

DEVELOPMENT OF A NOVEL FINE COAL CLEANING AND DEWATERING TECHNOLOGY

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ABSTRACT

The cleaning and dewatering of ultrafine (minus 44 micron) coal slurries is one of the biggest challenges faced by the coal industry. Existing commercial technologies cannot produce sellable products from these ultrafine streams; therefore, the industry is forced to discard this potential energy resource to waste impoundments. This practice also has the potential to create an environmental hazard associated with *blackwater* pollution. To address these issues, researchers at Virginia Tech have worked over the past decade to develop a novel separation process that simultaneously removes both mineral matter and surface moisture from fine coal particles. The first stage of the process uses immiscible non-polar liquids, such as straight chain hydrocarbons, to selectively agglomerate fine coal particles in an aqueous medium. The agglomerates are then passed through the second stage of processing where mild agitation is used to disperse and fully engulf hydrophobic coal particles into the non-polar liquid and to simultaneously reject any residual water and associated hydrophilic minerals entrapped in the agglomerates. The non-polar liquid, which has a low heat of evaporation, is then recovered by evaporation/condensation and recycled back through the process. The research work described in this document focused on the engineering development of this innovative process using batch laboratory and continuous bench-scale systems. The resulting data was used to design a proof-of-concept (POC) pilot-scale plant that was constructed and successfully demonstrated using a variety of fine coal feedstocks.

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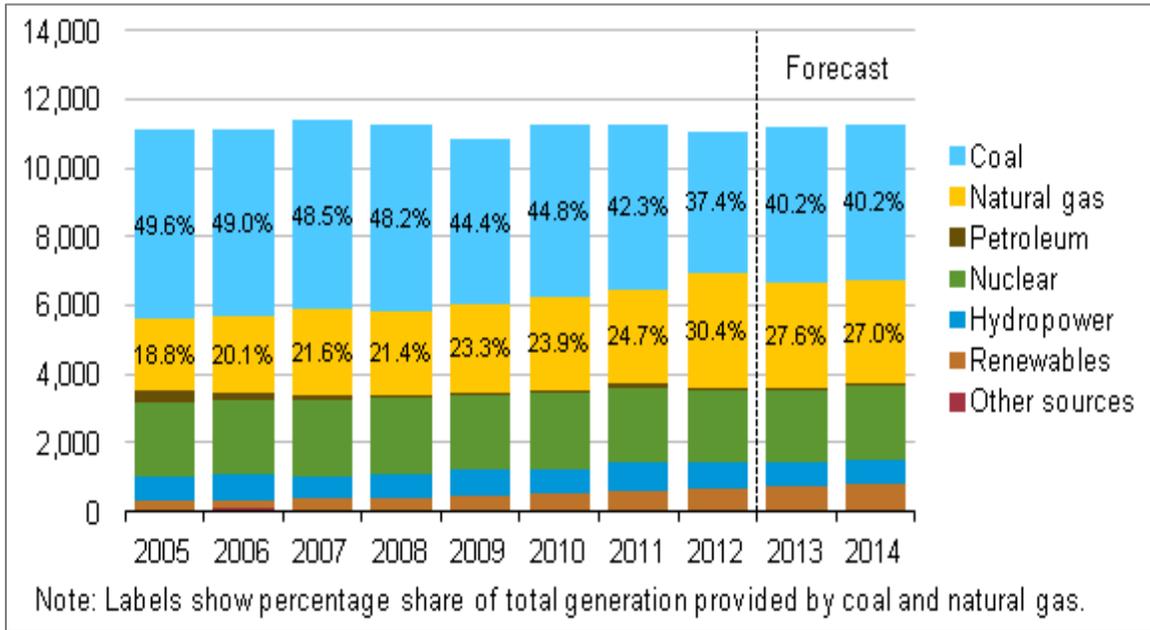
CHAPTER 1 – General Introduction

PREAMBLE

Coal has been fulfilling a high proportion of human energy needs from centuries. Though historically used as a domestic fuel, coal is now globally used by industries, especially in the generation of electricity. Coal is the largest and historically one of the cheapest fuels used for electricity generation in the United States and accounted for 37% of electric power generation in 2012. Since 2000, about 90% of all the coal consumed in United States has been used for electric power generation (EIA, 2013). The U.S. Energy Information Administration expects total consumption will increase by 7.1% from its current value in the next couple of years (refer Figure 1.1) due to higher electricity demand and increasing natural gas prices.

Coal mining grew aggressively during the Industrial Revolution, which started in the 1880's. Since then the mining practices have improved from men tunneling, digging and manually extracting the coal on carts to large surface and underground longwall mines. Mining at high production volume requires modern large machines such as draglines, trucks, conveyors, self-advancing longwall supports and high-capacity shearers. The large-scale extraction of coal through the 20th century in the traditional coalfields of the Eastern United States has resulted in a diminution of the mined coal quality, while mechanization has resulted in reduction in average particle size. These factors, in addition to the 1970's "energy crisis" and strict environmental standards, have forced the United States coal industry to find ways to produce marketable coal in a more efficient manner. Coal preparation, a process that improves the quality of coal and recovers coal particles from coal-rock run-of-mine material, has become more important as the mined product has worsened.

Coal preparation processes that remove unwanted impurities and increase the product heating content significantly improve coal quality. This methodology results in increased power plant capacity and reduced plant maintenance cost. Raw coal that emerges from a mine contains "bone" (clay/shale rock), pyrite, mercury and other types of impurities; these vary in amount depending on the particular coal seam and mining method used. Physical processes can remove many of the included non-combustible mineral impurities, whereas chemical processes can remove impurities, such as organically bound sulfur, that are part of the



EIA (2013), "Short-Term Energy Outlook", U.S Energy Information Administration, Report – June 2013

Figure 1.1 U.S. electricity generation (thousands MWH/day) by fuel (EIA, 2013).

complex chemical composition of coal and are impossible to remove by physical methods. In short, coal processing increases the heating value, lowers the transport cost per unit of heat, reduces emissions, and improves the marketability of the run of mined coal. There are currently 286 coal processing plants in the United States that clean approximately 67% (660 million short tons per year) of the total coal consumed in the United States (Coal Age, 2010).

Moisture is considered to be a contaminant in the final clean coal products. Excess surface moisture also reduces the heating value of coal, and can lead to severe handling and freezing problems. Additionally, it also increases the transportation cost of coal. Relative to energy loss, moisture and ash content are roughly equivalent (Luttrell, 2010), which is approximately 150 BTU loss for each additional 1% by weight.

LITERATURE REVIEW

The following literature review is designed to provide a brief overview of the current accepted practices for fine coal cleaning and dewatering circuits in coal preparation plants. Moreover, the literature review provides detailed background on the oil agglomeration process, which is a crucial aspect of the reported research. In addition, an overview of the previous scientific studies, which are the foundation of proposed technology, conducted at Virginia Tech is presented. In the final section, the research objectives and goals are discussed in detail.

1.1 Coal Preparation Practices – An overview

The earliest type of coal preparation employed were “hand pickers” to remove non-coal materials from coal. With the advent of mechanization, more sophisticated techniques were necessary to clean large amounts of smaller, more impure coal particles. As a result, coal preparation plant technology has evolved in close harmony with changing mining technology and practices.

Modern plants are designed in accordance with specific operational factors like raw coal characteristics, market specifications and demands, environmental requirements, applicable processing methods, and economics. Each of these factors dictates the role of different unit operations, sizing, cleaning, dewatering and drying in the final design of the coal preparation plant. A typical coal processing plant flowsheet can be represented by a series of sequential unit operations for coal particle sizing, cleaning and dewatering. This sequence of operations is called a circuit. Coal processing operations must be designed in multi-stage circuits for several different size fractions, since each coal preparation method has a limited range of applicability in terms of particle size. In the United States, processing plants typically include as many as four separate processing circuits for treating the coarse coal (above 10 mm), intermediate (10 x 1 mm), small (1 x 0.15 mm) and fine (below 0.15 mm) feed material. Figure 1.2 illustrates a typical flowsheet for a modern coal preparation facility.

The coarse coal cleaning processes typically involve Jigs or Dense Medium Vessels. For material in range of 10 x 1 mm, dense medium processes are used to efficiently clean run-of-mine coals, while screens and centrifugal dryers are used to efficiently dewater the clean coal products. Both coarse and intermediate coal particle separations are based on differences in the

relative densities (RD) of coal (1.3 RD) and associated impurities (2.0 RD). Particles in the size class between 1 and 0.15 mm are typically cleaned using water-based density concentrators including spirals, water-only cyclones, crossflow/teeter-bed separators or multi-stage combinations of these units. The only commercially viable process for treating particles finer than 0.15 mm is froth flotation. Particles smaller than 1 mm, which are more difficult to dewater due to a higher specific surface area, typically require the use of energy intensive devices such as screenbowl centrifuges or filters to remove the unwanted surface moisture. The problems associated with fine coal cleaning processes are complex. To address the issue and increase the plant productivity in this circuit, an emerging practice is to deslime the flotation feed using a classifying cyclone. The cyclone separates ultrafines (below 0.044 mm), which cannot be processed economically with the existing technologies and are thus discarded. Therefore, it is now paramount of importance to recover coal from these streams by developing a suitable method.

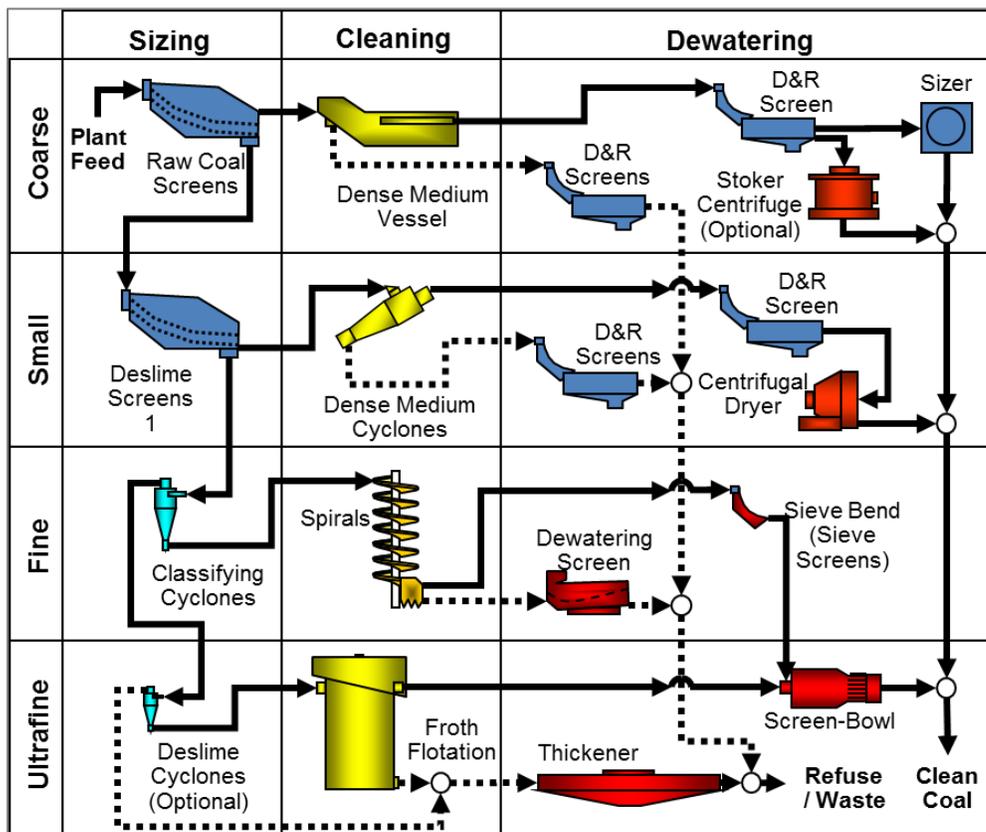


Figure 1.2 Generic modern coal washing plant flowsheet

1.2 Fine Coal Cleaning

Effective cleaning of fine coal (that is, both removal of impurities and moisture reduction) is mostly dependent on the economics, the capability and performance efficiency of the processing equipment, and the extent to which separation of the feed coal can be optimized. Currently, froth flotation is the only commercially practiced method for cleaning ultrafine coal in the United States. In previous years, oil agglomeration was another extensively studied method for fine coal cleaning, but could not grow and lost the significance due to several reasons. Due to its high cleaning and to some extent dewatering capabilities and its importance to this research, it is reviewed in detail in a separate section of this chapter.

1.2.1 Conventional Froth Flotation Process

Froth flotation is currently the preferred method for cleaning fine coal particles of size below 150 microns (minus 100 mesh). It is based on the differential wettability of particles; i.e., this surface-based process distinguishes between hydrophobic coal and hydrophilic mineral impurities (clay, pyrite etc.). In flotation, air bubbles are dispersed in water in which fine coal and mineral matter are suspended. Hydrophobic coal particles are selectively collected by a rising stream of air bubbles and form a froth phase on the surface of the aqueous phase, leaving the hydrophilic mineral matter behind. Higher-rank coal particles are usually hydrophobic and, therefore, can be attracted to air bubbles that are also hydrophobic through a mechanism known as hydrophobic interaction. Along with surface chemistry, particle and bubble size are two of the most important variables. Flotation works best for fine particles about 0.1-0.25 mm in diameter. Larger particles (greater than 0.25 mm) have a high probability of bubble-particle detachment, whereas smaller ones (less than 0.1 mm) have a low probability of bubble-particle collision.

While particle size determines which particles are most likely to float, bubble size controls the amount of particles that are able to float. The total surface area of the bubbles determines the carrying capacity of the froth. Therefore, smaller the bubble size, the greater the bubble-particle interaction. Several advanced flotation technologies have been successfully commercialized. Nonetheless, their primary focus is to create smaller bubbles inside the flotation cell. In previous years, Virginia Tech has successfully commercialized micro-bubble column technology (MicrocellTM), which showed high carrying capacity and energy recovery (Yoon et al., 1992) because of micron-size bubbles.

In a modern coal flotation circuit, the feed stream (minus 100 mesh) is first classified using a 6-inch classifying cyclone to remove ultrafines of size below 44 microns (minus 325 mesh). When the clean coal product reports to the froth phase, it is substantially free of mineral matter but contains a large amount of water. Finer particles have greater surface and greater capacity to adsorb water. Wet fine coal is difficult to handle, increases shipping costs and lowers combustion efficiencies. Therefore, the clean coal product is dewatered using various devices such as cyclones, thickeners, filters, centrifuges, and/or thermal dryers.

1.2.2 Problems with Fine Coal Processing

There are two reasons for the high costs of processing fine coals (0.15 x 0.044 mm): one is the low efficiency of cleaning, and the other is associated with the high cost of dewatering. The first problem has been resolved to a large extent by the advent of advanced coal cleaning technologies, such as the conventional and column flotation process, and advanced flotation methods such as MicrocellTM column flotation, StackCell[®] flotation, etc. These water-based processes are capable of recovering the fine coal from finely dispersed ash- and SO₂-forming minerals; however, it is difficult to remove the free water adhering to the surfaces of fine coal particles. The finer the particle, the larger the surface area and, hence, the more difficult it becomes to dewater. Typically, 100 x 325 mesh flotation concentrate contains 30-40% moisture after a mechanical dewatering process such as vacuum filtration, causing not only a loss of heating value, but also problems with handling and transportation. Some consider that cleaning fine coal replaces one type of inert substance (*e.g.*, ash-forming minerals) by another (*e.g.*, water), offering no financial incentives for coal companies to clean fine coals (Yoon and Luttrell, 1995).

In general, the cost of dewatering increases with decreasing particle size (as illustrated in Figure 1.3) and can become prohibitive with ultrafine particles, *e.g.*, particles finer than 0.044 mm (minus 325 mesh). In such cases, coal producers are forced to discard those because of unacceptably high moisture content and processing cost. The top size of the material discarded may vary from 0.15 to 0.044 mm (*i.e.* 100 to 325 mesh) depending on the value of the coal and demands imposed by the sales contract (NETL, 2009). Ultrafine coal is one of the primary components of the fine waste found in waste impoundments. The loss of the minus 44 micron material is especially tragic because coal particles that small are liberated extremely well. Large amounts of

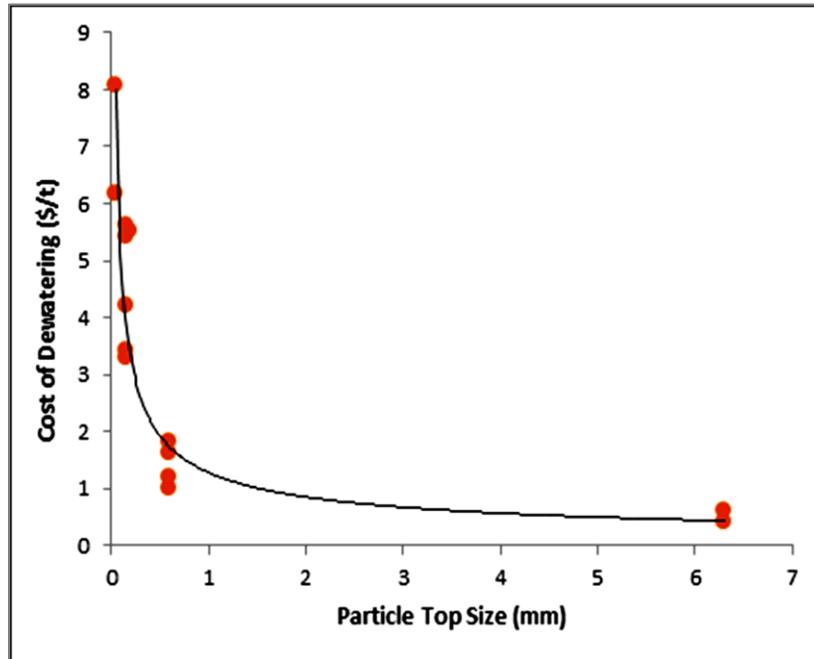


Figure 1.3 Effect of particle size on dewatering cost (\$/ton), (redeveloped, first published by Hucko in 1981)

fine coal have been discarded to numerous impoundments worldwide, creating environmental concerns. A study conducted by National Research Council under congressional mandate reports some 70 – 90 million tons of fine coal is being discarded to coal slurry impoundments annually by the United States coal industry (Orr, 2002). The industry estimates that so far approximately 2 billion tons of fine coal have been discarded in abandoned ponds, and 500-800 million tons are in active tailing ponds (Orr, 2002). This activity represents a loss of a valuable energy resource, loss of profit for coal producers, and the creation of a potential environmental liability.

1.3 Fine Coal Dewatering Methods

The solid-solid separation processes employed by modern coal preparation plants require large amounts of process water. After cleaning, the unwanted water must be removed from the surfaces of the particles. Small and fine coal (less than 1 mm) particles represent as little as 10% of the total run of mine coal and often contain one-third or more of the total moisture in the final coal product (Osborne, 1988). Existing fine coal dewatering processes, such as filtration, centrifuges, and thermal drying are expensive, inefficient, and consume a lot of energy (Osborne, 1988).

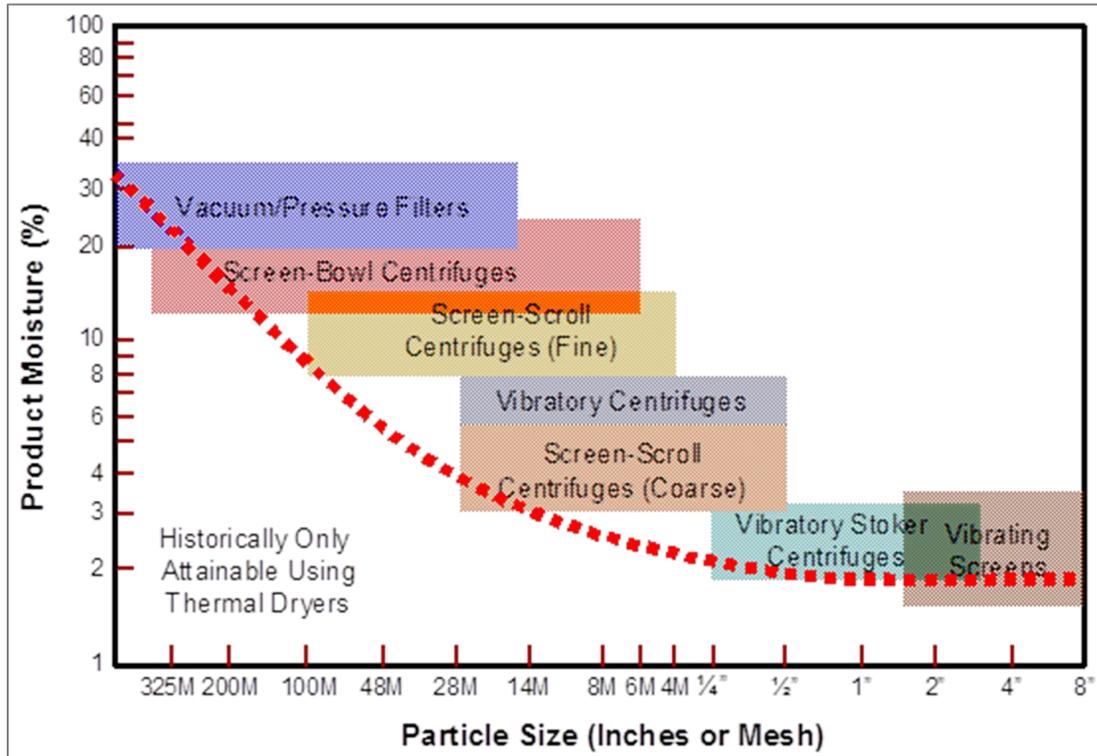


Figure 1.4 Dewatering methods with respect to size fraction of coal

Coarse coal particles larger than 5 mm are dewatered using screens. Shaking and vibrating screens are commonly used for this purpose. Moreover, sieve bends are generally used for preliminary dewatering of coal prior to vibrating screens and centrifuges. Particles of 5 x 0.5 mm size range are typically sent to basket type centrifuges for dewatering.

In this research document, three conventional methods of dewatering used for small size fraction are reviewed: screenbowl centrifugation, vacuum filtration, and thermal drying (refer Figure 1.4). Screen bowl centrifuges are widely used in coal industry to dewater the 1 mm x 0 size range of clean coal coming from froth flotation and spirals. Screenbowls are able to handle some ultrafine sizes and, therefore, are reviewed here, although they are usually reserved for coarser feeds than those studied in this research. If high coal recovery is desirable, then the fine coal (0.5 mm x 0) can be dewatered using vacuum filters. Vacuum filtration is the most common method for dewatering ultrafines. Although thermal drying produces the driest product, it is currently the least used of the three methods due to high cost and problems in obtaining environmental permits. Less than 10% of the existing United States coal plants still utilize thermal dryers for moisture control (Bratton, 2013), largely because of abovementioned issues. Latest developments and emerging technologies for dewatering and drying solids, such as

hyperbaric centrifugation technology, Nano-Drying method, etc., will also be discussed in the section.

