

PROCESSING LOW RANK COAL AND ULTRA-FINE
MINERAL PARTICLES BY HYDROPHOBIC–HYDROPHILIC
SEPARATION

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RIDDIHIKA JAIN

ABSTRACT

This thesis pertains to the processing of ultra-fine mineral particles and low rank coal using the hydrophobic–hydrophilic separation (HHS) method. Several explorative experimental tests have been carried out to study the effect of the various physical and chemical parameters on the HHS process.

In this study, the HHS process has been employed to upgrade a chalcopyrite ore. A systematic experimental study on the effects of various physical and chemical parameters such as particle size, reagent dosage and reaction time on the separation efficiencies have been performed. For this, a copper rougher concentrate (assaying 15.9 %Cu) was wet ground and treated with a reagent to selectively hydrophobize the copper-bearing mineral (chalcopyrite), leaving the siliceous gangue minerals hydrophilic. The slurry was subjected to a high-shear agitation to selectively agglomerate the chalcopyrite and to leave the siliceous gangue dispersed in aqueous phase. The agglomerates were then separated from dispersed gangue minerals by screening and the agglomerates dispersed in a hydrophobic liquid (n-pentane) to liberate the water trapped in the agglomerates. The chalcopyrite dispersed in the hydrophobic liquid was separated from the medium to obtain a concentrate substantially free of gangue minerals and moisture. The copper recoveries were substantially higher than those obtained by flotation. The HHS process was also tested on ultrafine mono-sized silica beads. The results were superior to those obtained by flotation, particularly with ultrafine particles. The HHS process has also been tested successfully for upgrading subbituminous coals. Low-rank coals are not as hydrophobic as high-rank coals such as bituminous and anthracite coals. In the present work, a low-rank coal from Wyoming was hydrophobized with appropriate

reagents and subjected to the HHS in a similar manner as described for processing copper. The results showed that the HHS process reduced the moisture substantially and increased the heating value up to 50% without heating the coal. Laboratory-scale tests conducted under different conditions, e.g., particle size, reagent type, reaction time, and pretreatments, showed promising results. Implementation for the HHS process for upgrading low-rank coals should help reduce CO₂ emissions by improving combustion efficiencies.

DEDICATION

I dedicate this work to my parents and my beloved Gaurav for their continuous love and support which gave me strength to do my work whole heartedly.

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Chapter 1: Introduction

1.1 Preamble

Chalcopyrite is the principal commercial source of copper. Presently, the mineral is recovered by flotation after grinding the ore to fine sizes for liberation. Similarly, flotation is used for the removal of silica from iron ore and phosphate concentrates. As ore grades becomes lower, it is necessary to grind an ore finer to achieve liberation (Johnson, 2005). However, flotation is inefficient for the recovery of fine particles below approximately 10 to 25 μm .

Spherical or oil agglomeration has been proposed as an excellent technique for recovering fine particles that are difficult to recover by flotation. Oil agglomeration involves addition of an immiscible liquid such as a hydrocarbon oil to an aqueous suspension of solids. Upon agitation, there will be a distribution of the oil over the surface of the hydrophobic surfaces, causing formation of liquid bridges or oil agglomerates. Addition of suitable collectors to the process results in selective mineral recovery. Recovering coal fines by oil agglomeration is a well-known process. However, recovering mineral particles with oil agglomeration is yet to be tried outside the laboratory (House, C. I. and C. J. Veal, 1989). Some work on cassiterite, ilmenite, hematite, barite and gold has been reported in the literature (House, C. I. and C. J. Veal, 1989).

Coal is used as a raw material for many chemical synthesis processes including metallurgy and fuels for power plants due to its low cost. In 2011, 42% of the electricity in United States used coal as its source of energy (EIA 2012). Over the coming years it is expected that the demand for coal will rise. An estimated 52% of the world coal reserves consist of sub-bituminous and brown coal also referred as low rank coal (LRC). With the impending energy crisis, it will be increasingly necessary to use LRCs. Although, low rank coal has low ash and sulfur contents, its high moisture content, low calorific values and spontaneously combusting characteristics makes it really difficult to utilize. So if it could be efficiently upgraded and converted into high-grade, high-heating coal, it would greatly contribute not only to a stable

energy supply but also to environmental conservation as SO₂ releases from the combustion plants contributes largely towards acidic rain.

From the Energy crisis in 1970, numerous research and development projects of conversion process for low rank coal started in several countries. Some of the conventional processes developed to reduce moisture content of the low rank coal involve heating LRC above the boiling point of water to vaporize the fluid. However, these processes have problems with the large latent heat of water vaporization which increases its energy consumption and the product becomes spontaneously combustible. As a result, the transportation and storage of processed low rank coal become very difficult. For this purpose, a new and innovative process to reduce the moisture content and increase the BTU value of low rank which can also solve the self-combustion issue has to be developed having two main benefits: utilization of low rank coal reserves around the globe to cater to energy needs and the environmentally friendly product with low sulfur content.

1.2 Objectives

Virginia Tech developed a patented process known as dewatering by displacement (DbD) in 1995 (Yoon and Luttrell, U.S. Patent No. 5,459,786) for dewatering of fine coal. The main aim of this research work was to extend the application of dewatering by displacement (DbD) process for processing of mineral particles in ultrafine size ranges as well as for up gradation of LRCs. The research focused on studying the changes in the properties of low rank coal and mineral (chalcopyrite and silica) with the test parameters.

For chalcopyrite and silica beads, the goal of this project was to develop a process to facilitate the recovery of mineral particle in ultra-fine size range. The project was focused on conducting laboratory-scale batch tests on different size fractions of both silica beads and chalcopyrite. The surface of the ore particles was modified using hydrophobizing agent. The modified ore was then subjected to oil agglomeration. The agglomerates were then dewatered either dispersing them in hydrophobic liquid or filtered in presence of hydrophobic liquid so as to facilitate the displacement of water by hydrophobic liquid.

For low rank coal, the goal of this project was to develop a process to remove the excessive moisture content without making it susceptible to spontaneous combustion. The coal surface was modified using different techniques to make it more hydrophobic. The modified coal was then subjected to oil agglomeration. The coal particles were then dispersed in hydrophobic liquid, which was recycled back into the process using double boiler and condenser unit. The resulting clean coal should contain less than 12% moisture to achieve higher BTU values. In all the experiments, pentane was used as hydrophobic liquid since it is affordable and can be easily recycled using evaporation and condensation.

The project was focused on conducting laboratory-scale batch tests using three different methods for making low rank coal surface hydrophobic in order to determine the most economic method which will facilitate the scaling up of the process. During the experiment processes, the low rank coal was made hydrophobic by surfactant coating, acid washing followed by esterification or low temperature oxidation followed by esterification. The resulted hydrophobic coal particles were subjected to oil agglomeration, which were then dispersed into hydrophobic liquid using mechanical agitation/vibration.

1.3 Organization

The thesis has been broadly categorized into four main parts. The introductory part gives an overview of the research objectives for both low rank coal processing as well as mineral processing.

The literature review section of this thesis deals into prior work conducted by researchers on the processing of low rank coal as well as oil agglomeration of mineral particles. It provides an overview to familiarize the readers with basic concept and terminologies that have been used in this research.

The experimental section is further divided into three parts. The first part describes the chalcopryrite processing by hydrophobic- hydrophilic separation (HHS) technique and compares with froth flotation. The second parts deals with processing of mono-sized silica by HHS and compares with froth flotation. Finally low rank coal processing by HHS technique is discussed.

Results of each of three subsections have also been included as part of the experimental section. The conclusion and recommendation section serves as the final section for this thesis. It reviews the scope and extent of the work carried out as a part of the research project and seeks to explain the probable future work that can be carried out as continuation of the research.

Chapter 2: Literature Review

2.1 Prior Work

2.1.1 Dewatering by Displacement

Virginia Tech developed a patented process known as dewatering by displacement (DbD) in 1995 (Yoon and Luttrell, U.S. Patent No. 5,458,786), and has been making improvements. In this process, a hydrophobic liquid is added to a coal slurry to displace the surface water. The displacement occurs because the hydrophobic liquid has a higher affinity for coal surface than water. The DbD process is depicted in *Figure 2-1* (a), in which a hydrophobic solid particle **1** leaves an aqueous phase **3**, and enters the hydrophobic liquid (oil) phase **2**. This step is spontaneous, when the change in Gibbs free energy (ΔG) normalized by particle surface area (A) is less than zero:

$$\Delta G/A = \gamma_{12} - \gamma_{13} < 0 \quad (1)$$

Combining Eq. (1) with Young's equation, one obtains the following relation,

$$\Delta G/A = \gamma_{23} \cos \theta < 0 \quad (2)$$

in which θ is the contact angle of oil on the hydrophobic surface as measured through water (3). According to Eq. (2), $\Delta G < 0$ when $\theta > 90^\circ$.

Figure 2-2 shows the contact angles of n-alkanes on a hydrophobic bituminous coal surface. As shown, the contact angles are greater than 90° . Therefore, the hydrocarbon oils can spontaneously displace water from the surface. Note here that ΔG becomes more negative with decreasing number of the carbons in the hydrocarbon chain. Therefore, a shorter hydrocarbon chain would be a better hydrophobic liquid to displace water from the surface of hydrophobic particles. One advantage of using a short chain hydrocarbon oil is that it can be readily recovered and recycled after the DbD process.

