced with the existing supply, due to expanding situation of industrial zones and population growth [5, 4]. The quality of Ethiopian coal is known by low heating value or energy content as well as high moisture content and volatile matter. This is observed to be a big challenge and has its own consequences when we look at it from the end user point of view. For example, when we consider the geographical location of

cement plants they are at minimum distance of 400km from the nearest coal source. Transporting bulk quantity over a long distance with trucks, as is the practice now, is not cost effective when there is high moisture content (35%) which is simply to be driven off in the process. Similarly, high ash content adversely affects the production process and ultimately the finished product quality. The higher volatile matter of the coal is liable to spontaneous ignition and hazards both during storage and application of coal powder.

Moreover, the characterization of the domestic coal and beneficiation of such coals to reduce the impurities and improve quality are not well investigated or studied properly yet. It has been found from the literature that very limited studies have been conducted on upgrading quality of low-ranked coal in developing countries, particularly in Ethiopia, by using the physical treatment, and no work has been done on energy enhancement of domestic coal by using the combination of physical and chemical treatment with minimum consumption of chemical reagents. Thus, the local plants such as cement and metallurgical steel industries are forced to depend on and use imported coals spending the highest cost of foreign-exchange. To fill this existing gaps and achieve import substitution, the current study aimed at upgrading locally available coal using the froth-flotation followed by sequential alkali-acid leaching methods. The main reason for selecting floatation method as a pretreatment before alkali-acid cleaning is that the technique requires low capital and operating cost, and is highly effective and efficient in reducing the impurities of the coal [4].

The flotation concentrate was then leached using the alkali-acid leaching procedures, sequentially, for purifying coal and its efficient utilization. The combined technique of the froth flotation and alkali-acid leaching was applied to minimize the consumption of chemical reagents used in chemical leaching, and hence, effective to upgrade quality of domestic coal for desired applications.

1.3 Objective of the Study

1.3.1 General Objective

The major objective of the current study is to carryout domestic coal beneficiation experiment and recommend workable solution to the improvement of its quality.

1.3.2 Specific Objectives

The specific objectives of the research are to:

- Carryout physical beneficiation of the sample coal by applying the froth flotation technique.
- Conduct chemical cleaning of the flotation treated coal by applying alkali-acid leaching method.
- Determine the proximate analysis, sulfur content and heating value of sample coal before and after treatments.
- Recommend workable operation condition to the improvement of quality of the domestic coal for the desired purpose.

1.4 Scope of the study

The main purpose of the thesis is to conduct study on characterization and energy enhancement of domestic coal using froth-flotation technique followed by sequential alkali/acid leaching method. The study is limited to coal sample collected from Dawuro area, Southwestern Region of Ethiopia considering the variables (factors) such as: particle size, collector dosage and frother dosage for flotation of raw coal, and alkali/acid concentration, leaching temperature and time for both alkali leaching and acid-leaching experiments. The experimental conditions (parameters) for each experiment are modelled and optimized using the RSM (response surface methodology) with a BBD.

In addition, the study covers proximate analysis (volatile matter, moisture content, ash content, and amount of fixed carbon), sulfur content, and heating value, which are determined for raw and treated (leached) coal samples, to analyze quality of the coal before and/or after the experiments done, sequentially.

1.5 Significance of the Study

The proper use of natural resource as important as coal needs the comprehensive participation of stakeholders. Besides to end-users, the role of researchers in the academic field is significant. The study focus is upgrading the domestic coal with low processing cost as compared as imported coal of the same energy content (or calorific value). Therefore, the student researcher believes that the findings of the current study will:

- Provide valuable information for enhancing calorific value of domestic coal so that end-users will be cost effective.

- Provide policy makers insights to consider central issues such as import-substitution of coal for future planning.
- Initiate investment on coal upgrading, which will in turn strengthen the economy of the country, save foreign currency, increase job opportunities, improve income of the family and community, and provide the opportunity for innovation and creativity.
- Use as a lesson and reference for future/other researchers who are conducting study or want to conduct/practice in the future, and also can help to educators and consultants for their practice of teaching and learning.

1.6 Limitations of the study

Limitations to the current study start from inadequacy of the relevant literature sources found on the subject matter here in Ethiopia as it is already mentioned that the application of domestic coal and associated challenges is a recent experience for the country and hence, there is hardly no enough investigation or previous study has done on the subject matter. In addition, the lack of infrastructure (road, rail, etc.) and collaborative working culture, and existing civil wars and instabilities in most coal deposit areas of the country, particularly in western Oromia, Benishangul Gumuz, and Southern parts are among the major limitations the researcher faced in sample coal collection.

1.7 Organization of the Thesis

The current thesis report is organized and presented as five main chapters with their respective subunits as follows. The first chapter is an introductory-chapter containing background, existing problem, objectives, importance/significance, scope, and limitations to the current study. The second chapter deals with the concept and relevant literatures review and lays the theoretical foundation for the current study. The third chapter presents the research materials and methodology adapted to undertake the current study. The analysis, presentation, and interpretation of the data gathered from experiments, findings and lessons learned were presented in the fourth chapter. Chapter-five, which is the final one, consists of main conclusions and possible recommendations suggested based on the findings of the study. Annexes of relevant documents, materials, and instruments were also included in the report.

CHAPTER TWO

2 REVIEW OF RELATED LITERATURES

To get an insight and provide a brief account of the concepts the procedures and practices of coal quality improvement found in the literatures and then apply them in addressing the research problem discussed, a synthesis of related literatures is reviewed and presented below.

2.1 Definition and Basic Concepts

To have a common understanding of key terms that will be used in the study and to create clarity the following definitions are given. The ranking of coal is based on the levels of geological metamorphosis, FC, and CV. As a basic rule, the harder the coal, the better its heating value and rank. According to the international standards organization such as ASTM, the ranking of the four types of coal from the densest to least dense in their carbon and energy values is as follows: *Anthracite:* is first-in-rank and has a heating value of 30 MJ per Kg; *Bituminous:* second-in-rank with heating (calorific) value of 18.8–29.3 MJ per kg; *Sub-bituminous:* the third-ranked having 8.3–25 MJ per Kg of CV; and *Lignite (brown coal):* fourth-in-rank with CV of 5.5 – 14.3 MJ per kg.

Ethiopia has different useful and valuable natural resources with great potential, among which is coal. Due to the expanding of industrial-development and country's high population-growth and, there is a highly increasing demand of energy from time to time, where the supply of energy is limited and not counterbalanced with the existing demand [4, 5, 6].

Based on the report by [7], the deposits and occurrences of coal resource of the country estimated at 600 million metric tons. The majority of the deposit as we can see from Table-1 below is found in the south-western part of the country including areas such as Yayo-Wittete, Achibo-Sombo, Moye, and Delbi. In Dawuro zone of South-Western Region of Ethiopian, a huge amount of coal-deposit has also been explored and additional exploration (and mining-activity) has started in Benshangul Gumuz region [5, 4, 8]. However, the existing coal resource of the country is identified by existence of high impurity (or low-grade), and hence, doesn't fulfill the desired quality and requirements for the intended

applications. Low-grade coals, having high amount of sulfur and ash contents and low carbon content, are characterized with low calorific values.

Table 1. Coal deposit by category in Ethiopia.

Locality	Estimated Reserve (in thousand tons)					Calorific Value (Kcal/Kg)
	A-Category (measured resource)	B-Category (indicated resource)	C_1 Category	C_2 Category	Sum (A+B+C)	
Delibi			6,455.02	7,561.71	14,016.73	2,392.80-7,543.80 (mmmf)
Moye			7,274.06	20,271.24	27,545.30	4,820.50-8,333.30
Yayu Witette	12,270.00	37,525.00	128,781.00		178,576.00	4,465.35-4,981.97 (dmmf)
Yayu Achibo Sombo			64,453.11	57,003.92	121,457.03	3,713.95-6,739.44 (mmmf)
Chilga				19,000.00	19,000.00	4,129.60-5,691.17 (mmmf)
Gojeb-Chilga				9,380.00	9,380.00	5,835.00 (mmmf)
Nejo				2,900.00	2,900.00	4,545.00
Total	**12,270.00**	**37,525.00**	**206,963.19**	**116,116.87**	**372,875.06**	

Source: [7]

Note: ***mmmf*** (*moist, mineral matter free*) basis: was used to calculate CV, using a theoretical base as if there were no mineral-matter, but includes moisture-content of the coal sample; and ***dmmf*** (*dry, mineral matter-free*) basis: was used to calculate calorific-value of coal, using a theoretical base as if there were no moisture (or mineral-matter) in the sample (ASTM D388-12; 2013, p. 390–396).

Still, coal is the most important and widely occurred fossil fuel, covering 64% of recoverable fossil resources of the world compared to oil (19%) and natural gas (17%) [9]. In general, coal is classified based on its quality and application as low-rank and hard coal. Considering percentage of the coal types with respect to their reserve worldwide, lignite (17%) and subbituminous (30%) are categorized under low-rank coal. Bituminous (52%) and Anthracite (1%) are grouped under hard coal. Such classification is best described in the following figure.

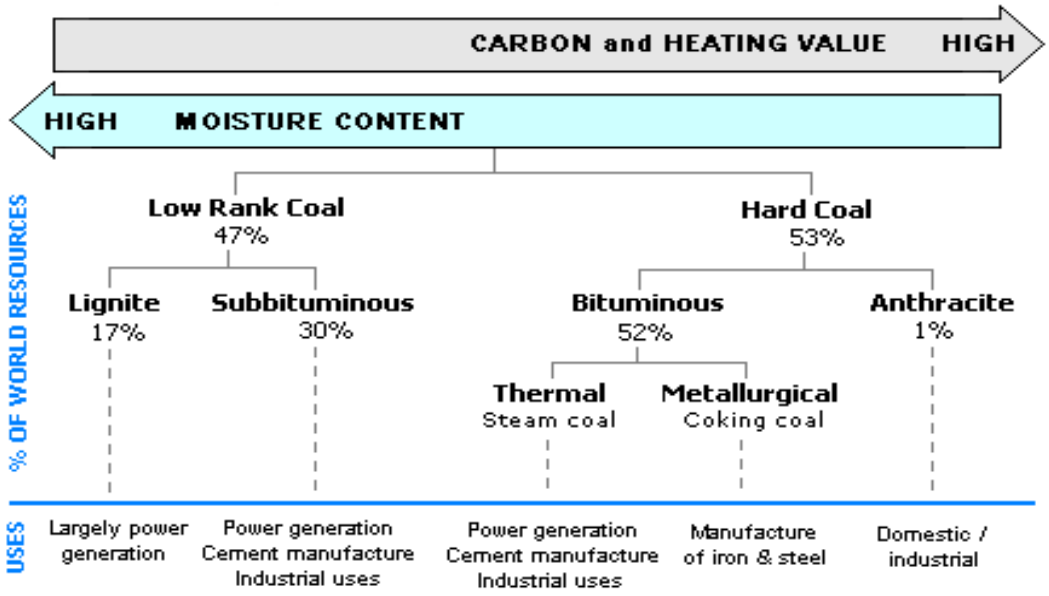


Figure 1. Classification of coal

Source: [18]

Despite the abundance of its reserve, the quality of Ethiopian coal grouped in the lignite to subbituminous classification described by: low heating-value, higher ash content (up to 50%), high moisture content (up to 35%), high volatile matter, and low to medium sulfur-content (1.5 – 3%).

Coal-dependent industries, which have played important roles in the modern world development, are expected to play a critical and dominant roles for the coming long-time, particularly, in most developing countries. Globally, the primary application of coal as sources of heat and energy shows [10]: for cement-production (over 90%), iron and steel-production (70%), electricity-generation (41%), transportation fuels, feedstock to produce chemicals, industrial-process heating, and household-heating and cooking.

According to [11], with the combined annual production of 6.35 billion tons coal, countries such as China, India, Indonesia, USA and Australia were considered as the top five coal (includes all grades) producing countries and ranked in the order they are listed, respectively. China, which produced about 3.94 billion tons, accounts for about 50.8 percent of the total production of the world. On the other hand, five countries namely Australia, Indonesia, Russia, USA, and South Africa are the biggest five exporters of coal to the global markets, for instance, these five mentioned countries shipped 84.5 percent of the total values sold at the international markets during the year 2021.

The statistical reports mentioned above show that despite the global initiative to reduce carbon-emissions due to the burning fossil fuels, it is not easily achieved and going to happen in the near-future. Countries having the potential coal resources are having greater opportunities and using it for achieving their developmental agenda and Ethiopia, owning enough coal resource, should be no exception. In Ethiopia, coal has been taken as a source of energy in different industries mainly cement and steel factories that are currently expanding in the country. Coal is used in cement industries for burning the raw-materials and metallurgical industries (like: iron and steel) for melting of iron with high temperature. Due to the high-impurity and low quality of domestic coal, these factories are forced to use and depend more on imported coal by spending high foreign exchange-rate to satisfy the growing demands of their industries [4, 8].

2.2 Industrial Uses of Coal

Broadly speaking, it will not be exaggeration if one says that coal is the basic raw material resource playing roles for the start of industrial development. Coal, which is a fossil-fuel, is considered far more plentiful than gas and oil. The degree of the undergoing change by coal, as it goes matured from the soft peat to hard anthracite, has important and significant effect on its chemical and physical properties and ultimately for what purpose it is applicable.

The most significant industrial uses of coal which are dominant until today are for energy use including in the electricity generation, cement production, iron and steel manufacturing, and also in the manufacture of different chemicals whereby the coal is first gasified and then after some treatments, the gases are utilized. Several kind of products can be produced from a by-product of refined coal tar to produce phenol, benzene and naphthalene by converting coal into gases by gasification processes. Thermal coal (for power plants and manufacturing of cement) and metallurgical coal (for manufacturing of steel) are terminologies alternatively used in the market [9].

According to reference [19], globally, the consumption of coal in 2022 reported above 8.3 billion tons, a new all-time high. Coal accounts for 36% of the world's electricity generation in 2022, which was 41% in 2007 [20]. The report also stated that the main coal consumers are China, India, USA, Russia, and Indonesia, which considered as the largest five coal-user countries in the world in 2022. The power plant is burning the coal to make steam to turn turbines and generate electricity. Besides, heat source from coal is used as raw materials in

variety of industries like bricks, limestone, and chemical products. The separated ingredients from the coal mainly ethylene and methanol, are used for production of synthetic fibers, plastics, tar, propylene-gas, Ammonia/Fertilizers, and Hydrocarbons [21, 22].

Although Ethiopia enjoys renewable energy source such as hydroelectric dam, solar and wind turbines for its power generation as a benefit of natural blessing, coal plays important roles in global power delivery. Data in WCA's website [23] states that still coal is the single and largest source of heat and electricity, and will also contribute about 22% in 2040, adding that this value is even higher in the newly emerging markets in areas of Southeast Asia as it will fuel 39 percent of heat and electricity in 2040. However, almost all of the cement plants in Ethiopia today are dependent on thermal coal for their manufacturing process. For the cement production, large amount of heat and energy are required (about 200 kg coal is required to make one ton product of cement) –an important component for the construction sector. Lime manufacturing is also dependent on coal as its source of energy [24].

Based on [25], coal is utilized in 70 % of the global production of steel as inputs and is required as a major component in several industrial processes. The production of steel ultimately delivers goods/services for economic growth, and needs health-care, clean water, well agricultural practices, access to affordable and reliable energy, telecommunications and better transport means. The future potential of Ethiopia's iron and steel manufacturing is expected to be significant and for this the domestic coal resource it has is going to be a good opportunity so long as it fulfils quality requirements.

Liquid fuels obtained from coal give alternative and viable option to conventional products of oil and can be applied in the supply of existing infrastructure. Currently, 'coal-to-liquids' gives 20% transport needs of South Africa, including the 7.5% jet fuel [10]. In this regard, there is room for Ethiopia to learn from. Prior to the production of petrochemical, several organic chemicals were produced from acetylene that made from the route of calcium carbide, in which coal was major feed stock. Various routes used for the production of inorganic and organic chemicals include: carbonization of coal and distillation of coal tar, gasification of coal and applying synthesis gas as feed stock for production of ammonia, liquefaction of coal by hydrogenation, and acetylene from calcium carbide. Coal is a potential source of multitude of industrial products that could be further used as feedstock in production of -value added products. The major products include ammonia, urea, methanol, and olefins [10].

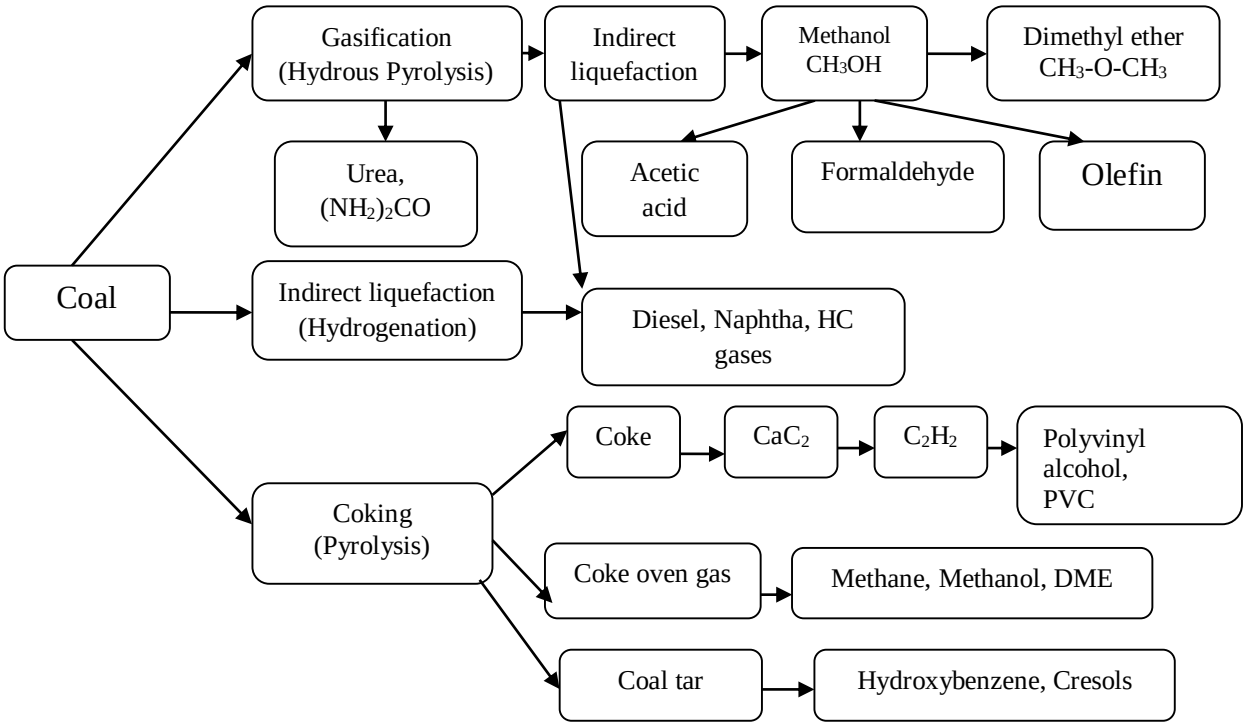


Figure 2. Derivatives of Coal.

Source: Korean Energy policy (2012)

2.3 Quality Considerations in Coal

The conditions of coal combustion are influenced mainly by the type of coal used and its processing. It is also fact and truth that the profitability of a specific industrial plant is affected by the quality of coal –as it equally affects ability of the plant to meet the environmental requirements. The main components that affect coal quality are its sulfur and ash content. Sulfur and ash are inorganic components that have no heating value. The higher the ash content of the coal indicates the lower its heating value. Typically, lower ranked (poor coals) have higher ash content, that is, 40% or more. Removing its ash content (which contains crustal materials having dirt and small rocks, and inorganic compounds: salts and metals, which have almost no heating value) through additives or washing increases the heating value of that coal [26].

They further stated that the existence of sulfur and ash in the chamber of boiler combustion of a power plant for example is being the factor for the increased maintenance (both scheduled and unscheduled) and factors for reduction of capacity (that is, generating electricity for fewer hours only). In addition, it results in higher ash accumulation due to incomplete combustion and increase solids' quantity, which have to be gathered by the

emissions' control devices. Sulfur and ash deposits on ductwork increases corrosion and reduced the expected life of the plant.

In the case of cement plants when VM, sulfur and ash contents of the coal used are high, production interruption happen due to clogging of preheater cyclones caused by the VM and sulfur compounds formed in the system. The ash content creates undesirable quality product which is going to be considered as reject affecting the profitability in a significant way. The coal combustion causes different environmental challenges mainly emission of particulate matter, NOx, SOx, toxic metals emission, and greenhouse gases. The direct coal utilization as stated above has different problems including: lower heating value; higher moisture contents and ash forming minerals; and environmental pollution. Enhancing quality of coal by lowering its sulfur and ash content is, hence, both economically and environmentally selective, beneficial and is an appropriate course of action [22].

2.4 Methods of Improving the Quality of Coal

The well-known problem for the use of poor (or low-ranked) coals is that it contains high moisture, ash and sulfur content with low carbon-content. Thus, the low ranked-coals need more beneficiation before utilization in order to increase their carbon-content and enhance heating value. The main purpose of low-ranked (or poor) coal beneficiation is, to minimize the inactive particle of mineral-matter, upgrade its combustion situation and quality, reduce the operation costs, minimize the pollutants' particulate, and minimize the associated transportation and storage costs [27, 14].