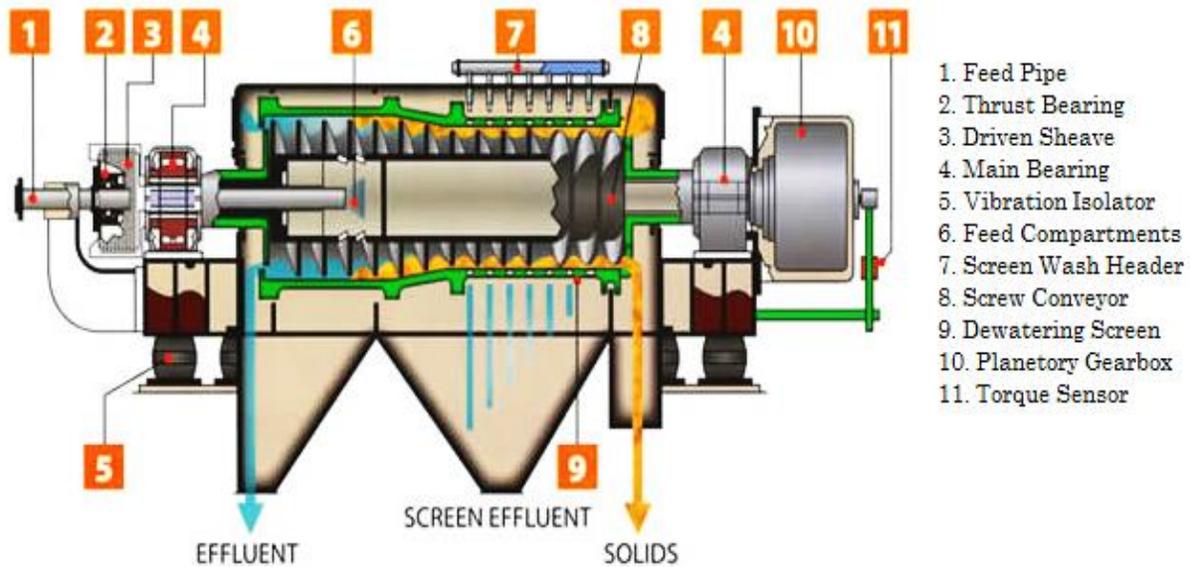
1.3.1 Centrifuges

Centrifugal dewatering is a solid-liquid separation technique in which solid particles are separated from a liquid by means of a combination of sedimentation and filtration mechanisms driven by centrifugal force. These devices spin either horizontally or vertically. The rotation generates centrifugal force, which separates water from fine coal, much like the spin-dry cycle of a laundry washing machine (Osborne, 1988).

Although gravitational sedimentation and centrifugation employ the same basic principle, i.e. differential density separation, the latter is a much faster process because of the centrifugal 'g' force applied to the particles. Most of the centrifugal dewatering devices used in coal industry operate at 50-3000 times the gravitational force. High g-forces cause solids to settle quickly into a compact cake and force water out through the pores (Osborne, 1988). Two types of centrifuge are commonly used in industry: solid-bowl and screen-bowl.

Bowl type centrifuges were first used in the coal industry in the mid-1960s with the introduction of the solid-bowl centrifuge. These centrifuges contain two rotating elements: the conveyor and the bowl. The bowl consists of a long cylindrical shaped region and a shorter cone shaped region. The conveyor, with one or more helical flights that follow the contour of the bowl, transports the material by rotating at a slightly slower or faster speed than the bowl (Osborne, 1988). The unit can have either a concurrent or a countercurrent feed arrangement. In the concurrent feed system, the pulp enters the centrifuge at the larger cylindrical section of the bowl, and the cake moves in the same direction as the effluent towards the conical end. Concurrent (solid-bowl type) operates at slower speeds as compare to countercurrent type, therefore they are found to be attractive in removal of coal tailings where acceptable product moistures are 35-45% in range.

Screenbowl centrifuges, as exhibited in Figure 1.5, are countercurrent machines and consist of a horizontal tube with a screw inside to move the material. The pulp enters the centrifuge near where the conical section starts and the cake moves in opposite to the effluent flow. The machine is equipped with an additional cylindrical screen that assists further water drainage. The first section of the horizontal tube is solid and removes the bulk of the water.



Decanter Machine Inc. (2013), www.decantermachines.com

Figure 1.5 Screenbowl centrifuge section diagram (Decanter Machine Inc., 2013)

The screen is made of tungsten carbide bars that have wedge profiles to prevent near size solid particles from getting stuck between the bars. As the feed comes into the horizontal tube section, it quickly forms a cake while the majority of the liquid and about half of the minus 325 mesh material flow over the adjustable weirs in the back of the machine (Keles, 2010). Solids settled under the acceleration force are carried up the slope of the cone by the helical conveyor, as in solid-bowl centrifuges. However, unlike solid-bowl centrifuges, thickened cake of solids pass over the cylindrical screen section where the remaining excess water is filtered through the cake and discarded (Osborne, 1988).

These centrifuges are high capacity, long life machines that can provide low moistures. The final moisture is directly related to the amount of minus 325 mesh feed material. For example, if a feed contains 30% minus 325 mesh, the product's moisture will be around 18% (Osborne, 1988). It should also be noted that some of this ultrafine material is discarded with the main effluent. Typically this effluent is not recycled, and any material in it is lost to the tailings. Final product moisture is also dependent on the centrifugal force. A higher operating speed will lead to lower moisture and a finer cut; however, screen-bowl centrifuges are generally not operated above 500g due to excessive wear (Osborne, 1988). Due to the strong dependence of product moisture on feed size distribution and limited centrifugal force, screen bowl centrifuges are generally used for dewatering fine material coming off of spirals, i.e. 1 x 0.15 mm.

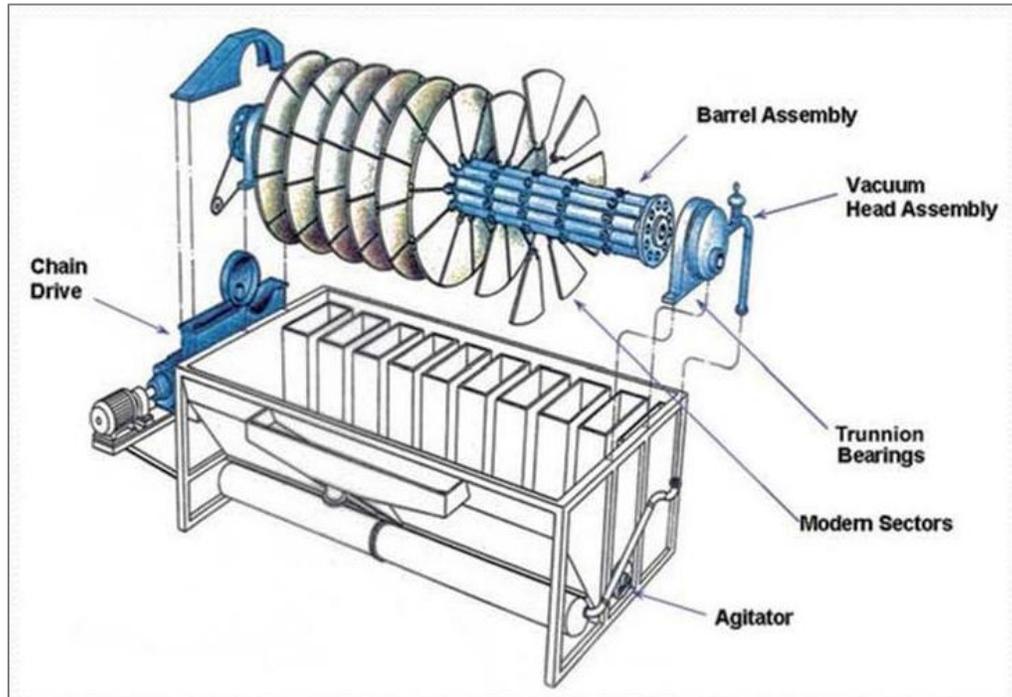
1.3.2 Vacuum Disk Filtration

Filtration is used to separate liquids from solids by passing the solid-liquid mixture through a permeable medium. The medium accumulates most of the solid particles while allowing the liquid to pass. In coal preparation applications, most are disc-filters utilizing vacuum and positive air pressure as the collection and dewatering mechanism.

Vacuum filtration is a highly effective method for dewatering fine coal containing a large proportion of minus 325 mesh (minus 44 micron) solids. These filters are basically porous cloth or fine-fabric screens to which a vacuum is applied. The vacuum draws water and solids to the screen surface, which traps the solids but allows the water to pass through.

The most common type in the United States is disc-filters (illustrated in Figure 1.6), which consist of vertical discs with fan shaped sectors covered in fine cloth. The hollow discs are under vacuum and submerged about half way in slurry. As the discs rotate, they pick up solids from the slurry. The cake dries as it is carried through the air, and then the dried cake is blown off by positive pressure before the segment is again dipped into the slurry (Osborne, 1988). Fine solids are trapped in the cake against the filter cloth, with recovery exceeding 97%. Moisture is typically in the 25-35% range, and reagents may be needed to reach the lower moistures. Flocculants are usually added to reduce screen blinding, reduce ultrafine losses, and aid in cake release, while cationic coagulants are occasionally used to increase the filtration rate.

These filters are popular because of their small footprint, high capacity, and low cost; however, they produce higher moisture levels and require more maintenance compared to some other filters. Other continuous vacuum filters include rotary drums and horizontal belt filters. Filtration may also be done by applying positive pressure instead of a vacuum; however, these filters are more expensive and are used rarely in the coal industry for dewatering clean coal products.



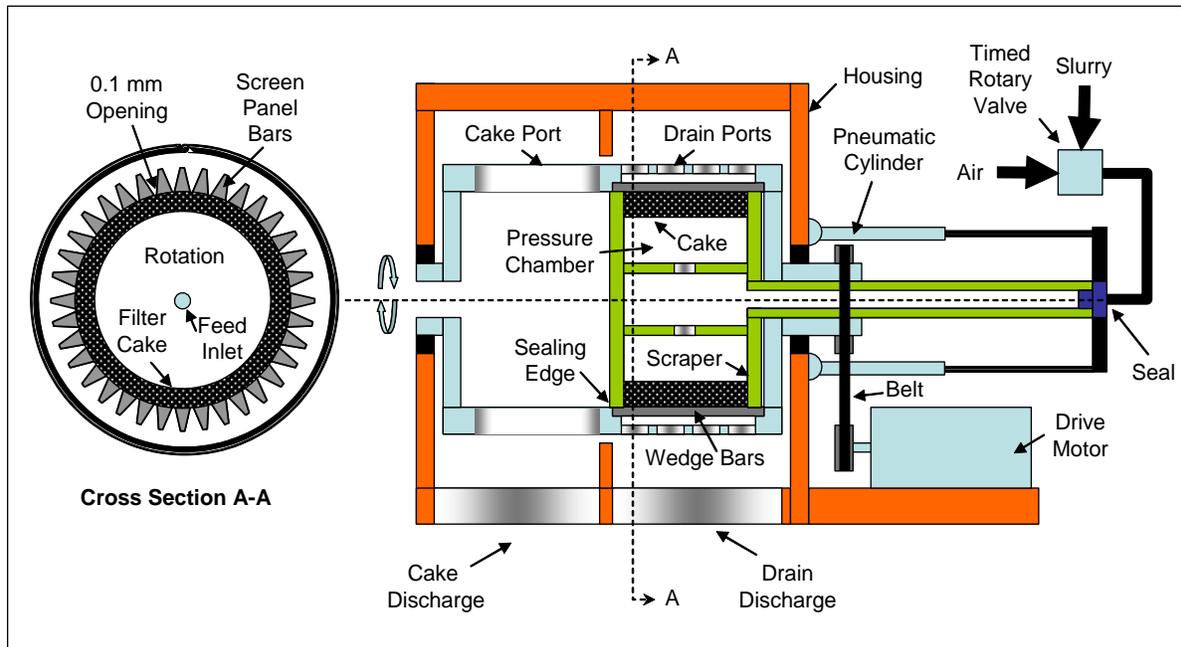
NFM (2013), National Filter Media, www.nfm-filter.com

Figure 1.6 Schematics of typical vacuum disc filters (NFM, 2013)

1.3.3 Hyperbaric Centrifuge System

One of the latest centrifugal bowl type separators is the Hyperbaric Centrifuge (commercially known as Centribaric™ Centrifuge), which was developed at Virginia Tech for ultrafine particle dewatering. The technology combines centrifugation and pressure filtration techniques within one process to substantially reduce product moisture. Keles et al. (2010) performed moisture-recovery analysis on a prototype hyperbaric filter centrifuge unit manufactured by Decanter Machines. The moisture values were reported in the range of 13 to 20% with solid recoveries in range of 83-96%. It was demonstrated through economic analysis that utilization of hyperbaric centrifuges in a coal plant would likely produce an attractive economic gain compared to utilizing only screen bowl centrifuges (Keles, 2010). The first commercial hyperbaric centrifuge unit (Figure 1.7), also manufactured by Decanter Machines, Inc., was tested by Walter Energy in 2009 by replacing the standard screenbowl centrifuge.

The most economic benefit observed on the commercial scale was the reduction in the amount of ultrafine solids reporting to the centrifuge through the effluent in the plant. The percent of solids reported was between 0.5 – 1%, with an ash value ranging from 30 to 50% as compared to 4 – 6% solids with ash value 14% from previously installed screenbowl centrifuge



Keles, S. (2010), PhD Dissertation, Mining & Minerals Engineering, Virginia Tech

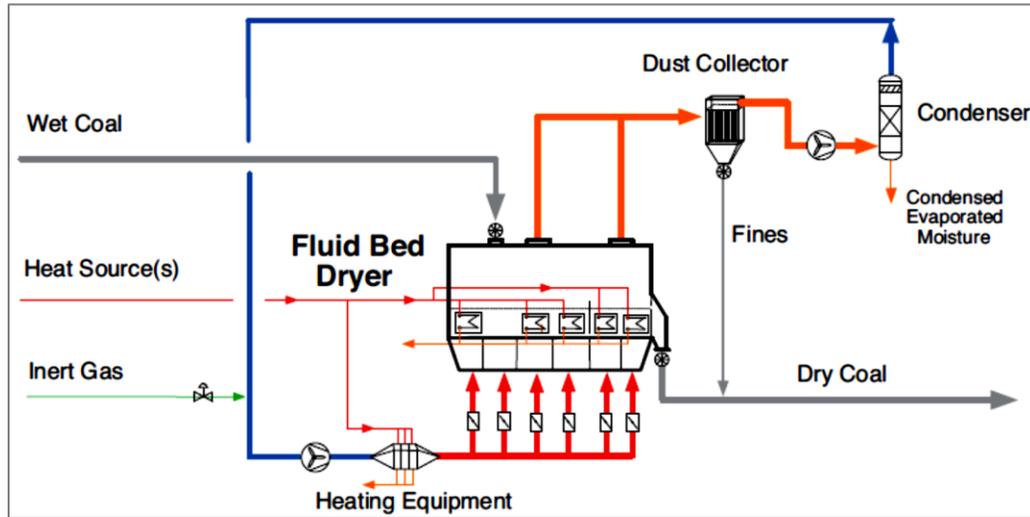
Figure 1.7 Simplified schematics of hyperbaric filter centrifuge (Keles, 2010)

main effluent. This improved the plant productivity to 20 - 25 tons/hour (Franklin et al., 2012). The only drawback with this technology is that it is highly energy intensive, and thus very costly to implement for a low price commodity such as coal.

1.4 Fine Coal Drying Methods

1.4.1 Thermal Drying

Thermal drying is not common in the United States as it is the most expensive unit operation in coal preparation (Osborne, 1988). Additionally, it is now extremely difficult to get permits to install new units in the preparation plants (Bratton, 2013). They are generally used on ultrafine coals whose large surface areas lead to high moisture contents. Thermal dryers are the only units that can consistently provide low moisture (<10%) with ultrafine feed, although they diminish the coking properties of coal. The coal begins to volatilize at temperatures greater than 90°C, while these units typically operate in range of 150-430°C. Thermal drying is justifiable only if the low moisture is worth the cost to reduce the possibility of freezing, to reduce heat loss during combustion, and to prepare the coal for coke making (Osborne, 1988).



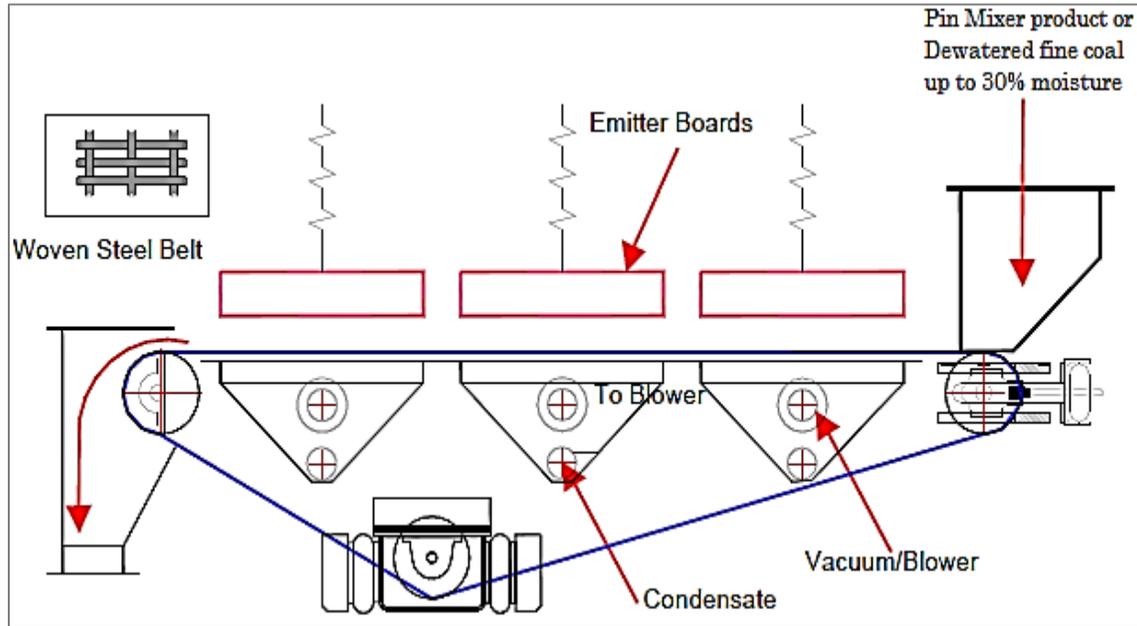
Jumah, R, and Majumdar, A, (2006), "Dryer Emission Control System", *Handbook of Industrial Drying*

Figure 1.8 Simplified flowsheet of fluidized bed direct heat exchanger coal dryer

Industrial coal dryers usually employ convection in direct heat exchange type dryers. In these type dryers wet coal is continuously brought into contact with hot gases in order to evaporate surface moisture (Osborne, 1988). The most common types of convective thermal dryers are: fluidized bed, flash, and multi-louvered (Jumah and Majumdar, 2006). In the fluidized bed dryer (outlined in Figure 1.8), the coal is suspended and dried above a perforated plate by rising hot gases. In the flash dryer, coal is fed into a stream of hot gases for instantaneous drying. The dried coal and wet gases are both drawn up a drying column and into a cyclone for separation. In the multi-louvered dryer, hot gases are passed through a falling curtain of coal, which carried by flights of specially designed conveyor.

1.4.2 Parsepco Drying Technology

Mohanty et al. (2012) reviewed several emerging fine coal drying technologies, of which Parsepco Drying Technology (PDT) is one of them. PDT employed medium-wave infrared radiation (MIR) in combination with a steel-belt dryer and a pin mixer (as described in Figure 1.9). This infrared drying system transfers thermal energy to the feed material (typically 25-30% moisture) to be dried in the form of electromagnetic waves, producing dry product that is constantly below 10% moisture level. Buisman (2010) indicated medium-wave infrared radiation is more effective than short-wave or long-wave infrared in moisture reduction. A pin mixer is used for ultrafine clean coal below 75 microns to prepare the



Buisman, R. (2010), "Coal Fine Beneficiation Using Liquid Coal Fuel", IQPC Presentation

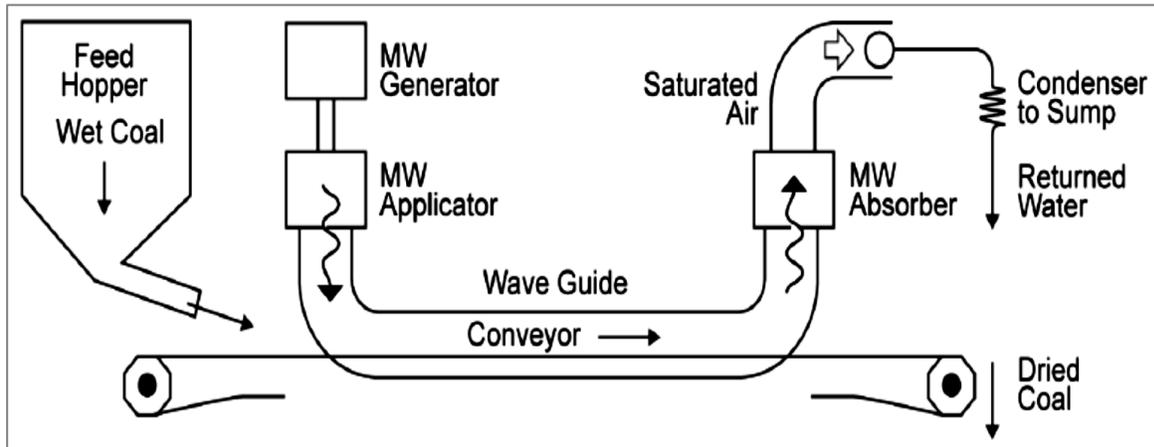
Figure 1.9 Schematic of Parsepco Drying Technology (Buisman, 2010)

feed for the dryer. It is reported that moisture levels in the range of 9-13% were achieved by drying product obtained from a plate-and-frame filter press (Buisman, 2010).

1.4.3 Drycol Process

The Drycol Process was first developed by DBAGlobal Australia. The process utilizes controlled application of microwave radiation for drying the fine coal fraction. Water molecules attached to the coal surface absorb energy from the radiation by dielectric heating—that is, by rotating rapidly as they attempt to align themselves with the microwave induced alternating electric field. The schematic for the process is shown in Figure 1.10. The molecular movement creates heat as the rotating molecules strike other molecules and put them in motion (Graham, 2007). The applied microwave energy passes through the carbon and acts directly on both free and inherent water.

Microwave drying is well known for its advantages, such as volumetric heating and faster drying rates. A commercial unit of capacity 15 tons per hour plant was tested and was able to dry low-rank coal from 28% to 12% moisture content (Graham, 2007).



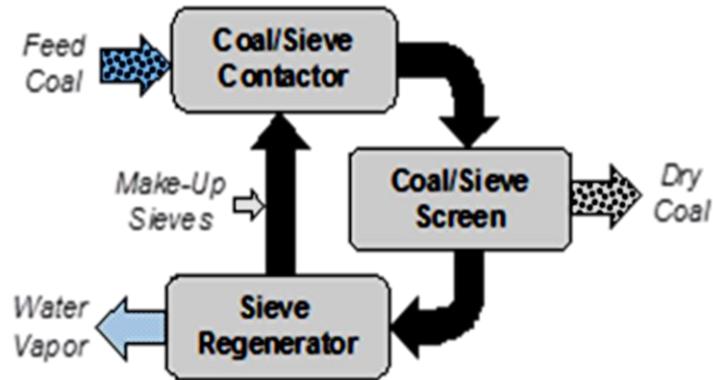
Graham, J. (2007), "Microwaves for Coal Quality Improvement: The Drycol Project", DBAGlobal Au.