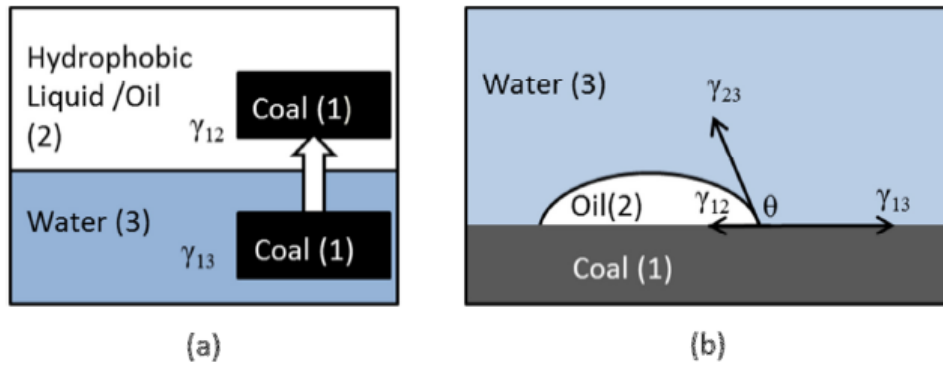


Figure 2-1: a) Schematic showing the displacement of coal, 1, from the water phase, 3, into the oil phase, 2; and b) the three-phase equilibrium between interfacial tensions (Redrawn from Yoon)

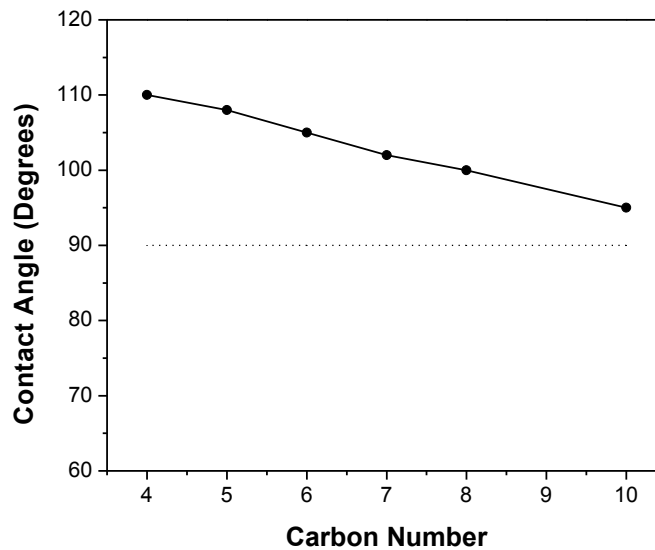


Figure 2-2-2: Contact angles of n-alkanes on a hydrophobic bituminous coal surface

When water is displaced during the DbD process, hydrophilic particles dispersed in it is also separated from the hydrophobic particles. In this regard, the DbD process is now referred to as hydrophobic-hydrophilic separation (HHS). For this process to work as a separation process, one type of particles must be rendered hydrophobic, while another type of particles is left hydrophilic as is obvious from the thermodynamic considerations noted above. Thus, one can upgrade a chalcopryite ore by rendering the copper mineral selectively hydrophobic using a

typical sulfide flotation collector such as xanthate or thionocarbamate. Ultrafine silica particles can also be separated from phosphate or iron oxides by selectively rendering the silica hydrophobic. For coal, it is not necessary to use a hydrophobizing agent as higher rank coals such as bituminous coal and anthracite are naturally hydrophobic. For subbituminous coals that are naturally hydrophilic, one can use appropriate hydrophobizing agents and subject them to the HHS process.

2.1.2 Low Rank Coal

Coal formation and reserve maturity determine the rank of coal. The rank of coal can be seen to be the degree of maturation that occurs as coal metamorphoses from peat to anthracite during the course of its formation process (Sondreal, E. et al, 1984)

Thus the sub-bituminous coal types and lignite can be seen to form low rank coal. This type of coal has low carbon content and hence, the energy output achieved on combustion is also lower. Thus, low rank coal refers to the coal type which has high moisture content and low heating value. Consequently the price of low rank coal which amounts to 50% of total coal is also lower compared to the higher ranks. It is imperative that low rank coal with its low pricing and larger reserve needs ample attention so as to benefit from the same.

Figure 2-3 describes the types of inherent moisture present in low rank coal. In total we can see five major types. Based on their characteristic properties, these can be classified as interparticle water, adhesion water, capillary water, surface adsorption, organic water and interior water (Kartikayen, M et al, 2009). These can be defined as follows:

- 1) Interior adsorption water is that which is deposited during formation and find itself bound to the coal micro-particles and capillaries.
- 2) Surface adsorption water, as the name suggests finds itself on the outer surface of the coal particles.
- 3) Capillary water is that which is found in the capillaries of coal particles.
- 4) Water found between two particles is termed as interparticle water.
- 5) Water which find itself adhering to the surface of the coal particles is adhesion water.

- 6) Organic water which is present as the carboxyl function group at the surface of coal particles.

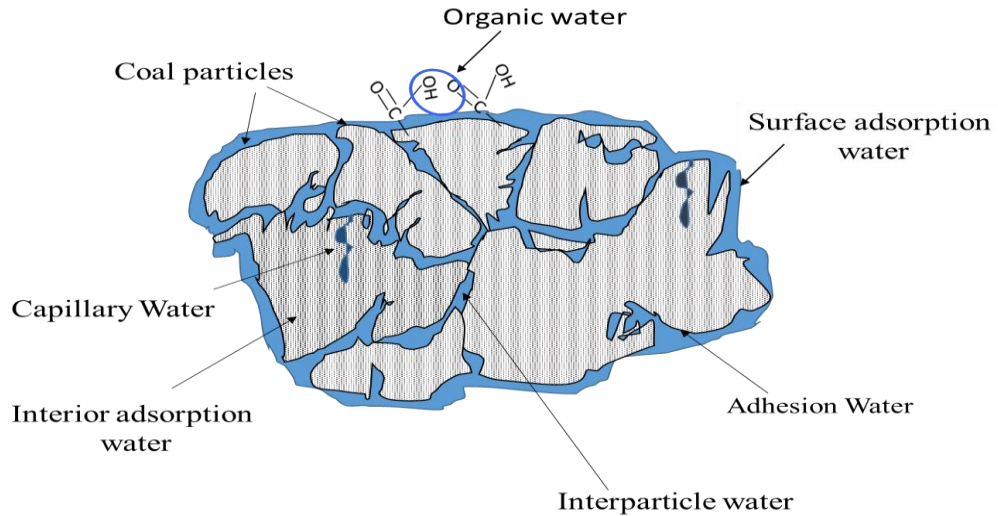


Figure 2-3: Inherent moisture structure in low rank coal

Traditionally this type of coal did not find preference for use in industries due to the additional costs involved in the transportation of the fuel due to high moisture and the low output in terms of energy content. The high moisture content of the low rank coal, or brown coal, makes it heavy in weight and with the energy output being not nearly as comparable to the higher ranks, it found its use near the mines for burning and heat generation processes.

However, over the years, low rank coal has been sought out for usage as fuel due to its characteristic low sulfur content which makes it an environmentally friendly substitute compared to its other sulfur-rich counterparts.

Another disadvantage of the low rank coal is the ease with which it combusts spontaneously. Spontaneous combustion occurs when low rank coal is dewatered at high temperature. Even at low temperatures, partial oxidation of the carbon takes place which releases heat and cause a rise in the temperature of the coal. This temperature increases gradually reaching a point at which spontaneous combustion takes place. Low rank coal has lower carbon content which increases the possibility of an oxygen adsorbent functional group to exist in its

structure in comparison to higher ranking coal thus making it more susceptible to oxygen adsorption both chemically and physically

In the techniques which have been employed so far to enrich the low rank coal, the inherent moisture present as the organically bound water in the coal is also driven out due to the drying techniques used. However, this causes the problem for the fuel composition as it makes the fuel easily susceptible to the spontaneous combustion.

2.2 Fine Particle Processing: Flotation

Froth flotation (*Figure 2-4*) is the most vividly used process in mineral industry for concentrating mineral in the size range $45\mu\text{m}$ to $150\mu\text{m}$. It is a physico-chemical separation process based on the wettability of particles. In flotation cell, air bubbles are generated in the pulp phase by agitator which selectively attached the hydrophobic minerals and carry them to the froth phase, while hydrophilic gangue particles remain in the bottom of the cell. The froth is then collected in the launder separating valuable mineral particles from gangue.



Figure 2-4: Chalcopyrite flotation using Lab scale Denver flotation cell

Flotation is controlled by both chemical and physical variables. Chemical Variables include reagent dosage, pulp pH etc. Physical variables include particle size, feed rate, pulp level, slurry density, aeration rate, impellor speed, conditioning time and froth height. The separation efficiency of the process is also effected by type and configuration of flotation cell.

The efficiency of flotation process is highly dependent on the surface properties of the mineral and gangue. The surface chemistry of the particle is controlled by addition of several chemical regents like frother, collector, activator, depressant and pH modifier. Although complex ore (like lead-Zinc sulfide ore) flotation process utilizes all of the reagents, single ore (like chalcopyrite or silica) flotation often utilizes only collector and frother. Collector is the organic surfactant which attaches on the surface of the mineral making it more hydrophobic and hence facilitates the bubble – particle attachment (Wills, 2005). Frother are hetero-polar surfactants consist of polar head and non-polar tail which are used to stabilize the froth and hence inhibit the breaking of particles loaded bubbles in the froth phase (Wills, 2005).

Flotation is most efficient for particle size ranging from 45 μ m to 150 μ m. At finer particle size, the bubble particle collision decreases, while for big particle, the probability of detachment from the bubble surface increases. Apart from particle size, bubble size also affects the efficiency of flotation process. Bubble size not only affects the recovery but it also affects the selectivity of the process.

Although selective attachment of valuable mineral to the air bubble is the major phenomena for recovery of valuable mineral, the separation efficiency of the flotation process is also affected by degree of entrainment in the water phase which passes through froth phase and physical entrapment between particles in the froth (Wills, 1995). The entrainment of unwanted gangue in the water phase is very common in the industry and can be minimized by adding several circuits to the flotation (rougher, scavenger and cleaner).

2.3 Oil Agglomeration

Selective oil agglomeration is commonly used to recover or separate fine particles dispersed in water through addition of oil. On contrary, as the particle size decreases below

50 μ m, the flotation process becomes less desirable due to decrease in selective recovery of desirable mineral particles and increase in processing cost (Hazra, Rao et al. 1988). Oil agglomeration is more economic and most effective in very fine particle size range as the particle is fully liberated.

2.3.1 History

Oil agglomeration has been used in mineral processing industry since 1920's for cleaning of coal. The earlier process involved agitating a mixture of dry solids and oil in water to separate oil wetted particles from water-wetted gangue minerals. The process has been subjected to several modifications since then. The process, in its early years of development, could not compete with the then existing processes due to the high cost of creating the agglomerates and low oil recoveries. However, in 1970's the development of oil agglomeration process was given impetus because of the sharp increase in oil prices. Though the principle of oil agglomeration process remained same, several patents were filed during this period. The process was even tested on several pilot plant units (Mehrotra et al., 1983). Other possible uses of the process, besides cleaning of coal like dewatering and waste water cleaning have also been explored. Several methods to employ oil agglomeration on low rank coal were also researched in late 1980's (Ikura and Capes, 1988). The oil glut in late 1980's once again made the oil agglomeration obsolete as an oil substitute was no longer needed (Mehrotra et al., 1983).