To solve problems related with the low-ranked coal and enhance its quality and applications, several researchers have been trying to develop different upgrading technologies of highly impure coal to minimize its impurities and fit with its desired applications. The recent techniques that have been developed and used for upgrading low-grade coal are mainly categorized as physical and chemical beneficiations. These techniques are used to increase the utility and cost-effectiveness of high ash and high sulfur-containing coal [3, 2, 12, 1].

Both chemical and physical purifying methods, which are more selective for the separation of minerals, need attention to reduce the challenges due to their high economic cost and low efficiency. Besides the expensiveness and cost, chemical-reagents that are used in applying these techniques for the purification of coal are dangerous, which need to be purified and treated before discharging [13, 14].

James and Gerhard [26] highlighted inorganic compounds can be removed prior to the coal combustion by washing the coal either at the plant itself or by applying mineral additives to it. “Beneficiation”, the industry term for improving quality of coal, improves the quality of the coal and produces benefits (both economic and environmental). Upgrading or improving of coal can be performed for several cases including de-mineralization, moisture removal, removal of dangerous constituents like mercury, sulfur, and others.

The reference [22] reviewed the improving of coal focusing on its processes of production, latest developments, and potential applications, indicated the history of chemical-cleaning of coal, in Germany, dated-back to 1940’s, where the processes were developed for the removal of ash forming minerals from physically-purified coal concentrates, involving heating of the coal concentrate (as a paste) with solution of alkali, followed by separation of solid-liquid, acid washing, and water washing. They elaborated the two basic cleaning-approaches of coal – physical and chemical. Physical treatment process is purifying the feed coal using uniquely physical processes, on the other hand, chemical cleaning can be categorized into two: using chemicals dissolving minerals or solvents in order to dissolve the ‘coaly-matters’. The first method (i.e., chemicals to dissolve minerals) produces ultra clean coal (UCC) by using alkalis or/and acids dissolving all minerals but leaving the organic coal-matrix under hydrothermal conditions. The second approach, production of AFC (ash free coal), is dissolving the coal’s organic components in organic solvent. In pure coal preparation process by physical treatment, separation of minerals are done by density-difference, and hence, the original structure of coal doesn’t change. Similarly, in the production process of UCC, there is no change in original structure of the coal; only the applied alkali (or acid) reacts with its mineral-matters. However, in AFC production (which dissolve solvents), organic matters dissolve in solvent while the mineral matters remain in residual, resulting in chemical changes in the original structure of the coal [22].

The model in figure shown below, used by the scholars and researchers clearly shows the ash content, which was initially up to 35%, was highly and significantly reduced in all cases of physical-cleaning (path-A), and in both types of chemical purifying methods, namely by alkali-acid method (path-B) and solvent-extraction method (path-C) in order to obtain UCC and AFC coal products, respectively. As the availability of low-grade coals is large, several researchers suggested that the importance of upgrading these low-ranked coals, hence, to enable the product acceptable and suitable for clean electricity-generation and protection of

the environmental. However, researchers suggested that some of the solvents used in the coal-leaching experiment like HF, HCl, HNO_3, and NaOH are toxic and expensive reagents and unless further research-work is done on their reduction or regeneration (reuse) of these chemicals to assure the cost-effectiveness and environmental-friendliness of the whole coal cleaning/leaching process [27, 1, 3].

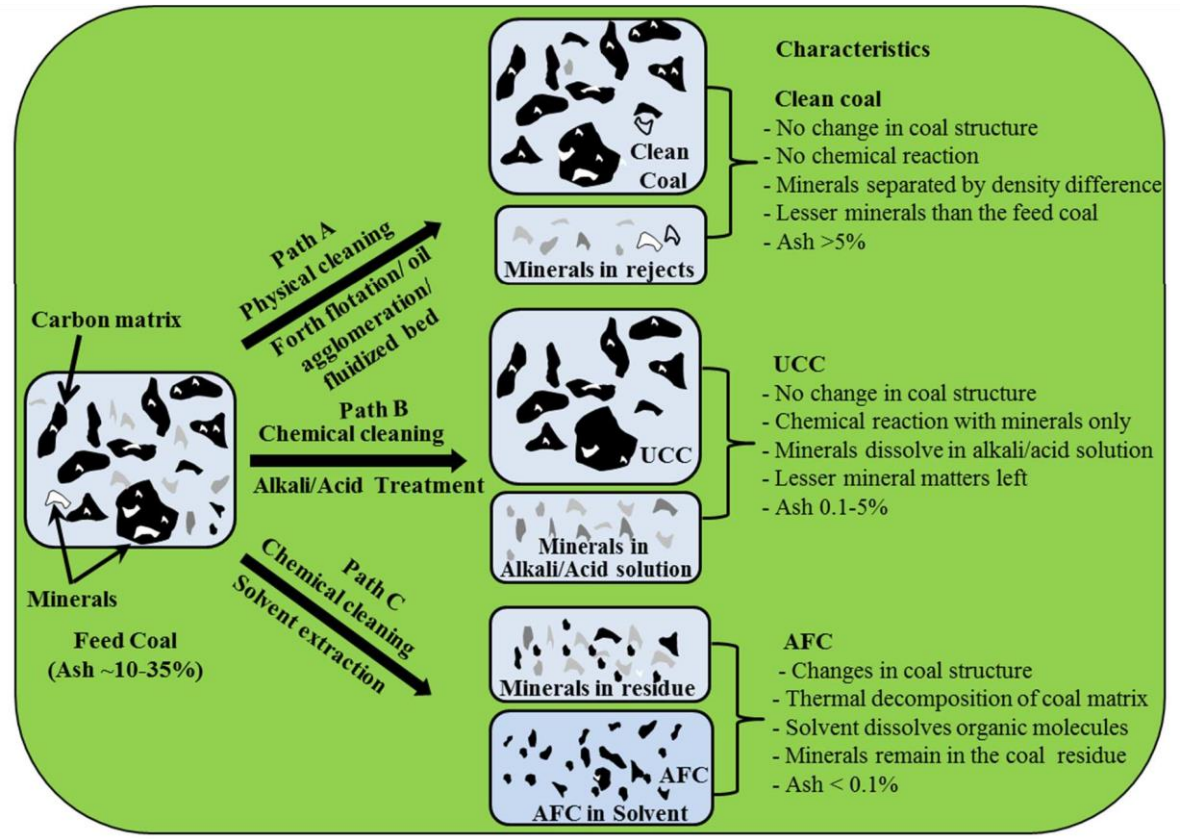


Figure 3. Conceptual diagram of producing: (a) Clean Coal (b) UCC and (c) AFC, and their characteristics.

Source: [22]

In fact the experimental test results of final products (UCC and AFC) were found to be affected by conditions and factors such as the acids or alkali concentration, leaching temperature and time, initial pressure, particle size, and its properties through proximate analysis and ultimate analysis [1, 27]. The physical beneficiation method by froth flotation technique, chemical cleaning method by alkali/acid treatment on Ethiopian low-quality domestic coal shall be the choice of the research and as [22] explained out, the physical treatment of the sample coal by froth-flotation technique is applied as a precondition for best achievement of result.

2.4.1 Physical Beneficiation Methods of Coal

Physical beneficiation is one of the most popular and common practices for the removal of impurities and improving of coal quality without any chemical alteration, as the method is mainly focused to separate impurities and coal based on the resulting difference in physical properties such as: the mineral-matters' size, specific gravity and magnetic-conductivity, and carbonaceous parts of the coal. Physical beneficiation method works well for coal with higher-quality rather than low-quality coal. Its other limitations are that only the pyritic-sulfur is removed and the gravity separation of the coal requires a larger feed size (greater than 0.5 mm), and is not suitable for separating minerals having chemical-bound [16]. Hence, physical beneficiation method is less effective for the treatment of coals with lower-grade particularly, for those high-sulfur containing coals and chemically bounded impurities within their coal matrix.

2.4.1.1 Froth Flotation

Froth flotation is known as one among the most widely used coal's physical-purification methods, which is done based on the difference of surface hydrophobicity and floatability between inorganic-minerals and organic-matter for fine coal purification. The basic principle of this method is hydrophobic-materials separation from the hydrophilic mineral-matter through the addition of appropriate chemicals-reagents (collectors, frother and air-application) [21].

The efficiency and effectiveness of separation depends on the differences between the coal-particles' wetting-capacity with the mineral-content found in aqueous phases [28]. In the process of separation, the establishment of stable situation is created and observed between the air bubble and coal's surface. In the treatment of coal using floatation, the coal particles used are wetted in aqueous-solution and agitated (stirred) in order to mix it with the collector-reagents used. Then hydrophobic coals-particles are attached to the resulting air-bubbles and hence rise to the surfaces of clean coal in the froth-zone by leaving behind the existing hydrophilic mineral-particles in tailings (suspensions). The formed foam is collected (or skimmed off), and followed by filtering process and drying for further analysis [29, 1].

Low-grade coal contains more of oxygen functional-groups commonly known as: hydroxyl, carboxyl, carbonyl, and phenolic-group functionalities. These functional-groups reduce the

ability of hydrophobicity of the coal-particle surface by increasing a lot of hydrogen-bond sites with molecules of the waters and forming of the hydration-films, which block absorption substances (i.e., oily droplets) [3]. Due to the oxygen functional-groups existence, the flotation of lower-ranked coal is very difficult. Different researchers have used chemical reagents to increase the performance and efficiency/effectiveness of the flotation. The chemical-reagents used as collectors for the coal floatation are (diesel-oil, kerosene, gasoline, and oxygenated-fuel-oil) and the reagent used as frother are (Methyl-isobutyl-Carbinol, methanol, polyethylene-glycol, pine-oil, n-octanol and oleic acid). The selection of the reagents for coal floatation is based on the viscosity, molecular weight and cost of that reagent [30, 17].

2.4.1.2 Collecting Mechanism of Flotation Collectors

The polar collectors are lying to spread on the surface of the coal and have high interfacial interaction energy with the surface of coal. This interaction mechanisms between collectors (oxygen-containing groups) with the coal surface's oxygen-containing sites are through hydrogen bonding or electrostatic interaction [29]. The interaction between coal surface and collectors is classified into two mechanisms. The first one is the interaction between the coal surface and collectors that appears through the reagent's polar groups interacts with the oxygenated functional groups on surface of coal through the bonding of hydrogen. The second approach holds the nonpolar chain's interaction with the carbonaceous sites on the surface of coal by displacing molecules of water from the surfaces [31, 14].

2.4.1.3 Factor Influencing Performance of Coal Floatation

The performance of flotation of lower-ranked coal is usually affected by different operating parameters like: reagent dosage, pulp density, air bubble, flow-rate and particle-size. But these all working-parameters are dependent on the types of floatation-cell used.

Airflow rate: - is one parameter that influences the floatation of coal which depends upon the amount of air-introduced into the flotation process, significantly influences the response of flotation. It also plays critical role for the froth establishment. The air-bubbles, introduced into the floatation, used for capturing case and carrying of coal particles' hydrophobic toward the froth phase by leaving the hydrophilic ash-minerals. As airflow rate increases the content of ash of the froth phase and combustible-recovery is also increases up to the maximum points and airflow-rate has a significant effect on the floatation-performances [4].

Particle-size: - It is one among the basic parameters in the process of flotation because it influences distribution of bubble-size, gas bubble-mineralization, the stability of bubble-particles aggregates through the particle-attachment/detachment-rates. But the coarse particle-size has bubble-particle buoyancy and particle-sizes increasing resulted in longer time of induction and the floatability deterioration [16, 16].

Pulp density: -is a parameter that influences coal floatation-process with bubble-size and mixing-characteristics –by increasing the solid-phase in the pulp that affects the pulp-viscosity and aggregate of bubble-particle overloaded that attaining high-densities. Then this aggregation of the particle leads to a greater number of coal particles that will sink than that of the floating one [16].

Reagent dosages: are the most significantly influencing-parameters of coal floatation by reacting with mineral-surface or coat to make the water-repellent and attachment of particle on the air-bubbles. The importance of reagents in coal floatation is to minimize the bubble-size and hence stabilize mobility of froth-phases [32, 16, 14]. Appropriate reagents' selection is important in flotation technique [1]. Several types of collector reagents are used for coal flotation. Kerosene and Diesel oils were applied in combination as collector for coal flotation. A combination of kerosene oil and diesel oil, in 1:1 ratio, was identified as a better and appropriate collector for coal flotation being under investigation [33]. It was found that a mixture of kerosene and diesel oils is more appropriate collector for coal flotation because of its hydrophobic property and enabled higher-recoveries. According to [4] diesel oil was proved to be a better collector for the coal samples flotation from Achibo areas of Southwest Ethiopia. In addition, in a few experiments previously conducted, different frother reagents such as pine oil, n-octanol, 'methyl isobutyl carbinol', and polypropylene glycol were applied to find out the effect of frother on flotation of coal. It was confirmed that the pine oil and n-octanol gave better stable froth in coal flotation. Both adsorb on surface of coal and have better collecting properties in flotation of coal [4, 34].

2.4.2 Chemical Beneficiation Methods

The chemical beneficiation is a method used for removal of mineral-matters (both organic and inorganic) from coal, which adequately reduces the ash content as well as the removal of harmful minerals to avoid the challenges associated with liquefaction, gasification, combustion effectiveness, and emissions minimization of airborne pollutants. The method

also involves the treatment of low-grade coal with the help of chemical solvents that use for the removal of particle that bounded strongly to the coal matrix and mineral matters. The chemical solvents that are used for leaching processing are alkali reagents (like KOH, NaOH, and $Ca(OH)_2$) and acids (like HCl, HNO_3, HF, and H_2SO_4). The leaching process is faster and directly affects the minerals within the coal without affecting its original structure. However, due to the uses of expensive solvent in chemical beneficiation, it's not widely recommended and employed on a commercial scale [21, 22]. Therefore, in order to enhance performance of the leaching process, further work needs and will be done to reduce the utilization of these reagents or minimize their consumption in the processes of coal cleaning while determining optimum parameters for other important leaching factors, which is of great concern and be considered in this study.

2.4.2.1 Alkali-Acidic Leaching

Studies confirmed that the alkali and acid- leaching procedures in combination play significant roles in significantly minimizing the higher ash-content in the coal – as the sodalites and sodalumino-silicates, which are formed due to the reaction with sodium-hydroxide and are largely acids soluble. Thus, sometimes, activity like mild acid washing also minimizes the extra compounds of sodium together with those acid soluble minerals exist in the ash. Further, in addition to kaolinites, quartz, and pyrites, the existing organic sulfur content is also minimized by the alkali-acid purification [17, 16].

The use and application of alkalis, acids, oxidants, leachants and different combinations of alkalis/acids are proved to be an effective and attractive alternative to demineralize and also desulfurize different low-ranked coals. Accordingly, higher demineralization and desulfurization results, about 80 – 90 percent, being achieved in coals of lower-grade, however, the expensiveness and costs associated with these chemicals still remain an issue to use them commercially for purifying coal [16]. Hence, work needs to reduce the application of those chemicals/reagents or apply the combination of chemical and physical methods to further minimize the consumption, and hence costs, of those reagents in coal cleaning and enhance its utilization. Moreover, the efficient ways of recovery or recycling of those chemicals and their disposal into water sources after leaching is receiving great attention and concern researchers considered [17].

According to the study conducted by [17], flotation as a pretreatment could reduce the ash and sulfur contents from 22.5% and 3.54% to 13% and 2.14%, respectively. Then, coal concentrate resulted from flotation technique was cleaned applying NaOH, and the total sulfur content was decreased to 1.10% with 54.77% sulfur-reduction and the ash became 17.5 %. Further, the NaOH-leached coal (after flotation) was leached again with 10 % HCl and the sulfur-content remain 1.10% and ash content of 8.1% with 59.27% ash-reduction was obtained. This shows that chemical cleaning with NaOH, after the flotation, can efficiently remove much content of sulfur, while chemical cleaning of NaOH-leached flotation concentrate can effectively remove much of the ash-content.

2.5 Coal Data Analysis for Quality Improvement

The coal data analysis is aimed mainly at determining the rank (or quality) of the desired coal, which is further, used for coal trading as the fundamental and basic consideration and coal's utilization. Generally, physicochemical determination and characteristics of coal data analysis includes three parameters as [16, 35]: (i) *the proximate analysis* (that includes ash-content, volatile-matter, moisture-content, fixed carbon); (ii) *the ultimate analysis* (such as: Hydrogen, Carbon, Nitrogen, Oxygen, Sulfur); and (iii) the coal's CV (heating value).

2.5.1 Proximate Analysis

The proximate analysis performed on the coal data is one of the basic and most widely used and the simplest method applied for the evaluation of coal properties and energy-value. It also provides vital information on the appropriateness of coal application for a specific purpose. The coal's proximate analysis before and/or after treatment is characterized by determining its ash, moisture, volatile matter, and fixed carbon [4, 16].

2.5.2 Sulfur Content

The sulfur content of the given coal is determined by applying the method of Eschka. The desired amount of the sample is weighed and mixed with Eschka mixtures (made from magnesium oxide (2g) and anhydrous sodium carbonate (1g)) in the porcelain-crucible. The resulted mixture is covered with Eschka mixture again to prevent the sulfur loss in the form of sulfur dioxide. Next, the porcelain-crucible containing the above mixture is put in a cold muffle furnace, and followed by gradual heating at 800 ^{o}C, for 60 minutes. During combustion, the sulfur compounds are reacted with the added Eschka mixture under the oxidized condition, and hence, converted to Na_2SO_4 and $MgSO_4$. Next, the product will be

digested by applying dilute HCl (1M) with appropriate stirring for 45-minutes. The solution (digested) will then be filtered into beakers and required drops of methyl orange is added to it until its color will be turned to neutral. Then, the obtained sample will be heated to the boiling-point and 10-ml $BaCl_2$ (10%) will be gradually added by stirring it continuously for 30-minutes. At the end, by thoroughly washing with hot water, and thus, after cooling down, the solution will be filtered and the formed Barium-Sulfate ($BaSO_4$) residue will be burned at 500 ^oC. It will be weighed and then used to compute the sulfur content; the detailed procedures and equation applied to calculate sulfur content is described in third chapter under the methods section [36, 37].

2.5.3 Calorific Value

Specific heat energy (calorific value) is an important parameter in coal data analysis that directly shows the heating value of coal particles. It is the most widely applied benchmark for the quality of coal. The calorific-value (CV) is described as higher heating value (gross calorific value) or lower heating value (net calorific value) [1].

Calorific value is computed from the obtained value of heat released as the sample coal is burnt in excess oxygen using bomb calorimeter with standard test method of coal analysis [38, 39]. It is performed using a Bomb calorimeter according to the standardized steps explained in the ASTM D 5865 [1].

An enough amount of oxygen (with pressure) is purged into the bomb for the complete-combustion and is covered with lid screwing. The purpose of lid screwing is to provide 2 electrodes and oxygen inlet valve. The bomb is put into the 'copper-calorimeter' weighting the distilled water that is surrounded with air jacket and water jacket to prevent heat loss because of radiation. Finally, the bomb is automatically-fired and the temperature that raised is recorded. It is continued until the jacket's temperature is reached equilibrium with the bucket temperature and the heating value is then determined by taking the difference between the initial and final temperatures [6, 8].

2.6 Comparison of Beneficiation Methods

The reference [40] studied demineralization aspects of Indian coals containing high ash and sulfur by applying chemical and physical beneficiations. They confirmed that physical treatment of coal is not very efficient and effective in finely dispersed minerals separation,

on the other hand, chemical cleaning uses expensive chemicals/reagents and results in generation of large amount of wastewater that needs purification before its discharge. Hence, the study concluded that the combined method applying physical and chemical purification considered as effective and attractive method for significant minimization of ash, requiring less capital or investment and producing less polluting wastewater.

The study conducted by [41] on chemical purifying of higher-ash coals of India to obtain lower-ash coal revealed that reduction of the ash value from the Indian coals by using caustic solution and then acid washing. They concluded that demineralization result was improved by reducing particle-size and increasing alkali concentrations, reaction time and temperature. A significant reduction of phosphorous-content and marginal-reduction of sulfur were observed after the acid treatment. The reference [42] studied the efficiency of desulphurization and demineralization processes to improve the application of lignite coal. They stated that in order to make the applications of coal environmentally friendly, treated it with the combination of physical and chemical methods. Physical treatment removes organic minerals on the surface structure that are attached to the coal, while chemical purification was an effective technique, however, due to utilization of chemicals, it is expensive than physical treatment. The study concluded that applying the combination of both methods is more efficient for desulphurization and demineralization of coal and reported the achievement of UCC by the combined technique.

The study conducted by [43] reported the reduction of ash content of raw-coal applying the chemicals NaOH, HCl, and H_2SO_4 by conduction a series of leaching tests on coal of different size by varying the leaching parameters such as temperature, time and concentration. The results showed that about 75% of ash was removed from the sample coal. Moreover, the study revealed that NaOH is a better leachant than HCl or H_2SO_4. They confirmed that decreasing the sample size improves the leaching potential, due to increasing surface-area, and the leaching has been improves by increasing leaching parameters (concentration, time and temperature).