Figure 1.10 Simplified Drycol Process flowsheet (Graham, 2007)

1.4.4 Nano Drying Technology

The Nano-Drying Technology (NDT™) system uses molecular sieves to wick water away from wet fine coal particles and does not require crushing or additional finer sizing of the wet coal to dry it. These molecular sieves are a form of nano-technology based particles, which are typically used for extracting moisture from airborne, aerosol and liquid environments. There are also known techniques for combining molecular sieves with solids, but no previous techniques included regeneration of the molecular sieves. Molecular sieves contain pores of a precise and uniform size. These pores are large enough to draw in and absorb water molecules, but small enough to prevent any of the fine coal particles from entering the sieves. Some molecular sieves can absorb up to 42% of their weight in water (Bland et al., 2011). Molecular sieves are used in the drying process because they are re-usable after the absorbed water is removed from the sieves by heating them in the microwave at 300°C (Bratton, 2013). The water in the molecular sieve turns into vapor at this temperature and is released into the atmosphere.

Bratton et al. (2012) conducted both bench scale and pilot scale parametric testing and statistical analysis on this technology. The study reported product moisture contents in the range of 5% to 10% for both minus 0.6 mm and minus 0.15 mm fine coal material from the feed carrying moisture in the range of 22% to 28%. A simplified schematics of the process is exhibited in Figure 1.11.



Bratton, R., Ali, Z., Luttrell, G., Bland, R., and McDaniel, B. (2012), "Nano Drying Technology: A New Approach for Fine Coal Dewatering", 29th Annual ICPC, Lexington, KY.

Figure 1.11 Simplified flowsheet for pilot scale NDTTM process (Bratton et al., 2012)

1.5 Oil Agglomeration

Another fine coal cleaning process that has been investigated in the past is selective oil-agglomeration. Several studies conducted on oil agglomeration process for fine coal achieved better combustible recoveries compared to conventional flotation process. The process is not preferred in the United States due to high costs associated with oil consumption, among other factors. The process is discussed in detail due to its importance in the novel technology proposed in this research.

1.5.1 Brief History

Oil Agglomeration, which is also referred to as selective agglomeration or spherical agglomeration, was first performed on coal in the early 1920's (Mehrotra et al., 1983); however, it was not until the 1970's energy crisis that the United States invested significant amounts of time and money into the potential uses of oil agglomeration. Though most of the testing during the 1980's focused on the cleaning ability of oil agglomeration, dewatering, and oil recovery were also explored to some extent. Since its introduction in 1921, the use of oil agglomeration was mostly investigated in laboratories and pilot plants. Several variations of oil agglomeration processes were developed over the years including the Trent Process (1921), the Convertol Process (1952), NRCC (1961), the Shell Pelletizing Separator Process (1968), the Olifloc Process (1977), the CFRI Process (1976), and the BHP process (1977). Several pilot plants were even constructed to test the feasibility of the method in continuous larger scale production

(Mehrotra et al., 1983). Most of abovementioned processes used light diesel oil as an agglomerants that could not be easily recovered, and thus increased the cost of the final product.

To address the issue, Smith and Keller (1981) employed fluoro-chloro derivatives of methane and ethane, which have low boiling points (40-159°F), so that the agglomerants could be readily recovered and recycled by gentle heating. However, these reagents are known to have undesirable effects on the atmospheric ozone layer, therefore could not be used on a large scale production. Keller (1984) disclosed a method (called the *Otisca T- process*) of oil agglomeration that utilizes short-chain hydrocarbons, such as, 2-methyl butane, pentane, and heptane as agglomerants. Agglomeration using low chain recoverable non-polar liquids as an agglomerant typically provides moisture only up to 40% by weight (Keller, 1985). These reagents also have relatively low boiling points, allowing them to be recycled. Being able to recycle an agglomerant is a significant step towards commercialization of the selective agglomeration process (Keller, 1984).

Another method to substantially reduce the amount of oil consumption was proposed by Capes (1989). In this low-oil agglomeration process, smaller agglomerates (<1 mm) are formed at low dosages of oil (0.5-5%) and are separated from mineral matter by flotation process rather than by screening. Similarly, Wheelock and Meiyu (2003) developed another method of selectively agglomerating coal using microscopic gas bubbles to limit the oil consumption to 0.3-3% by weight of coal.

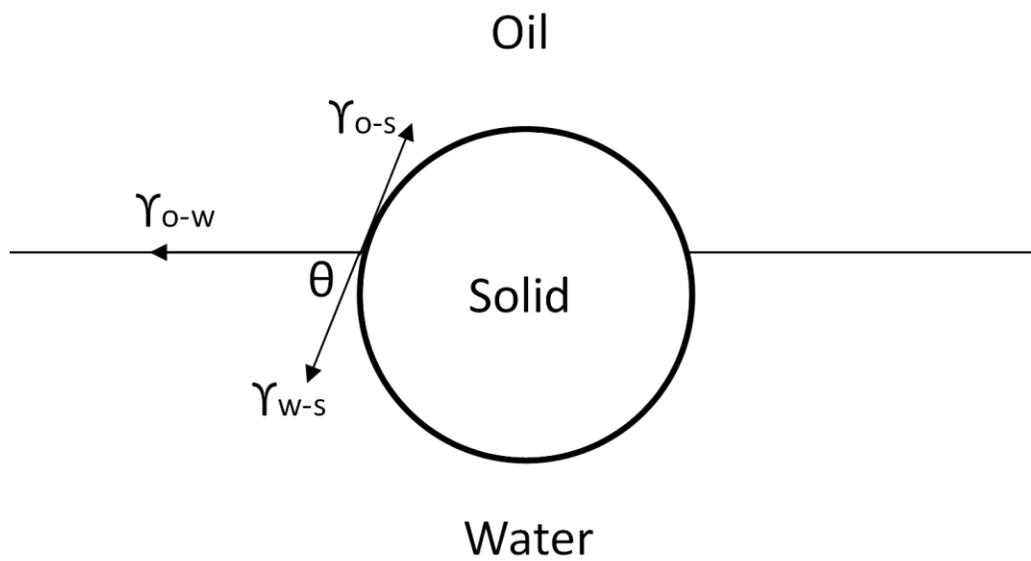


Figure 1.12 Interfacial forces on solid particle at oil-water interface

Chiang and Klinzing (1986) disclosed a method (called the *LICADO process*) for cleaning fine coal of mineral matter by selective transportation of particles across the water/liquid carbon dioxide interface. Additionally, the liquid CO₂ could be recycled. A report shows that clean coal products obtained using this liquid carbon dioxide process contained 5-15% moisture after filtration (Cooper et al., 1990).

1.5.2 Fundamentals

The selective oil agglomeration process is a solid/solid separation method. The treatment of coal fines in the aqueous suspension consists of separating the carbonaceous fraction from the ash-forming mineral matter. The separation technique in oil agglomeration involves the principle of preferential wetting of hydrophobic carbonaceous particles by hydrophobic liquid/oil. In the presence of an adequate amount of oil and sufficient mechanical agitation, the oil coated coal particles collide with each other and form into agglomerates. The agglomerate formation is due to the interfacial tension of the oil and the capillary attraction of the oil bridges between the particles. The mechanism of particle absorption by the bridging oil is explained in Figure 1.12. The position of the solid particle at the interface is governed by the relative values of interfacial tensions. From the balance of forces, only the following three conditions are possible, (a) if $\theta < 90^\circ$, the particle will tend to be drawn into the aqueous phase; (b) if $\theta = 90^\circ$, the particle will remain at the interface; (c) if $\theta > 90^\circ$, the particle will be drawn into the oil phase (Osborne, 1988). Having the angle θ , defined as the contact angle, greater than 90° is the prime condition for a successful oil agglomeration process.

Despite the fact that oil agglomeration has been studied extensively, the microscopic interactions are still not well understood. Coal is not-homogenous and consists of a patchwork of hydrophilic and hydrophobic sites (Keller and Burry, 1987); therefore, several conflicting theories exist on which liquid, oil, or water, acts as the bridging mechanism to form the agglomerates.

The first popular theory is that oil acts as a liquid bridge between coal particles (Keller and Burry, 1987). In the oil agglomeration process, oil is added to an aqueous suspension while being agitated. Under conditions of high-shear agitation, the oil breaks up into small droplets that collide with coal particles, spread on the surface of the particles, and form pendular bridges between them to produce agglomerates. The oil envelops the coal and bridges over the

hydrophilic sites. Though small droplets of water may remain bound to the hydrophilic sites, oil displaces the water from the hydrophobic sites and remains the dominant liquid in the agglomerates. As two oil-coated particles collide during mixing, the oil and its capillary attraction causes the particles to stick together and eventually form agglomerates.

A second opposing theory suggests that water actually acts as the bridging liquid. Many oils simply spread on hydrophobic coal surfaces, whereas water sticking to the hydrophilic sites forms water droplets with contact angles greater than 90° (Good and Islam, 1991). When two of these droplets meet, they form a bridge and the surface tension of the water pulls the coal particles together. The more the particles are pulled apart, the more the surface tension increases and forces these particles back together. In contrast to the first theory, hydrophobic liquids will break apart into two droplets when the bridge is stretched (Good and Islam, 1991). Oil simply coats the particles and provides an environment for the water bridges. There is little discussion on whether these theories are mutually exclusive or may both contribute to agglomerate formation.

1.5.3 Parameters

In the selective oil agglomeration process, the interaction that occurs between the hydrophobic particles and hydrophobic liquid, which also affects the kinetics of the process, is mainly controlled by three factors: (a) the free energy at the three-phase interface (the interface between water, coal, and the hydrophobic liquid), (b) the dosage of hydrophobic liquid, and (c) the mixing intensity (Capes and Darcovich, 1984).

Agglomeration should proceed when there is sufficient driving force, that is, the free energy is negative (Keller and Burry, 1987). This is highly dependent on the nature and choice of agglomerant used and the quality of coal in the process, and is thus governed by the interfacial surface tension between water, coal, and the oil. The higher the rank of coal the higher is the hydrophobicity of the coal surface. The thermodynamic model (proposed by Jacques et al., 1979) based on the oil bridging mechanism showed the relationship between the change in free energy with interfacial tensions with the following equation:

$$F_{II} - F_I = (\gamma_{o-s} - \gamma_{w-s}) + \gamma_{o-w}[(1 + n^3)^{\frac{2}{3}} - n^2] \quad [1.1]$$

Where F_I and F_{II} are the free energies of State I (when coal particle and oil droplet are fully dispersed in water phase) and State II (when coal particle is completely engulfed with oil in water phase, agglomerated state) respectively, γ_{o-s} , γ_{w-s} and γ_{o-w} are the interfacial tensions (refer Figure 1.12) and n is the ratio of the diameter of particle in State II to the diameter of particle in State I.

Previous studies (Keller and Burry, 1987; Skarvelakis et al., 1995) showed that coal cleaning decreases with the increase in density and viscosity of oil. This is due to the decrease in the interfacial tension between water and oil interface. The researchers found that chlorinated hydrocarbons and short-chain alkanes were more effective than saturated aliphatic hydrocarbons, which, at the same time, were better than aromatic hydrocarbons. The detailed analysis of the feasibility of the oil agglomeration process for all rank coals (anthracite, bituminous, sub-bituminous, and lignite) with these various types of agglomerants can be found in the literature (Keller and Burry, 1987; Skarvelakis et al., 1995).

Moisture held by agglomerates of fine coal is mostly due to the amount of water trapped between the void space in agglomerate and the moisture held on the particle surface. The amount of oil required cannot be determined without consideration of the mixing intensity. Intensive mixing such as that produced by high shear devices often generates rapid agglomerates through efficient oil dispersion and good particle contact. The early Trent Process employed low intensity agitation with high oil dosages and longer retention time to achieve agglomeration: on the contrary, the Shell process used high mixing speed and low retention time for agglomeration. Later processes, such as the Convertol and the Olifloc, used the combination of very high shear mixing, low oil dosages (2-7% by weight of coal) and very short retention time (Capes and Darcovich, 1984).

The next most important parameter for a successful agglomeration process is oil dosage. The amounts of oil used in the process are typically in the range of 5 to 30% by weight of feed coal (Tsai, 1982). At low dosages, agglomerates have larger void spaces between the particles, forming agglomerates that are filled-up with water. Here, fine mineral matter, *e.g.*, clay, is dispersed, which makes it difficult to obtain low-moisture and low-ash products. Researchers found indeed that the moisture content was in excess of 50% by weight when the amount of oil used was less than 5%. By increasing the oil dosage to 15%, the agglomerates were more compact and discreet in nature. They grew in size and were easy to drain the clay and mineral

matters with the suspending water phase. The void space in the interior of agglomerates was partially filled with oil, which resulted in a lower moisture and cleaner product. A dosage higher than 20% led to the formation of relatively hard and spherical agglomerates (Capes and Darcovich, 1984).

Keller and Burry (1987) increased the dosage of oil to 55-56% by volume to fill up the void spaces thoroughly, which practically eliminated the entrapment problem and produced super-clean coal containing less than 1-2% ash. However, the moisture content remained high. Keller (1985) also claimed that the typical agglomerates' moisture content was 40% by weight using fluorocarbons as an agglomerant. Depending on the type of coal tested, approximately 7-30% of the moisture was due to the water adhering onto the surface of coal, while the rest was due to the massive water globules trapped in the agglomerates (Keller and Burry, 1990).

1.5.4 Kinetics

Agglomerates growth kinetics depends on the aforementioned process variables and thus affects the recovery efficiency of the coal as well as its moisture content. Many studies were previously conducted (Rao and Vanangamudi, 1984; Skarvelakis et al., 1995) to determine the kinetics and mechanism for the batch-scale oil agglomeration process and to predict the size distribution of the agglomerates. The researchers showed the agglomerate growth rate follows second order kinetics and can be represented with the following equation:

$$\frac{t}{d_{50}} = \frac{1}{k_2 d_{50\infty}^2} + \frac{t}{d_{50\infty}} \quad [1.2]$$

Where, d_{50} is the size which allows 50% agglomerates to pass, $d_{50\infty}$ is the equilibrium size that can be obtained after a prolonged period of the agglomerating process, t is the agglomeration period and K_2 is the second order rate constant. The knowledge of the two constants, $d_{50\infty}$ and K_2 , for a given set of conditions, allows the growth of agglomerates as a function of agglomeration time and mean diameter of the coal particle to be predicted.

Thermodynamically, the kinetics of the agglomeration process is faster than the flotation method. This is because in flotation when an air-bubble contacts a particle its curvature changes. This creates an excess pressure (P) on the wetting film existed between the bubble-particle. The excess pressure due to curvature change (P_{cur}) is known as Laplace or capillary pressure. This pressure causes film thinning only up to a critical thickness. At critical thickness, electrical

double layer and van der Waals forces interact with each other and give rise to a disjoining pressure (Π). A pressure balance along the direction normal to a film shows that the excess pressure becomes equal to the capillary pressure minus disjoining pressure ($P = P_{\text{cur}} - \Pi$). In flotation conditions, both electrical double layer and van der Waals forces are repulsive (positive), causing the excess pressure to decrease and hence the film thinning process de-escalated (Sulman et al., 1905).

On the contrary, in oil agglomeration process the van der Waals forces are attractive (negative) while electrical double layer forces are negligible in the presence of non-polar liquid (oil). The negative disjoining forces increase the excess pressure on wetting film, thus escalate the film-thinning process beyond the critical thickness. Furthermore, Pan and Yoon (2010) identified that the higher the hydrophobicity of the particle (such as high-rank coals) the higher is the negative disjoining pressure. For the reasons, oil agglomeration process has faster kinetics and thermodynamically more favorable than flotation.

1.6 Otisca T-Process

The concept of Otisca T-Process is the key step in the proposed novel fine coal cleaning and dewatering technology and thus is separately discussed in detail. The process was disclosed by Keller (1984) and developed by Otisca Industries, Ltd. of Syracuse, NY. The process first employed heavy chloro-fluoro carbon (CFC) derivatives (1.25 – 1.7 SG), which have low boiling point and can be recovered by heating at low temperatures.

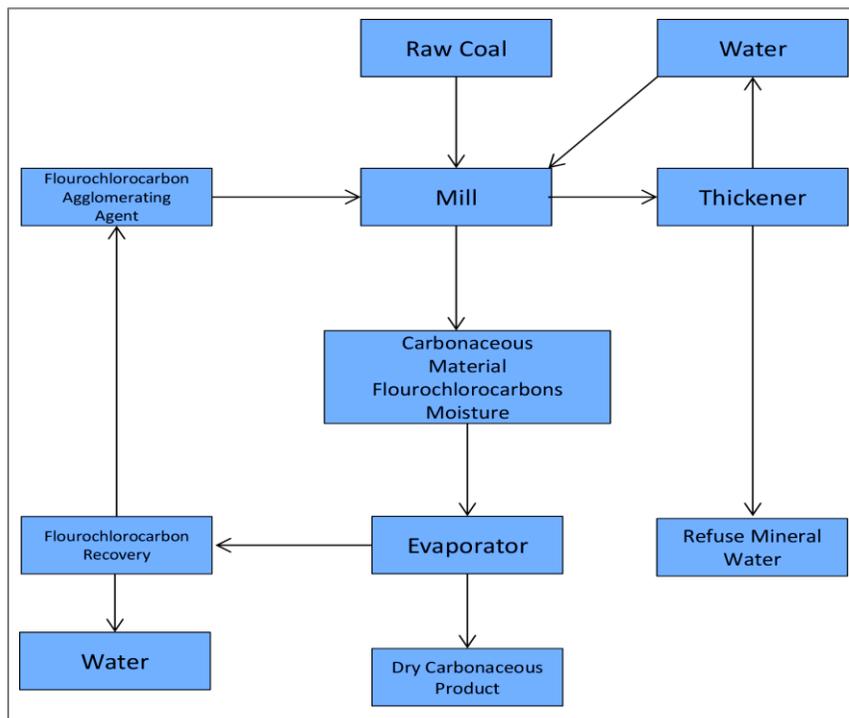
The Otisca process involved three steps: (a) particle size reduction of run-of-mine coal to 15 micron x 0 in presence of chloro-fluoro carbon, where the organic liquid forms a thin surface film on the newly exposed particle surface, (b) agglomeration of the carbonaceous material from coal-mineral matter-liquid system and separation of the agglomerates by gravity in a static bath using chloro-fluoro carbon as a medium, and (c) organic liquid recovery from both the clean coal product and reject (Keller, 1982; Keller and Rainis, 1980). A simplified flowsheet of the process is shown in Figure 1.13.

Keller (1982) showed that the process, when treating the grinded ultrafine size fraction (15 micron x 0), was able to achieve almost 100% carbon recovery (ash value 0.3%) from run-of-mine feed treated on a 200 pound/hour plant. The water content in the final product was reported as low as 8% by weight. Later, the company constructed and successfully operated a 15

ton/hour feed capacity pilot-scale facility with Island Creek Coal Co. in Bayard, West Virginia in late-1970s. The data collected from the plant showed energy recovery as high as 90% (Keller, 1982). The separation efficiency indicator, called the ecart probable, values obtained from 8-hour pilot-tests for different size fractions are outlined in Table 1.1. The results clearly indicated that as the size fraction decreases the ecart probable value increases (i.e., process efficiency decreases). However, the separation was much better in comparison to the other processing methods for fine (100 x 325 mesh) particle size fraction (Keller, 1982). In addition, the pilot-scale testing showed only 0.1% loss of organic liquid.

Table 1.1 Ecart probable values for Otisca Process at different size fraction feed (Keller, 1982)

Feed Size Fraction	Ecart Probable	Organic Efficiency%
3/8 x 1/4 inches	0.008	100
1/4 inches x 28 mesh	0.015	99
28 x 100 mesh	0.175	98
100 x 325 mesh	0.260	96
3/8 inches x 325 mesh	0.023	98



Keller, D, and Rainis, A., (1980), "Processes of Recovering Coal", US Patent No. 4186887

Figure 1.13 Simplified Otisca T-Process flowsheet (Keller and Rainis, 1980)

Following the initial success, the company constructed the first full-scale plant for American Electric Power (AEP) of rated capacity 125 tons/hour in early-1980s. The project received a setback when it was determined that the organic liquid recovery process was not economical and the plant was losing as much as 5% of chloro-flouro carbon, which escalated the clean coal product cost. Furthermore, scientists discovered that these organic liquids were a significant source of depleting the ozone layer in the earth atmosphere (Seaman, 1992). The company lost contract with AEP.

Keller (1984) switched the chloro-flouro carbons to short chain alkanes (such as pentane) in the process, and was able to produce a final product of similar carbon recovery. The Otisca Industries received couple of contracts from Florida Power & Light and General Electric respectively (Seaman, 1992). The process was only able to survive few more years, because in late-1980s, the energy crisis was over. The cost of the final Otisca product could not compete with the falling prices of oil. Later, the process utilized fine coal-water slurries from the preparation plants to produce high carbon recovery product, but the moisture (as-received) reported was high, on an average 40% by weight (Keller, 1985). Eventually, the Otisca-T process lost its significance and abandoned in early-1990s.

The Otisca process using short-chain hydrocarbons is a source of inspiration in developing the novel, innovative technology proposed in the research. Since surface forces get stronger for micron size particles, the researchers at Virginia Tech have developed an additional proprietary step to treat the 40% moisture agglomerated product, which can provide very low moisture as well as high combustible recovery at a very low energy input. The innovative method simultaneously cleans and dewateres ultrafine coal slurries by exploiting hydrophobic-hydrophilic surface properties of the particles with a hydrophobic liquid.

1.7 Foundation of Novel Proposed Technology

Consistent higher energy recoveries achieved in the oil agglomeration in comparison to flotation process and the successful demonstration of the Otisca T- Process using recoverable straight chain hydrocarbons provided motivation to the researchers at Virginia Tech to develop an innovative method for dewatering fine coal using the recyclable non-polar liquids. The dewatering is achieved by allowing the liquids to displace surface moisture. The agglomeration process has been expanded through research at Virginia Tech by developing an additional

processing step, i.e., the phase inversion step (from water-oil-water to oil-water-oil), which is capable of ‘drying’ (dewater) the fine clean coal at room temperature.

Yoon and Luttrell (1995) first disclosed the concept of dewatering-by-displacement (DBD) or hydrophobic-displacement, which is the foundation of the novel proposed technology. The researchers claimed that the method is capable of achieving the same level of moisture reduction as thermal drying at substantially lower energy costs, but did not mention the removal of mineral matter from coal. The beauty of the DBD method is its thermodynamic spontaneity in behavior compared to the thermal drying process, which is forced drying. The only energy requirement in the DBD method is the recovery of hydrophobic liquid, which can be achieved by gentle heating depending on the nature of the liquid. Figure 1.14 illustrates thermodynamic comparison between the DBD and thermal drying methods. In the latter, large amount of heat exceeding the latent heat of evaporation is required to remove all the water molecules which are deposited in multilayers. On the other hand, in the DBD method the only energy required is just to displace the water molecules in the bottom-most monolayer. The additional advantage of the novel concept is that the volatile matter is retained, thus it does not change the coal properties. Further, the explosion hazard is reduced, since high temperature heating is not involved.