2.3.2 Factors affecting Oil agglomeration

Oil agglomeration is the selective wetting of hydrophobic particle, in aqueous suspension, by oil. The process highly depends on the surface hydrophobicity of the particle and that of the oil. The interaction between hydrophobic liquid and hydrophobic particle is controlled by the surface free energies at the three interfaces, mixing intensity (high shear or Low shear), mixing time and amount of the hydrophobic liquid used. For most effective process, from thermodynamic standpoint, the surface free energies at solid/water interface and oil/water interface should be high than surface free energies at solid/oil interface (Mehrotra et al., 1983). From kinetics point of view, speed of agitation and total agitation time are the deciding factors. High sheer quickly forms agglomerates but limit the size of agglomerates to small diameters, whereas low sheer helps in growth of the agglomerates size. Optimum oil dosage and mechanical

mixing allows coal particles to collide and stick tighter by oil bridges and the growth of agglomerates incorporated by mixing time. Low oil dosage creates loose flocs structure whilst very high dosage results in formation of emulsion rather than agglomerates.

Selecting right kind of oil is very important for successful agglomeration process both from economic point of view and as well as selectivity of the process. Oils are conveniently divided amongst heavy oil and light oil depending on the viscosity of oil. Some researchers have shown that heavy oils are too viscous to be dispersed in the slurry while other researchers have shown that with longer mixing time, highly viscous oils are also capable of high recoveries. Some researchers have also concluded that heavy oils are less selective. It is also cited in the literature that very light oil could not make the particles sufficiently hydrophobic. In summary, the selection of oil is deeply affected by the surface properties of particles to be agglomerated and the method of mixing of oil (Mehrotra et al., 1983)

Since oil agglomeration is based on differences in surface properties of organic and inorganic matter, first being hydrophobic and later being hydrophilic, oil agglomeration is very difficult for low rank coal. The low rank coal can be made hydrophobic either by addition of hydrophobic collecting oil, and/or by adding surface active agents or electrolytes which adsorb on the coal surface and also modify the surface charges on both coal surface and oil droplets and hence aid towards the agglomeration process (Gürses et al., 1997). It is mentioned in literature that agglomerate rates for low rank coal can be improved by adding H^+ ions to the water phase or a small peroxide-group-containing chemical to oil phase. Using vacuum bottoms (highly viscous IPPL/Cold Lake) at high temperature for oil agglomeration of lignite has also been reported successful with 90% combustible recovery (Ikura et al., 1988)

2.3.3 *Methods Employed for Dewatering Of Agglomerates*

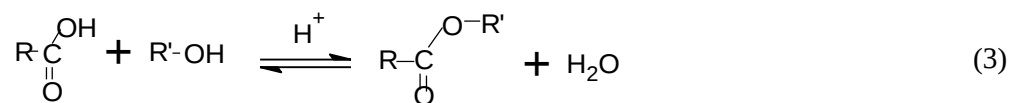
The moisture content in agglomerates mainly consist of the water droplets trapped inside the agglomerate and surface moisture. A significant amount of research has been done at Virginia Tech on reducing the moisture content of the agglomerates. Several technologies such as centrifuge, ultrasonic probe, dewatering by screen have been utilized for breaking and dewatering of agglomerates. Centrifugation was able to produce moisture as low as 7.5% with combustible recoveries in range of eighties to nineties (Kara 2008). A proprietary method of

breaking the agglomerates has also been developed at Virginia Tech. While separation efficiencies for both ultrasonic probe and the novel method were near 85% percentile when used for breaking coal agglomerates, it was discovered that method developed at Virginia Tech is the best process for breaking agglomerates with product moisture as low as 2.05% (Smith, Sarah 2012).

2.4 Esterification of Low Rank Coal

Esterification is the process of production of esters by heating carboxylic acid (-COOH) and alcohols in presence of a catalyst. The double arrows in the reaction shown below signify the reversible nature of the esterification reaction. The process of esterification, thus reaches equilibrium easily and to be able to drive the reaction more to the right, the Le Chatelier's principle is commonly adopted. According to this principle, upon increase of any one of the reactant concentrations, the reversible reaction under consideration can be driven forward to favor product formation.

The use of catalysts can also cause the reaction to move forward. In most cases, sulfuric acid is preferred for use as a catalyst favoring product formation. However, as part of this study, hydrochloric acid was used, since it is found to be more suitable for demineralization processes. A small quantity of catalyst is used, since catalyst consumption does not occur during the progress of a reaction and the rate is not impeded by the lack of the same at any point. Another method to increase the process rate is to supply heat to the esterification process. For the scope of this project, the economically optimum temperature of fifty degrees was used and all experiments for esterification were conducted at this temperature.



The rate of the esterification reaction is highly dependent on the structure of acid and alcohol, temperature, choice of catalyst, amount of the catalyst and amount ratio of acid to alcohol. Since esterification is equilibrium reaction, the rate of the reaction can also be increased by removing water from the final product. It has been cited in literature that methanol is the most

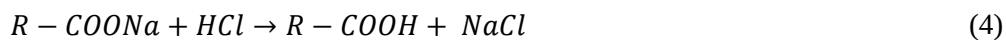
reactive and can esterify most of the carboxyl groups and the efficiency of the process decreases with increase in carbon chain length in alcoholic group as the structural hindrance increases.

It has been reported in the literature that for coal, the internal surface area inclusive of all capillaries and micro-pores is much larger than the external surface area. To make low rank coal suitable for esterification, the low rank coal is either subjected to demineralization or low temperature oxidation in order to create carboxyl acid group (-COOH) on the surface of low rank coal. The esterification process not only takes place at the coal surface, but the alcohol penetrates inside the pores as well. The shorter the alcohol chain length the more penetration into the pores increasing the hydrophobicity of low rank coal surface. The product obtained by esterification of low rank coal is hence suitable for oil agglomeration.

2.4.1 Pretreatment 1: Demineralization by HCl

Demineralization is the process of oxidizing and de-ashing low rank coal by treating it by aqueous solution of acid. The process is alternatively termed as chemical leaching and is one of the simplest ways to reduce inorganic impurities from brown coal (Wang et al., 1986, Yang et al., 1985). Shamaras et al. (1996) were the first to report the use of acid for efficient demineralization process. The most commonly used acids for demineralization are hydrochloric acid or other suitable mineral acids. The process effects both physical and chemical properties of coal and hence altering the suitability of coal for different process (Kister et al., 1988). It has been proven successful in removing all the chemically bound Na, Ca, Mg, Ba ions from the surface of low rank coal (Young and Niksa 1988), but quartz remain intact due to their insolubility in HCl (Vamuka et al., 2006). The mechanism of ion exchange at the surface of coal due to presence of HCl is explained by equation 3, which explains the formation of carboxyl acid as the main product. The penetration of acid in the pores of coal supports the formation of carbonyl or carboxylic groups and causes disappearance of aliphatic group (Kister et al., 1988). The extent of demineralization depends on acid concentration, particle size of the coal, temperature at which demineralization is carried out and total reaction time (Kister et al., 1988). Ash content in the final product reduces with increase in acid concentration (Vaccaro, Salvatore 2010). It has been reported by Kister et al. (1988) that as particle size decreases, more

oxygenated groups are formed upon demineralization, hence, showing the inverse trend for oxidation (surface reticulation effect).



In the past, the demineralization process is used as pretreatment to remove the mineral matter present on the surface of the coal so as to make low rank coal more hydrophobic and hence suitable for subsequent flotation process (Henkley, David W., 1974). The process has also been reported as pretreatment for preparing coal as a feed stock for liquefaction process (Polat, Chander et al. 1995). The process is used to produce ultra-clean coal (UCC) at elevated temperatures (Vijaya, N. et al., 2011)

2.4.2 Pretreatment 2: Low Temperature Oxidation

Oxidation of coal can be seen to be the consumption of oxygen by the fuel which occurs as adsorption onto the surface of the fuel. However, oxygen consumption and oxygen adsorption cannot be regarded to be the same. This is because the consumption of oxygen by coal is the result of oxygen adsorption as well as physical and chemical reaction at the surface pores and particle voids. Interaction between coal and oxygen can be classified as either physical or chemical adsorption process. While the physical adsorption is similar to condensation being that it is a nonspecific type of adsorption, chemical adsorption on the other hand is surface specific and involved forces which are stronger than those which results in physical adsorption. Thus, while physical adsorption can form either mono or multi-layer at the surface, chemical adsorption restricts itself to monolayer at the pores (Wang, Dlugogorski et al. 2003).

Oxidation of low rank coal at low temperature ($<100^{\circ}C$) is described by consumption of oxygen on both external surface and internal surface of the coal, resulting in formation of solid oxygenated complex species or humic acids, such as carboxyl (-COOH), carbonyl (-CO) and hydroxyl(-OH) groups in the coal matrix. Surface reaction between the coal and the oxygen was

found to be a first order reaction. This was because unlike first order reaction wherein the oxygen concentration would be expected to decrease exponentially with time, in the case of this particular reaction, the oxygen concentration declined linearly with time until the surface concentration became zero (Rehman, Hasan et al. 2007).

The oxygen adsorbs both chemically and physically on the surface of the coal. Thus, the oxidation process is effected by several factors including particle size, reaction temperature, composition and physical properties of coal. It is observed that the rate of oxidation reaction is inversely proportional to the particle size (Wang, Dlugogorski et al. 2003). However, the reaction rate reaches the maximum at some point after which the further decrement in size has no effect on the reaction rate (Rehman, Hasan et al. 2007). The effect of temperature on oxidation rate usually follow the exponential trend given by Arrhenius equation. It is reported in the literature that at 35°C, the dominant product species includes phenolic groups while at 70°C, the formation of carboxylic groups is predominant (Rehman, Hasan et al. 2007). Inherent moisture also plays important role in the oxidation of low rank coal as it act as catalyst in the oxidation reaction (Rehman, Hasan et al. 2007).

Chapter 3: Experimental Results & Discussion

The research conducted as part of this thesis delves on using of HHS separation technique for ore processing. The idea is novel, in that, not many researchers have explored the possibility of using this technique as a means for processing of low rank coal or for mineral chalcopyrite. The traditional flotation techniques exploit the hydrophilic hydrophobic properties of the ore-gangue mixture, using the bubbles to separate the hydrophilic gangue from the hydrophobic ore. This study builds upon the traditional techniques and takes into account the thermodynamics as well as reaction kinematics, which could influence the separation process.

Batch tests were conducted using different methods of hydrophobic – hydrophilic separation techniques on copper ore, mono-sized silica beads and low rank coal from Wyoming basin. This chapter is divided into three sections, one each for copper ore, silica beads and low rank coal respectively. The subsection for each experimental process is further divided to include description of the apparatus used for the process the methods employed, followed by the results and a discussion.