The research by [35] explored the demineralization mechanism and influence of leaching parameters on high-ash containing coal of Indian and also its characterization before and after treatment. The selected coal samples, prepared as particle size of 375, 230 and 180 µm, were tested with both alkali and acid treatments (each applied on raw coal) using different leaching values of concentration, time, and temperature. The demineralization was

improves, for both acid and alkali treatments with reduction of particle size and increasing leaching parameters. They investigated that particle-size of 180µm offered better demineralization for the sample coals at NaOH (30%) and H_2SO_4 (30%). The alkali (NaOH) leaching resulted in 46% and 42% demineralization for two selected coals, whereas acid-cleaning resulted in demineralization of 34% and 32%. The study concluded that better clean coal was obtained when the leaching factors and parameters of each factor were properly selected. They reported that the demineralization was better by the application of NaOH as compared to acid-based treated coals, and the study found that leaching with alkali concentration was more effective/efficient for coal demineralization.

The study conducted by [44] on pretreatment of coal using flotation from Hazro-Turkey for improving desulfurization applying aqueous NaOH. They reduced 58.54% ash, 79.34% pyritic sulfur, and 56.98% VM by flotation-pretreatment, and 69.59% coal concentrate. Further, the resulted coal concentrate was leached with NaOH solution, and its sulfur content (organic) was decreased by 59.27%. The result showed that, using the two methods in combination, the ash, sulfur, and VM contents were decreased by 63.13%, 88.06%, and 77.32%, respectively. The study concluded that two-step desulfurization and demineralization, using flotation pretreatment followed by leaching with aqueous caustic, was considered as an effective approach for preparation of clean coal with maximal yield.

In experimental study by [45], the sample coal was leached with sequential leaching processes using NaOH and then by HCl. The NaOH concentration was varied from 2.5M to 10M and conducted with 1.4N HCl. Effects of time and shaking-speed were analyzed at (1, 2, 3 and 4) hours and (0, 50, 100, 150 and 200) rpm, respectively. They investigated that the parameters: alkali concentration, shaking-speed and duration time were found the most affecting leaching parameters for the ash-content reduction of the coal. Accordingly, after 3-stages of chemical treatment, the ash was decreased from 35.3 % to 0.98 % and UCC was obtained with 10M NaOH solution and 1.4N HCl. However, they obtained such result with higher NaOH consumption, increasing cost of leaching.

The reference [46] reviewed the purification of high-ash containing Indian coals by applying physical, bio- and chemical beneficiations. The study stated that chemical purifications were superior to physical ones, however, they used expensive chemicals and resulted in wastewater with large quantities. Efficient beneficiation depends on the amount and type of minerals found in coal [47]. Therefore, [46] suggests a combined method of physical

treatment and followed by chemical method. [48] stated that even though physical or physicochemical purification are economical and easy to operate, they are not both efficient and advantageous for low-ranked coals due to: (1) drifty-nature, (2) poor-washability, (3) presence of finely disseminated and bound minerals, (4) requiring for larger size of coal particle (above 0.5mm) if gravity-based purification method is used, (5) coal's oxidized-nature that challenges its flotability during processes of flotation, and (6) requiring small feed-size (below 100μm) in the energy-intensive flotation process.

In the study by [13] on Zonguldak coal, flotation and two different sodium-hydroxide cleaning methods with a three-stage process of purification were applied to obtain a fine clean coal. The result showed that the ash percentage of the coal were decreased from 10.62 to 2.7 % with weight recovery of 27.2 % and from 10.6 to 1 % with weight recovery of 25.78 % with atmospheric cleaning and autoclave leaching, respectively. Hence, they concluded that, with the best experimental conditions, a coal product with 1% ash and 8,390 kcal/kg of CV was obtained, which meets the required standards for the coal-water slurry production to be used as a fuel in gas or oil boilers, coal boilers, and diesel engines,.

In general, applying the combination of chemical and physical methods for coal purification, considering the consumption of the chemicals has not been well studied. Moreover, the characterization of the domestic coal and beneficiation of such coals to reduce the impurities and improve quality are not well investigated or studied properly yet. It has been found from the literature that very limited studies have been conducted on upgrading quality of low-ranked coal in developing countries, particularly in Ethiopia, by using the physical treatment, and no work has been done on energy enhancement of domestic coal by using the combination of physical and chemical treatment with the minimum consumption of chemical reagents.

CHAPTER THREE

3 MATERIALS AND METHODS

3.1 Materials

3.1.1 Instruments and Apparatus

The instruments and apparatus used for experimental process in current study are: Jaw-crusher machine (RoHs53743), Centrifugal-miller (RETCH-56402) and Sieve-Shaker (RETCH-A200) all from Germany, and Adiabatic Bomb Calorimeter (MK-GSL-12, UK) at Laboratory of Geological Survey of Ethiopia; Wedag flotation cell (Groppel-98, Germany), Universal Hot-Oven (Jaico-fisher Scientific, 40GCEMD, India), Silica-crucible, Muffle furnace (XMT - F9), and Electronic-balance (AUW-320, Philippines) at AASTU (Industrial Chemistry laboratory).

3.1.2 Chemical Reagents

The chemical reagents which had been used for the experimental process of the current study were: Diesel oil collector (Industrial-grade), n-octanol (99%, Loba-Chemie private limited, India), NaOH (98 %, Sigma Aldrich, USA), NaOH (10%), USA), HCl (37 %, Sigma Aldrich, USA), Sodium carbonate anhydrous (99.9%, Sisco Research Laboratory private limited, India) to make Eschka mixture, Magnesium-oxide (97.5%, Sigma-Aldrim, Germany) to make Eschka mixture for sulfur determination, Barium Chloride ($BaCl_2$), and 5% HNO_3 (as solid digester in acid-leaching).

3.2 Methods of the Study

3.2.1 Experimental Design

The whole experimental procedures carried out in the current study and coal data analyses were summarized in figure below. It includes the raw coal sample preparation methods, flotation of coal sample followed by the sequential Alkali-Acid leaching, coal data analysis and calorific value determination. This experimental procedure of coal quality improvement was designed for both raw coal sample and sequentially treated (flotation concentrate and alkali-acid-leached) samples.

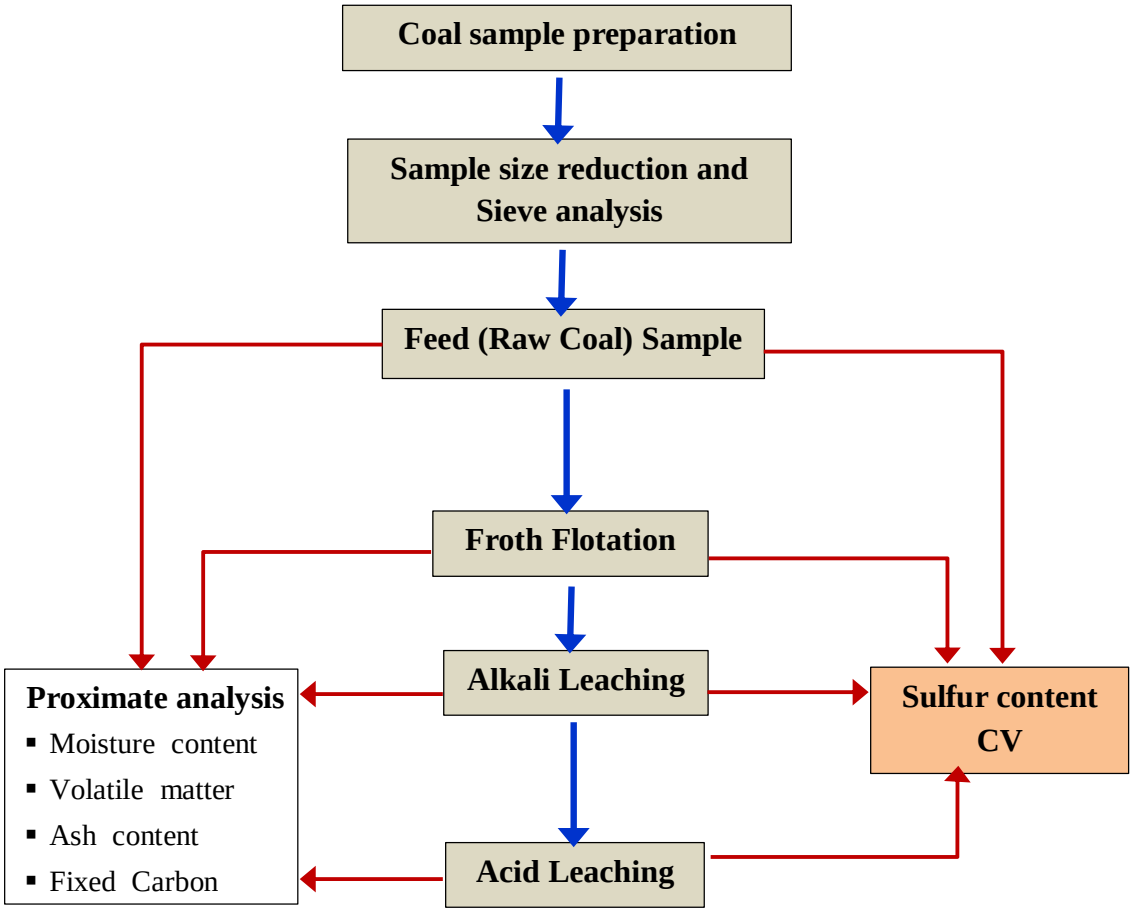


Figure 4. The overall experimental design of coal beneficiation using flotation technique, Alkali and then Acid-leaching, sequentially.

3.2.2 Coal Sample Preparation

The coal sample was obtained from Dawuro located in South-West Region of Ethiopia, which is one of the known coal deposit areas in Ethiopia. The coal sample, which was prepared based on the standards called ASTM (ASTM D-2013) used for preparation of coal by the Coal Mining Plant, was obtained from the nearby Cement Plant. The coal sample was dried in atmospheric air for 72 hours for removal of extraneous moisture from coal, and the dried coal sample was ready for size reduction in order to minimize the particle-size without changing the proportional weight.

First, the lumpy coal sample was crushed to reduce the size of the particle to 1–2 mm by using Jaw Crusher. Next, Centrifugal Miller was used to obtain the fine powders product approximately under 500 µm. Then, the milled particles (below 500 µm in size) was taken to the Sieve Shaker to separate the fine and coarse samples. Accordingly, the mesh sieve was arranged from higher to lower size as: (i) 60 mesh or 500–250 µm, (ii) 120 mesh or 250–125 µm, and (iii) 230 mesh or 125–63 µm. Finally, the fine powder product of the coal

sample of the current study, separated according to their size at three ranges of intervals, was stored in plastic bags, labeled and taken to the laboratory for the experimental analysis.

3.2.3 Flotation of the Coal Sample

3.2.3.1 Optimization of Coal Flotation Parameters

The flotation experiment was conducted at AASTU (Industrial Chemistry laboratory). The Design-Expert version 13 software is deployed in experimental design and to determine the optimal flotation parameters. The experimental conditions for flotation of coal samples were modelled and optimized using RSM (response surface methodology) using a BBD. A BBD, one of the standard RSM designs, is appropriate for fitting quadratic and higher models and it enables to optimize the applied parameters with the least number of experiments, and also to analyze the existing interaction among parameters. Moreover, RSM is a collection of important statistical and mathematical methods used to design and develop empirical models, improve/optimize parameters, and determine interactions among the influencing factors [49].

Three independent variables (called factors), each varied over 3 levels, were generated and then optimized. The ranges of parameters in flotation were organized and optimized by arranging the particle size of the sample coal at three ranges of intervals such as 500–250 μm (60 mesh), 250–125 μm (120 mesh), and 125–63 μm (230 mesh); the dosage of Diesel oil (as collectors) was using as 10.0 g/ton, 55.0 g/ton, and 100.0 g/ton; and n-octanol as frother stabilizer from 90.0 g/ton, 230.0 g/ton, and 370.0 g/ton, leading to 17 flotation runs. The study conducted by [4] on Achibo area coals in southwestern Ethiopian used different dosages of 0.047 kg/ton diesel oil (as collector) and 0.368 kg per ton frother (n-octanol).

Accordingly, the optimum parameters of particle size, collector dosage, and frother dosage were determined at the preliminary test, and then the entire experimental tests of this study were performed by using such optimum parameters. In this research, the entire flotation tests were conducted using the constant parameters of flow rate of 90 g/min and impeller speed of 2800 rpm as several studies recommended [50, 15, 32].

Finally, ash contents of feed coal and flotation concentrates were obtained and the performance of the process was calculated using equation:

$$\alpha_1 = \frac{A_1 - A_2}{A_1} * 100,$$

where, α_1 = percentage reduction in ash, A_1 = Ash percentage in coal sample before flotation, A_2= Ash percentage in coal sample after flotation.

3.2.3.2 Procedures of Coal Sample Flotation

In this research, the following procedures were applied to conduct the froth flotation experiments using the fine particle size of the sample coal.

1) The fine particle size of sample coal prepared earlier and Wedag flotation machine having capacity of 3L are used. Thus, 2.5L of distilled water is added to the flotation tank and then 90g of the sample coal is added and agitated for 3 min with stirring speed of 2,800rpm until the particles are fully wetted with the air valve being closed.
2) Next, drops of dosage of diesel oil (collector) is added and agitated again for 2 min while the air valve is closed. Then, required dosage of n-octanol (frother) is added, while air valve is opened in order to supply the air in the flotation cell to make the required bubble particles.
3) As formation the bubble begin, 0.5L water is added to fill the flotation cell. Then overflowing of the formed bubble particle is started and the flow particles are collected. The formation of foam and collection are continued until the white foam will be observed, indicating that all solid particles are attached to the oil collectors.
4) At the end, the particles collected are filtered and then dried in the hot oven at 80 ^{o}C and the concentrate yield is calculated by the equation given below [4, 13].

$$Yield\ \% = \frac{Mc}{Mf} \times 100$$

where Mc is weight of floatation concentrate, and Mf is weight of sample (feed coal) in grams.

The experimental coal flotation flow diagram is shown in Figure 5 below.

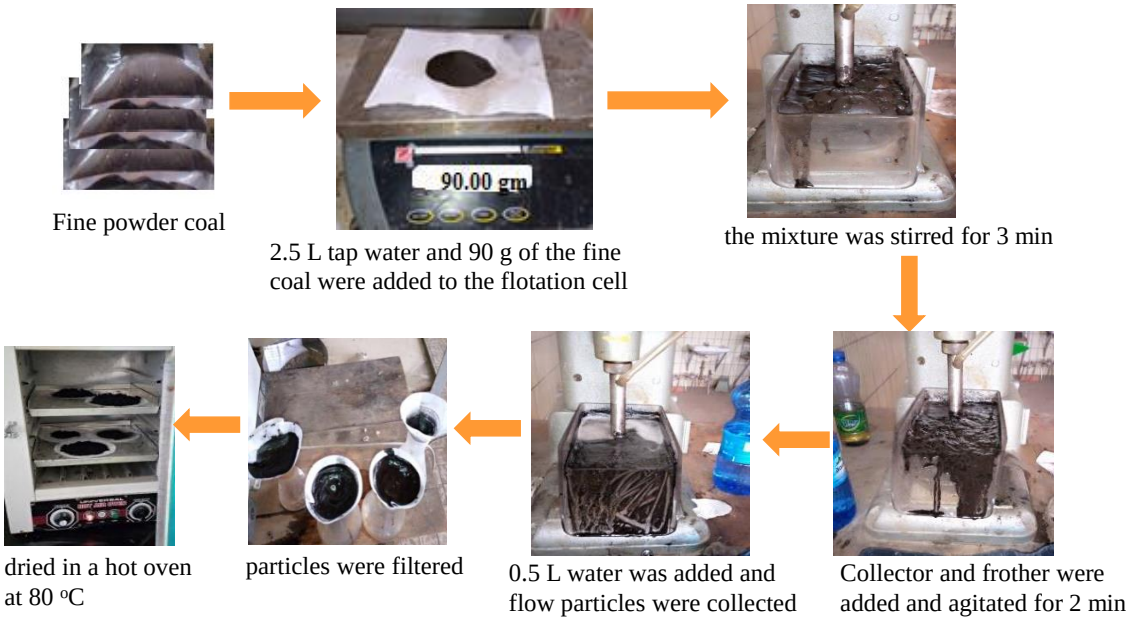


Figure 5. Coal flotation flow diagram.

3.2.4 Alkali Leaching

For the sequential Alkali-Acid leaching experiment, the flotation concentrate obtained from optimized particle size was used as feeds for alkali leaching followed by acid leaching tests. The chemical reagents that was deployed in this current include Sodium hydroxide (NaOH) and Hydrochloric acid (HCl). NaOH was used for the alkali-leaching of flotation concentrate and HCl was used for the acid-leaching of Alkali-treated flotation concentrate. HCl, along with the other acids, were also used to digest solids in alkali-leaching.

3.2.4.1 Optimization of Alkali-Leaching Parameters

NaOH-leaching experiment was carried out using the floatation concentrate coal particle sample. The NaOH was used as a solvent and the optimization of its parameter was done for this process. Design-Expert software (version 13) was applied for the design of experiment. The experimental conditions were modelled and optimized using RSM (response surface methodology) using a BBD. The independent variables such as sodium hydroxide concentration (1 mol/dm^3, 2.5 mol/dm^3, 4 mol/dm^3), leaching temperature (130 ^{o}C, 175 ^{o}C, 220 ^{o}C) [13] and contact time (40 min, 60 min, 80 min), leading to 17 leaching runs, were generated and then optimized. The NaOH concentration, leaching temperature and time were varied, and coupled with a agitation speed of 600 rpm, that was kept fixed.

Finally, ash contents of alkali-leached flotation concentrate were determined and performance of the process was determined using equation:

$$\alpha_2 = \frac{A_2 - A_3}{A_2} * 100,$$

where, α_2 = percentage reduction in ash due to alkali-leaching experiment, A_2 = Ash percentage in the sample before alkali-leaching (after flotation), A_3= Ash percentage after alkali-leaching.

3.2.4.2 Procedures for Alkali-Leaching of Flotation Concentrate Sample

The procedures to conduct the alkali-leaching on flotation concentrate is similar to [13, 51] and described as follows.

1) The flotation concentrate obtained from the optimized particle size of coal was treated with NaOH solution of a predetermined concentration from the three levels.
2) The agitating speed is kept fixed/constant at 600 rpm for the entire tests of experiment. The slurry was subjected to the desired level of temperature (from 130, 175 and 220 °C), for selected level of leaching time (from 40, 60, and 80 minutes).
3) The leached particle is filtered using 'what-man filter paper'. The filtrate is then, washed using 'double-distilled' water to get rid-of contaminations of due to process.
4) Finally, the filtered sample is dried with electric oven at 80 ^{o}C, and subjected to volatile matter, moisture, ash content, sulfur, CV, and other analyses.

3.2.5 Acid Leaching

3.2.5.1 Optimization of Acid-Leaching Parameters

Here, the HCl leaching tests were performed on NaOH-leached flotation concentrate. At this step, HCl is used as a leaching agent as it is less expensive than HNO_3 and to find out the optimal experimental conditions [13, 12]. Again, the Design-Expert (version 13) program was deployed for the design of acid-leaching experiment. Hence, the working conditions are modelled with BBD-based RSM.

The independent variables such as: HCl concentration (2, 4, and 6 mol/dm3), leaching temperature (40, 60, and 80 ^{o}C), and leaching time (1, 3, and 5 hours), leading to 17 runs, were obtained and optimized. The HCl concentration, temperature and time were varied and coupled with solid/liquid ratio of 5% and 530 rpm agitating speed that were kept fixed.

Finally, ash contents of HCl-leached products of alkali-leached flotation concentrate were determined and performance of this process is obtained using equation:

$$\alpha_3 = \frac{A_3 - A_4}{A_3} * 100,$$

where, α_3 = percentage reduction in ash due to acid-leaching, A_3 = Ash percentage before acid-leaching (after alkali-leaching), A_4 = Ash percentage after acid-leaching.

3.2.5.2 Procedures for Acid-Leaching of Alkali-treated Flotation Concentrate

The procedure of acid-leaching test that was used in current study is same to that applied by [12], which is described as follows.

1) For each test, alkali-leached floatation concentrate coal product was mixed with HCl solution of selected concentration level, and then agitated with 530 rpm.

2) Then, 15mL of the slurry is drawn with 0.45 μm micro-filter plunger syringe to separate the solids that is suspended from the leachate.

3) The liquid sample was diluted with 5% HNO_3 and then directly subjected to the desired analysis, while the solid samples were completely digested first, and the digestion solutions were analyzed. A comprehensive description of the digestion procedures can be found in a previous study [31].

3.2.6 Coal Data Analysis

The physical and chemical composition of sample coal were analyzed according to the coal analyses guidelines of national standards and international, i.e. 'American Society for Testing and Materials' (ASTM) standards used for analyses of coal [52]. To examine quality of the coal, different analyses such as: proximity analysis, total sulfur, and calorific value of raw, and flotation-treated, alkali-leached and acid-leached coal samples were carried out.

Design Expert (version 13) software deployed to perform analysis on the data of each experiment. To select the best fitting model, different statistical conditions including p-value, 'lack-of-fit', and 'R-Squared' values of several models were computed and compared. The 3-D 'response surface graphs' were plotted and used to investigate the influence of the variables. Software-generated formulas were created and evaluated. The experimental and predicted values were computed and compared.