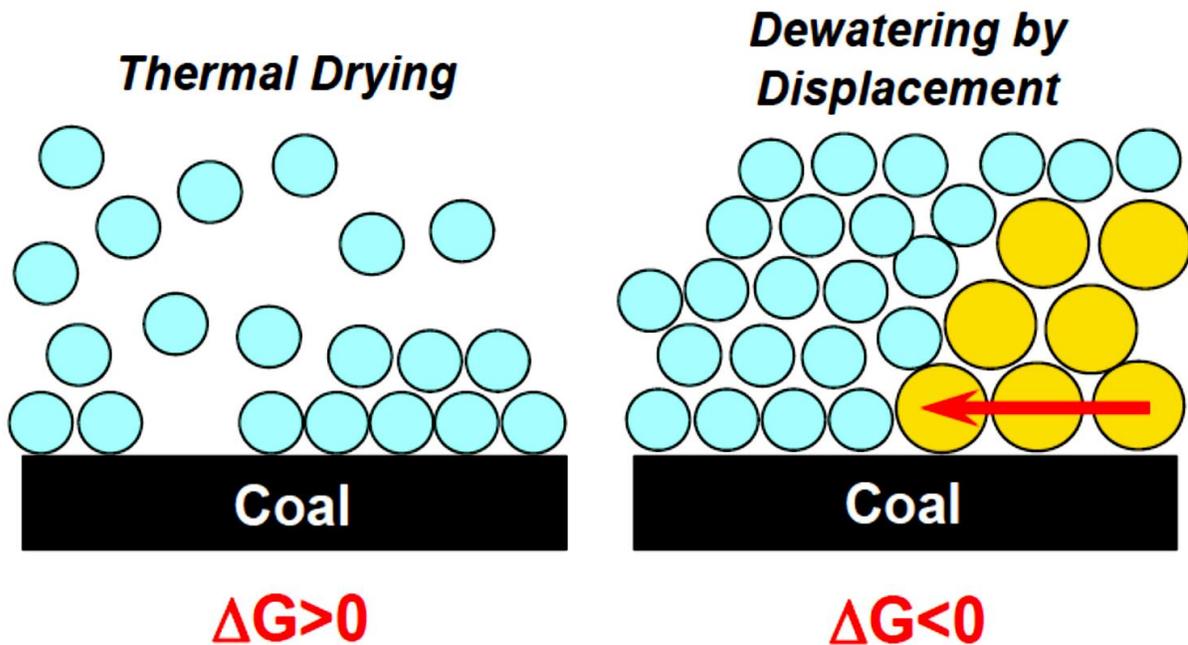


Figure 1.14 Thermodynamic comparison between thermal drying and the DBD process

1.7.1 Concept of Hydrophobic Displacement

The scientific evidences of hydrophobic forces were first measured and reported in the literature by Israelachvili and Pashley (1984). The research showed that these are attractive forces that generate between non-polar molecules in the presence of water. In case of high-rank coal, the coal particles in water are hydrophobic in nature and therefore, have high affinity towards the hydrophobic liquids, such as hydrocarbons. Due to the attractive hydrophobic forces between the two, the liquid quickly engulfs the coal particle and displaces the surface moisture. On the contrary, the clay is hydrophilic in nature, and therefore does not interact with the hydrophobic liquid. Since the novel concept of dewatering was driven by the hydrophobic interactions, it is also referred as hydrophobic displacement.

Dewatering-by-displacement (DbD) is a method of cleaning fine coal from its mineral matter and simultaneously dewatering the clean coal product by displacing the water adhering to the coal surface with a hydrophobic liquid. The displacement is achieved by using the phase inversion process (Yoon et al. 2011). Use of such a liquid allows coal particles to be engulfed (or transported) into the hydrophobic liquid phase, leaving hydrophilic mineral matter in the aqueous phase.

In order for the displacement to occur spontaneously, the thermodynamic analysis comparing a beginning state of coal (1) in water (3) and an end state of coal in a hydrophobic liquid (2) is shown in Figure 1.15. Application of Young's equation (by Thomas Young in 1805) yielded the following criteria for thermodynamic spontaneous dewatering. The change in Gibbs free energy (G) of displacement with respect to contact area (A) must be less than the difference between surface free energies at the coal/oil interface (Υ_{12}) and at the coal/water interface (Υ_{13}).

$$\Delta G_{\text{displacement}}/\Delta A = \Upsilon_{12} - \Upsilon_{13} < 0 \quad [1.3]$$

Furthermore, from thermodynamic equilibrium condition, shown in Figure 1.15, the following relationship can be established:

$$\Upsilon_{12} - \Upsilon_{13} = \Upsilon_{23} \cos\theta \quad [1.4]$$

Therefore, from Equations 1.3 and 1.4, the condition for displacement can be re-established as:

$$\Delta G_{\text{displacement}}/\Delta A = \Upsilon_{23} \cos\theta < 0 \quad [1.5]$$

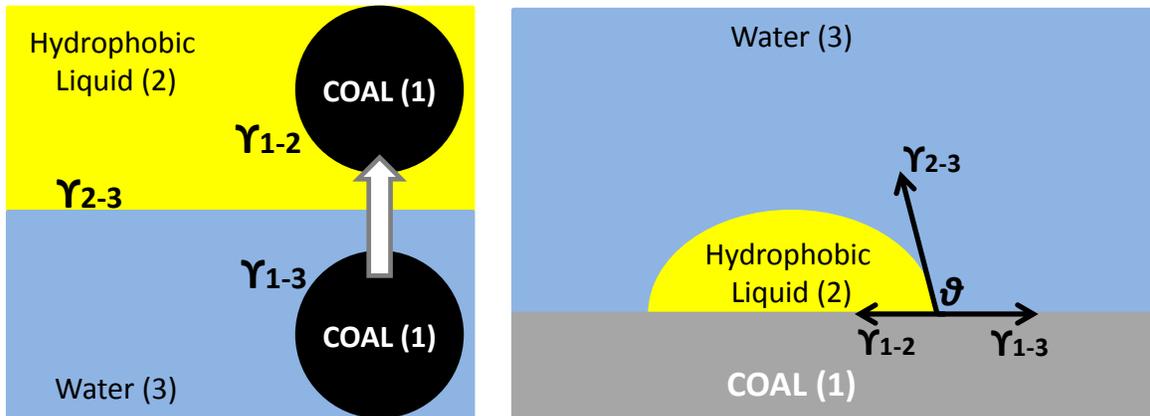
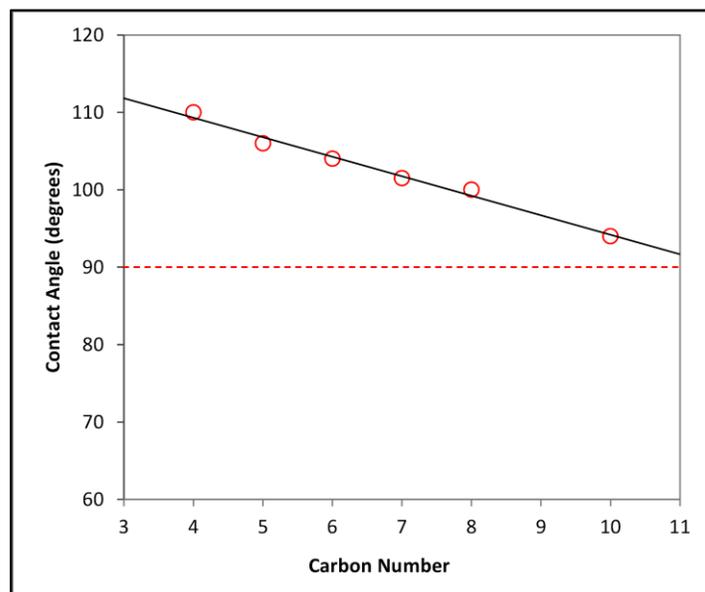


Figure 1.15 Schematics showing removal of a coal particle (1) from water (3) to hydrophobic liquid phase (2) with equilibrium contact angle, θ .



Yoon, R-H, Eraydin, M, and Freeland, C., (2011), "Cleaning and Dewatering Coal", WO 2011/094680

Figure 1.16 Contact angles of *n*-alkane hydrophobic liquids on the surface of a hydrophobic coal immersed in water, redeveloped (Yoon et al., 2011).

In other words Equation 1.5 indicates that a hydrophobic liquid will displace water from coal when the three-phase contact angle ' θ ' is greater than 90 degrees. Identifying the primary condition for displacement, Sohn et al. (1997) indirectly determined the equilibrium contact angles for several short straight chain hydrocarbon liquids (C₄-C₁₀) using the sets of Fowkes-Giriflaco equation (Equations 1.6-1.8), which only considers the dispersion component of the interfacial tension. The polar components of the surface tension will have little or no effect in hydrophobic interaction.

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d \gamma_2^d} \quad [1.6]$$

$$\gamma_{13} = \gamma_1 + \gamma_3 - 2\sqrt{\gamma_1^d \gamma_3^d} \quad [1.7]$$

$$\gamma_{23} = \gamma_2 + \gamma_3 - 2\sqrt{\gamma_2^d \gamma_3^d} \quad [1.8]$$

where superscript d refers to dispersion component of surface tensions. The equations work very well for non-polar liquids and solid surfaces (Sohn et al., 1997).

Figure 1.16 shows the relationship between calculated contact angle (θ) and carbon number. The contact angles of hydrocarbon liquid in water increased as the carbon number decreased. Liquefied butane (C4) had the greatest contact angle at 110° ; therefore, displacement of water by liquid butane is thermodynamically most favorable. Pentane had the next highest three-phase contact angle, which is 106° (refer Figure 1.16).

With the availability of three phase equilibrium contact angle, it is possible to measure the change in free energy per unit area between the two states as illustrated in the Figure 1.15 by the relationship established from the Dupre equation (by Lewis Dupre in 1869).

$$\Delta G_{\text{dis}} = \Delta A (\gamma_{13} - \gamma_{12}) + \Delta A \gamma_{23} \cos\theta \quad [1.9]$$

Therefore,

$$\Delta G_{\text{dis}}/\Delta A = \gamma_{13} - \gamma_{12} + \gamma_{23} \cos\theta \quad [1.10]$$

Also, the work per unit area required for displacement can be determined from the following thermodynamic calculations. The work of adhesion, the amount of work energy per unit area required to pull apart two phases/species (suppose A and B) in contact with each other in presence of third phase, is given by the following equation (by Harkins in 1928).

$$W_{\text{adhesion (A-B)}} = \gamma_A + \gamma_B - \gamma_{AB} \quad [1.11]$$

Similarly, work of cohesion, the amount of work energy per unit area required to pull apart single species in terms of its interfacial tension, can be written as:

$$W_{\text{cohesion (A)}} = 2\gamma_A, \text{ as } \gamma_{AA} = 0 \quad [1.12]$$

From the above relationships, the amount of energy required to pull one liquid in presence of other liquid on the coal surface can be calculated, given that the equilibrium contact angle and surface tensions are available. The lower the energy (i.e. more negative free energy), the more thermodynamically favorable the process will be.

In the thermodynamic states, illustrated in Figure 1.15, the work required per unit area to remove water drops (3) from the coal surface (1) in any medium (2) will be,

$$W_{321} = W_{13} + W_{22} - W_{12} - W_{23} \quad [1.13]$$

Therefore, using Equations 1.4, 1.11, to 1.13, work per unit area for displacing a water droplet from the coal surface can simply be described as:

$$W_{321} = \gamma_{23}(1 + \cos\theta) \quad [1.14]$$

Equations 1.9 – 1.14 were later used in the thermodynamic energy calculations for the process, which was investigated in detail during the early phase of the reported research and therefore, will be described in Chapter 3.

1.7.2 Previous Research at Virginia Tech

Studies in dewatering by displacement were initiated at Virginia Tech in 1995 and included thermodynamic analysis and batch-scale testing with liquid butane. Sohn et al. (1997) conducted batch-scale testing on a mid-volatile bituminous coal with liquefied butane (pressurized 25-35 psig at room temperature) due to its large three-phase contact angle and ease of recovery (boiling point, 30.2°F). When clean coal slurry was gently agitated with large amounts of butane in a pressurized vessel, the resulting dry coal powder gathered on top of the water phase. The concentrate (approximately 2 grams) was removed from the top of the powder, and the initial weight for the moisture was taken after the sample sat at room temperature for 90 minutes. Testing indicated this was the approximate amount of time needed for butane to evaporate. The best moisture, i.e. 1%, was reported with a butane-to-coal mass ratio of 2.0, a solid content of 5%, and a settling time of 10 minutes. Initial testing showed that the butane recovery would be high due to ease of evaporation and the minor loss of butane in the water.

Yoon et al. (2011) reported that significant amounts of the process water could be entrained into the organic phase in the form of large water globules stabilized by hydrophobic coal particles. It is well known that particle such as coal in oil, with three phase contact angles larger than 90°, stabilize water drops in the oil phase. This stabilization of water leads to the formation of water-in-oil emulsion (Binks, 2002). In general, the hydrophobic liquid containing dry coal particles and entrained water in the form of water-in-oil emulsion is phase-separated naturally from the aqueous phase containing hydrophilic mineral matter. This hydrophobic liquid

can be transferred to a size-size separator, such as screen, classifier, and/or cyclone, to remove the globules of water from the dry coal particles (Yoon et. al., 2011).

Smith (2008) conducted extensive laboratory-scale bench test investigation to examine several hydrophobic displacement (separation and dewatering) methods of oil agglomerated products with liquid n-pentane. The methods included: hand shaking, screening, air classification, centrifugation, filtration and displacement. The research was conducted to identify conditions for stable agglomerates and procedures to evaluate pentane loss/consumption from evaporation curves. The major parameter studied was the pentane-to-coal mass ratio, varying from 0.11 to 1.99. It was reported that spherical agglomerates (formed when the pentane-coal ratio was between 0.21-0.34) responded most efficiently for dewatering purposes by hydrophobic displacement. Very high moisture was reported in all the methods when the pentane dosage increased to the ratio higher than 1. This may be due to the formation of thick curd-*esque* stable water-in-oil emulsions with coal, as identified by Capes and Darkovich (1984).

The hand-shaking method was performed continuously for five minutes to achieve consistent results (Smith, 2008). The investigator reported that the lowest moisture observed was 16% by weight, with the formation of loosely-bound floc-like agglomerates. In addition, the combustible recovery was higher than 90% irrespective of the oil dosage. In the screening method, floc-like agglomerates were passed through a coarse sieve. This method was an innovative concept because the dry solids associated with the agglomerates were passed through the screen while the water globules stabilized with coal particles retained on the top of the screen. Shaking of the sieve caused the small water droplets to coalesce and roll over the sieve. The coating of coal prevented the coalesced water from wetting the screen. The lowest moisture reported was 6.5% but the recovery decreased drastically to only 30% with this method (Smith, 2008).

An air-classification method was implemented briefly as described in the corresponding study (Smith, 2008). The method utilized spherical agglomerates, and air was used to remove the top agglomerate layer floating on the top of aqueous phase. The method was not developed further due to the unpredictability of throwing water into the agglomerates, because of high air pressure. The research indicated that the method was not draining any water trapped in the voids of the agglomerates structure, thus retaining the moisture in the final product.

According to the Smith (2008), the centrifugation method appeared to be the best method both in terms of lower moisture and high recovery product. The lower moisture was attributed to an increase in centrifugal g-force with higher rotation speed (Capes and Darkovich, 1984). The product moisture observed in the bench scale experiments was as low as 7.5%, and recovery was always greater than 90% with a centrifugation spin time of 1 minute at 3280 RPM and a pentane-coal ratio 0.32. The higher dosage resulted in agglomerates clumping and sticking together when being fed to the centrifuge.

When the vacuum filtration method was employed during the investigation (Smith, 2008) for dewatering pre-cleaned agglomerates, the filtration of these agglomerates resulted in moistures in the range of 20-32%. Lower moisture was observed on samples containing less ultrafines material and more coarse solids (Smith, 2008). The research also reported that the higher moisture values were caused by the small water droplets in agglomerate voids that were retained in the filter cake.

In the displacement method, Smith (2008) filtered the homogeneous coal slurry with large amounts of pentane without using any oil agglomeration process step. The experimental study provided the product moisture content in the range of 22-28% by weight, when pentane was poured on the top of coal slurry phase being filtered. In theory, the liquid pentane should displace the last droplets of water as it filters through the cake; however this was not observed during the bench-scale experiments (Smith, 2008). The lowest moisture reported was 19.7% when the vacuum pressure increased to 24mmHg with a drying time of 1 minute.

In 2010, a low-temperature drying process was developed at Virginia Tech to reduce the moisture of coal agglomerates. The technology was applicable to coal agglomerates and filtered flotation concentrate with less than approximately 22% moisture (Freeland, 2010). Three devices were developed to explore the process: a static breaker, an air jet conveyor, and a centrifugal fan. In each device, the coal agglomerates or cake were subjected to a high, mechanical shearing force. Compared to the other two methods, the centrifugal fan consistently produced a low-moisture product (less than 2%) without plugging (Freeland, 2010).

The newly developed low-temperature drying technique required a high amount of airflow to dry the particles. The relative humidity and temperature of the ambient air have a large impact on the water carrying capacity of the air. It was discovered that the process worked best by heating the air to at least 48.9 °C (120°F) (Freeland, 2010). Unfortunately, heating the air

added an additional cost to the process. Based on the economic model developed to calculate the cost of an industrial scale low-temperature dryer unit, it was discovered that the thermal dryer requires \$0.18/ton less energy-cost than the low-temperature drying technology (Freeland 2010).

Smith (2012) continued the study on the aforementioned innovative screening method to achieve low moisture product (< 10 %) and high coal recovery by implementing multiple stages of screening. Apparently, multi-stage screening had no effect on the reduction of moisture and in improving combustible recovery. Next, Smith (2012) attempted to utilize a Teflon-coated mesh to prevent wetting of the sieve with coal-coated water. The study showed that the Teflon mesh works better for a brief period of time; however, as the shaking continues, the water droplets coalesce together and with coal particles and eventually result in a thick sticky coal-mass on the screen.

Although the innovative screening method produced single digit moisture, the screen size area requirement and low recovery made it almost impossible to develop the process in a practical industrial setting. In addition, blinding of the screen and the risk of wetting the sieve could not be easily controlled in the plant environment (Smith, 2012).

Smith (2012) later employed two critical modifications that assisted in the development of technology proposed in this research. *First*, a cylindrical column reactor was introduced after mixing (formation of emulsions) step. The column was initially filled with clean water and then with pure pentane to create a distinct two-phase system. The liquid pentane floated on the clean water due to its lower density. *Second*, an ultrasonic source of energy was implemented on a batch-scale, which was used for the dispersion of coal water-in-oil emulsions in bulk pentane liquid column. The coal-water in oil emulsions was first formed by intensive mixing in a kitchen blender with a high dosage of pentane. The overflow of the kitchen blender from a custom made port, which was mainly emulsions, was pumped into the separate column reactor. An ultrasonic probe, operated at a high frequency (20 KHz), was inserted below the oil-water interface in aqueous phase from the bottom of the liquid-filled column reactor. As the emulsions were pumped into the column, they started settling at the interface. The ultrasonic energy dispersed these emulsions at the interface leaving hydrophobic coal particles in the pentane column and releasing trapped globules with associated clay into the water phase. The dispersed coal in pentane was collected from the overflow port of the cylindrical column (Smith, 2012).

Smith (2012) identified that the method is ineffective due to the poor recoveries. Later, instead of dispersing emulsions, spherical agglomerates were tested using the same method. After several attempts and modifications, the method was successful. Although the dispersion of agglomerates with an ultrasonic probe was effective, several operational issues were observed. Since, the viability of the process involving ultrasonic energy was evaluated during the initial phase of the current research work; the details of the process are discussed in Chapter 2.

The aforementioned research activities from the past decade at Virginia Tech have played a significant role in determining the key factors in the development of the innovative combined cleaning and dewatering technology. From a thermodynamic point of view, the concept of hydrophobic displacement of surface water can produce product moisture at a level that can only be achieved by thermal drying. None of the methods explored previously can be scaled-up safely and economically, therefore, the biggest challenge is to develop a well-engineered system to demonstrate the concept of dewatering-by-displacement on a large-scale, which is necessary to commercialize this technology. This research, as described in further chapters, particularly the development and scale-up of a low energy mechanical device to break the agglomerates, has been a huge step forward in achieving this goal.

In the later stage of the research, a commercial name given to the proposed novel cleaning and dewatering method — called the *Hydrophobic-Hydrophilic Separation (HHS)* process. In later chapters, the innovative method will be referred with the new name.

1.8 Research Objectives

The objectives of this research are:

- To fully develop a well-engineered Proof-of-Concept (POC) pilot-scale plant for the innovative cleaning and dewatering technology that can be employed commercially to recover the finest coal particles that are now discarded due to their high moisture content.

This goal has been achieved by:

- Conducting the fundamental studies and developing a bench-scale low energy mechanical device for breaking the agglomerates.
- Conducting comprehensive batch-scale testing with the novel breaking device and defining the parameters governing the process that were used to scale-up the process.

- Developing a continuous bench-scale process to enable the design of mass-water-pentane balanced flowsheet that can be used for the selection of equipment for the construction of a POC pilot plant with a capacity 100 pounds/hour feed.
- Constructing and scaling-up of the novel mechanical breaking device for the required capacity.
- Conducting pilot-scale tests with several types of fine coal slurries with the newly constructed POC pilot plant to demonstrate the cleaning and dewatering capabilities of the innovative technology.
- Establishing engineering criteria and determining the process economics for the design and operation of an industrial demonstration plant that will be constructed by the project sponsor.
- To demonstrate the capability of the innovative process for reducing environmental impacts associated with the fine coal slurries while simultaneously creating a potential source of new revenue and profit for coal producers around the world.

1.9 Research Organization

This dissertation consists of seven chapters. The *first* chapter has provided detailed background information and a comprehensive review of the previous investigations that have a pivotal role in the development of this innovative technology. The *second* chapter discusses the batch-scale testing program and the development of a laboratory-scale mechanical device (the heart of this process), batch-scale test result and modifications that assisted in the development of a process engineering flowsheet for the POC pilot plant. The *third* chapter discusses the fundamental aspects and the scientific studies conducted for understanding the proposed technology. The *fourth* chapter illustrates the construction and engineering of a proof-of-concept (POC) pilot plant. In addition, shakedown testing with newly constructed POC plant and the preliminary pilot-test results are discussed. While the *fifth* chapter provides the complete pilot-scale testing program with results and evaluation of the POC pilot plant, the *sixth* chapter analyzes the different engineering models for each unit operation involved in the process. The models and analysis can be valuable in designing the demonstration plant for the sponsors. Finally, the *seventh* chapter summarizes the whole research work and proposed future recommendations that can help in improving the process.

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CHAPTER 2 – Batch-Scale Developments of the HHS Process

2.1 Introduction

In the coal preparation plants, froth flotation is the most recognized technique used for cleaning fine (150 microns x 0) coal (Osborne, 1988). Flotation is a water-based separation process, which requires industry to use a dewatering step to produce sellable products. The flotation concentrate (clean coal) is typically dewatered by conventional means such as vacuum filters, screenbowl centrifuges, or by advanced dewatering methods like the hyperbaric centrifuge technology (Schultz et al., 2012). Nonetheless, existing technologies cannot produce single-digit moisture values that can replace thermal dryers, which are very expensive (Osborne, 1988) and no longer considered as a viable drying option due to regulations and several restrictions in the United States.

Another fine coal cleaning process that has been explored in the past is selective agglomeration. Several studies conducted on the oil agglomeration process using fine coal feeds and short chain hydrocarbons achieved better combustible recoveries (Keller, 1985) compared to conventional flotation, but the process was not preferred in the United States due to high costs associated with oil consumption. Furthermore, typical moisture in the coal agglomerates is 40% by weight (Keller, 1985), which makes the product an undesirable commodity in the current market.