For HHS process, n-pentane by Alfa Aesar, was used to produce agglomerates. Pentane is colorless, immiscible liquid with density of 0.631 gm/cm^3 . The liquid and vapours are highly flammable. Pentane has a boiling point of 36°C . Pentane creates an explosive environment on reaching the concentration of 1.8% to 8% by volume are. The pentane used in the following experiment was HPLC grade and contains of minimum of 99% pentane by volume (Alfa Aesar 2009). Pentane was also used to create hydrophobic liquid phase for breaking and dewatering of agglomerates. To dewater agglomerates, 8 inch laboratory sieves of varying apertures were used or Buckner funnel is used. The Additional supplies and apparatuses used for the individual method will be discussed in the method's individual section.

3.1 Chalcopyrite Processing by HHS

Two methods of recovering Chalcopyrite from copper ore were employed: froth flotation and selective oil agglomeration followed by HHS. The experimental setup employed for each method is discussed in their respective sections.

3.1.1 *Froth Flotation*

A small scale Denver flotation cell was employed. A rougher concentrate from Utah copper plant was used in the experiments. The slurry was grinded in laboratory scale ball mill for varied time in order to study the effect of size on flotation recovery. Varied amount of potassium amyl xanthate was used as collector. The conditioning time was 2 minutes after addition of collector. MIBC (Methyl isobutyl Carbinol) frother was added to the floatation cell as was necessary to maintain a solid layer of froth. The pulp pH was kept approximately at 9.5 and calcium hydroxide used as was necessary to maintain the pH. Approximately 1 liter of slurry was floated at a time and the froth was manually paddled off until the floatable solids were depleted.

3.1.2 *Hydrophobic – Hydrophilic Separation*

To form agglomerates, a Ninja kitchen blender was used. A variable speed control drive was employed in conjunction with the blender so that both high and low sheer mixing environment could be created. A volume of copper ore slurry was poured into the blender and mixed on high speed setting for 50 to 90 seconds after addition of pentane. The volume of the pentane varied from 30% to 40% by weight of solid. Immediately after addition of pentane, an obvious phase separation could be observed. Heavier gangue containing water remained in the lower portion of the blender while less-dense golden chalcopyrite rested on the top of the blender. The high sheer mixing was followed by low sheer mixing, in order to facilitate the growth of the agglomerates in the size and hence enhance the dewatering stage. The blender was set to run on low sheer for additional 5 to 8 minutes by lowering the speed of the blender using a variable speed controller. The long time mixing allowed large agglomerates to form. The agglomerates were poured across a small-mesh screen (ranging between 140 and 400 mesh depending on agglomerate size) to dewater agglomerates.

The hydrophobic – hydrophilic separation took place in vibrating mesh or morganizer (Smith, Sarah 2012). It consists of a custom made glass column 5 inches high and 1.5 inches in diameter. A model 2007E electrodynamic shaker produced by Modal Shop INC. was used to disperse mineral particles into the pentane phase. A shaft with 2 mesh discs extended from the bottom of the shaker. The lower plate had an opening of 0.5 millimeters and the upper plate had an opening of 80 millimeters. The mesh disc pulsed at 35 hertz with an amplitude of 0.5 inches. The experimental setup is shown in Figure 3-1. Before the separation testing began, a water – pentane interface is formed in the glass column by pouring water at the bottom and pentane into the upper portion. The mesh disc were lowered into the column in such a way that the lower disc sat at the pentane / water interface. The overflow of morganizer was sent to the evaporation/condenser unit.

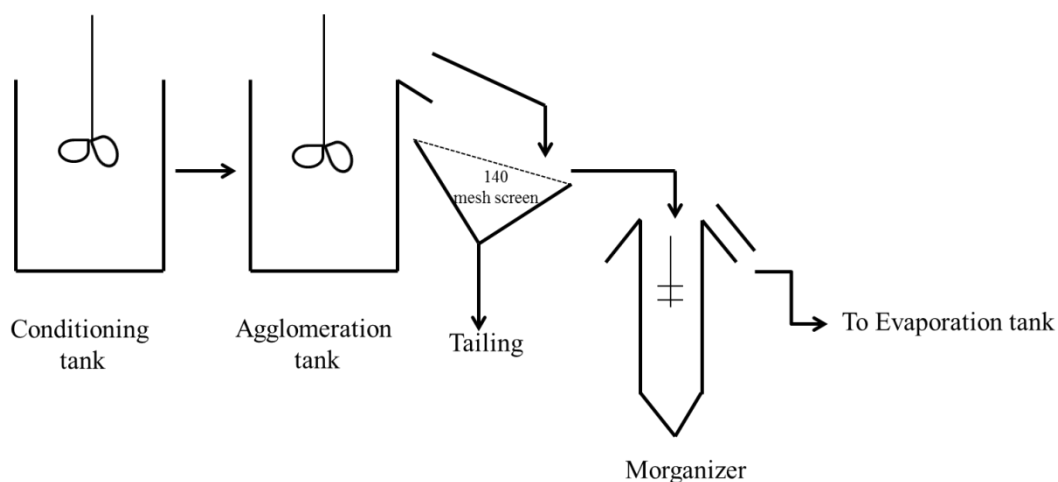


Figure 3-1 Experimental setup for Hydrophilic – Hydrophobic separation

The copper-pentane overflow from vibrating mesh was poured on the double boiler in order to evaporate the pentane (Smith, Sarah 2012). As the pentane evaporated, it travelled upward through the Teflon pipes and was condensed by two condensers employed in the circuit. In order for pentane to evaporate and condense properly, a pump was used to pump the displaced gas from the evaporation beaker into the reagent tank so as to minimize the pentane losses. The condenser unit is shown in *Figure 3-2*.

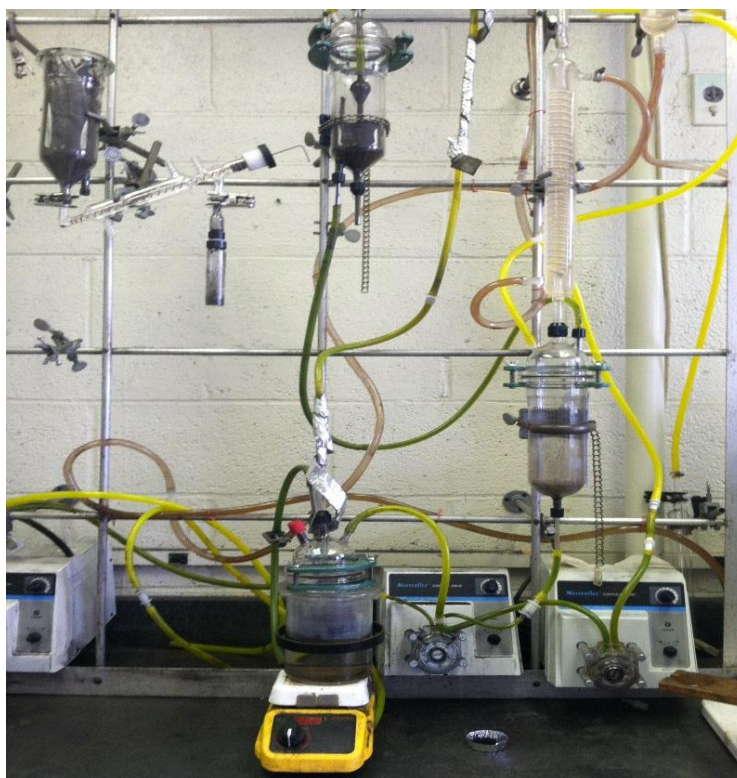


Figure 3-2: Evaporation Unit used to recover pentane

500 millimeter of copper slurry was added to the blender. High shear mixing was started immediately after adding 20 ml of pentane to the slurry. The pentane and slurry were mixed for 50 to 90 seconds to form small powder like agglomerates. It was then subjected to low shear mixing for 5 minutes so that agglomerates can grow in size. The agglomerates were dewatered on the screen.

The mechanical shaker was turned on and set to operate at 35 Hz. The agglomerates were removed from the screen using laboratory spoon-spatula and dropped on the morganizer. Immediately, the agglomerates dispersed into the pentane phase and gangue could be seen falling into the water phase. Pentane was slowly poured into the top of the column to overflow the chalcopyrite-pentane mixture. The process of adding more agglomerates and overflowing the column was repeated until enough amount of the product for grade analysis has been collected. If needed, ports at the bottom of the column were used to drain the gangue containing water so that the interface could be maintained at the same level as the lower disc.

The chalcopyrite/pentane product was then poured into the evaporation unit. The pentane was evaporated and condensed into the separate chamber, leaving behind dry chalcopyrite. The dry chalcopyrite was removed from the system and the final product moisture was calculated. Results from these experiments are discussed in section 3.1.3

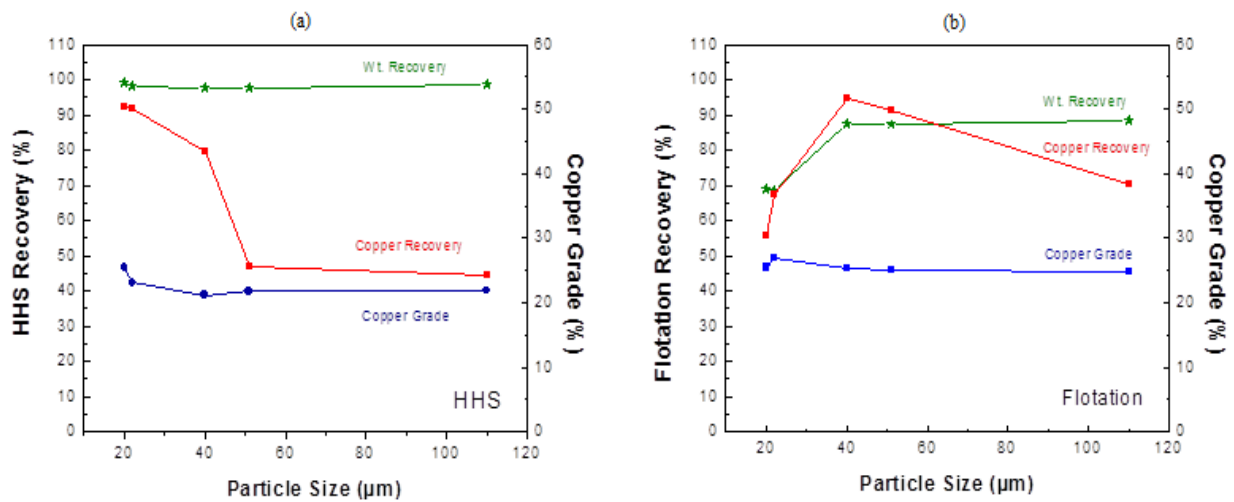
3.1.3 Results: Chalcopyrite Processing by HHS

The rougher concentrator from Utah copper plant with copper grade 15.9% was grinded in ball mill to obtain different size fractions. A Microtrac - X100 size analyzer was used to measure the size distributions of each size fraction and the 80 percent passing size of the fractions were found to be 100 μ m, 51 μ m, 40 μ m, 22 μ m and 20 μ m. The fractions were then subjected to both flotation and HHS and the weight recovery, grade and copper recovery was calculated at 17.6 lb. /ton dosage of potassium amyl xanthate, based on the grade analysis obtained from FLSmidth analytical lab, Salt Lake City.