3.2.6.1 The Proximate Analysis of Coal

The proximate analysis is used to identify the physical properties including: Moisture content (%), Volatile Matter (%), Ash content (%), and Fixed Carbon (%) of both raw coal and treated coal samples based on Standards of ASTM (D-3173, D-3174, D-3175, and D-5373). It gives important and critical information regarding the appropriateness of coal for a specific industrial or domestic application.

a) Moisture Content

Determination of moisture needs gentle coal heating at temperature slightly higher than boiling point of water that causes a weight loss from the given sample coal, which is called as *moisture.* Studies revealed that the moisture content of coals varies from 5 % to 70 %. Moisture is unwanted or undesirable content of coals since it reduces the heating value and its additional weight adds costs to the cost of transportation. The moisture content of air-dried, powdered sample coal is identified by heating weighed quantity of the given sample accurately in a silica crucible at $105^{o}C$ for 60 min in an electric oven. The loss of weight is computed by the difference in its weights. The percentage value of moisture is evaluated as:

$$Moisture\ (\%) = \frac{Loss\ in\ weight\ of\ sample}{Weight\ of\ air\ dried\ sample} \times 100$$

b) Volatile Matter

VM found in coal refers to the products of thermal decomposition liberate as sample coal is heated at high temperature in the absence of air. The percentage value of VL is computed by heating air dried sample using silica crucible covering with lid. Heating sample at 930 ^{o}C is carried out for seven minutes in a muffle furnace in the absence of air. Finally, the VL is computed as:

$$Volatile\ Matter\ (\%) = \frac{Loss\ in\ weight\ of\ sample}{Weight\ of\ air\ dried\ sample} \times 100 - Moisture\ (\%).$$

The volatile matter evolved consists of combustible gases including: H_2, CO, CH_4, and others/hydrocarbons, and incombustible gases such as N_2 and CO_2.

c) Ash Content

Ash is residue obtained after complete combustion of sample coal and consists of MgO, CaO, Al_2O_3, SiO_2, etc. The sample after determination of Volatile Matter is then heated using muffle furnace at 750 ^{o}C for 1 hour without lid. Next, it is cooled and then weighed.

The ignition, cooling and weighing activities are repeated till combustion is complete, which is determined by the residue's constant weight. The value of ash content is determined as:

$$Ash\ (\%) = \frac{Weight\ of\ Residue\ (Ash)}{Weight\ of\ dried\ sample} \times 100.$$

Ash is a non combustible inorganic matter which includes: alumina, silica, iron oxide, and small amount of magnesia and lime.

d) Fixed Carbon

Fixed carbon is the carbon amount that remains in the sample of coal after VL is removed out. Accordingly, the fixed carbon value in the sample is computed as,

$$Fixed\ Carbon\ (\%) = 100 - [Moisture\ (\%) + Volatile\ Matter\ (\%) + Ash\ (\%)]$$

Quality level of sample coal depends on percentage value of Fixed carbon; that should be as high as possible. Fixed carbon value varies inversely with VM. The more percentage value of fixed carbon indicates the higher calorific value of the coal.

3.2.6.2 Determination of Sulfur Content

To identify the sulfur content of coal applying the Eschka method, 1g sample is weighed in a porcelain crucible and then mixed with 3g of Eschka mixtures obtained by using 1g of anhydrous sodium carbonate and 2g of magnesium oxide). The resulted mixture is then covered using another 1g Eschka mixture to prevent sulfur losses as sulfur dioxide. Next, the crucible is placed in a 'cold muffle furnace' and then gradually heated at 800 ^{o}C for 60 minutes. During combustion, the sulfur compound obtained is reacted with Eschka mixture and converted to Magnesium Sulfate and Sodium Sulfate. Then, the resulting product is digested applying diluting HCl (1M) with appropriate agitation speed for 45 minutes. The digested solution is then filtered using beakers of 400 ml and 3 drops of methyl orange is added until the color will be become neutral. Next, the resulted sample is heated at boiling-point and 10ml $BaCl_2$ (10%) is added gradually, by agitating in continuous boiling for 30 minutes. At the end, after cooling down by washing thoroughly using hot water, the solution is filtered and the $BaSO_4$ (residue) formed is burned at 500 ^{o}C and then weighed.

The resulted $BaSO_4$ is thus used to determine the sulfur content using equation below [36, 37].

$$Sulfur\ \% = \frac{32}{233} \times \frac{Weight\ of\ BaSO_4\ formed\ (g)}{Weight\ of\ sample\ taken\ (g)} \times 100$$

3.2.6.3 Determining Calorific Value

Gross Calorific Value (GCV) - determined from the measured heat released as sample coal was burned in excess oxygen applying bomb calorimeter under the standard test method of coal analysis [38, 39]. The GCV is determined applying a Bomb Calorimeter based on the guideline explained in ASTM at D-5865 [1].

In this study, the calorific value and its analysis was determined by applying Adiabatic Bomb calorimeter in the Laboratory of Geological Survey of Ethiopia. About 1g of coal powder that weighed in nickel crucible was put in a bomb supporting it over the ring. Next, oxygen supply was purged into the bomb till pressure of 25 – 30atm obtained for totally completing the activity of combustion. Next, the bomb was put in the nickel bucket of the calorimeter, which was filled with distilled water of 2,000 ml. After power turned on, the initial temperature was recorded and as the temperature of bucket was equilibrated with that of the bomb, the bomb was fired. Then, by recording the maximum temperature of the reader, the bomb is removed and gradually, the knop valve is opened to release the residual gas pressure before removing the cap. All unburned fuse wire pieces at the bomb electrode are removed, straightened, and their length measured (in cm) to determine the net value of wire burned. At last, the bomb washing was find out using solution of sodium carbonate by using methyl orange indicator, and then, the gross heat combustion of both raw and treated samples are calculated applying equation:

$$GCV = \frac{tW - e1 - e2 - e3}{m}$$

where $t =$ Temperature change in ^oC; $W =$ Energy equivalent of calorimeter (Cal/^oC); $e1 =$ correction in calories for heat formation of nitric acid; $e2 =$ correction in calories for heat formation of sulfuric acid; $e3 =$ correction in calories for heat combustion of fuse wire; and $m =$ mass of the sample coal taken (grams).

CHAPTER FOUR

4 RESULTS AND DISCUSSIONS

4.1 Optimization of Experimental Parameters

In this study, the Design Expert (version 13) software and the BBD-based RSM with three factors were used for the sequential coal flotation and alkali-acid leaching experimental procedures. The results determined by the experiments are subjected to ANOVA for the response variable to test the significance level of the model and identify the importance level of the independent variables for each experimental design. Further, three dimensional response surface plots obtained by Design-Expert program were used to further understand influences of these variables, relation between those variables and response variable. The factors including their levels of BBD for experimental activities are presented in Table 2.

Table 2. Factors with BBD-based levels and constant parameters for the experiments.

Experiment	Factor	Coded Factor	Level		
			-1	0	1
Froth Flotation	Particle size (µm)	A	63	125	250
	Collector dosage (g/ton)	B	10.0	55.0	100.0
	Frother dosage (g/ton)	C	90.0	230.0	370.0
	Feed rate (g), fixed		90		
	Impeller speed (rpm), fixed		2800		
Alkali-Leaching	NaOH concentration (mol/dm^3)	A	1	2.5	4
	Leaching temperature (deg C)	B	130	175	220
	Leaching time (min)	C	40	60	80
	Stirring speed (rpm), fixed		600		
Acid-Leaching	HCl concentration (mol/dm^3)	A	2	4	6
	Leaching temperature (deg C)	B	40	60	80
	Leaching time (hour)	C	1	3	5
	Solid/liquid ratio (%), fixed		5		
	Stirring speed (rpm), fixed		530		

4.1.1 Experimental Results for Coal Flotation

Based on a BBD of response surface methodology, the percentage eradication of ash of concentrate from flotation is the function of particle size, collector dosage, and frother dosage. To identify the effects of the three parameters presented in Table 2 on the performance of flotation, 17 experiments were conducted in the laboratory. The ash reduction percentage of coal resulted from the flotation experiment is presented along with the design matrix in Table 3 as follows.

Table 3. BBD-based experiment design and results of flotation experiments.

Run	Factor 1 A:Particle size micro	Factor 2 B:Collector g/ton	Factor 3 C:Frother g/ton	Response 1 Actual ash reduction percent
1	250-125	100	370	63.75
2	250-125	55	230	70.86
3	250-125	10	90	57.46
4	250-125	10	370	60.61
5	125-63	55	370	73.84
6	500-250	100	230	51.94
7	250-125	100	90	59.81
8	500-250	55	90	45.95
9	125-63	10	230	65.33
10	250-125	55	230	65.97
11	125-63	100	230	71.64
12	500-250	10	230	48.00
13	250-125	55	230	68.48
14	250-125	55	230	68.69
15	250-125	55	230	69.58
16	125-63	55	90	70.06
17	500-250	55	370	54.31

4.1.1.1 Regression Model and ANOVA for Flotation of Coal

The results of experiment, obtained based on BBD model, were evaluated by the polynomial model of regression. From the results of coal flotation described in Table 3, the function for the reduction of ash content is expressed as a function of particle size (A), collector dosage

(B), and frother dosage (C). Equation (4-1) shows the relationship between ash reduction (AR_1) and independent variables. For the current coal flotation experiment, quadratic equation is selected as the best model as:

$$AR_1 = 65.45 - 10.08A + 1.91B + 2.62C - 0.3707AB + 1.28AC + 0.1966BC - 1.16A^2 - 5.06B^2 - 3.25C^2 \quad (4\text{-}1)$$

In this model, all variables are in coded values and the results obtained from the experiments were subjected to ANOVA for the response variable. ANOVA is a known and credible tool to determine the importance level of variables [49].

The importance level of the main linear, interaction, and quadratic influences of variables was identified based on P-value. Each factor having P-value less than 0.01 is considered as highly significant variable and value of 0.01–0.05 is significant. Moreover, in statistical analyses, variable having P-value above 0.05 is usually considered as 'non-significant'. The ANOVA results for the developed model are described in Table 4. Accordingly, as seen in Table 4, the lower probability value ('P-value' < 0.0001) with 'F-value' (38.36) implies that the model is high significant at confidence level of 95 %. The lower 'P-values' show that the variables play a better important role in influencing the response and 'P-values' above 0.1 show the model terms are 'insignificant'. In this case, A, B, C, B^2, and C^2 are significant model terms for ash reduction. The result shows that, the ash reduction depends more on the particle-size. Moreover, the "Lack-of-Fit F-value" of 1.09 with 'P-value' of 0.4493 (> 0.05) for ash reduction confirms that "the Lack-of-fit" is not significant for the model.

From the model summary statistics (Table 4), the values of "R-Squared" or R^2 of ash reduction is 0.9801, indicating that the quadratic equation of the response has the capacity to model the system within the given experimental domain. Moreover, the "Predicted R^2" of 0.8217 is in reasonable agreement with the "Adjusted R^2" of 0.9546. Figure 6 represents predicted values against actual values for ash reduction, and the actual and the predicted values found using Equations (4-1) are presented in Annex-2.

Furthermore, the plot of residual for the prediction values of ash reduction is shown in Annex-3, and as it can be observed, the values of residual are distributed uniformly (Annex-3), which indicated that Equations (4-1) fitted well for data from experiments.

Table 4. Analysis of variance for response surface quadratic model in flotation of coal.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	1159.72	9	128.86	38.36	< 0.0001
A-Particle size	813.48	1	813.48	242.14	< 0.0001
B-Collector	27.60	1	27.60	8.22	0.0241
C-Frother	52.17	1	52.17	15.53	0.0056
AB	0.5809	1	0.5809	0.1729	0.6900
AC	6.98	1	6.98	2.08	0.1928
BC	0.1546	1	0.1546	0.0460	0.8363
A^2	4.24	1	4.24	1.26	0.2985
B^2	107.81	1	107.81	32.09	0.0008
C^2	44.38	1	44.38	13.21	0.0083
Residual	23.52	7	3.36		
Lack of Fit	10.58	3	3.53	1.09	0.4493
Pure Error	12.94	4	3.23		
Cor Total	1183.24	16			

Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	3.92	0.8309	0.7919	0.7348	313.84	
2FI	4.39	0.8374	0.7399	0.5340	551.43	
Quadratic	**1.83**	**0.9801**	**0.9546**	**0.8217**	**210.97**	**Suggested**
Cubic	1.80	0.9891	0.9563		*	Aliased

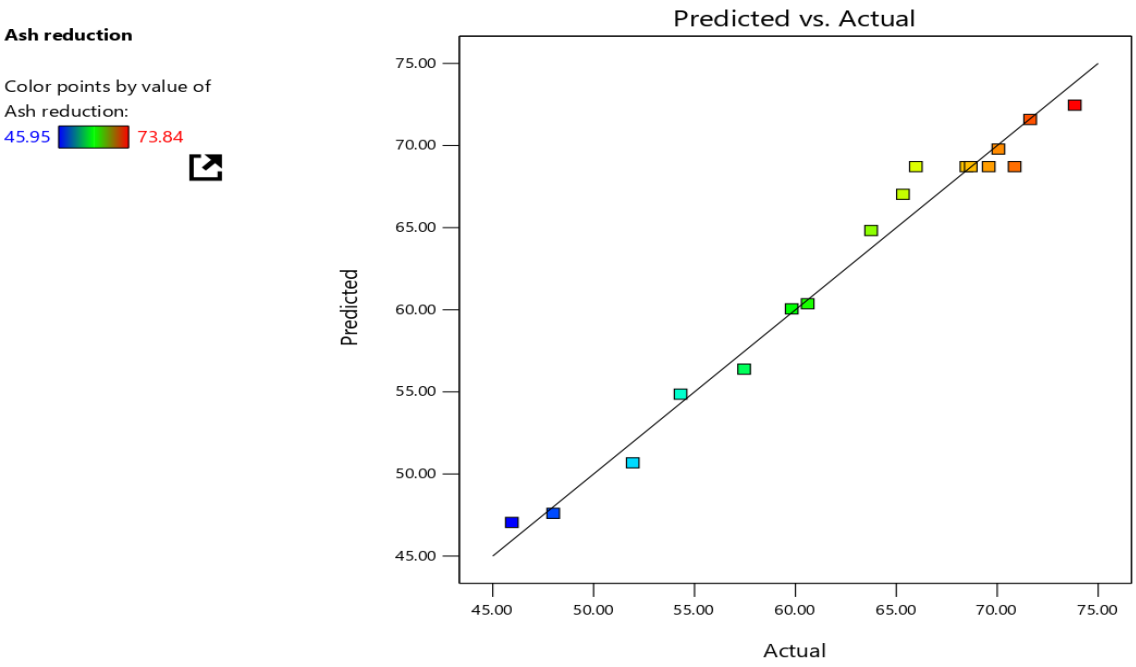


Figure 6. Relationship between actual and predicted values of ash reduction for flotation.

4.1.1.2 Effect of Variables on Ash Reduction in Flotation

The 3D plots response surface were used for better understanding of the interaction effects of these variables, the relations between factors and ash reduction. Three plots are shown in Figure 7 as 3D response surface. Since the model has three factors, one of factor was held fixed at the middle level for each plotted figure. Figure 7 (a) shows the simultaneous effect of particle size and collector dosage on ash reduction at the middle level of frother dosage. As can be observed, a higher ash reduction percentage (i.e., lower content of ash) can be achieved at a low particle size with a collector dosage around the center level. When the collector dosage keeps fixed value, ash reduction increases (or ash increases) sharply with the reduction of particle size. When the particle size keeps constant, ash reduction increases with collector dosage first and decreases with collector dosage after the dosage is over its center level. Hence, from the result, it can be explained that ash reduction depends more on the particle size than the dosage of collector.

Figure 7 (b) shows the effect of particle size and frother dosage on ash reduction at the middle level of collector dosage. It shows that higher ash reduction is obtained at the lower particle size and higher frother dosage. As the particle size is kept to be constant, the ash reduction rises with the increase of collector dosage in a low trend; but ash reduction rises sharply with increasing in particle size, which clearly indicates that particle size plays important role in effecting ash reduction in flotation of the sample coal.

Figure 7 (c) shows the influence of collector dosage and frother dosage on ash reduction at the middle level of the particle size. As shown from the result, a higher ash reduction (or lower ash content) is obtained at values above the center level for both frother and collector dosages. When the collector dosage is below its center level, ash reduction increases with the rise of frother and collector dosages. After the collector dosage is over the center level, ash reduction decreases with the rise in both collector and frother dosage.

Factor Coding: Actual

Ash reduction (percent)

Design Points:

Above Surface

Below Surface

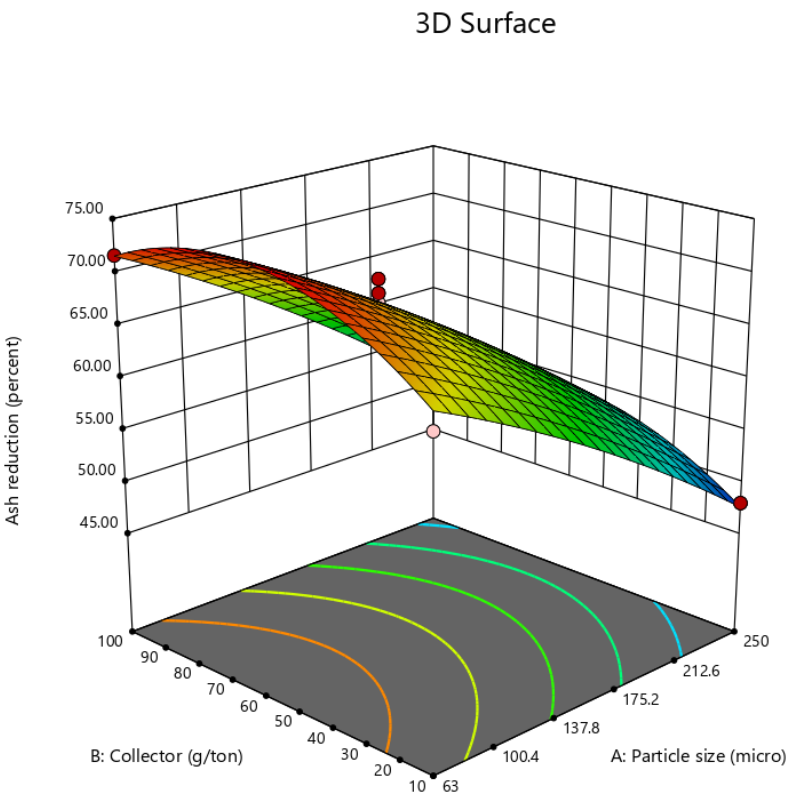
45.95 73.84

X1 = A

X2 = B

Actual Factor

C = 230



(a)

Factor Coding: Actual

Ash reduction (percent)

Design Points:

Above Surface

Below Surface

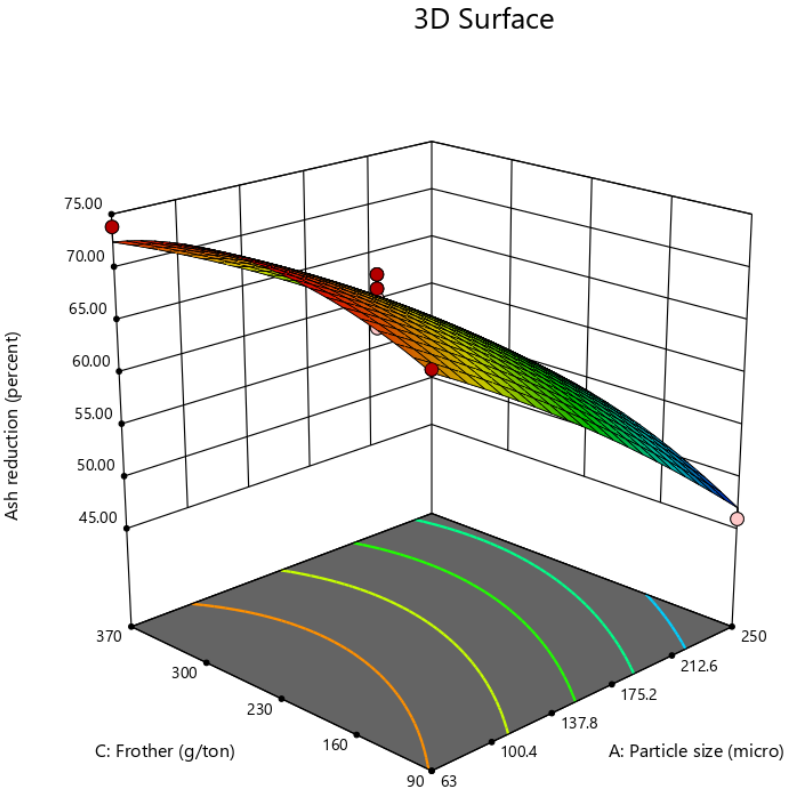
45.95 73.84

X1 = A

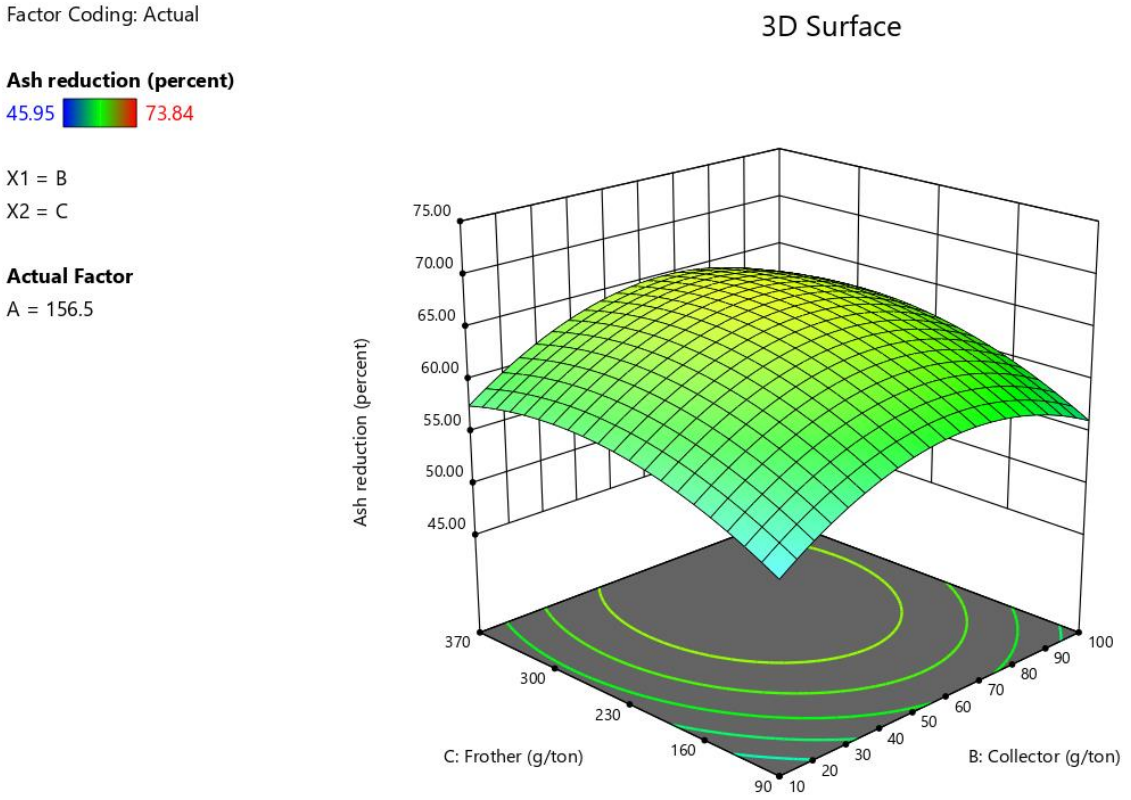
X2 = C

Actual Factor

B = 55



(b)



(c)

Figure 7. The effect of (a) particle size and collector dosage on ash reduction (with Frother dosage at the middle level), (b) particle size and frother dosage on ash reduction (with collector dosage at the middle level), and (c) collector dosage and frother dosage on ash reduction (with particle size at the middle/center level).