In light of this, researchers at Virginia Tech developed an innovative technology involving the concept of dewatering by displacement, which was first proposed by Yoon and Luttrell (1995). Since surface forces get stronger for micron size particles, an additional proprietary separation stage was added to treat the agglomerated coal. The novel technique simultaneously cleans and dewateres well-liberated fine coal feedstocks (some of which are currently discarded) and provides a final product with low single-digit ash and moisture contents at a very low energy.

The proposed technology is called the *Hydrophobic-Hydrophilic Separation (HHS)* process. The theoretical concept of hydrophobic-hydrophilic separation was tested on a bench-scale reactor using several coal-feed samples from the United States to demonstrate the thermodynamics behind the proposed process. The bench-scale unit was specifically designed to

serve the purpose of identifying and evaluating key process parameters, which later will be helpful in the scale-up of the process. This chapter discusses the development of the HHS process bench-scale systems, designing of a novel low-energy dispersion device, and engineering analysis of batch-scale testing data for the development of the process flowsheet.

2.2 Experimental Procedures

This section describes the HHS process laboratory testing by various methods utilizing non-polar hydrophobic liquids to separate both moisture and mineral matter impurities from fine coal samples. Several challenges were encountered during the development of batch-scale testing process and, therefore, several modifications to the process were required, which will be discussed in later sections. Two methods for breaking the agglomerates, including the use of a novel vibrating mesh design, were evaluated using fine coal samples from major coal preparation plants in the United States.

2.2.1 Material and Method

During the course of development and testing, the only hydrophobic reagent used was n-pentane liquid. Pentane, because of its low boiling point (98°F), is easy to evaporate and recover by condensation. Liquid pentane (C₅H₁₂) is a colorless, immiscible liquid and short-chain aliphatic hydrocarbon with an alkyl radical group, which is hydrophobic in nature. The density of n-pentane is 0.626 g/cm³; therefore pentane liquid floats on top of water in a pure pentane-water system. Table 2.1 outlines some of the physical and chemical properties of n-pentane. For bench scale experiments, n-pentane (98% pure) was procured from Alfa Aesar.

The experimental set-up included a regular kitchen blender (Black & Decker BLC12650) equipped with variable speed controller for high/low shear mixing, a 60 mesh sieve for separating agglomerates from the “dirty” aqueous phase, and custom-made glass columns designed and manufactured at the Virginia Tech (Figure 2.1). The coal agglomerates retained on the top of the sieve were poured manually from the top in the glass column, which was initially filled with n-pentane liquid and water. During the initial course of batch testing, an ultrasonic probe was initially used. Later, a low-energy vibrating-mesh device was developed for dispersion of the agglomerates.

Table 2.1 Physical and chemical properties of n-pentane

Properties	Data (units)
Molecular Weight	72.15 g/mol
Boiling Point at 1 atm	36.1°C (98 °F)
Surface Tension	0.016 N/m at 20°C
Liquid water interfacial tension	51.9 dyne/cm
Vapor (gas) specific gravity	2.5 (compare to air 1.0)
Latent heat of vaporization	153.7 btu/lb
Solubility with water	0.04 mg/L
Viscosity	0.000298 N-sec/m ² at 20°C
Specific Gravity	0.626 at 20°C
Ideal gas heat capacity	0.397 btu/lb at 20°C



Figure 2.1 Customized bench-scale reactors used for laboratory testing

2.2.2 Batch Testing Samples

Several fine (150 x 44 μm) and ultrafine coal (44 μm x 0) samples were tested from northern and central Appalachian coalfields. Most of these coals were low-volatile bituminous coals, which are hydrophobic in nature. Samples of screenbowl main effluent (below 44 micron) were procured from the Bailey and Buchanan plants from Consol Energy and the Beckley and Sentinel plants from Arch Coal. A sample of 6-inch deslime cyclone overflow, which was also

minus 44 micron, was taken from Arch's Cardinal and Leer preparation plants. Another set of fine coal flotation feed samples was procured from the Kingston plant at Alpha Natural Resources.

2.3 Initial Testing with Ultrasonic Energy

The batch-scale tests were initially performed with Bailey's screenbowl main effluent samples using ultrasonic energy to break the agglomerates. The feed samples contained 41.1% ash value by weight on a dry basis and contained more than 90% minus 44 micron particles. The coal samples, when procured, were decanted to obtain feed slurry with a high percent solid.

2.3.1 Study with Emulsions

The feed was first diluted to 6% solids by weight using fresh water. Equal volumes of hydrophobic liquid and coal slurry were mixed in a 600 mL container using a kitchen blender at low intensity. The mixing was continued until the phase separation was visibly observed. The resulting product consisted of two layers. The upper layer, which was a mousse-like thick coal mass, consisted of coal-water-oil emulsions floating on top of water. The bulk of the water and hydrophilic mineral matter separated and settled to the bottom of the blender. The clean coal mass with pentane floating on the aqueous phase was separated using a 60-mesh sieve. It was observed that the coal mass retained on the screen had large water globules stabilized by fine coal particles in oil, which appears like a paste.

The paste-like coal mass was then fed into a 1.5-inch diameter glass column equipped with multiple overflow ports at different heights. The column was initially filled with clear pentane and water. An ultrasonic probe manufactured by Qsonica (Model: Q700) operating at a frequency of 20 kHz was mounted at the bottom of the column so that the tip of the probe remained in the water phase as shown in Figure 2.2. As the probe operated, the water-in-oil emulsions were broken in a way that water trapped within the emulsion drained out of the hydrophobic liquid (n-pentane) phase. Three distinct phases existed within the reactor. The lowest phase in which the tip of the ultrasonic probe was submerged consisted of water and ash. Over time, a buildup of emulsions formed at the oil/water interface. The uppermost layer was mostly hydrophobic liquid with dry coal powder dispersed in it. As the top layer from the mixer

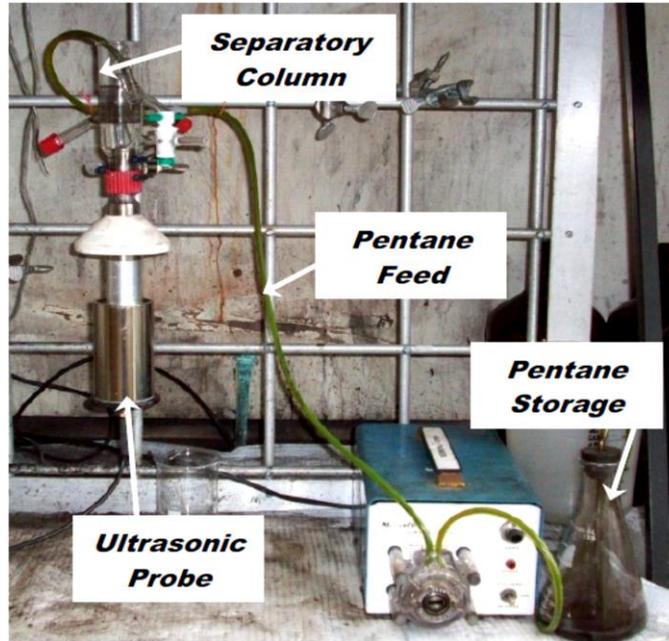


Figure 2.2 Experimental setup used for breaking agglomerates using ultrasonic probe

was fed into the column, the hydrophobic liquid and suspended coal particles exited the column through an overflow port.

After a certain time period, the emulsion layer became too thick for the ultrasonic waves to effectively break. Eventually, the column filled up with the emulsions and coal began to exit the column from the tailings port located at the bottom of the reactor. This method was effective only for initial time period, and after a long operating time (around 20 to 30 minutes), breaking emulsions with ultrasonic waves became ineffective. The product sample received in the first few minutes of the test mostly contained clean liquid pentane with a very small amount of coal (< 0.2% solid concentration), but not enough to conduct any analysis. Therefore, moisture and ash values could not be determined for these small products. Similar procedures were followed in later test runs by changing operating parameters such as mixing intensity, reducing feed percent solids, increasing agglomeration retention time and reducing oil dosage in order to eliminate the formation of these stable emulsions.

2.3.2 Study with Agglomerates

Due to the low throughput and inability to continuously run the process with emulsions, other coal and hydrophobic liquid products that could be fed into the separatory column were explored. It was observed that when the oil dosage was reduced to less than 30% by weight and

the residence time was increased, the fine coal from the feed slurry formed loosely bound spherical shape coal agglomerates. Later, the retention time was reduced by employing high-intensity mixing for the first few seconds, followed by low-intensity mixing for one minute. The spherical agglomerates formed by this procedure were very easy to disperse (as compared to emulsions) in the pentane column and therefore followed in further batch-scale testing.

Samples from the Bailey preparation plant screenbowl main effluent and Kingston plant flotation feed were tested with this method. Coal agglomerates were prepared by mixing 600 mL of slurry (6% solids) and 10 mL of hydrophobic liquid in the variable speed kitchen blender. For the initial 20 seconds of mixing, the blender was operated at a high speed to ensure a high-shear mixing environment. With high-shear mixing, micro-size agglomerates were observed. To grow the agglomerates, the blender was turned down and operated at low shear for another 40 to 60 seconds. The spherical agglomerates formed floated on top of the water phase. The agglomerates were poured across a 60-mesh screen to remove “dirty” water containing unwanted impurities of mineral matter. The water fell through the screen, while the agglomerates remained on top. In addition, no large stable drops of water were observed in this procedure. The loosely bound spherical agglomerates were large, usually with top sizes in the range of 0.8-0.9 mm, and had fairly low moisture values (35 – 55% by weight). By changing mixing time and hydrophobic liquid dosage, agglomerate size and moisture varied as well.

The ultrasonic probe described in the previous process was used to break the agglomerates. The column was filled with a small volume of water so that the water level was approximately 1 inch above the probe tip. The remainder of the column was filled with pentane up to the overflow port. Then, the coal agglomerates were poured into the hydrophobic liquid phase. The agglomerates broke up and coal particles dispersed into the hydrophobic liquid phase almost immediately. Additional hydrophobic liquid was pumped continuously from the top of the column for continuous flushing of the dispersed solids. The overflow was collected in a beaker and the hydrophobic liquid was evaporated at 40°C, leaving behind the dry clean coal product. Due to a higher product solids content (1-2% solids), the throughput with this method was much higher than the emulsion method. In addition, no build-up of stable emulsions at the oil/water interface was observed during the test runs. Unfortunately, a major issue was observed after a long operation time. Due to excessive heat caused by the large energy input, the probe started boiling the water.

Table 2.2 Batch-scale test results with agglomerates using ultrasonic probe

Kingston Coal, Beckley, Alpha Natural Resources				
Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
54.52	1.19	4.53	92.00	89.95
	1.16	4.38	92.44	90.54
	1.07	4.87	90.56	87.97
	1.10	4.05	91.67	89.45
Bailey Coal, Consol Energy				
41.11	1.15	3.06	86.94	89.94
	8.42	2.43	84.19	87.30
	0.60	3.36	86.97	90.01
	1.01	3.60	87.41	90.43

phase inside the reactor. Therefore, the tests were only conducted for a small time period, usually less than 10-15 minutes. The test was repeated multiple times with both the feed samples. The clean coal and tail samples were collected and analyzed for each test. Table 2.2 provides a complete set of test results. The achieved moisture of the final clean coal product was below 2% by weight and combustible recoveries as high as 90% were obtained, indicating the process can separate unwanted components from coal using the concept of hydrophobic displacement.

2.3.3 Development of Semi-Continuous Bench-Scale System

The detailed schematic of the newly constructed semi-continuous bench-scale system is shown in Figure 2.3. The whole apparatus was designed and assembled using in-house facilities at Virginia Tech. The continuous bench-scale system has five major units: a mixing vessel, a phase separator, a settling vessel, an evaporator and condenser, and a reagent recycling vessel. The preliminary batch-scale testing provided crucial information, such as the process is ineffective with emulsions and very effective with agglomerates. This is because the coal-hydrocarbon liquid mixture produces a very stable emulsion with high pentane dosage in strong mixing conditions. Trial-and-error testing indicated that the stable emulsion could not be broken with simple agitation, or sound waves, or with high frequency ultrasonic waves, in the separatory column (phase separator). Spherical agglomerates were prepared with two stages of mixing and a low dosage of pentane. In the existing system, high-shear mixing was hard to implement with the small glass units, therefore the mixing chamber was only used for low-shear mixing. The high-shear mixing was achieved with a kitchen blender and pumped into the mixing vessel.

The phase separator was assembled with a high-frequency ultrasonic probe at the bottom of the vessel. To overcome the issue of excessive heating, the test cell was equipped with a cooling water jacket. The overflow from the mixing vessel, which contains coal agglomerates and the hydrocarbon liquid, creates an interface of water and hydrocarbon liquid in the phase separator reactor. The ultrasonic energy from the aqueous phase was used to break and disperse the coal agglomerates. The dispersed particles moved into the pentane phase and eventually released water and associated ash-bearing minerals into the aqueous phase. Phase separator columns of different height were used to determine the optimum pentane column height. It was observed that low column heights worked better. The poorer performance may be due to the lower energy per unit volume associated with the taller columns.

The biggest challenge faced during the operation was to keep the water-oil interface level constant in the phase separator. Due to the low column height, the interface level was hard to maintain, which led to the formation of stable emulsions produced by the ultrasonic energy inside the reactor. Furthermore, no screen was employed in the existing system after the high/low shear mixing vessel, because screening was hard to implement in the small-scale continuous circuit. This also promoted the formation of stable emulsions, as lots of water from the mixing vessel reported with the agglomerates. Because of these operating issues, further test runs with this approach were discontinued. In later test runs, the tailing from the phase separator was pumped constantly at high speed so that the interface height could be controlled.

Once the dispersion process in the phase-separator reactor appeared to work, the clean coal in the bulk hydrocarbon liquid from the phase separator was pumped to a settler vessel, where coal settled with time and was transferred into the evaporator, while liquid hydrocarbon reported back to a reagent tank from overflow of the settling vessel. The evaporator used was a closed glass jar with vapor ports, which was placed in a hot water container mounted on a hot plate. The temperature inside the glass jar was maintained between 40°C to 50°C. The hydrocarbon from the settler inside the jar eventually boiled out and was captured using a two-stage condenser that passed the pentane back into the reagent tank. The condenser was equipped with a water chiller unit that maintained the cooling water at 5°C.

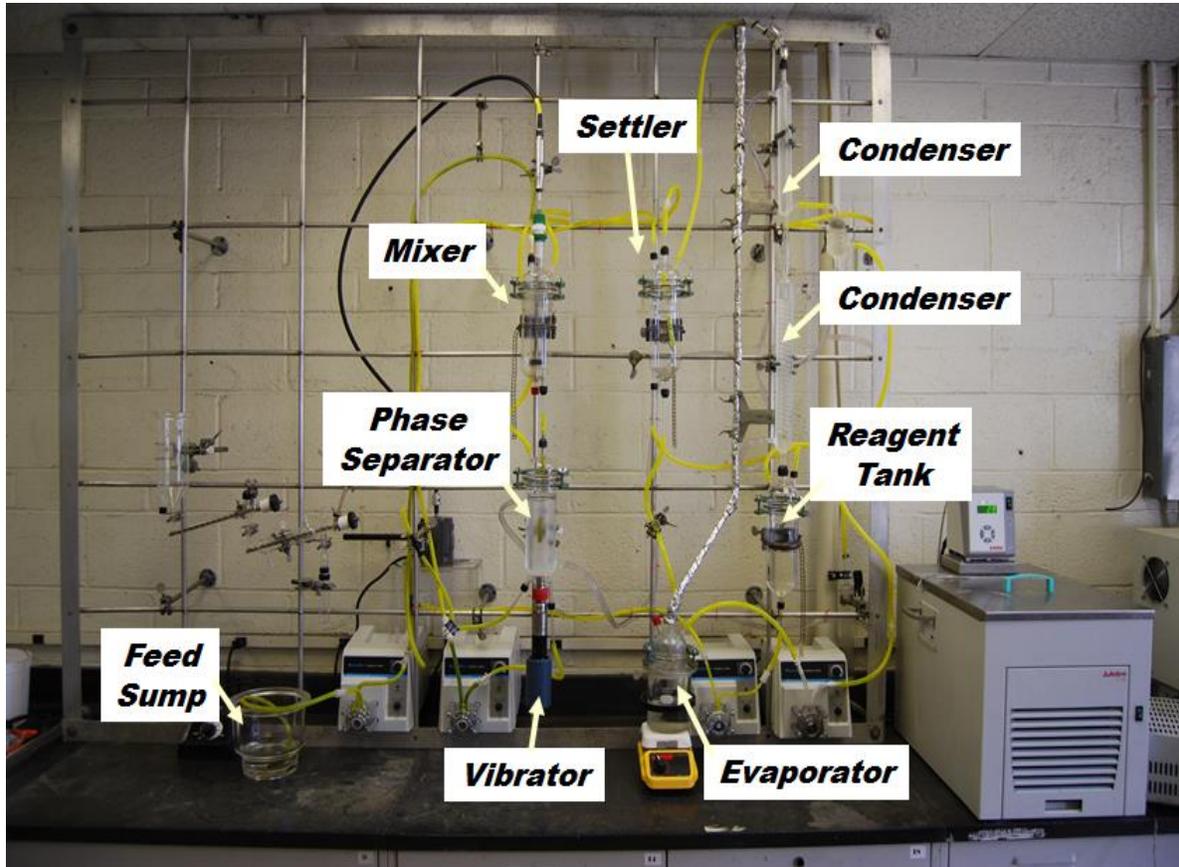


Figure 2.3 Constructed bench-scale continuous testing circuit developed for HHS Process

Table 2.3 Continuous system test results using ultrasonic probe

Screenbowl Main Effluent, Bailey Coal, Consol Energy				
Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
40.4	5.5	4.9	80.1	82.4
	5.5	5.0	81.4	85.5
	3.8	3.3	80.1	83.9
	2.0	5.5	83.2	87.3
	0.9	5.0	80.6	84.8

The clean low-moisture coal product obtained in the jar was collected manually once all the pentane was evaporated and was subjected to moisture and ash analyses. Multiple tests were conducted under the same operating conditions. Table 2.3 shows the complete set of test data for this system. As shown, the moisture and ash contents in the final products were below 6% with recoveries as high as 87.3%.

2.3.4 Dispersion with Ultrasonic Energy – Discussion

Using an ultrasonic probe for breaking emulsions proved to be ineffective for the process. The maximum overflow concentration of product achieved was 0.2% solids by weight. The low quantity of product sample made it impossible to analyze for moisture and ash contents. It was observed that the ultrasonic vibrations did not actually break the emulsions but rather split the emulsions into smaller and smaller emulsions. It must be noted that ultrasonic energy is a high-energy source, which is only concentrated close to the probe tip rather than uniformly distributed in the whole pentane column.

The water-in-oil emulsions formed in the method were very stable in nature, which makes it harder to break them. It was observed that, due to the high dosage of hydrophobic liquid, water droplets stabilized by coal particles were found suspended in the oil phase. It is well known that hydrophobic particles, such as micron-size coal, with three-phase contact angles greater than 90° can act as “particle surfactants.” Therefore, these particles can stabilize water droplets in the bulk oil phase and form water-in-oil emulsions (Binks, 2003). These emulsions, which are highly stable in nature, contain 60 to 80% water and resemble “chocolate mousse” (Fingas and Fieldhouse, 2004).

On the contrary, the fine coal spherical agglomerates typically have 40% moisture by weight (Keller, 1985) and do not contain stable water globules, as was found in emulsions. Breaking agglomerates using ultrasonic vibrations was successful both in cleaning and dewatering coal. The main advantage of using agglomerates over emulsions was a higher throughput in the product. When agglomerates were introduced in the reactor, they quickly dispersed into the pentane column. Consistent low moistures and high recoveries were achieved with the dispersion of agglomerates.

While the breaking of agglomerates with ultrasonic vibrations was successful, a major operating issue was encountered in using the probe, i.e. heating of the pentane and water column. The ultrasonic probe operated at a frequency of 20 kHz, which caused the tip to heat excessively. The probe was always placed in the water phase to isolate the pentane phase from the ultrasonic tip. However, after approximately 15 minutes of operation, the probe would generate enough heat to boil the water, which in turn caused the pentane layer to boil. After operating for approximately 20 minutes, large cavities started appearing at the tip of the probe, and the glass column was very hot when touched. It is believed that the water directly against the tip was hot

enough to boil, causing these cavities. At that point, the tip of the probe was very hot and was considered to be unsafe for further operation. Therefore, experiments were never conducted for longer than 25 minutes. Even though the results were highly impressive, this issue generated a serious threat in scaling-up the technology.

Another problem was the cost associated with scaling up of ultrasonic source of energy. It is not economical considering the market value of the product. Due to the severe issues with safety and scale-up of the ultrasonic technology, other possible designs for breaking the agglomerates were explored that could be more readily utilized on a commercialized scale.

2.4 Development of Batch-Scale Vibrating Mesh

Spherical agglomerates are held by intermolecular forces (Kendall, 1988), which are weak range forces. Interfacial thermodynamics of the process, which will be discussed in detail later in this document, showed that the high amount of energy provided may overcome free energy associated with cohesion of water droplets released after agglomerates dispersion, and therefore can hinder their coalescence mechanism. The thermodynamics also showed that the energy requirement is very low for a pentane liquid to displace a water drop from the coal surface in the three-phase mixture. In light of this, a simple mechanical device was explored that could serve the purpose of effectively breaking of agglomerates, keep the dispersed particle in suspension, and accelerate the process of coalescence of water droplets.

Richardson and Thorpe (1995) developed a simple mechanical device for dispersion that is used in the dairy industry. The apparatus was designed to measure milk coagulation time and rigidity in formation of fermented dairy products. This apparatus included a flat disc-shaped probe that was suspended on a wire placed into a fermented dairy product-making vessel filled with milk. The probe was reciprocated through a small vertical distance within the coagulating milk in the vessel. This mechanical device was installed on the top of the tank with the disc completely submerged in the milk and operated at constant low frequency below 2 Hz (Richardson and Thorpe, 1995).

This Richardson and Thorpe (1995) concept was modified and implemented in the current work for the purpose of breaking agglomerates and promoting water coalescence in the pentane column. Similar to the abovementioned device, where particles of milk fat find each other and coagulate, the developed mechanical vibrating device may assist the released water



Figure 2.4 Constructed vibrating mesh lab scale unit.

droplets in finding each other and coalescing. The shaker was designed only to create up-down motion. A thin shaft with two variable size mesh discs of aperture 0.5 mm and 80 micrometer was connected to an electro-dynamic shaker, manufactured by Modal Shop INC model 2007E. Considering that frequency and amplitude of vibration are important parameters in controlling vibrating energy, the shaker was equipped with a variable speed controller device, which provided frequencies ranging from 0 – 60 Hz at variable amplitudes. The discs diameter was kept close to the inside diameter of the reactor to provide maximum surface area for dispersion. The two meshes (0.5 and 0.08 mm aperture) were separated one inch apart with the bottom disc connected at the end of the shaft. The complete assembly is exhibited in Figure 2.4.

2.4.1 Experimental Procedure with Vibrating Mesh

Prior to dispersion, similar methods were used to form the coal agglomerates utilizing the kitchen blender. The separation took place in a custom-made glass reactor that was 5-inches high and 1.5-inches in diameter. The reactor was initially filled with water only up to one-third of the total height. The newly developed vibrating mesh device was inserted inside the reactor from the open top such that the lower disc was just above the water surface. The reactor was then filled

with pentane liquid just below the overflow port. The schematic of the laboratory testing system is shown in Figure 2.5.