Table 3-1 shows the results obtained by flotation and HHS. As the particle size decreases below 40 μ m , all the copper recovery, copper grade and weight recovery increases for HHS while the trend is opposite for flotation . *Figure 3-3(a)* shows the ability of HHS process to produce high recoveries even at fine size fractions which is in accordance with the findings cited in literature for oil agglomeration (House, C. I. and C. J. Veal, 1989). *Figure 3-3(b)* shows the decrement in copper grade, copper recovery and weight recovery for flotation process after particle size decreases below 40 μ m. With decrement in particle size, the concentration of surfactant per unit area decreases for both flotation and agglomeration but increasing the agglomeration time and low sheer mixing increases the recovery of HHS process and hence contribute towards the high recoveries of HHS process at lower size fractions. Table 3-2 focuses on the results obtained by flotation and HHS for particle size of 22 μ m.

Table 3-1: Results and of flotation HHS

Particle Size (μm)	Flotation			HHS		
	Wt. Recovery (%)	Cu Grade (%)	Cu Recovery (%)	Wt. Recovery (%)	Cu Grade (%)	Cu Recovery (%)
110	88.3	24.7	70.4	98.7	21.9	44.5
51	87.2	25.1	91.2	97.7	21.7	47.0
40	87.5	25.4	94.7	97.7	21.1	79.4
22	68.6	26.9	67.4	98.3	23.1	91.9
20	68.9	25.4	55.4	99.3	25.4	92.3

**Figure 3-3: Effect of particle size on wt. recovery, copper grade and copper recovery of (a) Hydrophilic-Hydrophobic Separation process (b) Flotation****Table 3-2: Concentration of chalcopyrite by flotation Vs. HHS at 22 μm particle size**

Process	Products	Weight		Assay % Cu	Distribution %	Moisture %
		G	%			
Flotation	Conc.	151.1	68.6	28.0	67.4	-
	Tailing	69.2	31.4	8.41		
	Feed	220.3	100	15.9		
HHS	Conc.	238.21	98.3	23.1	91.9	0.14
	Tailing	4.04	1.7	3.51		
	Feed	242.25	100	15.9		

The agglomerates, formed using copper ore of 80% passing particle size of 22 μ m, were dewatered by pouring them into the morganizer. The pentane overflow saturated with copper ore particles was collected and poured into the condenser unit for pentane recovery. Moisture content of the resultant product was calculated. Table 3-3 shows the results of the experiment conducted on copper agglomerates to decrease their moisture content.

Table 3-3: Moisture content and solid recovery of final product from Morganizer

Test No	Agglomerate Moisture (%)	Product Moisture (%)	% Solid Recovered
1	59.02	0.14	1.62
2	48.56	0.58	2.02
4	65.19	0.49	1.98

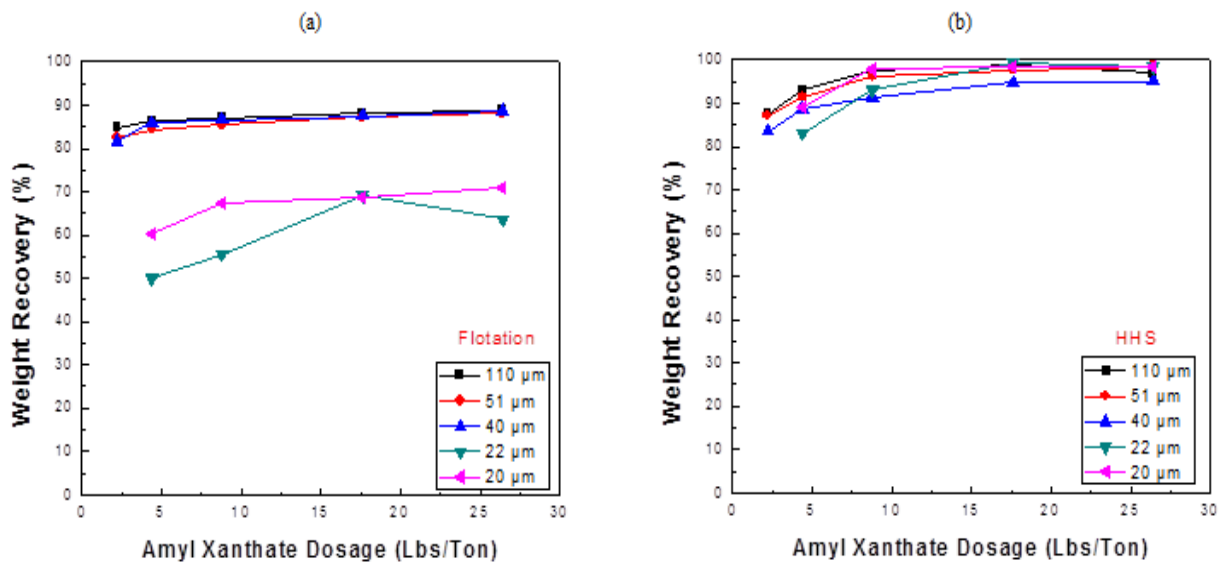
A second set of experiments were performed to study the effect of changing the potassium amyl xanthate (KAX) dosage ranging from 2.2 lb. /ton to 26.4 lb. /ton on the weight recovery of both flotation and HHS process. Table 3-4 shows the results obtained by flotation. It is evident that as the particle size decreases beyond 40 μ m, flotation weight recovery decreases irrespective of the collector dosage. Table 3-5 shows the results obtained for hydrophobic-hydrophilic separation process. The weight recovery of the HHS process increases with increases in hydrophobizing reagent dosage even at the finer size, showing that HHS process is suitable for fine particle sizes as well. Figure 3-4 (a) and (b) shows the variation in weight recovery with change in KAX dosage for different particles sizes.

Table 3-4: Effect of KAX dosage on weight recovery from Flotation

Amyl Xanthate Dosage (Lbs./ton)	Flotation Wt. Recovery For Different D80 Particle Sizes (%)				
	Particle Size 110 μ m	Particle Size 51 μ m	Particle Size 40 μ m	Particle Size 22 μ m	Particle Size 20 μ m
2.2	84.8	82.4	81.6		
4.4	86.3	84.4	85.8	50.1	60.1
8.8	87.0	85.4	86.6	55.6	67.4
17.6	88.3	87.2	87.5	68.9	68.7
26.4	88.7	88.1	88.6	63.7	70.9

Table 3-5: Effect of KAX dosage on weight recovery from HHS

Amyl Xanthate Dosage (Lbs./ton)	HHS Wt. Recovery For Different D80 Particle Sizes (%)				
	Particle Size 110 μm	Particle Size 51 μm	Particle Size 40 μm	Particle Size 22 μm	Particle Size 20 μm
2.2	87.4	87	83.5		
4.4	93	91.4	88.6	83.0	89.2
8.8	97.4	96.2	91.3	93.1	97.8
17.6	98.7	97.7	94.7	99.3	98.3
26.4	96.8	98.5	95.0	98.4	98.5

**Figure 3-4: Effect of Amyl xanthate dosage on weight recovery at different particle sizes by (a) Flotation (b) HHS**

3.2 Mono-sized Silica Processing by HHS

Two methods of recovering silica were employed: froth flotation and selective oil agglomeration followed by HHS. The experimental method and apparatus are described in their respective sections.

3.2.1 Froth Flotation

The flotation tests were conducted in a one liter laboratory scale Denver floatation cell. The material used in the flotation was technical quality glass spheres obtained (nominal size 35 μ m and 75 μ m) obtained from pottery industry. These samples were hydrophobized in a 4×10^{-6} M solution of dodecylamine hydrochloride (DAH) collector, which was prepared in advance in bulk by completely dissolving DAH in pure ethanol so as to ensure the uniformity in all tests. The conditioning time was 2 minutes after addition of collector. MIBC (Methylisobutyl Carbinol) frother was added to the floatation cell as was necessary to maintain a solid layer of froth. Approximately 1 liter of slurry was floated at a time and the froth was manually paddled off until the floatable solids were depleted.

3.2.2 Hydrophobic – Hydrophilic Separation

To form agglomerates, a Ninja kitchen blender was used. A variable speed control drive was employed in conjunction with the blender so that both high and low sheer mixing environment could be created. Silica along with desired volume of water was poured into the blender and mixed on high speed setting for 50 to 90 seconds after addition of pentane. The volume of the pentane varied from 15% to 20% by weight of solid. Immediately after addition of pentane, an obvious phase separation could be observed. The agglomerated silica particles floats on the top of the blender. The high sheer mixing was followed by low sheer mixing, in order to facilitate the growth of the agglomerates in the size and hence enhance the dewatering stage. The blender was set to run on low sheer for additional 5 to 8 minutes by lowering the speed of the blender using a variable speed controller. The agglomerates were poured across a 140 mesh screen to dewater agglomerate. The agglomerates were dewatered either by Morganizer or using Buckner funnel.

100 grams of silica particles along with 500 millimeter of water were added to the blender. The silica particles were hydrophobised either by 4×10^{-6} M solution of dodecyl amine hydrochloride (DAH) collector, which was prepared in advance in bulk by completely dissolving DAH in pure ethanol so as to ensure the uniformity in all tests, or by coating silica beads with octadecyltrichlorosilane (OTS, 95% purity Alfa Aesar) followed by rinsing the hydrophobized surface with toluene (99% purity, Fisher Chemical). High sheer mixing was started immediately

after adding 30 ml of pentane to the slurry. The pentane and slurry were mixed for 50 to 90 seconds so as to form small powder like agglomerates. It is then subjected to low shear mixing for 5 minutes so that agglomerates can grow in size. The agglomerates were dewatered on the 140 mesh screen.

For dewatering of agglomerates by Morganizer, the mechanical shaker was turned on and set to operate at 35 Hz. The agglomerates were removed from the screen using laboratory spoon-spatula and dropped on the morganizer. Immediately, the agglomerates dispersed into the pentane phase (Figure 3-5) and the hydrophobic silica particles stay in the pentane phase. Pentane was slowly poured into the top of the column to overflow the silica-pentane mixture. The process of adding more agglomerates and overflowing the column was repeated until enough product for moisture analysis had been collected. The silica/pentane product was then poured into the evaporation unit. The pentane was evaporated and condensed into the separate chamber, leaving behind dry silica beads. The dry silica was removed from the system and the final product moisture was calculated.