By using the BBD-based RSM experimental model, the maximum ash reduction of 73.84 percent was found at particle-size of 63 µm (i.e., 63-125 µm), collector-dosage of 55 g per ton and frother-dosage of 370 g per ton for the flotation of coal sample. Hence, the entire experimental tests of this study were conducted using such determined optimum conditions, further, to investigate the extent of ash reduction and quality improvement of the coal sample using the sequential alkali-acid leaching as follows.

4.1.2 Experimental Parameters for Alkali-Leaching

In this experimental process, the extent in further ash reduction in flotation concentrate was determined by the application of alkali (NaOH) leaching. The influence of concentration (sodium hydroxide), leaching temperature and duration of time on ash reduction was investigated on flotation pretreated concentrate. The ash reduction percentage of clean coal due to the alkali-leaching experiment is given together with the design matrix as follows.

Table 5. BBD-based experiment design and the results of NaOH-leaching experiments.

Run	Factor 1 A:NaOH Concentration Mol/dm^3	Factor 2 B:Temperature deg C	Factor 3 C:Time min	Response 1 Actual ash reduction percent
1	2.5	175	60	50.69
2	2.5	175	60	52.04
3	2.5	130	40	25.38
4	1	220	60	71.88
5	2.5	175	60	49.47
6	1	130	60	56.70
7	4	175	80	34.04
8	4	220	60	41.63
9	4	130	60	23.02
10	2.5	175	60	48.46
11	2.5	220	80	58.37
12	2.5	175	60	53.48
13	2.5	130	80	29.21
14	1	175	40	65.05
15	1	175	80	68.40
16	2.5	220	40	38.29
17	4	175	40	24.14

4.1.2.1 Regression Model and ANOVA for Alkali-Leaching

Based on BBD design, the results of experiments were evaluated by the polynomial model of regression. Equation (4-2) displays the relations between ash reduction (AR_2) and the three independent variables (A: NaOH concentration, B: Leaching temperature, and C: Leaching time). A quadratic equation, selected as the best model, is given as follows:

$$AR_2 = +5083 - 117.40A + 9.48B + 4.64C + 0.8602AB + 1.64AC + 4.06BC + 3.79A^2 - 6.31B^2 - 6.71C^2 \quad (4\text{-}2)$$

In this model, all variables are in coded values and the results of the experiments were subjected to the statistical analysis of variance (ANOVA) for the variable, ash reduction. The importance level for the main linear, quadratic, and interaction effects of factors was determined based on 'P-value'. The ANOVA results for the developed model are shown in Table 6. As revealed from the result, the F-value (54.10) with very low probability ('P-value'

< 0.0001) reveals that the model developed for the ash reduction in NaOH-leaching is reliable and highly significant at confidence level of 95%. In addition, A, B, C, BC, A^2, B^2, and C^2 all are significant model terms for ash reduction, as their 'P-value' are below 0.05. However, AB and AC (with 'P-value' great than 0.05) are not significant model terms for ash reduction. The result shows that the ash reduction depends more on the NaOH concentration followed by temperature.

Moreover, the "Lack-of-Fit F-value" of 3.23 with 'P-value' 0.1433 (> 0.05) for ash reduction confirms that the "lack-of-fit" is 'insignificant' for the model. The R^2 value of ash reduction is 0.9858, indicating that the selected quadratic equation of the response is capable in modeling the required system within the given domain (Table 6). The actual (and predicted values determined by Equations (4-2) are presented in Annex-2, while Figure 8 displays predicted values against actual values for ash reduction. Furthermore, as it can be seen from the residual plot for the prediction values of ash reduction (Annex-3), the 'residual' values are distributed uniformly, implying that Equations (4-2) fitted well the resulted experimental data.

Table 6. ANOVA for response surface quadratic model of the alkali leaching.

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	3810.28	9	423.36	54.10	< 0.0001
A-NaOH Concentration	2422.23	1	2422.23	309.51	< 0.0001
B-Temperature	719.22	1	719.22	91.90	< 0.0001
C-Time	172.53	1	172.53	22.05	0.0022
AB	2.96	1	2.96	0.3782	0.5580
AC	10.71	1	10.71	1.37	0.2803
BC	66.02	1	66.02	8.44	0.0228
A^2	60.47	1	60.47	7.73	0.0273
B^2	167.58	1	167.58	21.41	0.0024
C^2	189.40	1	189.40	24.20	0.0017
Residual	54.78	7	7.83		
Lack of Fit	38.79	3	12.93	3.23	0.1433
Pure Error	15.99	4	4.00		
Cor Total	3865.06	16			

Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS
Linear	6.51	0.8574	0.8245	0.7291	1047.24

2FI	6.87	0.8780	0.8049	0.4877	1979.96	
Quadratic	**2.80**	**0.9858**	**0.9676**	**0.8330**	**645.64**	**Suggested**
Cubic	2.00	0.9959	0.9834		*	Aliased

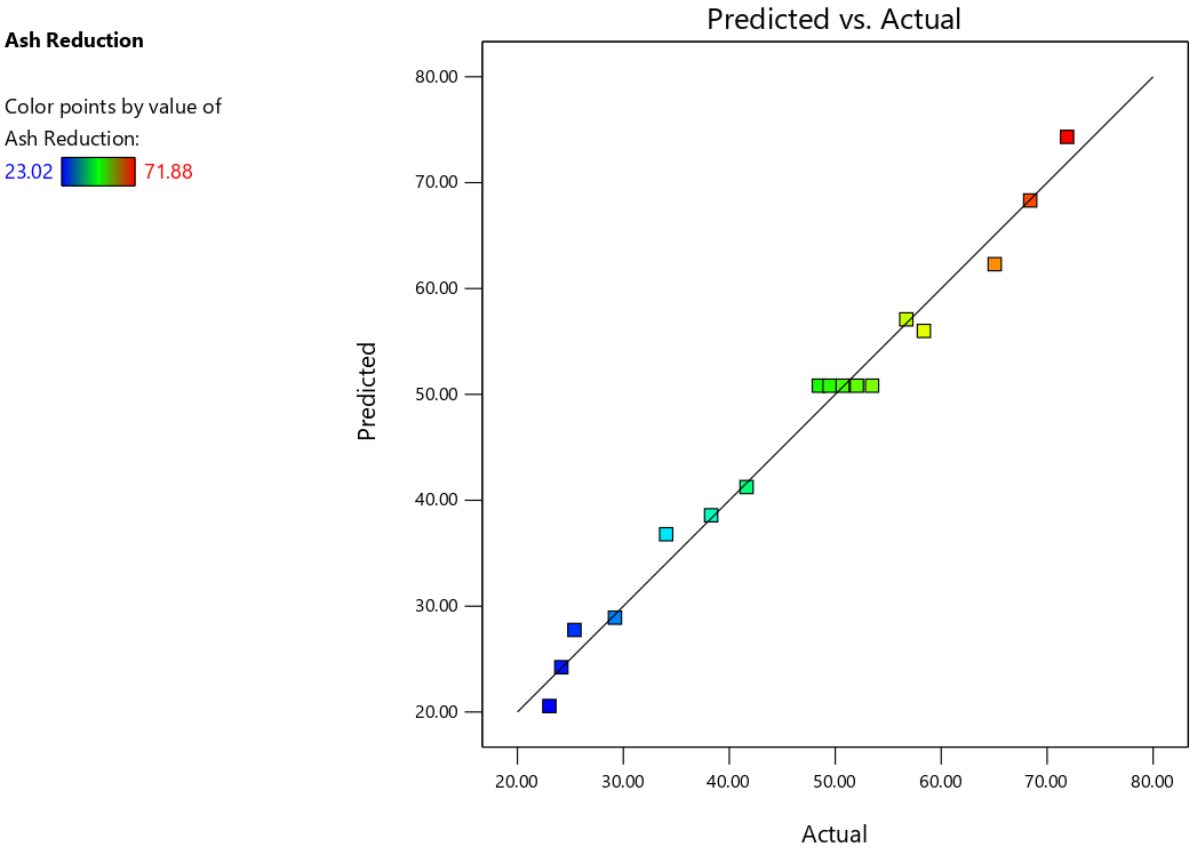


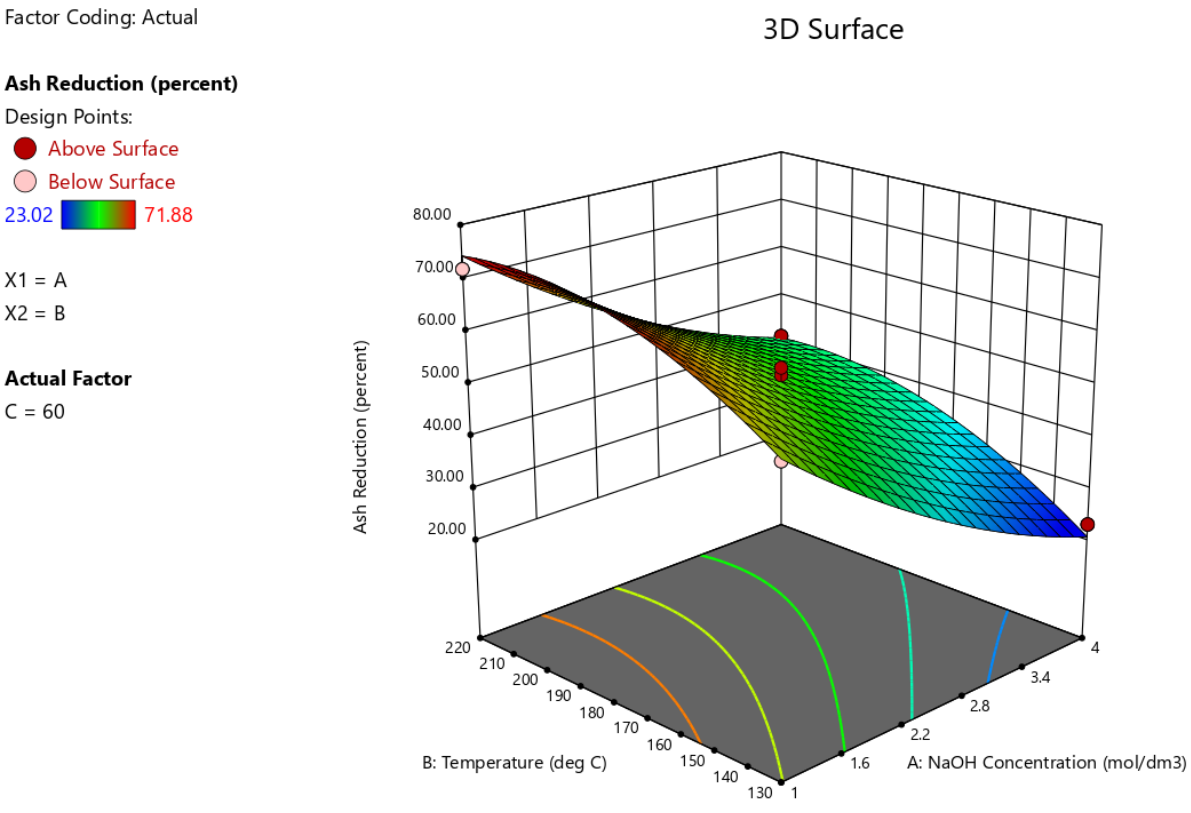
Figure 8. Relationship between actual and predicted values of ash reduction for alkali-leaching

4.1.2.2 Effect of Variables on Ash Reduction in Alkali-Leaching

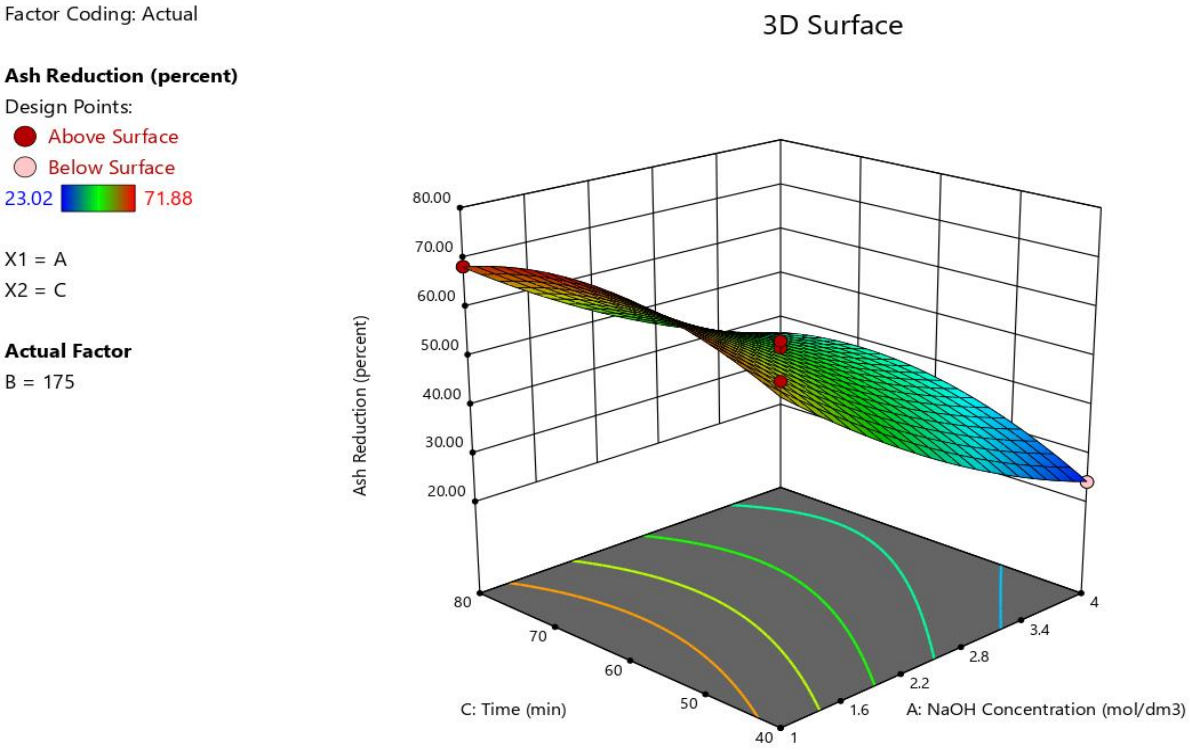
The 3D plots of response surface were used for better understanding of the interaction effects of the three alkali-leaching variables, and the relations between factors and ash reduction. One of factor was put fixed at the middle level for each graph. Figure 9 (a) shows the effect of NaOH concentration and leaching temperature on ash reduction (with leaching time at the middle level). As can be seen, the ash reduction percentage rises with the increase of leaching temperature and decrease of leaching concentration. Keeping the leaching time at the center level (60 min), the higher ash reduction (i.e., lower ash content) is achieved at a higher temperature with a lower alkali leaching concentration. Hence, from the figure, it can be seen that ash reduction depends on both leaching concentration and temperature.

Figure 9 (b) shows the influence of NaOH concentration and leaching time on ash reduction, keeping leaching temperature at the center level (175 ^{o}C). The ash reduction percentage increases with decreasing leaching concentration and steady increase of leaching time. When the leaching concentration is kept fixed/constant, the ash reduction increases due to increasing in contact time in a low trend; but ash reduction sharply decreases with the rise of leaching concentration, showing that ash reduction influenced more by the alkali-leaching concentration than leaching time.

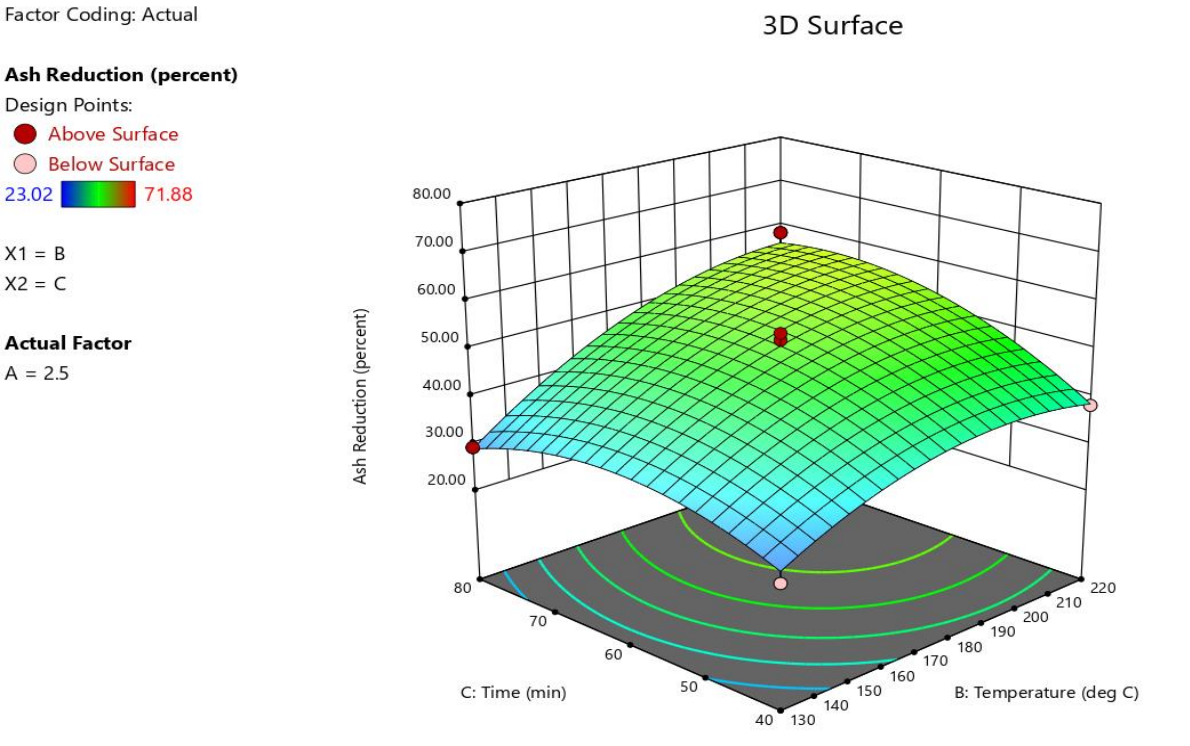
Figure 9 (c) shows the simultaneous effects of leaching temperature and time on ash reduction (with NaOH concentration at the center level). As shown from the result, a higher ash reduction (or lower ash content) is obtained at higher leaching temperature and time. When leaching temperature keeps constant, ash reduction increases with the increase of time of contact first and finally reduces with the increase of time. On the other hand, keeping leaching time constant, ash reduction better increases due to increase in temperature. The relations between factors/variables and ash reduction revealed that the interactions of leaching temperature against time has a significant influence on ash reduction, which is in line with the ANOVA results (Table 6).