The electro-dynamic shaker, which controls the vibrating mesh device, was operated at a constant frequency throughout the testing period. Agglomerates were then poured from the top of the reactor. The fine coal particles from agglomerates started dispersing almost immediately (as visually observed) in the pentane column leaving the residual water and mineral matter in the aqueous phase. The dry coal in pentane liquid was collected from the overflow port of the reactor in a glass beaker. The evaporator-condenser unit, which was designed for the continuous bench-scale system, was used to evaporate and recover the pentane consumed in the process. The pentane-free clean coal product was collected manually from the evaporator glass vessel and analyzed.

The novel mechanical vibrating-mesh device worked very efficiently as the analysis results showed similar moisture and recoveries as obtained using the ultrasonic probe. The biggest advantage with this system is that it is *very safe* to use. The method also utilizes only a small amount of energy and produced very high quality products. Also, due to the inherent simplicity of the vibrator, the device can be scaled-up. Another crucial observation was that this method provided a much higher throughput due to the higher solids content of the overflow product (up to 12% solids). It is believed that the vibrating device also creates a uniform energy distribution in the reactor, unlike the ultrasonic probe.

2.5 Batch Scale Results – Mechanical Vibrating Mesh

Breaking agglomerates with the novel low-energy mechanical vibrating mesh was used in both cleaning and dewatering fine coal material. The dispersion rate of the fine particles was observed to be higher compared to previous methods, which resulted in higher throughputs and lower moisture clean coal products. Several coal samples were tested, from metallurgical coal to steam coal, as well as particle size ranges from minus 325 mesh (screenbowl main effluent and 6-inch diameter “deslime” cyclone overflow) to minus 100 mesh (flotation feed). Results from the testing of each coal sample are discussed separately in this section.

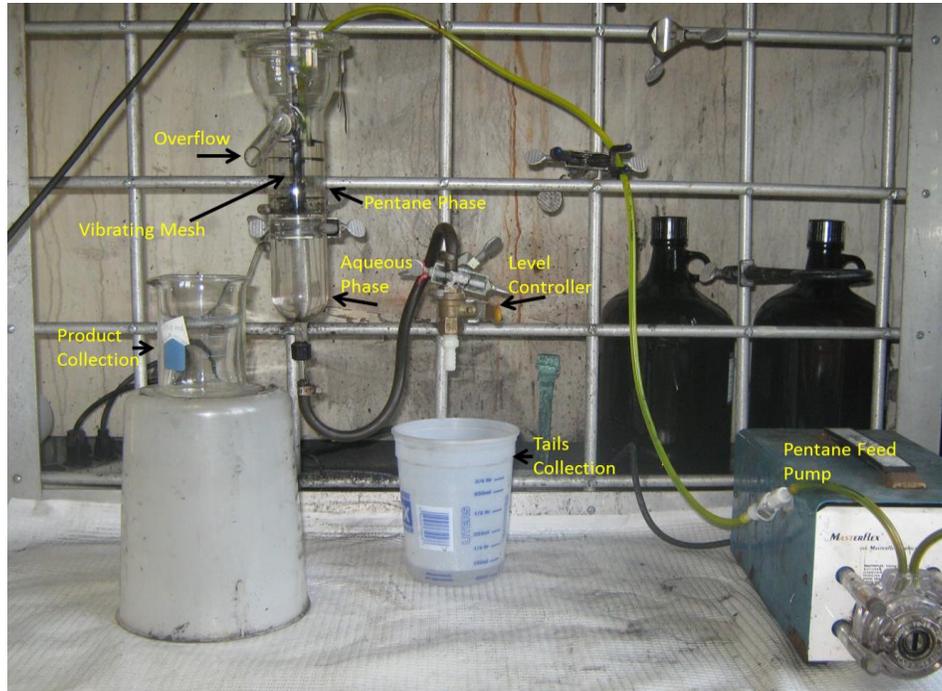


Figure 2.5 *Constructed bench-scale experimental set up for testing vibrating device*

2.5.1 Screenbowl Main Effluent

Screenbowl centrifuges are commonly used to dewater flotation products in coal preparation plants. The overflow of the centrifuge bowl, which is the main effluent, is rejected into thickeners as waste. It is well known that the effluent loses almost 50% of the ultrafine (minus 325 mesh) particles from the flotation concentrate (Luttrell, 2011). At the preparation plants, this stream usually has flotation chemicals, such as frothers and collectors. Also, it has very low percent solids by weight, typically 3-6 % in range.

Four different screenbowl main effluent samples were tested — two each from Consol Energy and Arch Coal. The samples were procured from Consol’s Bailey and Buchanan plants and from Arch’s Beckley and Sentinel plants. Tables 2.4 – 2.7 summarize the test results of screenbowl main effluent using the HHS process bench-scale system. As shown, the process produced consistently low moistures and high coal recoveries. The combustible recovery on metallurgical coals, such as those from the Buchanan, Beckley and Sentinel plants, was exceptionally high (96 – 99%) in all the batch-tests, while the steam coal recovery from Bailey plant was as high as 90%. As anticipated, the moisture percentage in the final product was in single digits for all types of coal, indicating the HHS process is ideally suited to recover lost coal in discarded streams from preparation plants.

Table 2.4 Batch test results from Bailey screenbowl main effluent

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
40.4	4.8	3.8	86.1	89.6
	4.1	5.0	86.1	89.8
	4.9	6.4	86.9	90.7
	3.9	4.3	85.8	89.4
	2.3	4.6	77.0	80.9
	2.0	3.3	81.7	85.4
	2.5	3.9	84.1	87.9
	4.3	4.0	86.4	89.9

Table 2.5 Batch test results from Buchanan screenbowl main effluent

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
11.3	8.1	2.3	84.0	98.0
	6.1	2.0	84.3	98.0
	6.8	2.7	83.8	98.1
	3.3	2.4	82.9	97.9
	5.2	2.3	81.7	98.0
	2.8	2.2	83.0	97.8

Table 2.6 Batch test results from Beckley screenbowl main effluent

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
10.7	7.4	3.2	88.4	98.9
	3.8	3.1	79.4	97.7
	2.1	3.1	77.6	97.5

Table 2.7 Batch test results from Sentinel screenbowl main effluent

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
13.7	5.5	5.0	75.6	96.5
	4.9	5.0	76.3	96.7

2.5.2 Deslime Cyclone Overflow

In United States, a modern practice in the coal preparation industry is to remove ultra-fine particles (minus 325 mesh) from the flotation feed by using 6-inch diameter classifying “deslime” cyclones (Bethell and Barbee, 2007). This practice increases the recovery of coarser coal from the flotation process and improves downstream dewatering performance. The overflow from the cyclone, which contains all 325 mesh material from raw feed, is typically rejected to

Table 2.8 Batch test results from Cardinal 6” deslime cyclone overflow

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
53.6	3.1	2.8	84.2	78.8
	3.5	3.9	88.0	84.7
	3.8	2.9	87.2	83.4
	10.6	3.0	85.0	80.1
	9.1	3.7	89.4	86.7

Table 2.9 Batch test results from Leer 6” deslime cyclone overflow

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
50.9	3.4	3.6	89.3	87.9
	6.1	4.5	87.3	85.5

tailings thickeners. The percent solids in deslime cyclone overflows are typically higher (6-8%) compared to screenbowl main effluents. In addition, since it is a run-of-mine raw feed, the stream is completely free of chemicals.

Two deslime cyclone overflow samples were tested, both from Arch Coal. The samples were procured from the Cardinal and Leer preparation plants, both of which process high-grade bituminous coals that are sold into the premium metallurgical coal market.

The results shown in Tables 2.8 – 2.9 indicate that the HHS process can achieve high combustible recoveries in range from 79-88% with product moistures between 3-10%. The HHS process also responded very well with the deslime cyclone overflow feed and, therefore, can be used to recover this process stream.

2.5.3 Flotation Feed

The objective of this portion of the research study was to develop and demonstrate the HHS process for recovering coal from ultrafine discarded streams. However, the scope of this technology is not limited, and the ultimate goal would be to modify the existing fine coal circuit by replacing the flotation process with the HHS technology, provided it responds well to upgrading of flotation feeds.

In light of this, two different flotation feed samples were tested with HHS process. The feed size is typically composed of 100 x 325 mesh particles. Samples were procured from

Table 2.10 Batch test results from Bailey flotation feed samples

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
44.9	1.1	5.5	87.1	88.7
	0.7	4.6	87.7	89.2
	2.7	3.0	88.7	90.0
	1.5	3.1	88.5	89.8
	3.2	3.4	87.9	89.2
	4.7	3.2	89.2	90.5
	1.6	3.4	89.1	90.4
	1.0	3.5	89.1	90.4
55.7	1.8	4.7	90.6	87.4

Table 2.11 Batch test results from Kingston flotation feed samples

Feed Ash %	Product Moisture%	Product Ash %	Reject Ash %	Combustible Recovery %
52.6	0.7	3.2	91.6	90.1
	1.0	3.6	91.7	90.3
	0.7	3.5	91.4	89.9
51.0	1.1	4.2	90.0	88.9

the Bailey Preparation Plant, which owned by Consol Energy and is located in the northern Appalachian Coalfields, and the Kingston preparation plant which owned by Alpha Natural Resources, and is located in the central Appalachian Coalfields.

Batch test results of flotation feed tested with the novel technology bench-scale system consistently achieved exceptionally low moisture and high combustible products, as exhibited in Tables 2.10 – 2.11. The combustible (carbon) recovery on Bailey’s and Kingston’s coal samples were as high as 90.4% and 90.1%, while the moisture percent was in range of 0.7-4.7% and 0.7-1.0%, respectively.

2.5.4 General Observations

The low energy mechanical vibrating mesh was proven to be very successful in breaking the agglomerates during the batch-scale testing. This method can be scaled up and is economical and safe to use as compared to the alternative approach of ultrasonic vibration. This innovative breaking device creates a uniform hydrodynamic shear field in the hydrophobic reagent column, which effectively disperses the coal particles and keeps them suspended in the column. Furthermore, the mesh design and low vibration frequency promotes water coalescence in the hydrophobic liquid phase, which is crucial for moisture reduction.



Figure 2.6 Final tail and product samples produced from HHS process bench-scale system

The vibrating mesh device was proven to be highly effective in producing consistently low moisture and ash values. In addition, the mesh provided higher percent solids in the overflow as compared to the ultrasonic device, which considerably increased the throughput productivity from the process. In the method, no formation of stable water-in-oil emulsions was observed during any of the test runs. The bench-scale system of HHS process demonstrated excellent cleaning capabilities with ultrafine particles, as illustrated in Figure 2.6. The photograph corresponds to final reject samples with ash contents of 80-90% and a final clean coal product with less than 5% moisture and ash. For an efficient separation, the bottom screen of the mechanical vibrating mesh device must be just above the water-pentane interface inside the column, otherwise the formation of micro-emulsions were observed after long periods of operation.

The major operating parameters that control the input vibration energy were found to be the vibrational frequency (f) and the amplitude of the vibrations (A). It was observed that these parameters affect the process efficiency individually and in the combination of each other. In addition, it was also observed that the ratio of the amplitude of vibration and pentane column length also affects the product quality. In light of this, parametric studies were conducted focusing the effect of vibration energy and length ratio on product moisture. The details are

discussed in Chapters 3 and 4, as these two criteria were considered for the development of vibrating mesh reactor for the HHS process Proof-of-Concept (POC) demonstration plant.

2.6 Bench-Scale Testing Results - Discussion

The results obtained from bench-scale testing of HHS process have successfully demonstrated that the concept of dewatering by displacement can be implemented for the efficient cleaning and dewatering of ultrafine particles. To evaluate the cleaning capabilities of the process, recovery-rejection curves were plotted for all the samples tested on bench-scale, as illustrated in Figure 2.7. The diagonal lines represent the separation efficiency of the process. The “*separation efficiency*” is a performance level indicator based on carbon recoveries and ash rejection values. Mathematically, the separation efficiency is defined as the recovery of desirable material in a given product minus the recovery of undesirable material in the same product. In the case for coal cleaning, the separation efficiency (E) can be obtained from Equation 2.1.

$$E = R - (100 - J) = R + J - 100 \quad [2.1]$$

In this equation, R is the combustible recovery and J is the ash rejection. R represents the percentage of combustible matter present in the feed that reports to the clean coal, while J represents the percentage of ash present in the feed that reports to the reject.

The performance evaluation of a process using separation efficiency is useful, as both recovery and rejection terms normalizes the variation in the feed. As shown in Figure 2.7, the separation efficiency achieved using the HHS process was very high in all the cases, although some small variations are noted because of differences in the feed ash of each stream. In the case of the screenbowl main effluent feed samples, which are typically 10-15% ash, almost all of the carbon from the feed is recovered. In cases involving the deslime cyclone overflow or flotation feed samples, which are typically much higher in ash, the data showed that almost all the ash from the feed is discarded in the tailings.

The biggest advantage of the proposed novel process is the moisture reduction associated with fine particles. Conventional dewatering methods produce moistures between 10-30%, which is still above most market specifications (typically 6-8% surface moisture). These traditional methods also require low water content in the feed for efficient dewatering. Screenbowl centrifuges produce 16-18% moisture product and can accommodate up to 35% water in the feed (Keles, 2010), but this technology typically loses half of the minus 325 mesh coal particles

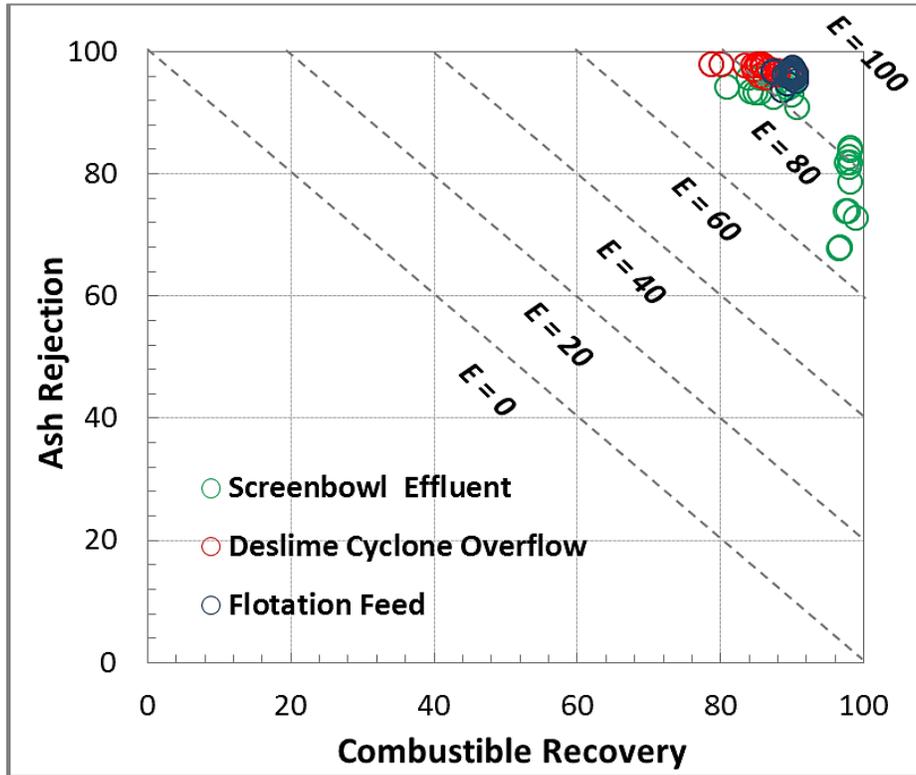
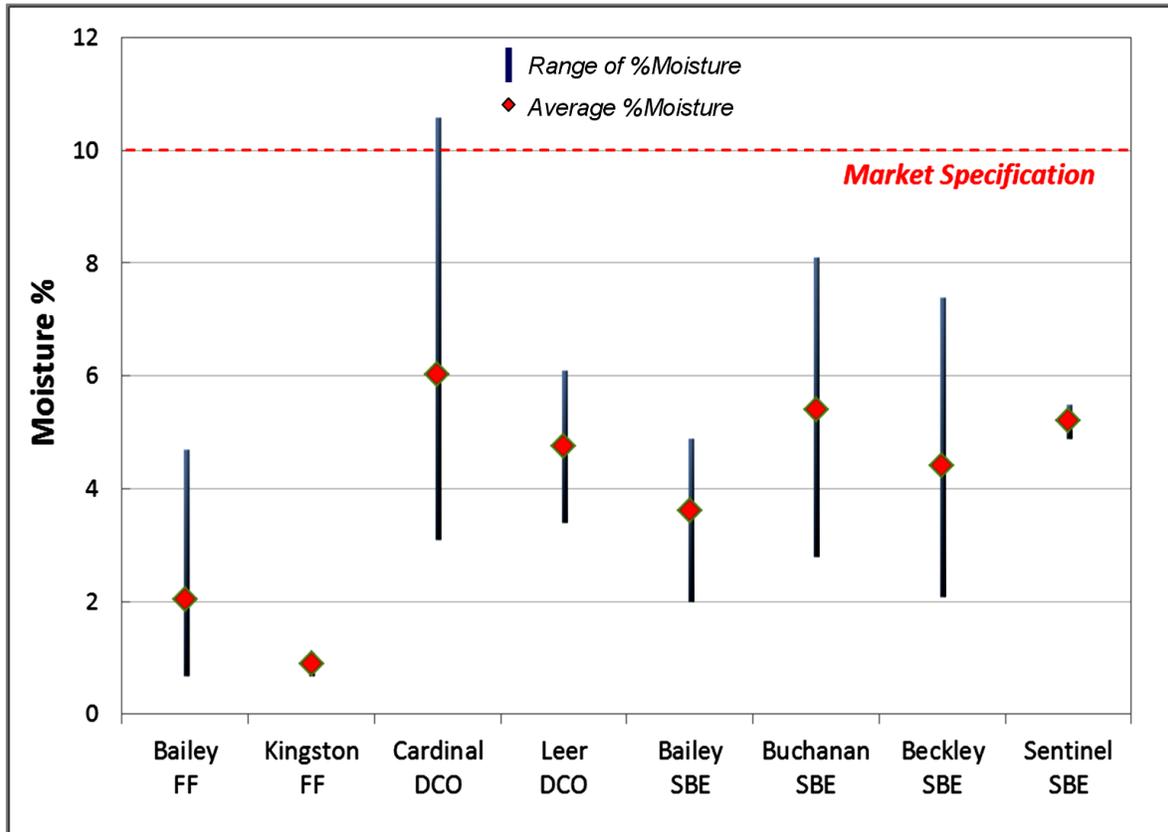


Figure 2.7 Separation efficiency data for the HHS process bench-scale system

(Luttrell, 2011). Vacuum disk filters, which were once popular in the United States, produce 22-25% moisture products from higher moisture feeds and recover up to 97% of the solids (Osborne, 1988). An advanced technology, hyperbaric centrifugation system, can produce as low as 13% moisture product from 10% solid feed (Keles, 2010), although few industrial installations of this technology have been implemented due to the high capital cost of this unit. The laboratory test results have showed that the HHS process is far superior to any of these existing dewatering technologies. The bench-scale system has demonstrated that a low moisture product (below 10%) is possible by using HHS process, which in the past could only be achieved by thermal dryers.

Figure 2.8 depicts the range and average values of clean coal product moisture (percentage by weight) of each coal sample tested on HHS process bench-scale system. The moisture achieved is below the target moisture of 10% in almost all of the test runs, which demonstrates the highly efficient dewatering capabilities of the novel technology.



Abbreviations: FF – Flotation Feed; DCO – Deslime Cyclone Overflow; SBE – Screenbowl Main Effluent

Figure 2.8 Product moisture% ranges with average values obtained from HHS process bench-scale system

One important factor that was also evaluated during the batch scale testing is the dosage of pentane in the agglomeration process. Dosage increases as the particle size gets finer. For example, the pentane dosage had to be increased for the screenbowl effluent coal samples up to 25-30% by weight of dry feed to attain successful spherical agglomeration. This value is much higher than the 10-15% by weight pentane dosage required for the flotation feed sample. The reason is due to the increase in the total surface area in the ultrafine particles.

2.7 Hydrophobic Liquid Consumption and Recovery

Consumption or loss of pentane in the process is one of the most crucial aspects for a successful commercialization of proposed technology, both in terms of economics and environmental regulations. Although the process produces low moisture and highly clean product, a high loss in producing a low commodity product like coal can hinder its development.

Data for the solubility of pentane in water (40 mg/L at 20°C) is well known, but no information for the loss of pentane associated with coal, either via absorption or adsorption, has been published. In order to estimate the loss associated with clean coal product, basic attempts were made at a batch-scale to quantify the loss of pentane theoretically as well as experimentally. It is important to mention that the pentane absorption in coal may depend on many design parameters and heat exchanger efficiencies and, therefore, can be estimated precisely only at a large scale.

A theoretical model was developed based on the mole concept. Consider the clean fine coal product collected in a sealed jar of 1 liter volume at standard temperature and pressure (STP) conditions. Assuming the voids are completely occupied by trapped pentane vapors, a linear relationship (shown in Figure 2.9) can be established between pounds of pentane in a ton of fine coal and the void fraction using the ideal gas equation. For example, for a 20% of void fraction (which is the available volume of pentane gas), relative loss associated with coal product would be 1.88 lbs/ton of coal at 20°C. Similar predictions can be made for ultrafine coal particles. The typical bulk density of coal powder is 0.641 g/cm³. Considering the clean coal particle density 1.25 g/cm³ and with 10% moisture, the available void fraction for pentane vapors is 42.3%. From the Figure 2.9, the predicted pentane loss would be approximately 3.97 lbs/ton.