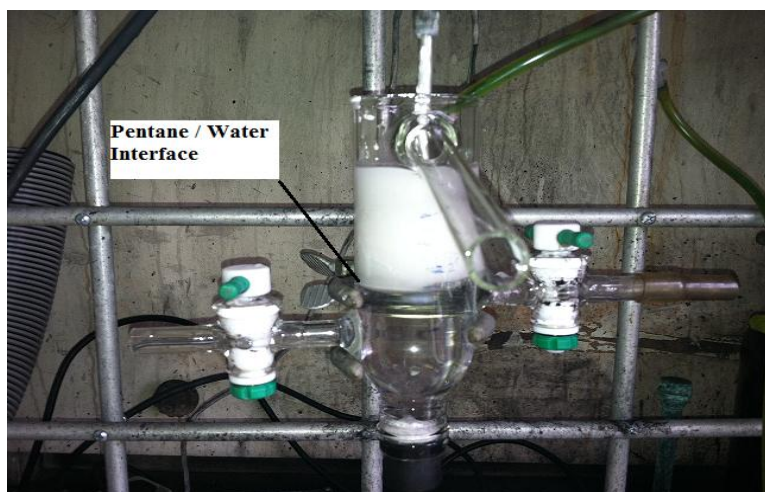


Figure 3-5: Complete dispersion of silica particles in pentane phase (above pentane water interface) in Morganizer

Buckner funnel was employed as another method for dewatering of agglomerates. The funnel was connected to pump in order to pump out the water / pentane. The Buckner funnel was lined with Whatman ashless filter paper and the agglomerates were poured over the filter paper. Pentane was continuously poured over the agglomerates until the overflow from pump no more contain water droplets. The filter cake is then subjected to moisture determination.

3.2.3 Results: Mono-sized Silica Processing by HHS

Silica beads (nominal size 35 μm) are subjected to both flotation and hydrophilic-hydrophobic separation. A previously prepared 4×10^{-6} M solution of DAH is used as the hydrophobizing reagent for this set of experiment. Table 3-6 shows the results of the experiments. Figure 3-6 shows a clear difference between the recoveries of flotation and HHS

Table 3-6: Effect of DAH dosage on recovery of flotation and HHS

DAH dosage	HHS Recovery (%)	Flotation Recovery (%)
1.1	80.12	41.35
2.2	90.22	50.12
4.4	92.6	52.17
8.8	95.74	78.23

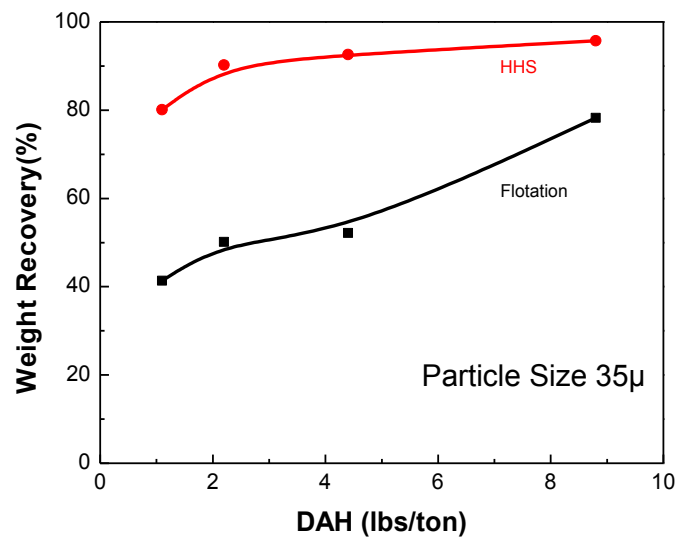


Figure 3-6: Effect of DAH dosage on weight recovery of flotation vs. HHS

A different set of experiment was performed to study the effect of both hydrophobizing agent (OTS or DAH) and dewatering technique on moisture of the final product from HHS process. Table 3-7 shows the results of the experiments.

With OTS coated silica, moisture content less than 1% is achievable using Morganizer. Whereas with DAH coating, the final product has moisture content varies from 5% to 6%. Same trend is observed while using filtration for dewatering which confirms that OTS coated silica is more hydrophobic than DAH coated silica. Results also show that dewatering process is more efficient for particle size of 75 μ m than for particle size of 35 μ m.

Table 3-7: Moisture contents of the product of HHS process for OTS coated vs. DAH coated

Size (μ m)	Technique	Moisture (%)	
		OTS Coated	DAH
35	Morganizer	.680	5.17
35	Morganizer	1.02	6.12
35	Morganizer	0.92	5.89
35	Filtration	9.15	12.42
35	Filtration	8.12	9.95
35	Filtration	7.89	15.12
75	Filtration	3.12	4.99
75	Filtration	3.89	5.82
75	Filtration	2.18	6.13

3.3 Low Rank Coal Processing by Hydrophobic-Hydrophilic Separation

The sample used for the testing in this section was obtained from Wyoming basin and had an as received (AR) moisture content of 28%, 8398 AR BTU/lb value and 8.5% dry ash content. The hydrophobization of low rank coal was achieved using three techniques. In the first technique, the low rank coal was coated with reagent U (Span 80) and Diesel mixture (1:2 ratio) or Span 20 and Diesel mixture. In second technique, the coal was first demineralized using HCl acid and then subjected to esterification. In third method, the coal was first subjected to low temperature oxidation followed by esterification. The hydrophobized coal was then agglomerated in Ninja kitchen blender, which was used in conjunction with the variable speed drive to control the speed of the blender. The hydrophobized coal was poured into the blender and mixed on high speed setting for 50 to 70 seconds after addition of pentane. The volume of the pentane varied from 20% to 30% by weight of solid. The agglomerated low rank coal

particles float on the top of the blender. The high sheer mixing was followed by low sheer mixing, in order to facilitate the growth of the agglomerates in the size and hence enhance the dewatering of agglomerates. The blender was set to run on low sheer for additional 5 to 30 minutes by lowering the speed of the blender using a variable speed controller. During low sheer mixing, a small amount of pentane was also added to facilitate the bridging between the agglomerates and also to incorporate for the pentane loss occur during long low sheer mixing. The agglomerates were poured across a 140 mesh screen.

For dewatering, the agglomerates were dropped into the 250 ml glass beaker, filled with 100 ml of pentane, using spatula and then agitated by hands for 5 to 10 minutes to facilitate breaking of agglomerates and dispersion of coal in pentane. The coal/pentane product was then poured into the evaporation unit. The pentane was evaporated and condensed into the separate chamber, leaving behind dry coal. The dry coal was removed from the system and moisture of final product was calculated using ASTM method for moisture determination. The products are then packed in sample bags and sent to Precision testing lab Inc, West Virginia for conducting BTU analysis. The ash analyses was performed using LECO Model 601-400-600.

A set of experiments were conducted to study the effect on immersion of sample in pentane. Theoretically pentane dislodges the water molecules from macro pores and capillaries of the fuel sample in consideration. Initially the coal sample was immersed in pentane. Continuous stirring using spatula was done to ensure that adequate molecular interaction took place between the coal and pentane. The pentane/coal solution was then poured into the evaporation unit. The dry coal was removed and analyzed for moisture content and BTU values.

3.3.1 *Hydrophobization of Low Rank Coal Using Reagent Surfactant*

In this technique, 150 ml of coal slurry with 20% solids was conditioned with desired amount of surfactant, being Span 80 or Span 20 solution in diesel in 1:2 ratio, for 5 minutes to ensure the maximum hydrophobization of the coal surface. Both Span 80 and Span 20 mixture is prepared in large quantity in advance by mixing 1 amount of surfactant with 2 amounts of diesel

in order to ensure uniformity in all tests. The hydrophobized coal was then subjected to the agglomeration followed by dewatering process.

Figure 3-7 shows the (a) agglomerates formed using this technique and (b) tailings obtained upon screening the agglomerates.

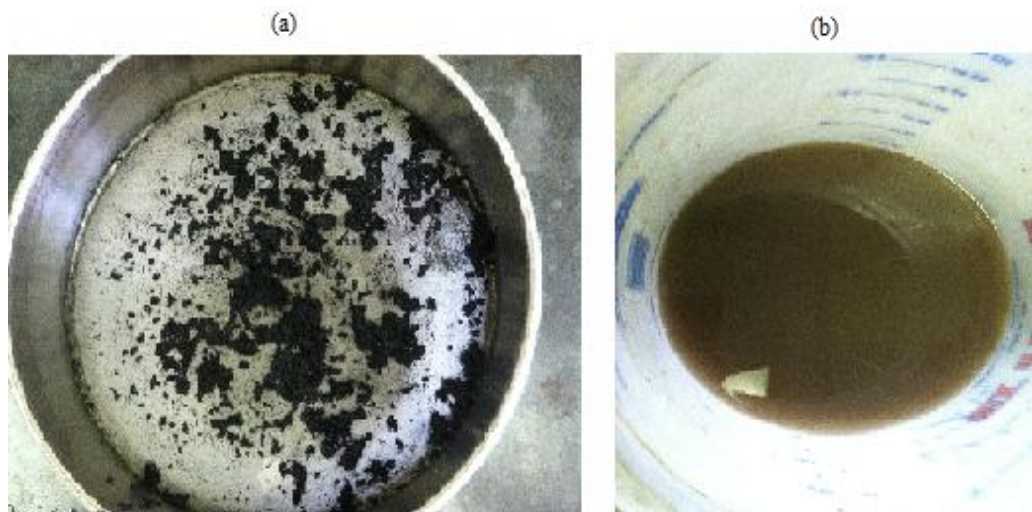


Figure 3-7: (a) Agglomerates formed using Span 80 (b) Tailing obtained by screening the agglomerate

3.3.2 *Hydrophobization of Low Rank Coal by Demineralization Followed by Esterification*

In this technique, 20 grams of coal was mixed with 100 ml of 0.1M HCl in a 250 ml beaker. The beaker was then placed on Thermo Scientific stirring hot plate. The demineralization/ acid washing process was carried out at 50°C along with continuous stirring. The processing time was varied from 1 to 4 hours. Figure 3-8 shows the experimental setup for demineralization. The acid washed coal was then filtered using conical funnel lined with Watman ashless filter paper. The filter cake was then poured in the 250ml glass beaker and to that 100 ml of ethanol was added along with 10 μ l of 1M HCl. The esterification was also carried out at 50°C along with the continuous stirring for 3 hours. The ethylated coal was then filtered using conical flask and the filter cake is then subjected to agglomeration followed by dewatering.