(a)



(b)



(c)

Figure 9. The influence of (a) NaOH concentration and leaching temperature on ash reduction (leaching time at the center level); (b) NaOH concentration and leaching time on ash reduction (leaching temperature at the center level); and (c) leaching temperature and time on ash reduction (NaOH concentration at the center level).

By using the BBD-based RSM experimental model, the maximum ash reduction (71.88 percent) was found at leaching concentration 1 mol/dm^3, leaching temperature 220 ^oC and leaching time 60 minutes for the alkali-leaching experiment. Hence, the remaining tests of this study were conducted applying such optimum parameters to investigate the extent of coal quality improvement employing acid-leaching on alkali-leached of flotation-pretreated concentrate.

4.1.3 Experimental Parameters for Acid-Leaching

In this part of the study, the extent of ash reduction in NaOH treated flotation-concentrate was again investigated by using HCl leaching. The influence of HCl concentration, leaching temperature and contact time on ash reduction was investigated on alkali-leached flotation-concentrate. Based on the BB-based experimental design of RSM, the ash reduction percentage of clean coal is determined and given together with the design matrix as follows (Table 7).

Table 7. BBD-based experiment design and results of HCl-leaching experiments.

Run	Factor 1 A:HCl Concentration Mol/dm^3	Factor 2 B:Temperature deg C	Factor 3 C:Time hours	Response 1 Ash reduction percent
1	4	60	3	34.81
2	2	60	1	44.60
3	4	80	5	39.55
4	4	60	3	38.70
5	4	40	1	24.05
6	4	40	5	23.88
7	2	60	5	41.19
8	2	40	3	37.88
9	2	80	3	49.40
10	6	60	5	26.29
11	6	60	1	17.79
12	6	80	3	29.97
13	6	40	3	16.96
14	4	80	1	26.35
15	4	60	3	32.52
16	4	60	3	37.55

17	4	60	3	34.24

4.1.3.1 Regression Model and ANOVA for Acid-Leaching

According to BBD, the experimental results were developed and analyzed by the model of polynomial regression. The quadratic equation was again suggested as the best model for the acid-leaching on alkali-leached flotation-concentrate. The relationship between ash reduction (AR_3) and independent variables (such as: A: HCl concentration, B: Temperature, and C: Leaching time) in acid-leaching experiment is shown by Equation (4-3) as follows:

$$AR_3 = +35.57 - 10.26A + 5.318B + 2.26C + 0.3726AB + 2.98AC + 3.35BC + 0.9952A^2 - 3.01B^2 - 4.10C^2 \quad (4\text{-}3)$$

The significance of the model and importance level for linear, quadratic, and interaction effects of factors were determined based on 'P-value'. The ANOVA results for the developed model and variables are shown in Table 8. Accordingly, the F-value (26.12) with very low probability ('P-value' < 0.0001) implying that the model developed for the ash reduction in HCl-leaching is highly significant and reliable at 95% confidence level. In addition, A, B, C, AC, BC, B^2, and C^2 all are significant model terms for ash reduction, as their 'P-values' are less than 0.05. However, AB and A^2 (with 'P-values' above 0.05) are 'insignificant' model terms for ash reduction. The result also revealed that the ash reduction depends more on the HCl concentration followed by leaching temperature. Moreover, the "Lack-of-Fit F-value" of 0.7093 with 'P-value' 0.5950 (> 0.05) indicates that the 'lack-of-fit' is not significant for the model.

The R^2 values of ash reduction is 0.9711, indicating that the quadratic equation of the response has the capacity to appropriately model the system within the given domain (Table 8). The residual plot for the prediction values of ash reduction (Annex-3) for acid-leaching experiment shows that the residual values are distributed uniformly, indicating that Equations (4-3) fitted correctly the experimental data. Furthermore, Figure 10 shows predicted values verses actual values for ash reduction and the predicted and actual values obtained by Equations (4-3) are presented in Annex-2.

Table 8. ANOVA for the response surface quadratic model of the acid-leaching.

Source	Sum of Squares	df	Mean Square	'F-value'	'P-value'
Model	1305.31	9	145.03	26.12	0.0001

A-HCl Concentration	841.60	1	841.60	151.57	< 0.0001
B-Temperature	225.77	1	225.77	40.66	0.0004
C-Time	41.03	1	41.03	7.39	0.0298
AB	0.5552	1	0.5552	0.1000	0.7611
AC	35.46	1	35.46	6.39	0.0394
BC	44.76	1	44.76	8.06	0.0251
A^2	4.17	1	4.17	0.7511	0.4148
B^2	38.15	1	38.15	6.87	0.0343
C^2	70.68	1	70.68	12.73	0.0091
Residual	38.87	7	5.55		
Lack of Fit	13.50	3	4.50	0.7093	0.5950
Pure Error	25.37	4	6.34		
Cor Total	1344.18	16			

Model Summary Statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	4.26	0.8246	0.7841	0.6807	429.19	
2FI	3.94	0.8847	0.8155	0.6066	528.86	
Quadratic	**2.36**	**0.9711**	**0.9339**	**0.8099**	**255.58**	**Suggested**
Cubic	2.52	0.9811	0.9245		*	Aliased

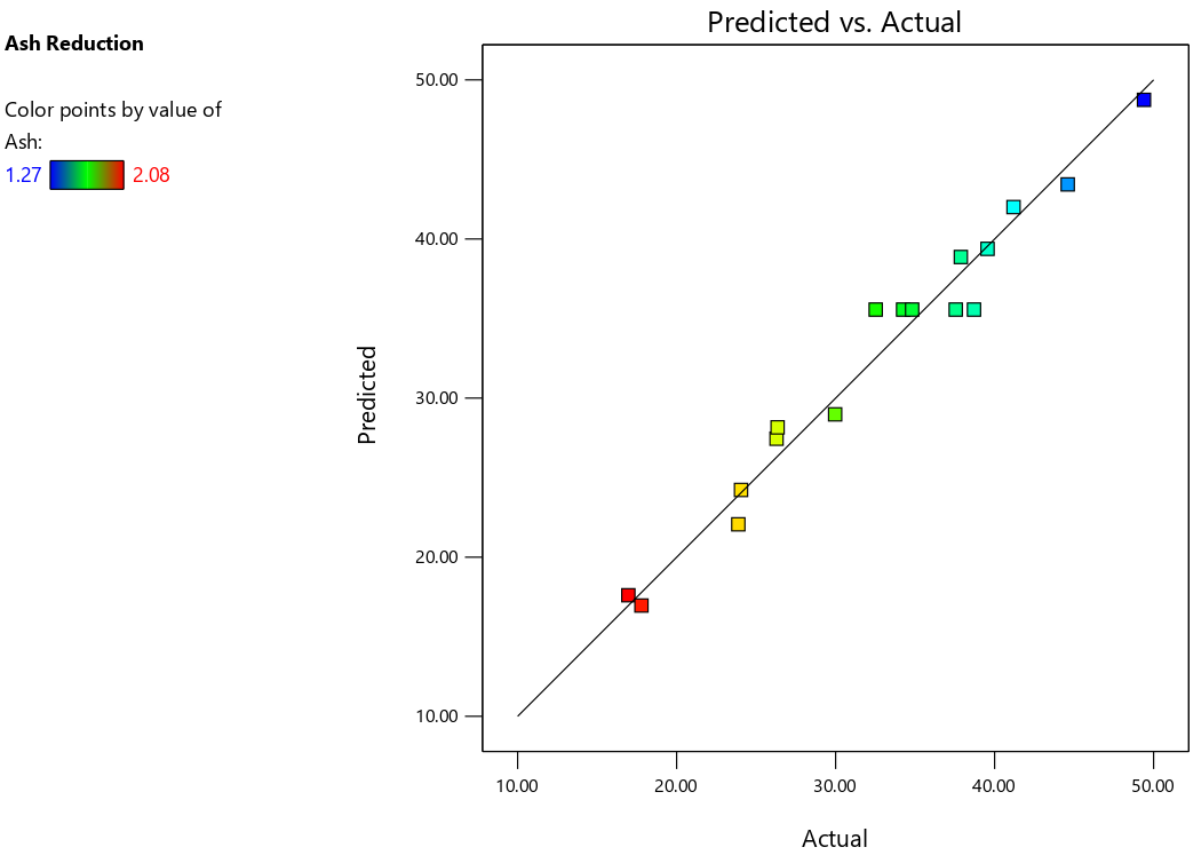


Figure 10. Relation between actual and predicted values of ash reduction for acid-leaching

4.1.3.2 Variables' Effect on Reduction of Ash in Acid-Leaching

For better understanding of the interaction influences of the three acid-leaching factors, and the relationships between variables and ash reduction, the 3D (three dimensional) graphs of response surface were used. Figure 11 (a) shows the influence of HCl concentration and leaching temperature on ash reduction (with leaching time at the middle level). As observed from the plot, the ash reduction percentage rises with the increases in leaching temperature and decrease of HCl-leaching concentration. Keeping the leaching time at the center level (3 hour), the higher ash reduction (i.e., lower content of ash) is obtained at a higher leaching temperature with a lower leaching concentration.

Figure 11 (b) shows the influence of HCl concentration and leaching time on ash reduction, fixing leaching temperature at the center level (60 ^{o}C). When the leaching time is below 3 hour, ash reduction increases (or ash content decreases) with the decrease of HCl concentration. After the leaching time is over 3 hour, ash reduction decreases with the decrease of leaching concentration. Thus, the higher ash reduction (lower ash content) is achieved at lower leaching concentration and center level of leaching time. The relation between factors and ash reduction shows that the interaction status between leaching concentration and contact time has a significant influence in affecting ash reduction, which is supported by the ANOVA results (Table 8).

Figure 11 (c) shows the simultaneous impact of leaching temperature and contact time on ash reduction (with HCl concentration at the center level). When the leaching time is below 3 hour, ash reduction increases (or ash content decreases) due to the increase in leaching temperature. However, after the time is over 3 hour, ash reduction decreases with the rise of leaching temperature. Thus, the higher ash reduction (lower ash content) is obtained at higher leaching temperature with center level of leaching time. The relation between independent variables and ash reduction confirms that the level of interaction between leaching temperature and time has a significant effect in determining ash reduction that is in agreement with the ANOVA results (Table 8).

Factor Coding: Actual

Ash Reduction (%)

Design Points:

Above Surface

Below Surface

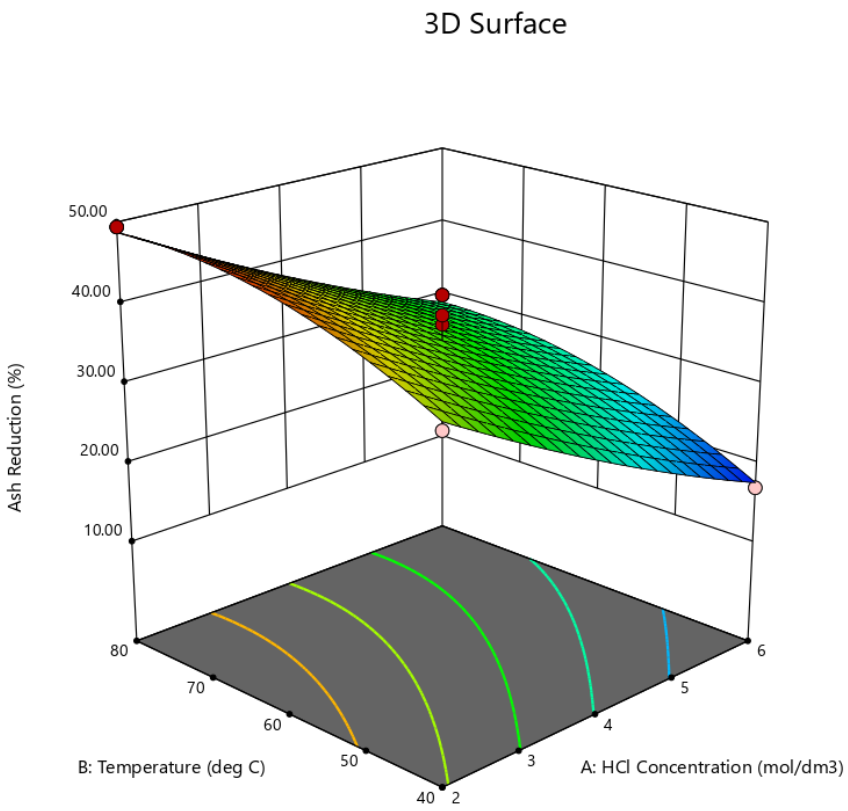
16.96 49.40

X1 = A

X2 = B

Actual Factor

C = 3



(a)

Factor Coding: Actual

Ash Reduction (%)

Design Points:

Above Surface

Below Surface

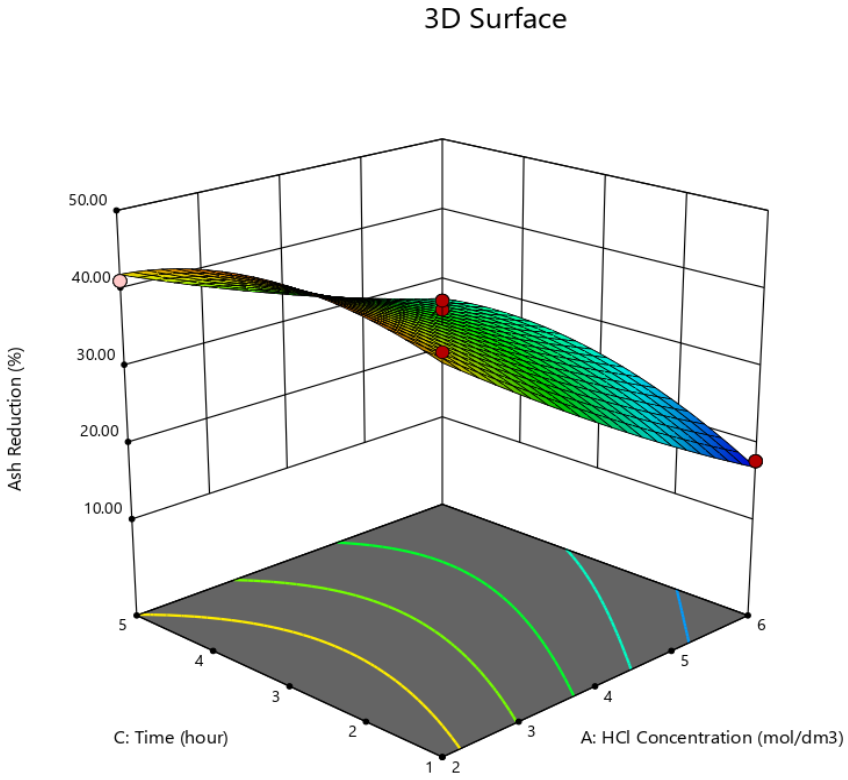
16.96 49.40

X1 = A

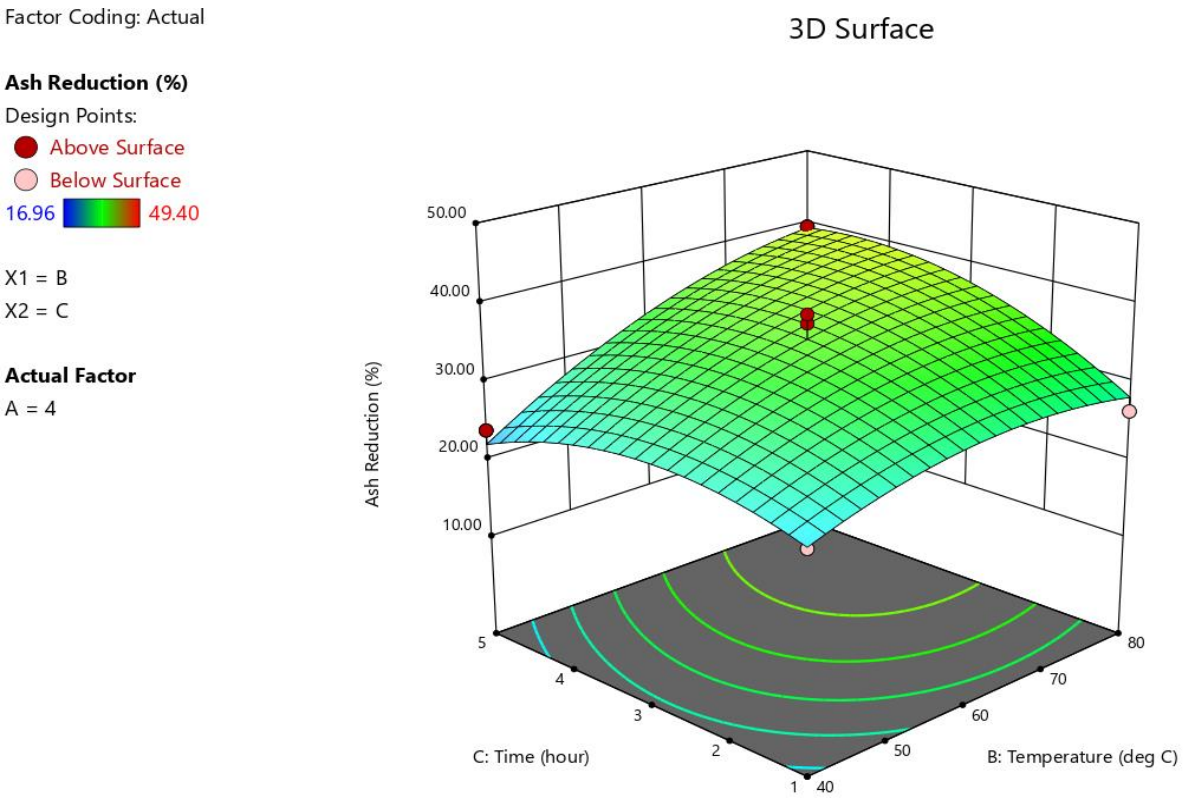
X2 = C

Actual Factor

B = 60



(b)



(c)

Figure 11. The impact of (a) HCl concentration and leaching temperature on ash reduction (leaching time at the center level); (b) HCl concentration and leaching time on ash reduction (leaching temperature at the center level); and (c) leaching temperature and time on ash reduction (HCl concentration at the center level).

From the HCl-leaching experiment conducted on NaOH-leached flotation-pretreated concentrate, the maximum ash reduction of 49.40 % (i.e., the ash content of 1.27 %) was found at acid-leaching concentration 2 mol/dm^3, leaching temperature 80 ^{o}C, and contact time 3 hours.

4.2 Optimization of Parameters for the Ash-Reduction

The important part of conducting the experimental study is to compute the optimum flotation and leaching process conditions where maximum value of ash reduction can be obtained. Optimization of both flotation and leaching parameters were conducted applying the method of numerical optimization. The required contour plots using optimum flotation or leaching) conditions for the maximum ash reduction percentage was displayed in Figure 12.

From the results of optimization conditions shown in Table 9, the optimum operating conditions for maximizing reduction of ash by the flotation process were obtained as particle

size 63-125 µm, collector dosage 64 g per ton and frother dosage 64 g per ton. The experimental and predicted values for the reduction of ash from sample coal were obtained as 74.70% and 74.77% at optimum conditions, respectively. Similarly, optimal conditions for maximizing the ash reduction by the alkali-leaching were obtained at 1.02 mol/dm^3 NaOH concentration, 210.06 ^{o}C leaching temperature and 65.71 min contact time. The experimental and predicted values for the reduction of ash from flotation concentrate were obtained as 75.94% and 75.88% at optimum conditions, respectively. Finally, the optimal conditions for reduction of ash by the acid-leaching were at 2.00 mol/dm^3 HCl concentration, 79.68 ^{o}C reaction temperature and 3.64 hours leaching time, and the predicted and experimental values for the ash reduction were obtained as 49.17% and 49.26% at optimal conditions, respectively.

A comparison of results between the predicted and experimental values shows that the absolute error was obtained as 0.07%, 0.06% and 0.09% for flotation, alkali-leaching and acid-leaching stages, respectively. This shows that from optimization process conducted, the experimental values obtained for the percentage reduction of ash were determined closer to that resulted as prediction by the developed models. Hence, it can be concluded that the developed models for each stage could predict the reduction of ash accurately.

Table 9. Optimal conditions and ash reduction models validation using numerical optimization.