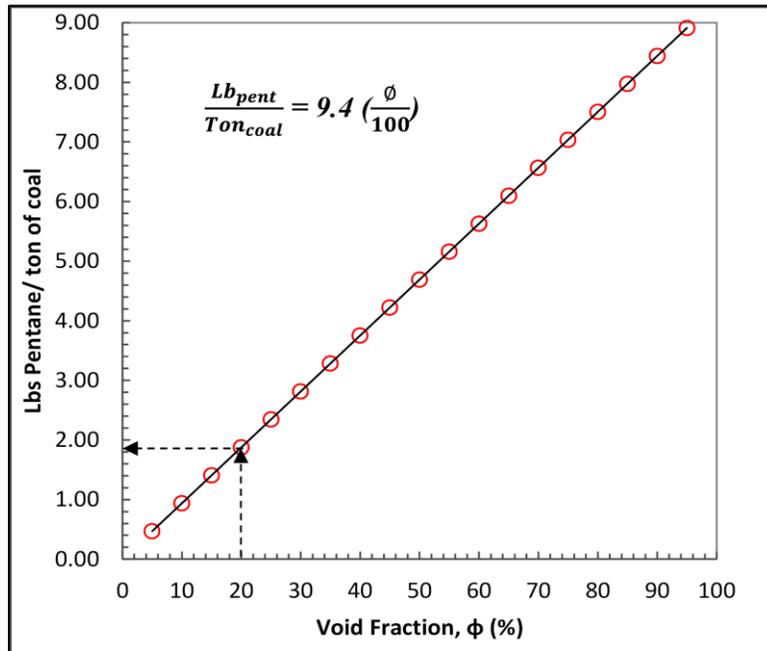


Figure 2.9 Empirical analyses for estimation of pentane loss/ton of coal relative to void fraction

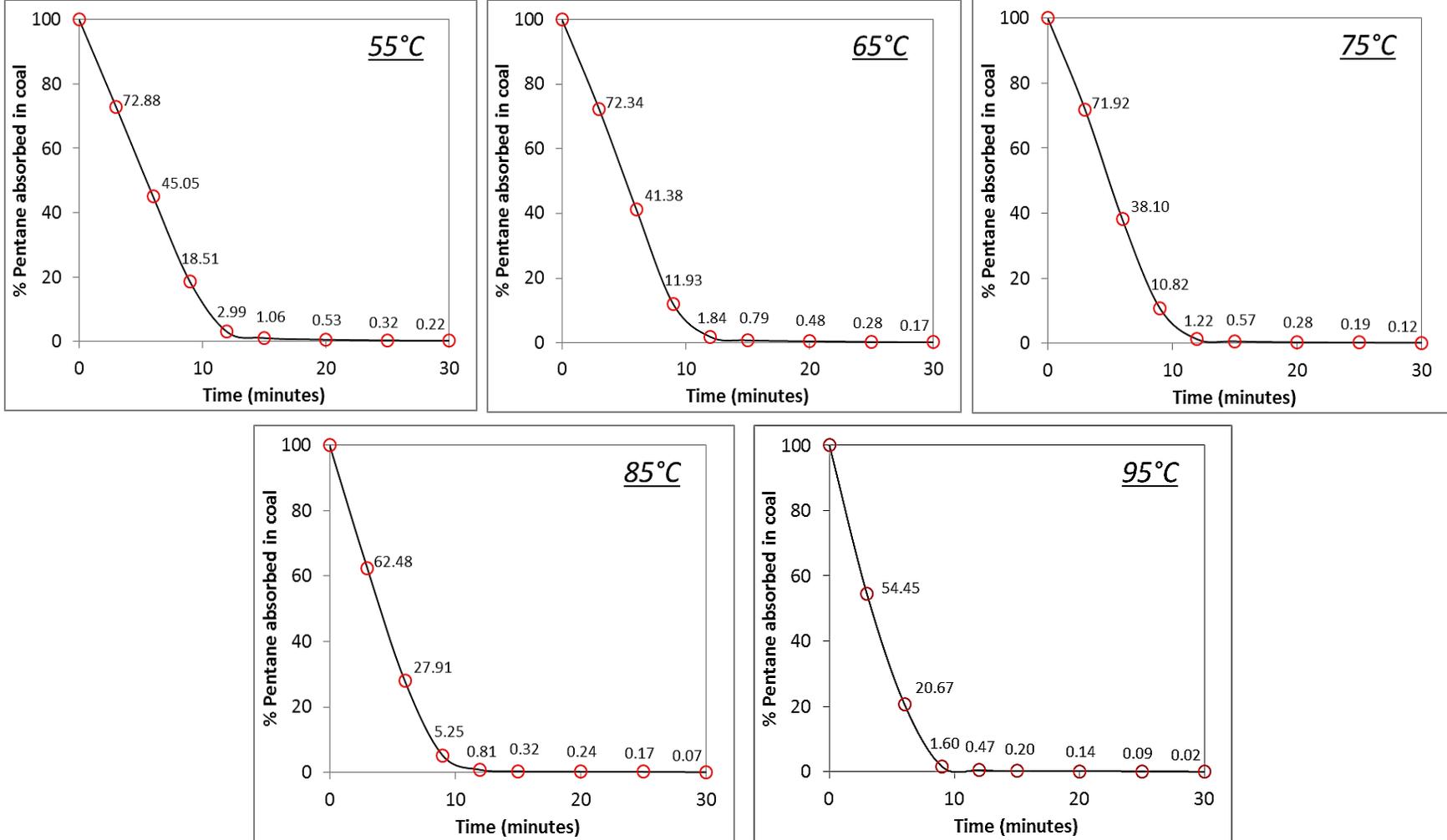


Figure 2.10 Percent pentane losses associated with coal at different temperatures

A series of experiments was conducted to evaluate the loss of pentane with ultrafine dry coal powder. Equal amounts of dry coal powder, in separate sealed glass vials, were completely soaked with pentane liquid and left overnight. After that, each vial was heated in isothermal conditions for different time period (ranging from 0 – 30 minutes) and the weight percent gain in the dry coal samples was recorded with respect to time (at every 3 minutes interval). The gain was assumed to be due to pentane absorption. The procedure was used to develop pentane absorption rate curves for five different temperatures (55 - 95°C), as exhibited in Figure 2.10. The study indicated that the rate of evaporation of pentane increased as the temperature increased. Clearly the inflection point on these graphs shows two rate constants for evaporation with a sharp inflection point. Initially, the rate is higher, as the bulk of pentane is easily available for evaporation at the surface. After crossing the inflection point, the rate decreases drastically as only a small amount of pentane may be trapped in between the coal particles void space or absorbed/adsorbed with coal. Table 2.12 summarizes the recorded loss of pentane after 30 minutes at each temperature.

Table 2.12 Estimated pentane loss after 30 minutes from experimental studies at different temperatures

Temperature (°C)	Pentane Loss (pounds of pentane/metric ton of coal)
55	4.85
65	3.75
75	2.65
85	1.54
95	0.44

2.8 Conclusions

The HHS process serves two purposes: cleaning and dewatering of fine coal particles. In many current coal processing plant circuits, ultrafine particle (44 micron x 0) streams — screenbowl main effluents and 6-inch deslime cyclone overflow — are not processed and are lost as waste to tailings thickeners. There is no existing technology available that can clean and dewater this ultrafine material economically. In addition, flotation is a widely accepted process for treating fine particles (150 x 44 microns) but is a water-based process. Consequently, the

dewatering cost associated with the flotation product exponentially increases the cost of the final product as particle size is reduced.

Studies conducted using a batch-scale HHS unit showed that too much or too little energy input is detrimental to the separation performance. Too little energy results in inadequate breakup of coal agglomerates, poor dispersion of coal particles into the pentane phase, and slow coalescence of water droplets in the pentane column. Too much energy results in the formation of coal-water-pentane emulsions that are very difficult to destroy once formed. In light of these limitations, a low-energy vibrating mesh device was developed for dispersion of agglomerates and water coalescence, which performed very effectively. The successful laboratory-scale testing with various types of fine coal feedstocks showed that the HHS process can fulfill the needs of coal industry by recovering and dewatering discarded ultrafine coal streams, thus increasing the productivity of existing preparation plants. Furthermore, attempts were made in determining the loss of pentane associated with coal, which is highly critical for the successful commercialization of the process. Data obtained using both theoretical and experimental approaches were found to be consistent and suggest that the expected losses are within acceptable levels.

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CHAPTER 3 – Fundamental Studies for the HHS process

3.1 Introduction

While the fine coal fraction (minus 150-micron particles) is often recovered in coal preparation plants using froth flotation, an emerging practice is to remove and discard the ultrafine fraction (minus 44 micron) from the flotation feed because of associated low recoveries and high dewatering costs (Bethell and Barbee, 2007). In light of this, researchers at Virginia Tech have developed an innovative technology, called the *HHS (Hydrophobic-Hydrophilic Separation) Process*, utilizing the concept of hydrophobic displacement to simultaneously recover and dewater well-liberated ultrafine particles. The concept of hydrophobic displacement of water from a hydrophobic coal surface in the presence of hydrophobic liquid is a thermodynamically favorable process. The condition for this displacement to occur is based on the three-phase equilibrium contact angle, which must be greater than 90°.

The HHS technology involves the selective oil agglomeration process as an initial step, combined dewatering-cleaning (the novelty in the process) as a second step, and oil recovery as the third step. The successful development of a bench-scale system for the process has proven that the HHS concept is feasible at a small scale by providing consistent low-moisture high-quality coal products from variable coal feedstocks. As for any new process, scientific studies are equally important as the engineering data in the further development of the technology. These investigations provide a better understanding of the mechanisms that control the process.

Several scientific studies with variable coal types (Capes et al, 1974; Keller, 1981; Capes and Germain, 1982; Wheelock, 1982; Slaghuis and Ferreira, 1987; Drzymala et al, 1988; Skarvelakis et al, 2006) can be found on the oil agglomeration process, but the focus of these studies is mostly on optimizing the coal cleaning (recovery) aspects and very little on moisture reduction (Capes and Germain, 1982; Smith, 2008). In a standard coal agglomeration method, which uses low chain recoverable non-polar hydrocarbons, product moistures are typically reduced to 40% by weight (Keller, 1985). As dewatering of ultrafine coal slurry is an integral part of the proposed technology, this chapter outlines scientific investigations conducted to identify two key mechanisms:

- how moisture is trapped in an agglomerate structure, and
- how moisture is released in the unique dewatering step of HHS process.

Based on these investigations, a theoretical model for the HHS process is proposed that is supported by the thermodynamics of the system.

3.2 Agglomerates Characteristics

The three crucial governing factors that affect the oil agglomeration process (Capes and Darkovich, 1984) are:

- free energy relationships at the three phase (oil-water-solid) interface,
- dosage of an agglomerant (bridging liquid) with respect to carbon content in the feed, and
- mixing conditions such as time, intensity and method of mixing.

The free energy relationships for the pentane-water-coal system have been discussed earlier in Chapter 1. It was identified that the liquid pentane makes a 106° equilibrium contact angle in the three-phase system and, therefore, quickly wets the hydrophobic coal surface. The other factors are explored here particularly to study their effect on agglomerate structure using liquid pentane, which is important to determining how moisture gets trapped in the agglomerates of ultrafine coal particles.

3.2.1 Agglomerate Structure

Typically, there are three types of structures that can form depending on the amount of oil used during the formation of agglomerates. These are pendular type, funicular type, and capillary type (Capes and Jonasson, 1989). An agglomeration study was conducted with mono-size (75 micron) hydrophobized silica particles under a microscope. Figure 3.1, taken with the camera of the microscope, illustrates with solid particles formed floc-like structures in a pendular form when using small amounts of the bridging liquid. With higher additions of bridging liquid, these pendular agglomerates consolidated into more compact funicular structures. Finally, with high quantities of bridging liquid, the agglomerates become are more compact, like pellets where the bridging liquid is in the capillary state and the aqueous phase is left out from the agglomerate structure. An excessive dosage of oil resulted into a formation of highly stable water-in-oil emulsions, which resembles a mousse in terms of consistence.

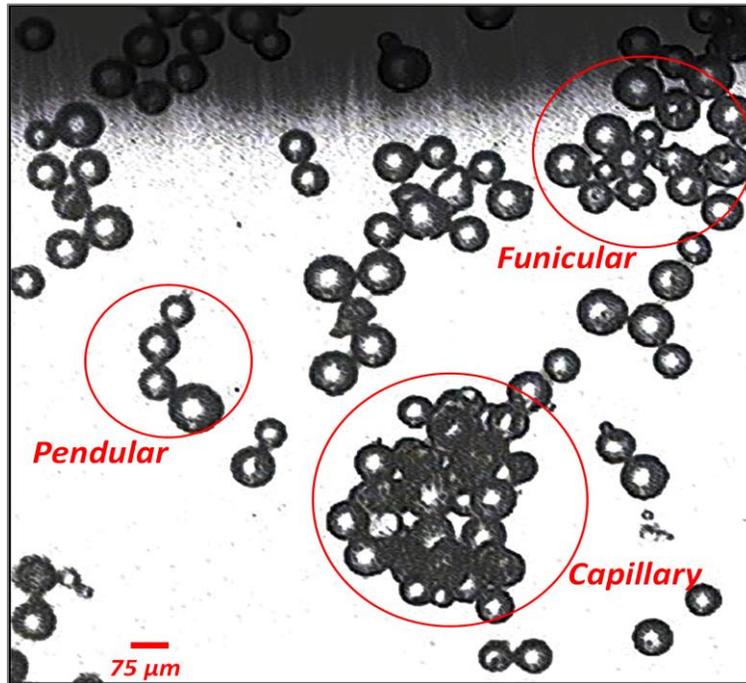


Figure 3.1 Image showing types of agglomerate formed with 75 micron silica particles

3.2.2 Entrapment of Moisture in Agglomerate Structure

Water can be trapped in any agglomerate structure by three possible ways, as exhibited in Figure 3.2. *First*, the bulk of water is associated with water droplets that are stabilized by micro-agglomerates. *Second*, a good proportion of moisture is trapped in the void spaces inside the micro-agglomerate structure and *finally*, by nature, water likes to be attached on any hydrophilic site available on coal particle surface. For ultrafine coal particles (minus 44 microns), the latter is expected to be the least likely scenario, as coal and clay particles are usually well liberated for ultrafine particles.

In order to better identify the dominant mechanism responsible for water entrapment, several microscopic investigations were conducted with fine coal particles (150 micron) in the presence of a bridging liquid (pentane). A dilute slurry (5% solids by weight) containing fine coal was prepared and agglomerates were formed by adding a small dosage (5% by weight) of pentane. The agglomerates were screened and analyzed under the microscope. As both water and pentane are clear liquids, it was hard to make a distinction between the two phases. After few minutes, due to the radiant heat of microscope bulb, the pentane liquid starts expanding, enough to clearly identify the oil bridges between the particles. The micro-photograph, shown in Figure

3.3(a), was taken as soon as the pentane started expanding, which eventually evaporated in the atmosphere. For better moisture assessment, the same experiment was repeated with a high dosage (30% by weight) of pentane, and a small amount of fluorescein was mixed with the slurry. The fluorescein is soluble in water and insoluble with pentane. Once the agglomerate formed, rather than screening, a small portion of the floating agglomerate was sucked into a glass tube and examined under the microscope. The photograph, shown in Figure 3.3(b), of floating agglomerates on top of the water surface clearly shows the entrapment of fluorescein dyed water in fine coal agglomerate.

The preferred size fraction processed in the HHS technology is ultrafine minus 44 micron particles. Due to limitations with microscope magnification, similar images could not be generated for this particle size range. To investigate moisture entrapment in agglomerates formed using ultrafine coal particles, the coal slurry was mixed with fluorescein and the formed agglomerates were screened out from the bulk water. The agglomerates were collected on a glass plate and examined under the microscope. Figure 3.4(a) shows a photograph of agglomerates, which appear to be dry. These agglomerates were then squeezed between the two glass plates and a photograph was taken as shown in Figure 3.4(b). The image clearly indicates a good proportion of fluorescein dyed water droplet releasing from the agglomerate structure when the agglomerate was mechanically squeezed between the two glass plates.

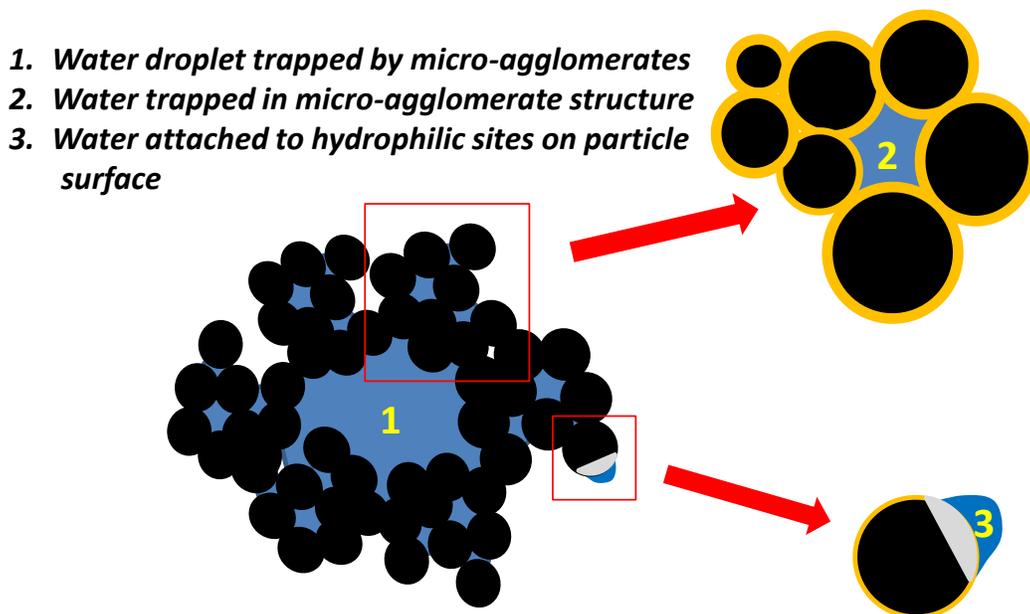


Figure 3.2 Schematics showing entrapment of moisture in agglomerates

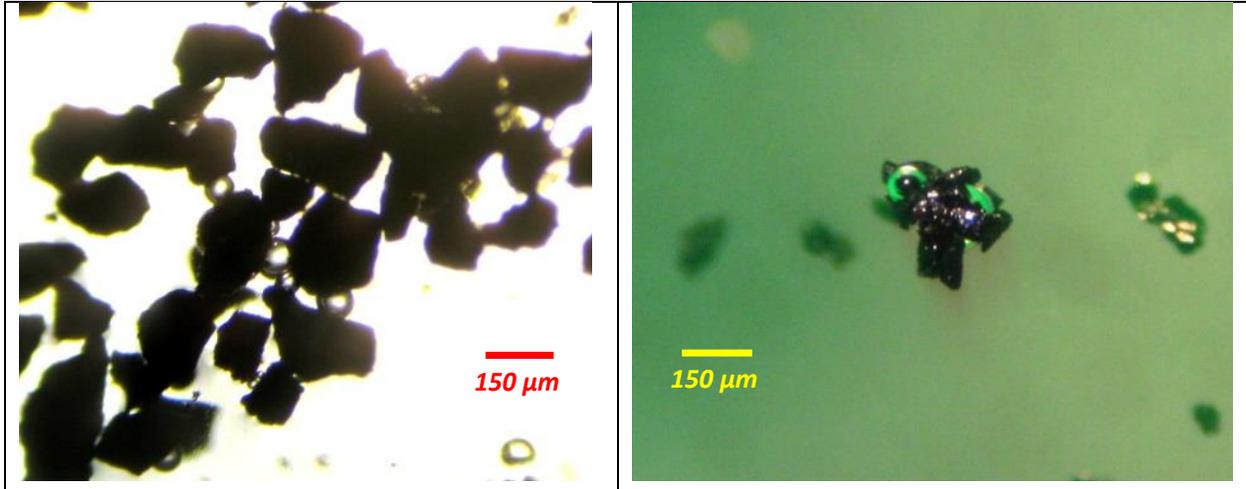


Figure 3.3 (a) Image identifying oil bridges between fine coal particles (b) Image of floating agglomerate identifying fluorescein dyed moisture trapped in its structure

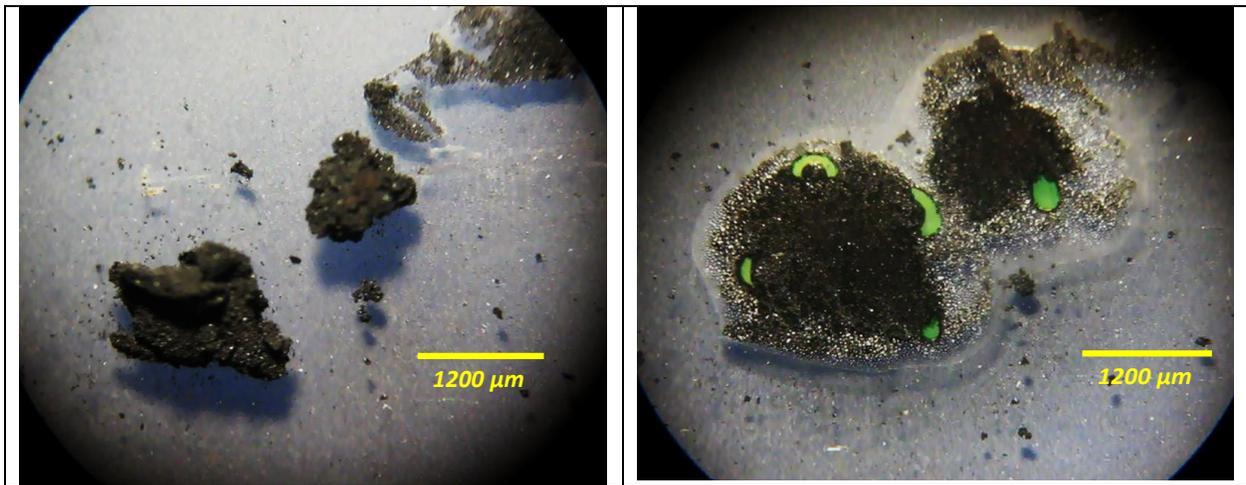


Figure 3.4 (a) Image showing agglomerates of ultrafine particle (b) Image showing entrapped moisture released from the agglomerates, when pressurized

3.2.3 Effect of Oil Dosage on Entrapped Moisture

As identified in the aforementioned studies, it appears that water gets trapped in the void spaces of the agglomerate structure and occupies most of the available volume space. Increasing the amount of bridging oil should reduce this volume of water and, therefore, reduce the amount of water entrapped. To corroborate this theory, bench-scale oil agglomeration experiments were conducted with different dosages of liquid pentane at a fixed mixing intensity and mixing time. Schematics shown in Figure 3.5, plotted between percent by weight of water entrapped for

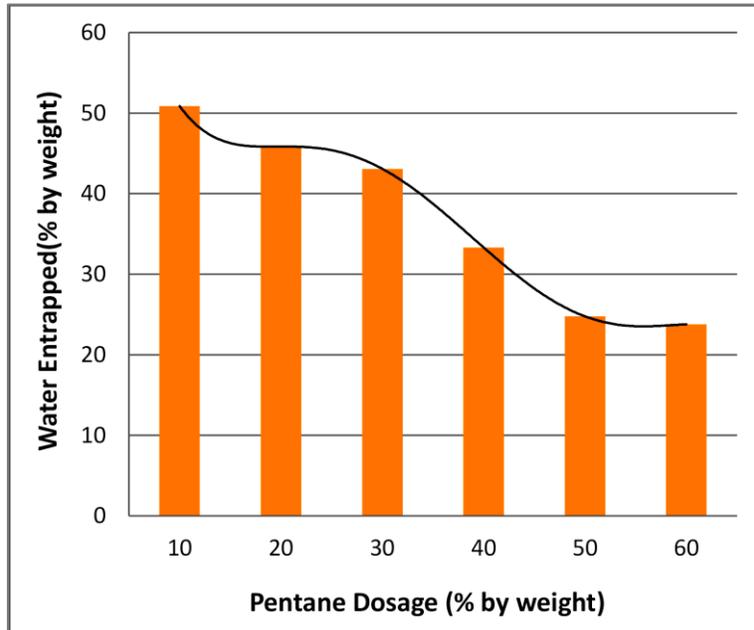


Figure 3.5 Effect of oil dosage on entrapment of moisture in agglomerates

different oil dosages, indicate a significant decrease in agglomerate moisture as the oil dosage was increased up to 50% by weight of solids. Dosages higher than 50% did not contribute further reduction of moisture from the agglomerates, suggesting that all available void space was filled at this dosage level.

3.2.4 Impact of Mixing Time and Intensity on Agglomerates

The mixing time and intensity of agitation play a very important role in the oil agglomeration process, particularly in defining the size distribution of agglomerates. An investigation was conducted with ultrafine coal agglomerates formed by varying impeller speed at a fixed retention time and vice versa. The agglomerates were screened and a small sample was spread on a clear white sheet. Photographs were taken utilizing a macro lens from a digital camera for each scenario and analyzed using image processing software (IMAGE-J) to determine the size distribution of agglomerates, as depicted in Figure 3.6 and 3.7.