Figure 3-8: Experimental setup for demineralization

3.3.3 *Hydrophobization of Low Rank Coal by Oxidation Followed by Esterification*

In this technique, 20 grams of coal was placed in oven at 70°C for time ranging from 1 hour to 8 hour. The oxidized coal was then poured in the 250ml glass beaker and to that 100 ml of ethanol was added along with 10 μ l of 1M HCl. The esterification was carried out at 50°C along with the continuous stirring for 3 hours. The ethylated coal was then filtered using conical flask and the filter cake is then subjected to agglomeration followed by dewatering.

3.3.4 *Results: Low Rank Coal Processing by HHS*

Hydrophobization of Low Rank Coal Using Surfactant The method was successful in both decreasing the moisture content as well as increasing the BTU/lb value of the final product.

Table 3-8 (a) and (b) shows the result of HHS testing on Wyoming coal using reagent U and span 20. From the both tables, it can be seen that increasing the reagent dosage resulted in increase of BTU values and decrease of moisture content for the Wyoming coal samples which were tested. Additionally, increasing the low sheer mixing time also resulted in decrease of moisture content of the product. Both the reagents were successful in hydrophobizing the coal

surface leading to the finding that sorbitan group was capable of adsorbing on the surface of low rank coal thus altering the hydrophobicity of the surface.

Table 3-8 (a): Results of HHS Testing on Wyoming Coal Using Reagent U (Span 80)

Reagent U Dosage (lbs/ton)	Shear Time (min)	Agglomerate Moisture%	Product Ash%	Product Moisture %	Combustible Recovery%	Ash Rejection %	Product AR BTU/lb
33.3	30	27.1	5.8	20.8	66.2	53.5	9814
33.3	15	44.6	6.2	38.2	95.9	26.7	7562
44.7	30	42.6	6.3	33.0	71.1	45.2	8194
50	30	28.1	6.0	4.1	95.5	29.4	11759
50	15	43.6	5.2	6.7	90.5	42.9	11543
50	5	46.2	5.8	6.0	87.1	38.8	11560

Table 3-8 (b): Results of HHS Testing on Wyoming Coal Using Span 20

Reagent U Dosage (lbs/ton)	Shear Time (min)	Agglomerate Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb
55.5	30	62.9	5.9	5.6	11880
55.5	20	50.3	5.9	7.9	11147
55.5	5	63.6	6.6	17.7	9134
44.5	30	67.9	6.2	5.9	11739

3.3.4.1 Hydrophobization of Low Rank Coal by Demineralization Followed by Esterification

The low rank coal obtained from the Wyoming basing was sieved into different size fractions using sieves having openings of 75µm, 300µm, 600µm, 1.18mm, and 6.3mm. All the size fractions are then subjected to acid washing for 4 hours followed by esterification for 3 hours. Table 3-9 shows the effect of particle size on moisture content and as received BTU/lb of the final product. From the table, It can be seen that product BTU increases with increases in

particle size. It can also be deducted from the table that moisture content of the final product decreases with increase in particle size.

Figure 3-9 shows the increasing trend for BTU values and decreasing trend for product moisture.

Table 3-9: Effect of particle size on Moisture content and product AR BTU/lb.

Particle Size Range (μm)	Particle mean Size(μm)	Agglomerates Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb.	% AR BTU increase
-350+75	212.5	40.3	3.20	9.92	10827	28.92
-600+350	475	25.62	3.20	9.82	11019	31.21
-1180+600	890	28.34	2.87	8.4	11216	33.56
-6300+1180	3740	37.63	2.30	6.27	11529	37.28

Effect of acid concentration was also studied in a different set of experiments. Low rank coal in the size fraction 1.18mm to 600μm was subjected to demineralization using HCl with concentrations 0.005M, 0.01M, 0.05M, 0.1M and 0.15M. Table 3-10 shows the results for this experimental set. From Table, it can be seen that steady increasing of the acid concentration results in the corresponding increase of product BTU values along with a trending decrease in both product moisture content and ash values. However, these trends continue up to an optimum value of 0.1M concentration of HCl, beyond which increasing concentration brought about negligible changes in the characteristics. The trends can also be noted from the Figure 3-10.

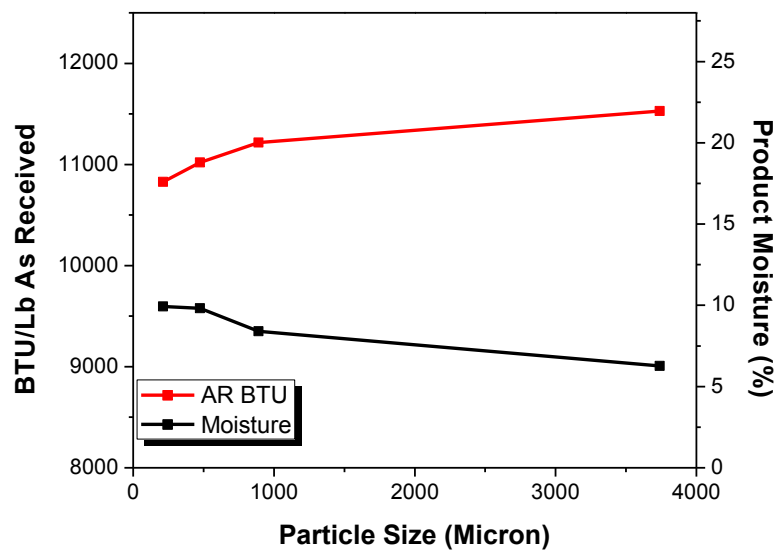


Figure 3-9: Effect of particle size on as received BTU and moisture content of the product obtained by HHS

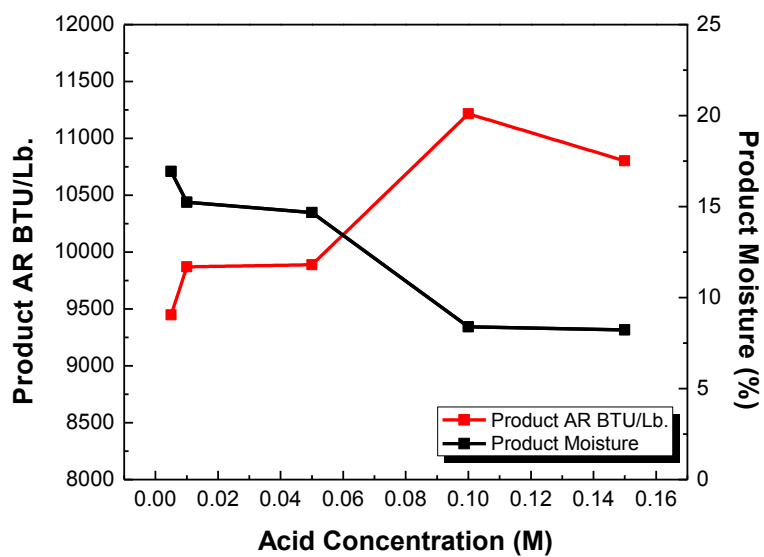


Figure 3-10: Effect of acid concentration on product BTU and moisture content

Table 3-10: Effect of acid concentration on the product characteristics

Acid Concentration(M)	Agglomerates Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb.	% AR BTU increase
0.005	21.27	6.48	16.93	9448.38	12.51
0.01	29.06	2.86	15.24	9869.45	17.52
0.05	22.18	3.20	14.67	9888.04	17.74
0.1	20.34	2.87	8.40	11215.50	33.55
0.15	18.32	2.84	8.23	10801.33	28.62

A set of experiments were conducted to study the relation between acid wash time and factors such as ash, BTU and moisture content of the final product. The trends can be seen in Table 3-11. On increasing acid wash time, the ash content was found to lower significantly however, on further increase of acid wash time no such marginal difference was seen as the values were found to cluster around 3%. The values for moisture content was found to decrease with decrease in acid was time, correspondingly the values for product BTU was found to increase with increase in acid wash. Figure 3-11 also shows the continuous increase in BTU values and decrement in product moisture in correspondence with the increase in demineralization time.

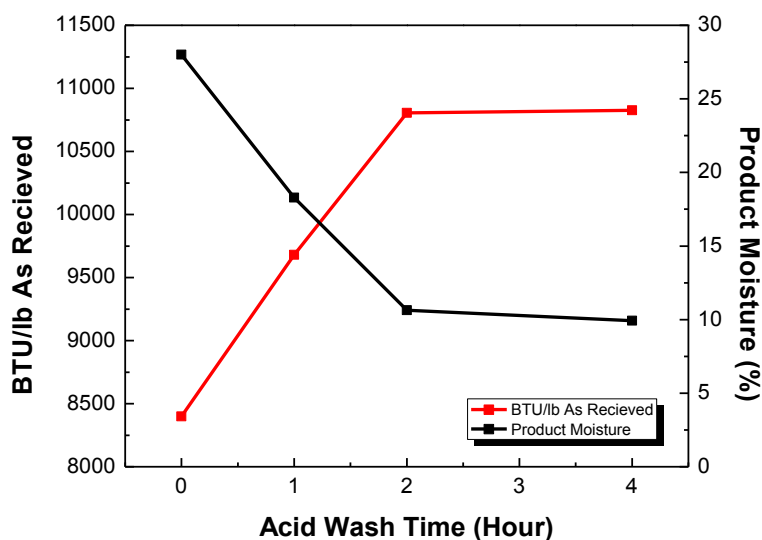
**Figure 3-11: Effect of acid wash conditioning time on product BTU and moisture content**

Table 3-11: Effect of acid wash conditioning time on the product characteristic

Acid Wash Time	Agglomerates Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb.	% AR BTU increase
0	-	8.5	28	8398	0.00
1	28.39	3.36	18.28	9680	15.27
2	25.62	3.40	10.64	10806	28.67
4	39.54	3.20	9.92	10826	28.91

Another set of experiments were conducted to find the optimum alcohol for esterification process. It could be seen that on increasing the hydrocarbon chain length in alcohol, there was a corresponding increase in product moisture and a decreasing trend was observed in product BTU values signifying that methanol is the most appropriate alcohol for the esterification of low rank coal followed by ethanol and higher chain length. The trends can be noticed in Table 3-12. The same has been diagrammatically represented in the Figure 3-12. The findings can be justified by the fact that the smaller the chain length of the alcohol, more easily it can penetrate inside the pore structure and form ester at the capillaries and hence making coal more hydrophobic.