Parameters				**Ash Reduction %**	
Flotation	**Particle size (µm)**	**Collector (g/ton)**	**Frother (g/ton)**	**Predicted**	**Experimental**
Optimum conditions	63-125	64	258	74.77	74.70
Alkali-Leaching	**Alkali concentration (mol/dm^3)**	**Temperature (oC)**	**Time (min)**	**Predicted**	**Experimental**
Optimum conditions	1.02	210.06	65.71	75.88	75.94
Acid-Leaching	**Acid concentration (mol/dm^3)**	**Temperature (oC)**	**Time (hours)**	**Predicted**	**Experimental**
Optimum conditions	2.00	79.68	3.64	49.17	49.26

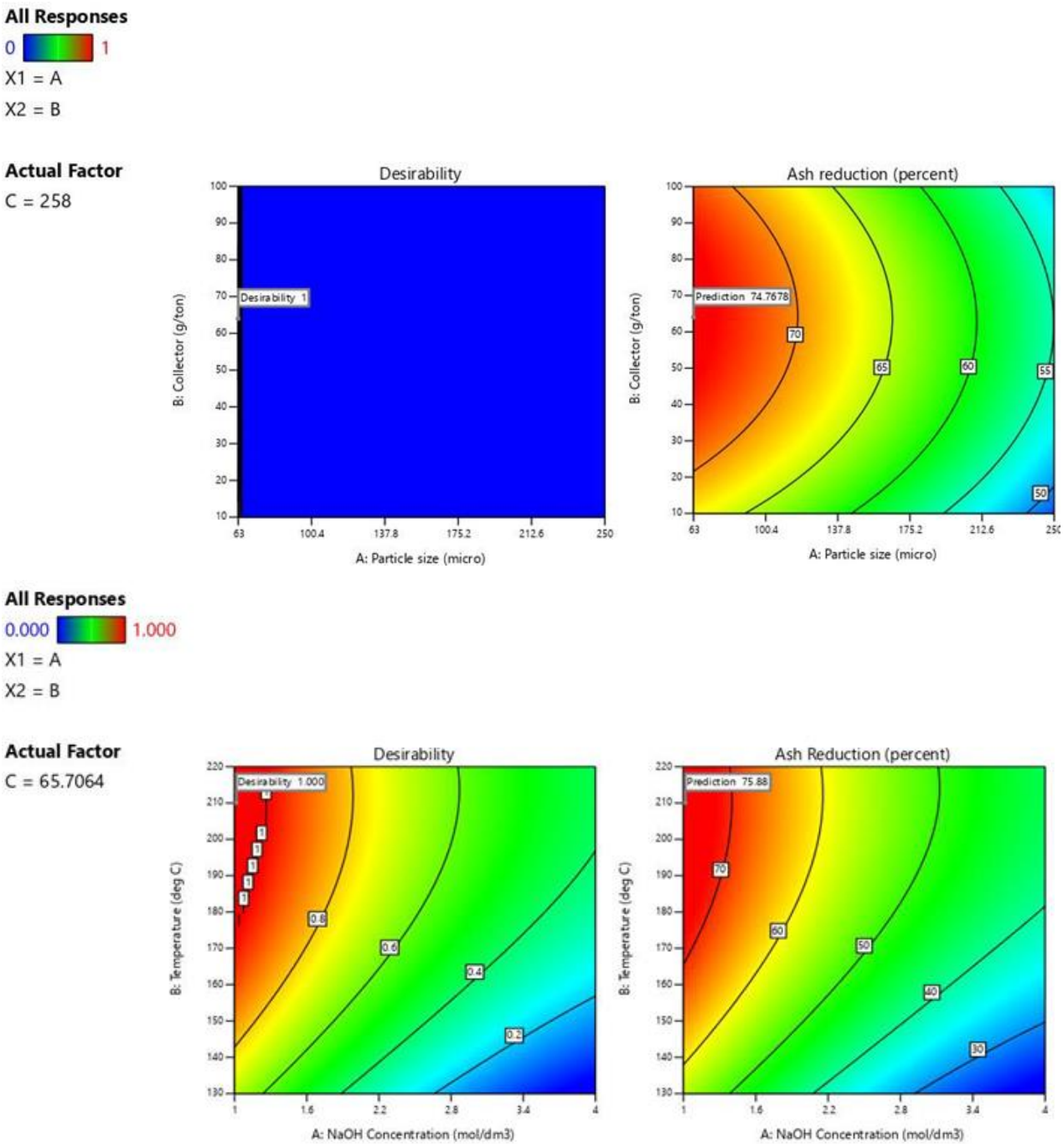


Figure 12. Contour plot of factors on ash reduction at optimum condition.

4.3 Proximate and Sulfur Content Analysis

4.3.1 Moisture Content

The result of proximate analysis of raw, flotation treated, alkali leached, and acid leached coal samples is described in Table 10. The result confirms that the moisture content for raw coal was 10.67%. The highest moisture value indicates lower carbon content that lead to lower heating value and higher storage and transportation costs [8]. By carrying out froth

flotation, alkali leaching, and acid leaching sequentially, the moisture content was 8.79%, 6.31% and 4.05%, respectively. The result revealed that the moisture content is significantly reduced by applying the above three-stage cleaning that applied sequentially (Figure 13). The same results were reported by [4], which reduced moisture content from 11.81–20.27% to 8.12–14.02% for Achibo, Sombo and Dabaso coal samples using the froth-flotation technique.

4.3.2 Volatile Matter

As can be seen from the result, the raw sample has the highest volatile matter of 30.34% (Table 10). The higher VM shows the coal having lower-rank and increasing VM also increases amounts of combustible gases, which directly reduces amount of fixed carbon in the coal and consequently, reduces its heating value. Finally, in current study, the volatile matter decreases and shows improvement by applying the flotation technique that followed by the alkali/acid leaching, sequentially (Figure 13). The result is in line with [4], which reduced volatile matter of coal samples from 22.74–34.85% to 21.92–30.64% using the flotation technique.

4.3.3 Ash Content

The raw coal sample of this study has higher value of 33.73 % ash content (Table 10), which is within the interval found in previous study (10.2 % – 54.6 %) in the south-west area of Ethiopia [5]. The higher and increase of ash content reduces the burning capacity of the coal, influences its combustion efficiency, increases costs of storage, and causes for the large slagging. The ash content and its behavior observed at high temperatures influence the handling of ash, which is employed in the process of utilization of coal. At high-temperature, coal ash become sticky and eventually, forms molten slag. As volumes of high impurity reduce burning efficiency of the coal, the increase of its ash content leads to reduced quality and rank.

The results shows that after the sequential experimental processes: flotation treatment followed by alkali-acid leaching, the ash content of flotation concentrate (8.92%), alkali-leached coal (2.51%) and acid-leached coal (1.27%) is reduced by about 73.84 %, 71.88 %, and 49.40 %, respectively (Figure 13). This reveals that the ash content of the sample significantly reduced by carrying out the above mentioned sequential coal treatment processes. Similar results were reported by the study [4] that reduced ash content from

22.47–36.58% to 7.49–13.62% for the study coal samples, using the flotation technique. Comparable results were also obtained by [14] as 8.27% ash content and [1], which reduced the ash content from 25.97% to 7.80%, applying flotation on low-ranked coal. Further, the results of this study are supported by [17, 47], applying flotation and alkali/acid leaching methods to clean low-ranked coal.

4.3.4 Fixed Carbon

The value of fixed carbon indicates the rough estimation of the coal's heating value. In this study, the contents of fixed carbon for the raw coal sample is 25.26 % (Table 10). The lower value of fixed carbon is that due to the higher contents of VM, ash, and moisture value of the coal.

The fixed carbon content for the treated sample obtained after flotation followed by alkali-acid sequential beneficiation experiments are 55.43%, 70.68%, and 77.43% for flotation concentrate, alkali-leached and acid-leached coal samples, respectively. The highest value of fixed carbon resulted in treated/leached coal samples leads to a higher calorific value. Hence, increasing the content of fixed carbon was leads to improvement in heating value and decreasing ash content.

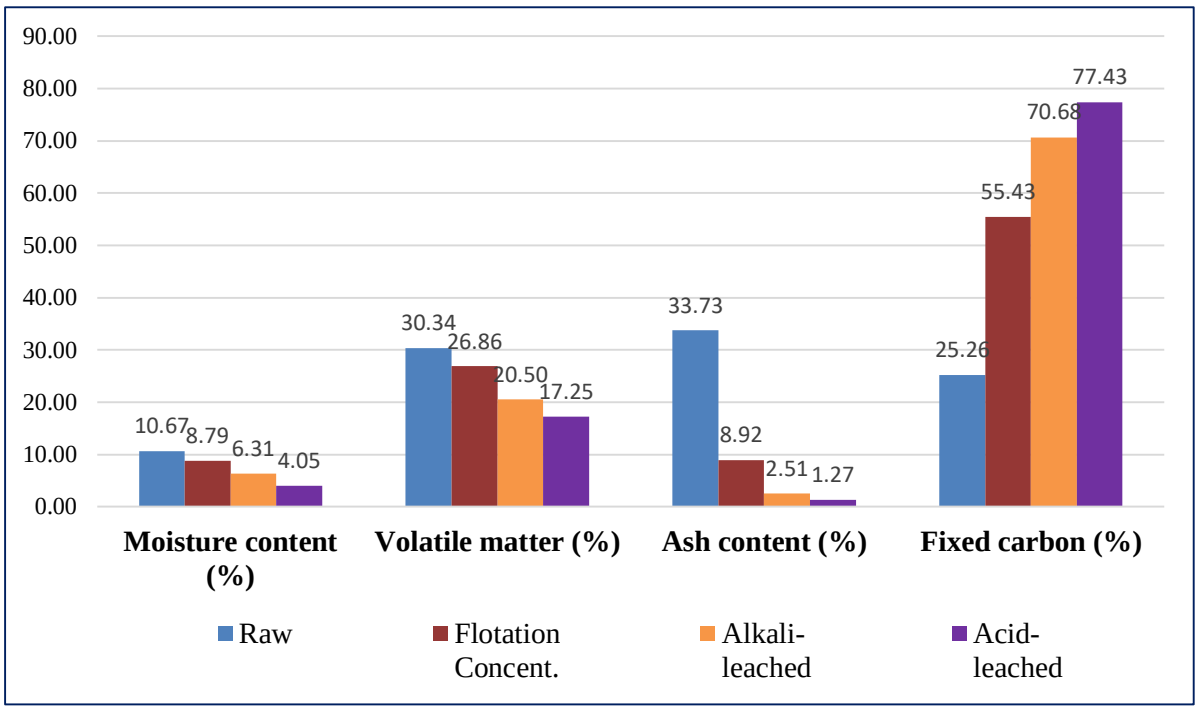


Figure 13. The results of proximate analysis of the raw, flotation-treated and leached samples of coal.

4.3.5 Sulfur Content

The results of sulfur for the raw, flotation-treated, alkali-leached, and acid-leached samples are shown in Table 10. The percentage of sulfur for raw coal was found to be 0.67%. By carrying out froth flotation, alkali leaching, and acid leaching sequentially, the moisture content was 0.45%, 0.38% and 0.37%, respectively. The result confirmed that the percentage of sulfur is significantly reduced by applying flotation and then alkali-acid leaching methods, sequentially (Table 10). The results of this study are supported by the studies [4], which reduced sulfur content from 0.57–1.9% to 0.25–0.41% applying flotation, and similar results were obtained by [13] apply flotation and acid-alkali leaching, and [17, 47], using flotation and chemical leaching methods to upgrade low-ranked coal..

Table 10. The results of proximate analysis and sulfur content of raw and treated coal samples

	Raw Coal (LMM-1)	Flotation Concentrate (LMM-2)	Alkali-leached Coal (LMM-3)	Acid-leached Coal (LMM-4)
Moisture content (%)	10.67	8.79	6.31	4.05
Volatile matter (%)	30.34	26.86	20.50	17.25
Ash content (%)	33.73	8.92	2.51	1.27
Fixed carbon (%)	25.26	55.43	70.68	77.43
Sulfur content (%)	0.67	0.45	0.38	0.37

4.4 Calorific Value

The heating value (or calorific value) analysis resulted from the experiment is shown in Table 11 and the value for the raw coal sample was found to be 3643.08 kcal/kg. As can be seen, by applying the mentioned sequential treatments, the calorific value was increased to 4,996.24 kcal/kg, 6,195.29 kcal/kg, and 7,124.58 kcal/kg for flotation concentrate, alkali-leached coal, and acid-leached coal, respectively. It indicates that the coal 'beneficiation' by applying froth flotation technique followed by alkali-acid leaching is an appropriate approach to improve the heating value of the sample coal.

Thus, after each treatment, the CV of the coal was improved due to the removal of its impurities by applying chemical reagents (Figure 13). The significant increment in values of fixed carbon and significant reduction of ash content play role for the increment of heating

value of the sample coal. This further revealed that the results of calorific value obtained are confirmed by ASTM standards, stating that quality of coal above 5,000 kcal per kg is better used as source of energy in steel and cement industries [35, 53].

Table 11. CVs of raw and sequentially treated coal samples.

Product	Weight (%)	Ash (%)	Sulfur (%)	HHV (kcal/kg)
Feed/raw sample	100.00	33.73	0.67	3,643.08
Flotation Concentrate	51.90	8.92	0.45	4,996.20
Alkali-leached coal	45.10	2.51	0.38	6,195.29
Acid-leached coal	43.51	1.27	0.37	7,124.58

4.5 Comparison with Previous Studies

The current domestic coal beneficiation study was carried out by applying the froth-flotation and alkali-acid leaching experiments, sequentially, for removing the unwanted materials and upgrading the quality of Dawuro coal, located in South-western Region of Ethiopia. The three factors BBD-based RSM experimental design was employed for each of the three sequential experiments.

4.5.1 Results of Raw Coal Flotation

In this study, the particle-size and dosages of reagents (diesel oil as collector and n-octanol as frother) are independent variables (factors) that optimized, whereas flow-rate and impeller speed are kept constant during the entire flotation process. In the coal flotation particles, after the addition of diesel oil as a collector and condition for a time period of 1-minute, big bubbles formation was observed in which particles were seen not attached to oily bubbles' surface. However, after the addition of n-octanol (frother) and increasing the time of conditioning to about 5-minutes, small bubbles were stabilized. Then, the formed foam particles were skimmed off and then filtered by using "What-man filter-paper" to separate the residue clearly from its resulted solution. The filtrates of both residue and flotation concentrate were dried and subjected for the analysis and characterization.

The results of the froth-flotation tests show that the maximum ash-reduction of 73.84% with 71.75% clean-coal recovery yield was obtained at the optimal conditions of 125-63 μm particle-size, 55 g/ton diesel-oil (collector-dosage), and 370 g/ton n-octanol (frother-

dosage). With such optimum conditions, the results revealed that relatively a higher-quality clean coal was obtained by reducing the ash content from 33.73% to 8.92% and sulfur content from 0.67% to 0.45%, and consequently, content of fixed carbon has been increased from 25.26% to 55.43% and the heating-value was improved from 3,643.08 kcal/kg in raw-coal to 4,996.20 kcal/kg in flotation-concentrate. This shows that the developed flotation process was effective for both ash and sulfur contents removal and produced a higher-quality-clean coal compared to the raw coal.

The result found in the current study was in line with that of the study conducted by [4] using the flotation method for improving quality of Ethiopian coal samples from Achibo, Sombo and Dabaso areas. They reported that froth-floatation was effective technique and increased the calorific-values of the samples above 5000 kcal/kg –obtaining clean coal yields of 77.5%, 73.5% and 67.9% with ash contents of 7.49%, 10.74% and 12.68% for the three areas, respectively, at optimum parameters of 0.0472kg/ton Diesel-oil (collector), 0.3689kg/ton N-octanol (frother), particle-size of 125-63 μm, and agitation speed of 2800 rpm. The result of this study was also comparable to the results by [14] – obtaining 80.7% yield of clean coal with 8.27% ash content at 10 kg/ton Diesel-oil (as collector), 500 g/ton MIBC (as frother), particle-size of 125–74 μm and impeller speed of 2000 rpm; and [1], which obtained a high quality clean coal for industrial utilization purpose by reducing the ash and sulfur contents from 25.97 % to 7.80 % and 5.78 % to 1.37 %, respectively; increasing content of fixed carbon from 35.15% to 55.81% and improving calorific-value from 2,820 kcal/kg in raw-coal to 5,813.8 kcal/kg in flotation-concentrate.

4.5.2 Results of Alkali-Acid leaching on Flotation-Pretreated Concentrate

In this part of the study, first, flotation-concentrate was treated by using NaOH-leaching with different concentration, and different leaching temperature and time. Then, NaOH-treated flotation-concentrate was again treated with HCl-leaching with different leaching concentration, temperature and time. Accordingly, the maximum ash-reduction of 71.88% and 49.40% were obtained at the optimum conditions (1 mol/dm^3 NaOH concentration, 220 ^{o}C leaching temperature and 60 minutes contact time) and (1 mol/dm^3 HCl concentration, 80 ^{o}C temperature and 3 hours leaching time) for alkali and acid leaching experiments, respectively. The experimental results for the treated coal samples show that the ash content was 2.51% and 1.27% and sulfur content was 0.38% and 0.37% with calorific values of 6,195.29 kcal/kg and 7,124.58 kcal/kg for alkali-leached flotation-pretreated concentrate

and finally acid-leached sample, respectively. The overall finding of the study revealed that the calorific value of Dawuro coal is upgraded to the expected level for the desired application applying the flotation followed by alkali-acid leaching with less consumption of the leaching chemicals that applied at the higher leaching temperature.

The study by [13] determined the optimal flotation parameters for the cleanest coal concentrate production of Zonguldak coal as solid-liquid ratio (w/w) of 10%, 300 g/ton kerosene (as collector), 20 g/ton Aerofroth 70 (as frother), and 1000 g/ton Na2SiO3, and under such optimal conditions, they obtained a concentrate with 41.57% recovery and 5.63% of ash content. Further, using flotation followed by the HCl-leaching experiments, they confirmed that temperature implied a significant influence on the ash removal from the sample; with the best conditions (3 hours and 2 mol/dm^3 HCl-solution at 80 ^oC), 32% of ash was removed from the flotation concentrate, and a product with 3.7% ash and 0.38% sulfur was obtained by applying flotation, followed by HCl-leaching. Moreover, applying flotation, HCl and NaOH leaching methods sequentially, they reported that a product with 1% ash, 0.37% sulfur and 8390 kcal/kg of heating-value was obtained under the best experimental conditions by using the sequential process mentioned in their study.

Similarly, the results of this study are supported by [17], which reported that flotation reduced the ash content from 22.5% to 13% and sulfur from 3.54% to 2.14%. Then, they leached flotation concentrate using NaOH, and the total content of sulfur was reduced to 1.10% with 54.77% sulfur-reduction but the ash content was increased to 17.5%. Further, the NaOH-leached concentrate was leached again with 10 % HCl and ash content of 8.1% with 59.27% ash-reduction was obtained but the sulfur-content remain 1.10%. This shows that flotation followed by aqueous-caustic leaching can effectively remove much of sulfur, while acid cleaning of NaOH-leached flotation concentrate can effectively remove much of the ash-content. Further, the results of this study are in agreement with that of [47], applying alkali/acid leaching methods to upgrade low-ranked coal.

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

This domestic coal beneficiation study was carried out by applying the froth-flotation and alkali-acid leaching experiments, sequentially, for removing the unwanted materials and upgrading the quality of Dawuro coal, located in South-western Region of Ethiopia. Flotation experiments were conducted on raw coal by considering particle-size, collector dosage, and frother dosage as independent variables. Further, alkali-leaching and then acid-leaching experiments were carried out on alkali-leached flotation concentrate by considering leaching concentration, temperature and time as variables. The test results indicated that the models determined for ash reduction were found to be statistically significant for ash reduction in flotation, alkali-leaching and acid-leaching experiments. Results revealed that particle-size of the coal for flotation pretreatment and leaching concentration followed by leaching temperature for both alkali and acid leaching play important role in effecting the ash reduction.

Accordingly, the maximum ash-reduction of 73.84%, 71.88% and 49.40% were obtained at the experimental conditions (125-63 μm particle-size, 55 g/ton diesel-oil as collector-dosage, and 370 g/ton n-octanol as frother-dosage), (1 mol/dm^3 NaOH-concentration, 220 ^oC leaching temperature and 60 minutes contact time), and (2 mol/dm^3 HCl concentration, 80 ^oC temperature and 3 hours contact time) for flotation pretreatment, alkali and acid leaching experiments, respectively.

The experimental results for the treated/leached coal sample shows that the ash content was 8.92%, 2.51% and 1.27%; and percentage of sulfur content was 0.45%, 0.38% and 0.37% with 4,996.20 kcal/kg, 6,195.29 kcal/kg and 7,124.58 kcal/kg of calorific values for flotation concentrate, alkali-leached and acid-leach coal samples, respectively. Hence, we concluded that:

- Flotation technique gives the higher results when applied on coal samples with lower particle-size and alkali-leaching on flotation-pretreated concentrate and acid-leaching on alkali-leached flotation concentrate both give higher values/results of coal quality by increasing leaching-temperature while decreasing leaching-concentration with fixed time.

- Applying froth-flotation followed by alkali-acid leaching experiments, with the optimum conditions, is effective to upgrade the quality of the sample coal with low ash content of 1.27% and sulfur content of 0.37%, which below 1 %, and hence, suitable to use for the intended purpose as an energy source in industries like cement and steel.

The overall finding of the study revealed that the calorific value of Dawuro coal is enhanced to the expected level to apply for the desired application using the froth flotation pretreatment followed by alkali-acid leaching with less concentration of the leaching chemicals that applied at the higher leaching temperature.

5.2 Recommendations

Based on the findings of this study, the following recommendations are suggested.