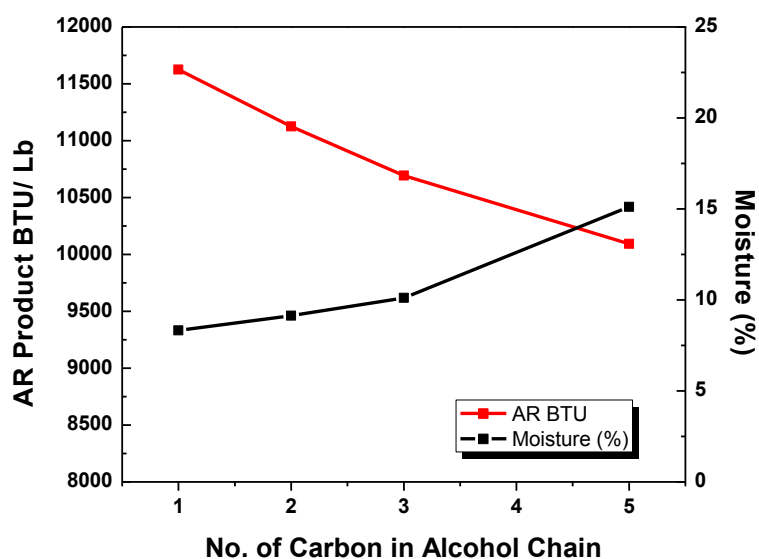
**Figure 3-12: Effect of increasing alcohol chain length on product BTU and moisture content**

Table 3-12: Effect of alcohol chain length on the product characteristic

Alcohol	Agglomerates Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb.	% AR BTU increase
Methanol	25.39	2.35	8.32	11625	38.43
Ethanol	30.92	3.20	9.14	11125	32.47
2-propanol	29.82	0.93	10.12	10693	27.33
1-Pentanol	31.05	3.8	15.12	10092	20.17

Table 3-13: Effect of particle size on product obtained by dispersion in pentane

Particle Size Range (µm)	Product Moisture %	Product AR BTU/Lb. (%)	Percent BTU change
-350 +75	7.3	10749	27.9
-600 +350	11.3	10282	22.4
-1180 + 600	13.7	10101	20.8
-2360 +1180	14.2	10078	20.0
-3360 +2360	14.5	10154	20.9
-12700 +3370	15.2	9795	16.6

Table 3-14: Moisture content of the product obtained from overnight immersion in pentane

Particle Size µm	Product Moisture %
-350 +75	7.4
-600 +350	8.3
-1180 + 600	8.9
-2360 +1180	9.6
-3360 +2360	10.0
-12700 +3370	13.8

The results of the experiments conducted to study the influence of immersion of fuel sample in pentane, without any treatment, can be seen in Table 3-13. It is evident from the table that the process works better for finer sizes. As the particle size increases, the BTU values

decreases and correspondingly product moisture increases. The immersion time of particles in pentane was increased to overnight in the second set of experiment and the final product moisture is calculated. It can be seen from Table 3-14 that increasing the immersion time has positive impact on moisture reduction which confirms the replacement of capillary moisture and interparticle moisture by pentane. From Figure 3-13, it can be noticed that increases in immersion time have positive impact on moisture reduction of middle range particle sizes because the increment in immersion time helps the penetration of pentane into the pores and hence cause the moisture reduction. However, the moisture content of very fine sized particles and very coarse sized particles are unaffected by the increment in immersion time. It can be justified by the fact that for very fine particle size, the pentane penetration into the pores is quick due to large surface area and hence the increment in immersion time didn't help much. For coarse particles however, the penetration is very difficult due to minimum surface area.

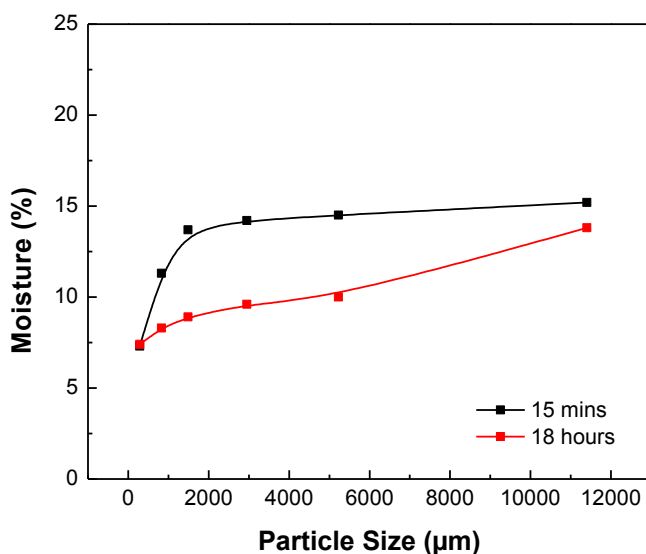


Figure 3-13: Effect of immersion time in pentane on different particle sizes

3.3.4.2 Hydrophobization of Low Rank Coal by Oxidation Followed by Esterification

The low rank coal obtained from the Wyoming basing was sieved into different size fractions using sieves having openings of 75μm, 300μm, 600μm, 1.18mm, and 6.3mm. All the

size fractions were then subjected to low temperature oxidation for 2 hours followed by esterification for 3 hours.

Table 3-15 shows the effect of particle size on moisture content and as received BTU/lb of the final product. It can be seen from the table that the process has minimal effect of ash content of the feed. However, with decrease in particle size, the significant increase in BTU values was noted along with significant decrease in moisture content of the feed coal which is in accordance with the finding in literature (Rehman, M. et al, 2007) supporting the hypothesis that smaller particles have large surface area for oxygen exposure. The trend in BTU values and moisture content of the coal can be seen in Figure 3-14.

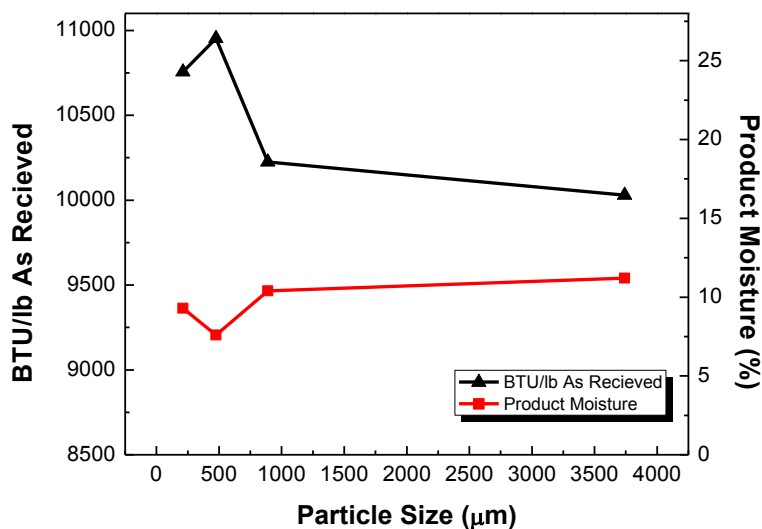


Figure 3-14: Effect on particle size product properties obtained from HHS using low temperature oxidation

Table 3-15: Effect of particle size on product BTU and moisture content

Particle Size Range (μm)	Particle mean Size(μm)	Agglomerates Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb.	% AR BTU increase
-350+75	212.5	27.3	7.2	9.3	10755	28.07
-600+350	475	15.2	7.4	7.6	10952	30.41
-1180+600	890	19.4	7.8	10.4	10225	21.80
-6300+1180	3740	20.8	7.5	11.2	10029	19.4

Another set of experiments was conducted on low rank coal in the size range 350 to 600 micron, to study the relation between oxidation time and factors such as ash, BTU and moisture content of the final product. The trends can be seen in

Table 3-16. The oxidation helped in decreasing the moisture content of the product as well as in increasing the heat values. But further increment in oxidation time have no or minimal effect on the moisture and BTU values.

Table 3-16: Effect of oxidation time on product BTU and moisture content

Oxidation Time	Agglomerates Moisture%	Product Ash%	Product Moisture%	Product AR BTU/lb.	% AR BTU increase
0	-	8.5	28	8398	-
1	15.5	7.48	10.26	10524	25.31
2	15.75	7.41	7.57	10952	30.41
4	16.53	7.31	8.93	10690	27.29
8	20.12	7.42	10.89	10241	21.94

Chapter 4: Conclusion and Recommendation

A hydrophobic–hydrophilic separation (HHS) technique has been developed and tested for processing of mineral particles in ultrafine size range as well for upgrading low rank coals. In case of mineral processing in ultra-fine size range, the HHS process was found to be promising, and can be used as an alternative to flotation for particles finer than 40 μm in size. In case of low rank coal, the HHS process can be used to increase the heating (BTU) values decreasing the moisture content.

The study showed that application of the HHS process for the processing of chalcopyrite gave copper recoveries approximately 20% higher than flotation particularly at finer particle sizes. Even at coarser particle sizes, the HHS process gave weight recoveries that are comparable to flotation. However, the copper grades were lower.

It has been observed that the HHS tests conducted on a mono-sized silica beads gave a minimum 25% higher recoveries than flotation at finer particle sizes. It has been found also that the higher the hydrophobicity of silica particles, the higher the silica recoveries and the lower the moisture of the products. The silica particles coated with OTS gave better results than the silica particles coated with DAH, which can be attributed to the hydrophobicity difference.

It has been found that the HHS process is also useful for separating water from a low-rank coal and hence increasing its heating value. The process requires that the low-rank coal be rendered hydrophobic by using appropriate reagents. When using the Reagent U as hydrophobizing agent, the moisture of the coal was reduced to less than 10% by weight from the moisture content of 28% by weight in the raw coal. As a consequence, the heating value of the processed coal was increased substantially. However, process required large amounts of the hydrophobizing agents for the HHS process to be effective.

In the present work, a low rank coal was hydrophobized by esterification with short-chain alcohols before subjecting the coal for the HHS process. Before the esterification, the low-rank coal sample was treated by an acid treatment to increase the surface concentration of the carboxylic acid groups. The acid treatment also helped ash rejection possibly by a dissolution mechanism. Another methods employed to increase the surface concentration of carboxylic acid

groups was to purposed oxidize the low-rank coal. The results showed that purposeful oxidation of a low-rank coal helped the esterification process and thereby increased the BTU content of the feed. However, the oxidation followed by esterification was not as effective as acid treatment by esterification for ash rejection.

Although all of the experimental test work has been conducted at bench-scale laboratory tests, they lay a path for future studies. Further, only a limited number of samples have been tested. Therefore, additional work is necessary to better understand the mechanisms involved and improve the process.

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