- As the current study employed a three-stages coal beneficiation procedures using flotation technique followed by the sequential alkali-acid leaching methods with less consumption of chemical concentrations, future and interested researchers should conduct studies on the purification and reusing/recycling of the chemicals after the alkali-acid leaching in order to further improve the efficiency and performance of the three-stages coal beneficiation methods developed in this study.
- Based on the possibilities of enhancing the domestic coals for the intended purpose, policy makers and stakeholders should take special attentions in order to initiate and facilitate potential investors to the domestic coal upgrading business activities.
- Future researchers use the findings of this study as reference and should conduct further studies on domestic coal improvement by using different coal samples available at different parts and potential sources of the country, and considering cost effective analysis of the proposed sequential beneficiation procedures and comparing its performance with the other methods.

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Annex 1

Coefficients showing importance of the independent variables

(a) Coefficients in terms of coded factors for flotation experiment

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	65.45	1	0.9120	63.29	67.61	
A-Particle size	-10.08	1	0.6480	-11.62	-8.55	1.06
B-Collector	1.91	1	0.6652	0.3338	3.48	1.05
C-Frother	2.62	1	0.6652	1.05	4.19	1.05
AB	-0.3707	1	0.8915	-2.48	1.74	1.05
AC	1.28	1	0.8915	-0.8235	3.39	1.05
BC	0.1966	1	0.9165	-1.97	2.36	1.0000
A^2	-1.16	1	1.04	-3.62	1.29	1.07
B^2	-5.06	1	0.8933	-7.17	-2.95	1.01
C^2	-3.25	1	0.8933	-5.36	-1.13	1.01

(b) Coefficients in terms of coded factors for alkali-leaching experiment

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	50.83	1	1.25	47.87	53.79	
A-NaOH Concentration	-17.40	1	0.9891	-19.74	-15.06	1.0000
B-Temperature	9.48	1	0.9891	7.14	11.82	1.0000
C-Time	4.64	1	0.9891	2.31	6.98	1.0000
AB	0.8602	1	1.40	-2.45	4.17	1.0000
AC	1.64	1	1.40	-1.67	4.94	1.0000
BC	4.06	1	1.40	0.7550	7.37	1.0000
A^2	3.79	1	1.36	0.5660	7.01	1.01
B^2	-6.31	1	1.36	-9.53	-3.08	1.01
C^2	-6.71	1	1.36	-9.93	-3.48	1.01

(c) Coefficients in terms of coded factors for acid-leaching flotation experiment

Factor	Coefficient Estimate	df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	35.57	1	1.05	33.07	38.06	
A-HCl Concentration	-10.26	1	0.8331	-12.23	-8.29	1.0000

B-Temperature	5.31	1	0.8331	3.34	7.28	1.0000
C-Time	2.26	1	0.8331	0.2948	4.23	1.0000
AB	0.3726	1	1.18	-2.41	3.16	1.0000
AC	2.98	1	1.18	0.1915	5.76	1.0000
BC	3.35	1	1.18	0.5591	6.13	1.0000
A^2	0.9952	1	1.15	-1.72	3.71	1.01
B^2	-3.01	1	1.15	-5.73	-0.2948	1.01
C^2	-4.10	1	1.15	-6.81	-1.38	1.01

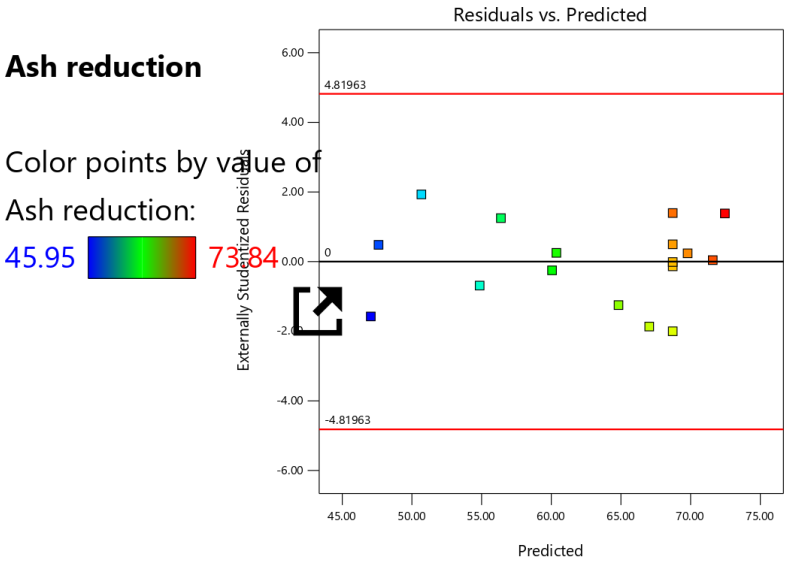
Annex 2

Actual and predicted values of ash reduction.

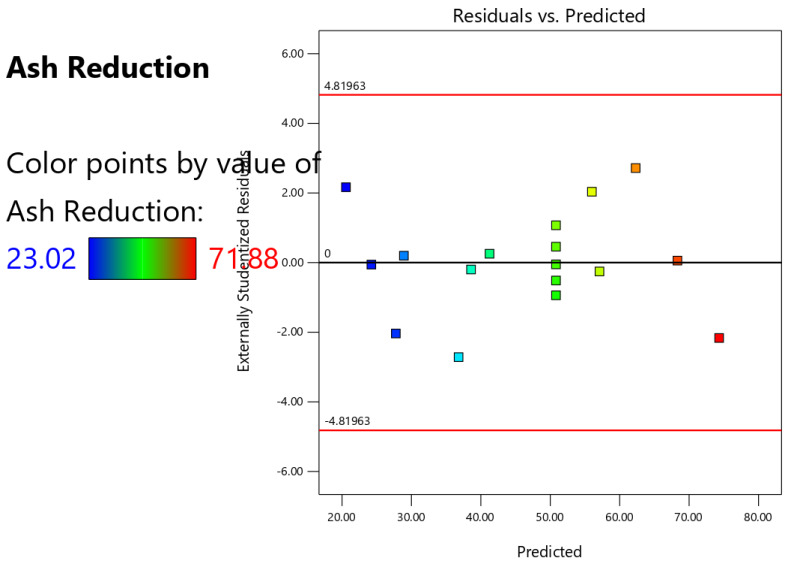
	Flotation Technique			Alkali-Leaching			Acid-Leaching		
Run Order	Actual Value	Predicted Value	Residual	Actual Value	Predicted Value	Residual	Actual Value	Predicted Value	Residual
1	63.75	64.83	-1.07	50.69	50.83	-0.1360	34.81	35.57	-0.7539
2	70.86	68.72	2.15	52.04	50.83	1.21	44.60	43.43	1.16
3	57.46	56.38	1.07	25.38	27.75	-2.37	39.55	39.38	0.1728
4	60.61	60.37	0.2403	71.88	74.33	-2.45	38.70	35.57	3.14
5	73.84	72.46	1.38	49.47	50.83	-1.36	24.05	24.23	-0.1728
6	51.94	50.68	1.26	56.70	57.09	-0.3825	23.88	22.07	1.81
7	59.81	60.06	-0.2403	34.04	36.79	-2.75	41.19	42.01	-0.8208
8	45.95	47.05	-1.10	41.63	41.25	0.3825	37.88	38.87	-0.9917
9	65.33	67.03	-1.70	23.02	20.57	2.45	49.40	48.75	0.6480
10	65.97	68.72	-2.74	48.46	50.83	-2.37	26.29	27.45	-1.16
11	71.64	71.59	0.0486	58.37	56.00	2.37	17.79	16.97	0.8208
12	48.00	47.61	0.3932	53.48	50.83	2.65	29.97	28.98	0.9917
13	68.48	68.72	-0.2396	29.21	28.91	0.2971	16.96	17.61	-0.6480
14	68.69	68.72	-0.0233	65.05	62.30	2.75	26.35	28.16	-1.81
15	69.58	68.72	0.8610	68.40	68.32	0.0854	32.52	35.57	-3.04
16	70.06	69.79	0.2727	38.29	38.59	-0.2971	37.55	35.57	1.99
17	54.31	54.86	-0.5526	24.14	24.23	-0.0854	34.24	35.57	-1.32

Annex 3

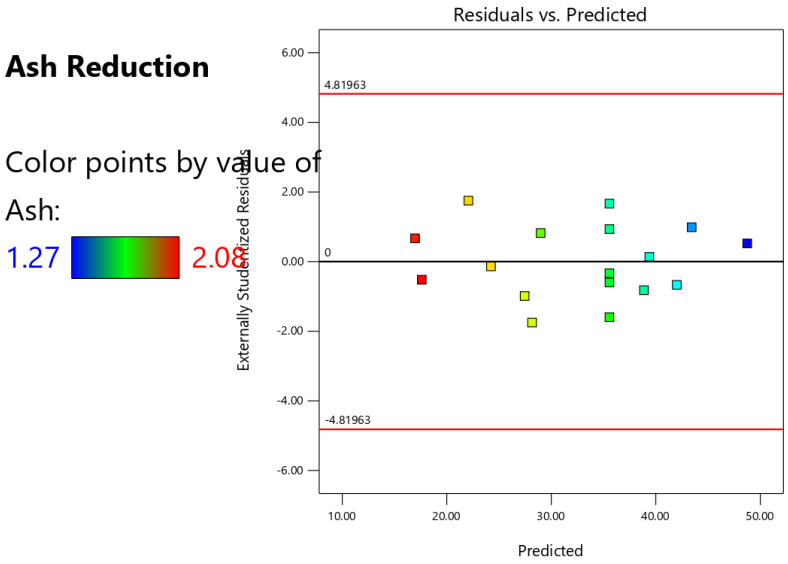
Residual plots for predicted ash reduction



(a) Flotation experiment



(b) Alkali-leaching experiment



(c) Acid-leaching experiment

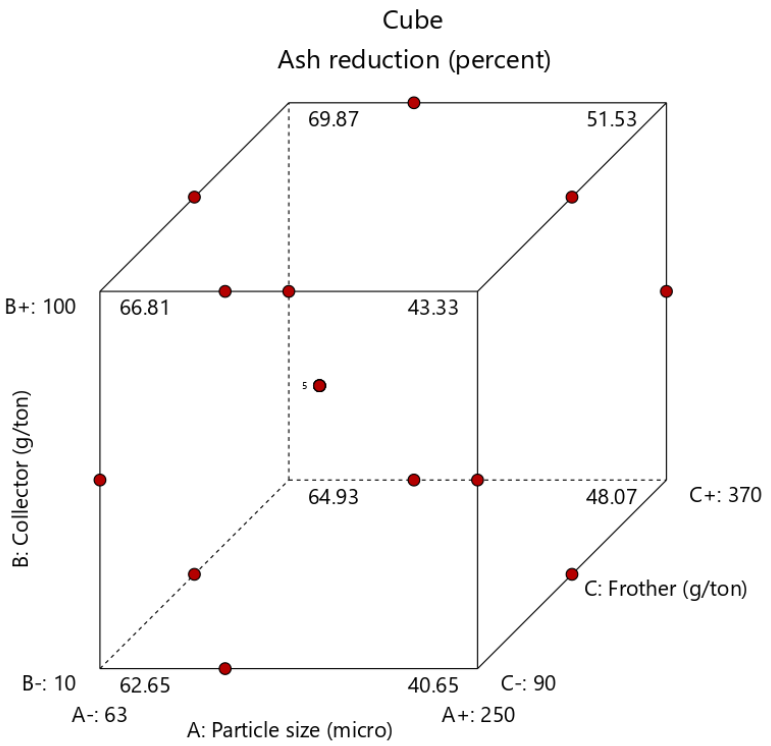
Annex 4

3D or Cube plots for predicted ash reduction

Factor Coding: Actual

Ash reduction (percent)
X1 = A
X2 = B
X3 = C

Predicted values shown

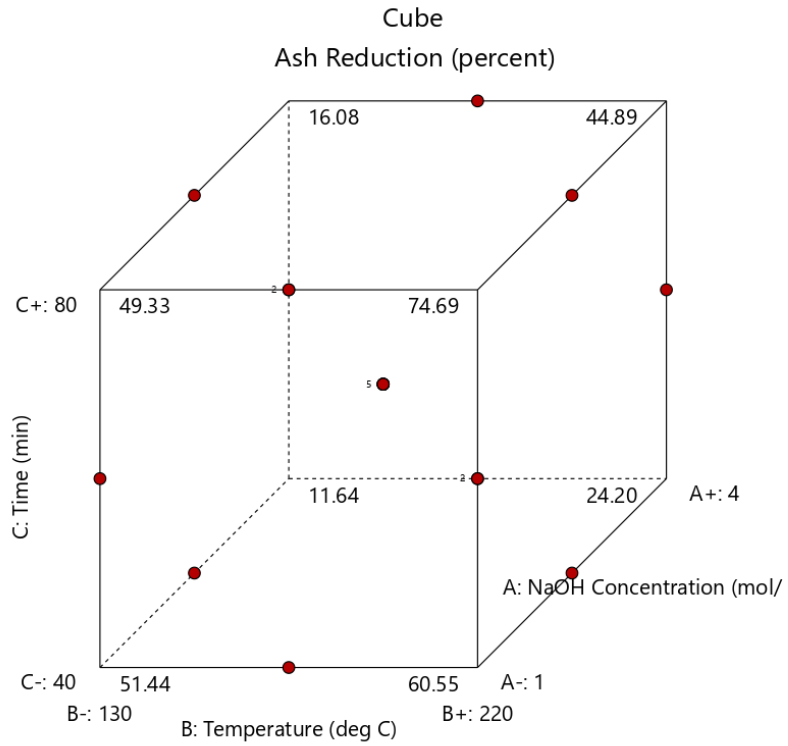


(a) Coal flotation experiment

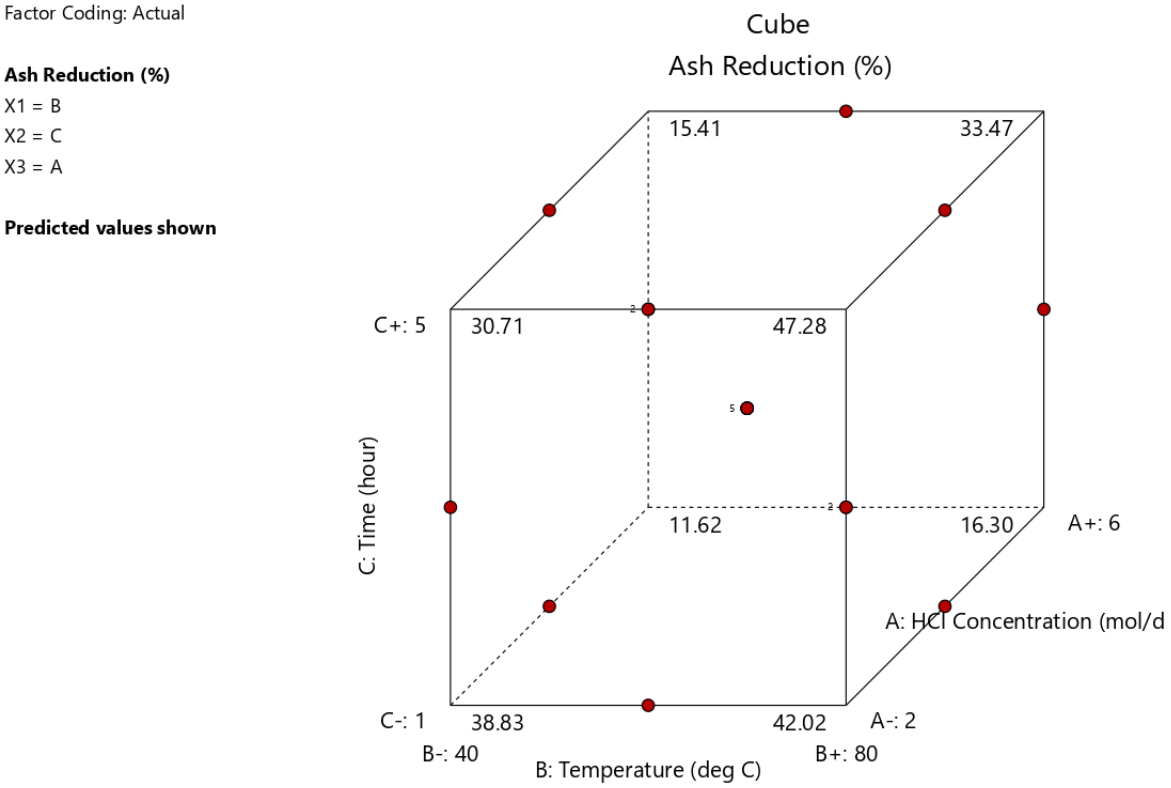
Factor Coding: Actual

Ash Reduction (percent)
X1 = B
X2 = C
X3 = A

Predicted values shown



(b) Alkali-leaching experiment



(c) Acid-leaching experiment

Annex 5

Reports of the Coal Beneficiation Experiments

Results of proximate analysis, sulfur content and calorific value of raw coal

	GEOLOGICAL INSTITUTE OF ETHIOPIA	**Doc. Number: GLD/F5.10.2**	**Version No: 1**
	Geochemical Laboratory Desk		Page **1**of **1**
Document Title:-	**Hydrocarbon Analysis Report**	**Effective date:**	**Nov. 2022**

Customer Name:-Leager Minwuyelet Meleak

Issue Date:- 20/09/2023

Sample type: -Coal

Request No:-GLD/RN/198/23

Sample Preparation:- 60 Mesh

Report No:- GLD/TR/2275/23

Date Submitted:-30/08/2023

Number of Sample:- One (01)

Elements to be determined:-(Moisture,Volatile matter, Fixed carbon and Ash), Calories & Sulfur.

Method of analysis:- Proximate Analysis, Adiabatic Calorie Metter and Gravimetric Method

Collectors' Code	Moisture %	Volatile Matter %	Fixed carb on %	Ash %	Calorific Value Cal/gm.	Sulfur %	Weight of Sample
LMM-1	10.67	30.34	25.26	33.73	3643.08	0.67	3.60 kg

Note: - This result represent only for the sample submitted to the laboratory.

Analysts
Bethelhem Tefera
Shashe Haile

Approved By
Alemnesh Abate

Quality Control
Negash Worku

Results of proximate analysis, sulfur content and calorific value of flotation concentrate

	GEOLOGICAL INSTITUTE OF ETHIOPIA	**Doc. Number: GLD/F5.10.2**	**Version No: 1**
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Document Title:-	**Hydrocarbon Analysis Report**	**Effective date:**	**Nov. 2022**

Customer Name:-Leager Minwuyelet Meleak

Issue Date:- 20/09/2023

Sample type: -Coal

Request No:-GLD/RN/199/23

Sample Preparation:- 60 Mesh

Report No:- GLD/TR/2276/23

Date Submitted:-30/08/2023

Number of Sample:- One (01)

Elements to be determined:-(Moisture,Volatile matter, Fixed carbon and Ash), Calories & Sulfur.

Method of analysis:- Proximate Analysis, Adiabatic Calorie Metter and Gravimetric Method

Collectors' Code	Moisture %	Volatile Matter %	Fixed carbon %	Ash %	Calorific Value Cal/gm.	Sulfur %
LMM-2	8.79	26.86	55.42	8.92	4996.20	0.45

Note: - This result represent only for the sample submitted to the laboratory.

Analysts
Bethelhem Tefera
Shashe Haile

Approved By
Alemnesh Abate

Quality Control
Negash Worku

Results of proximate analysis, sulfur content and calorific value of alkali-leach following flotation technique

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Document Title:-	**Hydrocarbon Analysis Report**	**Effective date:**	**Nov. 2022**

Customer Name:-Leager Minwuyelet Meleak

Issue Date:- 20/09/2023

Sample type: -Coal

Request No:-GLD/RN/201/23

Sample Preparation:- 60 Mesh

Report No:- GLD/TR/2278/23

Date Submitted:-08/09/2023

Number of Sample:- One (01)

Elements to be determined:-(Moisture,Volatile matter, Fixed carbon and Ash), Calories & Sulfur.

Method of analysis:- Proximate Analysis, Adiabatic Calorie Metter and Gravimetric Method

Collectors' Code	Moisture %	Volatile Matter %	Fixed carbon %	Ash %	Calorific Value Cal/gm.	Sulfur %
LMM-3	6.31	20.50	70.68	2.51	6195.29	0.38

Note: - This result represent only for the sample submitted to the laboratory.

Analysts
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Shashe Haile

Approved By
Alemnesh Abate

Quality Control
Negash Worku

Results of proximate analysis, sulfur content and calorific value of acid-leached alkali-treated flotation concentrate

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Document Title:-	**Hydrocarbon Analysis Report**	**Effective date:**	**Nov. 2022**

Customer Name:-Leager Minwuyelet Meleak

Issue Date:- 20/09/2023

Sample type: -Coal

Request No:-GLD/RN/202/23

Sample Preparation:- 60 Mesh

Report No:- GLD/TR/2279/23

Date Submitted:-08/09/2023

Number of Sample:- One (01)

Elements to be determined:-(Moisture,Volatile matter, Fixed carbon and Ash), Calories & Sulfur.

Method of analysis:- Proximate Analysis, Adiabatic Calorie Metter and Gravimetric Method

Collectors' Code	Moisture %	Volatile Matter %	Fixed carbon %	Ash %	Calorific Value Cal/gm.	Sulfur %
LMM-4	4.05	17.25	77.43	1.27	7124.58	0.37

Note: - This result represent only for the sample submitted to the laboratory.

Analysts
Bethelhem Tefera
Shashe Haile

Approved By
Alemnesh Abate

Quality Control
Negash Worku