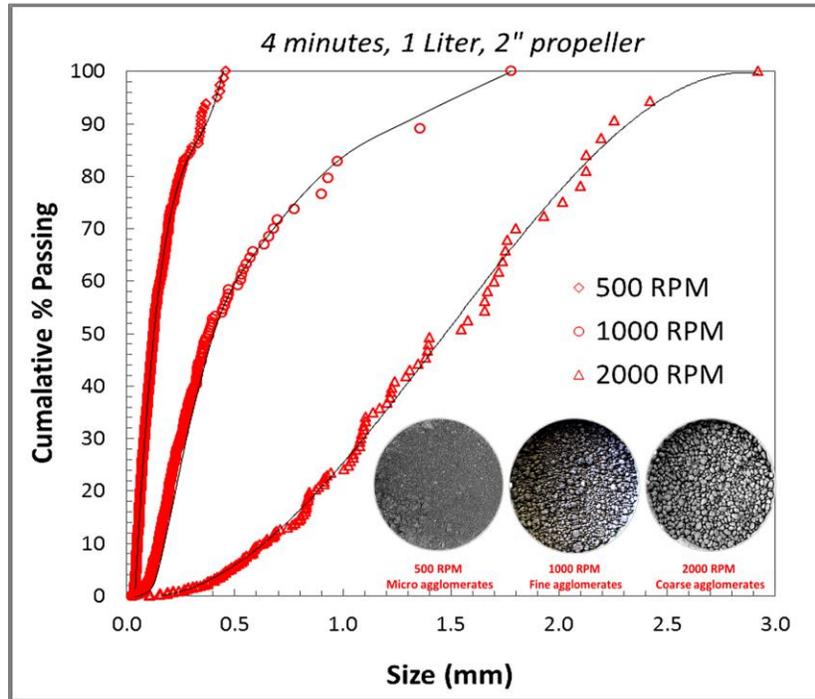


Figure 3.6 Agglomerates size distribution at varying impeller speed

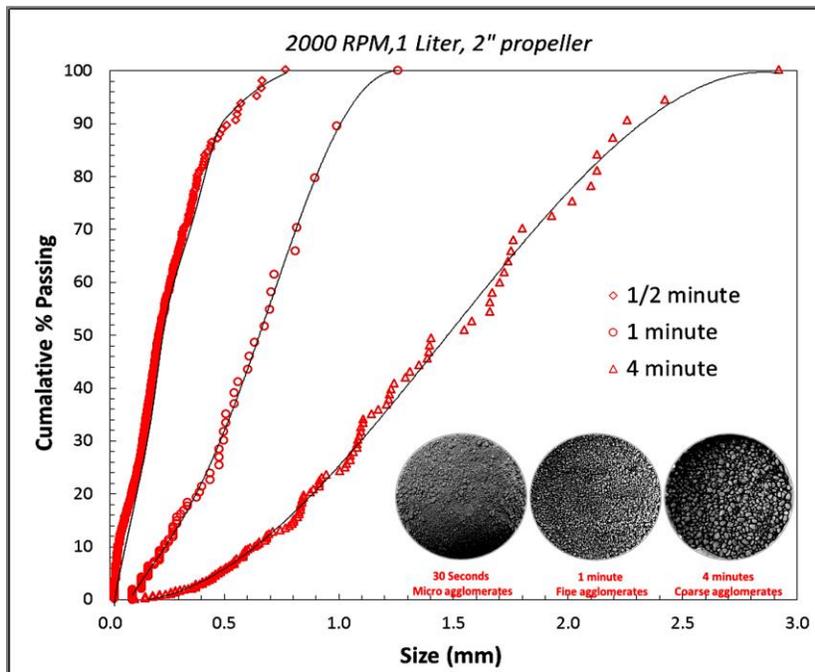


Figure 3.7 Agglomerates size distribution at variable mixing time

At 2000 RPM and 4 minutes of mixing time, agglomerates were large, compact and distributed uniformly. When the impeller speed was reduced, the intensity was not enough to disperse the oil completely and engulf particles. A wide range of size distribution was observed with a high percentage of micro-agglomerates. On the contrary, at a constant 2000 RPM, but with a variable mixing time, agglomerates were observed more uniformly distributed even at short agglomeration times.

The data also indicated that the agglomerate size distributions implicitly defined the amount of moisture trapped in agglomerates pore volume. A uniform size distribution, as found with high agitation speed, provided a high percentage of coarser (up to 3 mm) and more compact agglomerates. This tight structure resulted in a small amount of trapped moisture as exhibited in the trends shown in Figure 3.8. However, a wide distribution with high percentage of micro-agglomerates (less than 0.5mm), which were generated with low agitation speed, resulted in a large amount of water entrapment in agglomerates. Even though the available pore volume in the micro-agglomerates is much lower, it was observed that some of these agglomerates were stabilizing large water globules, which might have caused increase in moisture.

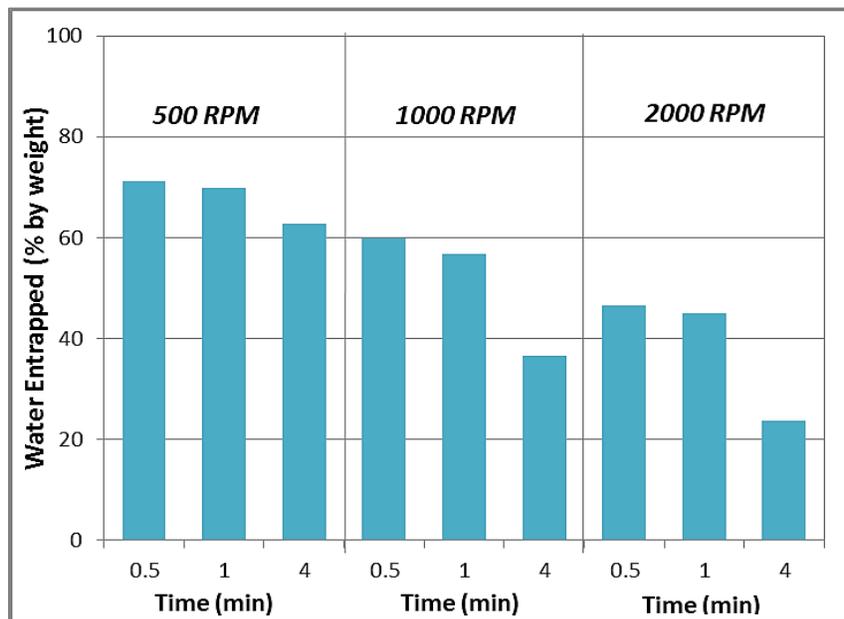


Figure 3.8 Moisture entrapment with variable residence time and impeller speed

3.3 Impact of HHS Process – A Comparison with Agglomeration

The basic difference between the HHS Process and the conventional oil agglomeration process is an additional stage of coal dispersion/water coalescence after the standard agglomeration step. This novel step is based on dispersion mechanism, i.e. the breakup of the agglomerates in a hydrophobic liquid. In this step, coal agglomerates are passed into a liquid pentane column for dispersion. The hydrophobic dispersed coal particles stay in pentane, while the trapped moisture from the agglomerates is released and settles to the bottom of pentane column. Hydrophilic ash-bearing minerals, such as clay, also like to be with the water and are rejected with the moisture. Thus, this novel step serves a dual purpose of cleaning and dewatering the ultrafine coal particles.

Figure 3.9 clearly depicts the advantages of the additional step in producing premium quality coal. In the study, two sets of agglomerates were prepared from a deslime cyclone overflow reject stream at different dosages of pentane. One of the two sets of samples was subjected to the novel step of coal dispersion / water coalescence, while the second otherwise identical sample was handled as in any standard oil agglomeration test. The samples were analyzed and the results indicate a significant drop in the clean coal product moisture (red circles vs. blue circles) and an increase in the combustible recovery (red squares vs. blue squares) up to 90%.

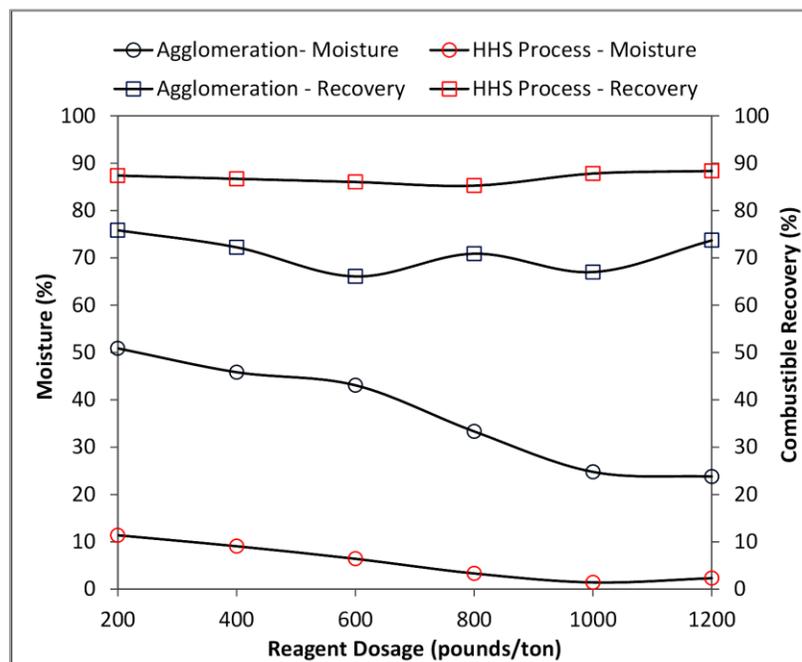


Figure 3.9 Comparison of HHS Process with Oil-Agglomeration in terms of product quality

3.4 Dispersion of Agglomerates

The dispersion of agglomerates formed from ultrafine particles in a hydrophobic liquid is a key part in the innovation of the novel proposed technology, as discussed in aforementioned study. Therefore, it is necessary to understand the mechanism, particularly in the proposed process, to identify the critical aspects of the process. More knowledge generated through scientific studies provides better understanding of the phenomenon occurring in the reactor, which is vital for successful scale-up of the HHS process.

Dispersion can be regarded as the result of two separate, though simultaneous, processes: de-agglomeration and homogenization. De-agglomeration is the breaking of aggregates to smaller agglomerates or individual particles, whereas in homogenization, each component is redistributed with its parent component to achieve a more homogeneous mass (Patterson and Kamal, 1974).

To better understand the dispersion process, it is important to have a fundamental knowledge of the inter-particle forces that lead to agglomeration. The wetting mechanism of liquid hydrocarbon on the coal surface without water is controlled by weak van der Waals force (Keller and Burry, 1987). This force becomes significant when the particle size is less than 1 micron. Other stronger forces may include those due to pendular moisture in the interior of agglomerates, bridging forces at the point of contact when hydrophilic gangue particles are present in the agglomerates, and mechanical forces from the interlocking of irregular shape particle (Hartley et al., 1985).

Dispersion due to agitation in a liquid medium is governed by a competition between the hydrodynamic shear forces acting on the fine coal agglomerates created by agitation in the liquid medium and the cohesive inter-particle forces holding the agglomerate together. These hydrodynamic forces can be determined by studying the strength and geometry of the shear stress field, while the cohesive forces can be evaluated from particle – particle interaction and packing arrangements of the agglomerates. Detailed studies on these forces are available in the published literatures (Rumpf, 1962; Kendall, 1988; Israclachvili, 1991; Bika et al., 2001; and Boyle et al., 2005).

De-agglomeration in the presence of a shear hydrodynamic field can occur in two ways, either individually or in combination, by rupture and by erosion (Pontente et al., 2002). *Rupture* is the spontaneous process of breaking agglomerates into smaller agglomerates due to the

imposed hydrodynamic stress, by collision between two or more agglomerates and by collision of agglomerates with the dispersion device. *Erosion* is the removal of primary particles from the top layer of the agglomerates, mostly when the shear hydrodynamic field exceeds the cohesive forces of these particles bonded at the agglomerate surface. Both cases involve the creation of new interfaces between the agglomerate/particle and the liquid medium.

In HHS process, all of the above dispersion theories can define the mechanism partially, as it is unknown how the released moisture behaves in the system. From an engineering standpoint, it is necessary to investigate both kinetics and thermodynamics of the process. Kinetic studies provide information related to the rate of dispersion, whereas thermodynamics studies help determine the behavior of fine water droplets released after breaking of the agglomerates.

3.5 Kinetics Studies of Dispersion

In agglomerate dispersion, two mechanisms occur simultaneously. These are breaking of agglomerates (de-agglomeration) and suspension of particles in hydrophobic liquid phase (homogenization). For kinetics studies, the rate of homogenization can be determined with ultrafine dry coal powder poured in the oscillatory dispersion device on the bench-scale system, as no breaking mechanism is involved with dry powder feed. Similarly, the combined rate for both mechanisms can be determined with the agglomerates formed utilizing the same coal feed under otherwise identical operating conditions. Thus, the difference in rates provides the net rate for de-agglomeration in the reactor.

Figure 3.10 shows the solid concentration ratios in the reactor at a given time for both the scenarios. In case of dry coal powder, almost all the particles were recovered from the reactor (shown with red circles). However, when agglomerates were tested under similar conditions, some of the particles were retained in the reactor. Therefore, to attain the rate associated with steady-state conditions, a series of kinetic tests was conducted in batches with equal quantities of agglomerates. When the first batch of agglomerates was poured into the reactor, a substantial amount of coal remained at the oil-water interface (as shown with green squares) even at a long residence time. The test was continued until the overflow from the reactor was visually free of solids. Then, the second batch of agglomerates was poured into the system and kinetic test was conducted. Again, a small portion of solids remained in the reactor (shown with green triangles).

When the third batch of agglomerates were introduced, almost all the particles were recovered (shown with green diamonds), which indicates a steady state condition was reached in the reactor.

The deviation in the rates between steady state dispersion of agglomerates and homogenization of dry coal powder can be used to determine true rate for de-agglomeration mechanism. Figure 3.11 depicts the two recovery plots for the mechanism. The individual recovery curve can be considered as a residence time distribution plot for breaking of coal agglomerates in the liquid pentane inside the reactor while the cumulative recovery plot defines the percentage of agglomerates that break in the reactor at any given time.

It is important to mention that the kinetic tests were conducted at conditions considered to be optimal for the HHS process bench-scale unit. The curves are expected to shift or vary once the operating parameters are changed in the reactor. Considering the novelty of the process, a detailed parametric study with a similar procedure can provide a better knowledge of the system best suited for this technology.

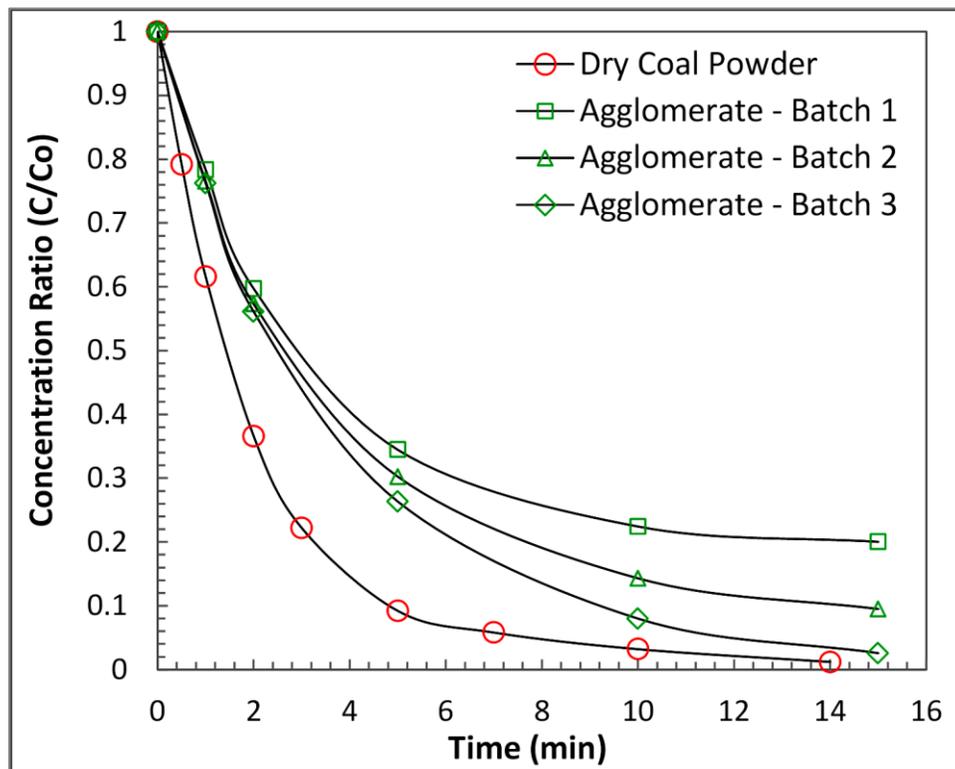


Figure 3.10 Kinetic rate studies for dispersion mechanism in HHS process

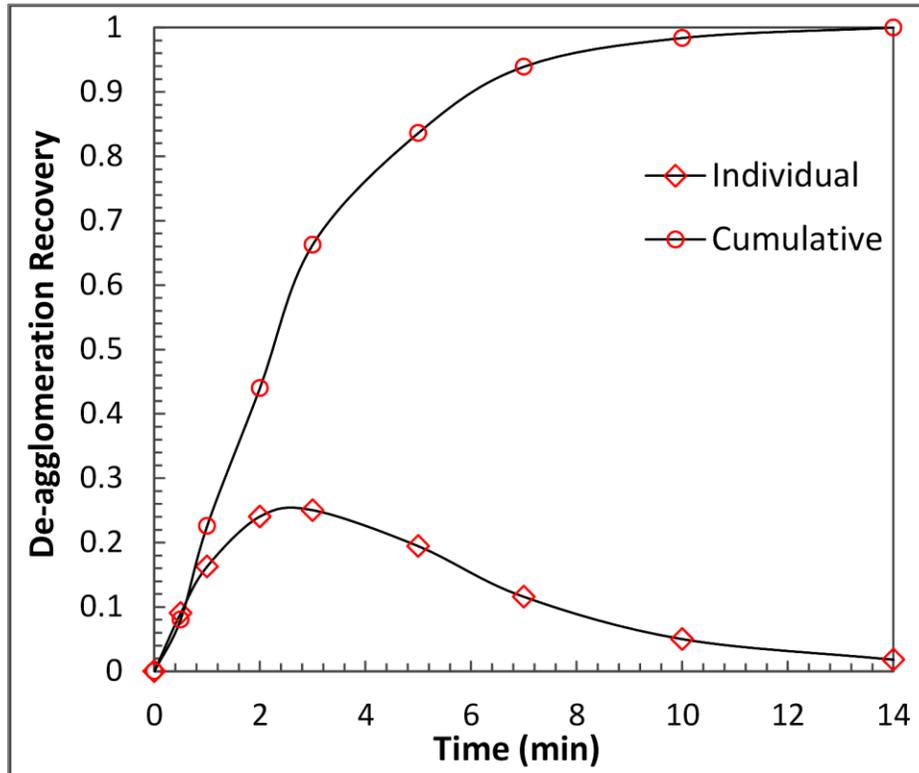


Figure 3.11 Kinetics of de-agglomeration mechanism in HHS process

3.6 Thermodynamic Studies – Proposed Theory

The concept of dewatering by displacement was first disclosed by Yoon and Luttrell (1995). The idea was to exploit the natural affinity of hydrophobic particle surface with a hydrophobic liquid, which makes the process thermodynamically favorable. In previous years, several studies were conducted at Virginia Tech to develop the concept into an engineering system that could recover ultrafine coal particles, which are currently discarded. Smith (2012) introduced an additional stage after a standard agglomeration process for dispersion using an ultrasonic device, which can be considered as a large development, though it added another dimension in the process.

One of the key outcomes of the current research is the development of low-energy vibrating-mesh device for dispersion, which is safe and can be scaled up. The batch-scale reactor for dispersion is a cylindrical column initially charged with clear water and liquid pentane and equipped with the vibrating-mesh device such that the bottom mesh is located just above the pentane-water interface. The vibrating mesh in the pentane column creates a uniform

hydrodynamic shear field inside the reactor that promotes agglomerate breakup, coal dispersion, and water coalescence.

Agglomerates, when introduced into the two-phase reactor, break in the hydrodynamic shear field created by vibrating energy either by rupture or by erosion mechanism. When agglomerates break in the reactor, they constantly generate new coal surfaces and eventually disperse all parental particles associated with the agglomerate in the pentane column. The kinetic data indicated that the breakup is a slow process, although thermodynamics also plays a pivotal role in defining the system.

The study on structure of ultrafine coal agglomerates has showed that the agglomerates are held together by pendular bridges formed by liquid pentane between the particles and that the bulk of the moisture is trapped in the structural voids. The combined moisture content is typically 40% by weight (Keller, 1985), though it can vary depending upon coal rank, oil dosages, and mixing time and intensity. During the breakup of agglomerates, the moisture trapped in the pore volume of the agglomerates gets exposed to bulk pentane, which eventually displaces (releases) the moisture from the particle surface. This phenomenon, which has been described by Yoon and Luttrell (1995), creates a complex three-phase system inside the reactor.

Thermodynamically, the work per unit area required for separation (defined as a reversible work) of water (3) from coal surface (1) in the bulk pentane (2) can be calculated from energy balance and the Young's equation. From energy balance,

$$W_{132 (sep)} = W_{13} + W_{22} - W_{12} - W_{32} \quad [3.1]$$

From the work-interfacial tension relationships and Young's equation, Equation 3.1 can be re-written as:

$$W_{123 (sep)} = \gamma_{23}(1 + \text{Cos}\theta_{123}) \quad [3.2]$$

Keller and Burry (1987) estimated surface tension between liquid pentane and water (γ_{23}) is 51.9 mJ/m². Sohn et al. (1997) estimated the three phase equilibrium contact angle (θ_{123}) is 106°. Therefore, from Equation 3.2, the work per unit area required to separate a drop of water by pentane from the coal surface is calculated to be 37.6 mJ/m².

The above relationships help to explain how and why moisture is displaced from the coal surface, but the unknown the behavior of released water droplet, which still exists in the pentane column, is not well understood. Theoretically, these fine size droplets should report in the

overflow with clean coal and pentane, as density is almost negligible for micron-size species. However, the consistently low moistures in the clean coal product obtained with the bench-scale testing suggests otherwise. In light of this, a theory is proposed, which indicates an additional phenomenon is occurring in the system.

The proposed theory is partially based on the free energy for attachment/detachment defined for spherical micron-size particles and partially on the free energy of cohesion. The free energy for attachment/detachment equation is widely used in colloidal sciences (Binks, 2002) to identify the minimum energy required for a particle of radius “r” at the water/oil interface to detach into either of the bulk phases. Assuming an ultrafine coal particle to be spherical with radius “r”, the free energy for detachment at the water-coal-pentane interface can be determined by Equation 3.3.

$$\Delta G_{int/Detach} = \pi r^2 \gamma_{23} (1 \pm \cos \theta_{123})^2 \quad [3.3]$$

The two terms in parentheses are added when particle is detached from water phase and subtracted when particle is detached from the pentane phase. Furthermore, the free energy of attachment can be defined as:

$$\Delta G_{int/Attach} = -\Delta G_{int/Detach} \quad [3.4]$$

Clearly, Equation 3.4 shows the energy for attachment is always negative and, therefore, is always a thermodynamically favorable process. On the other hand, the free energy for detachment (Equation 3.3) is always positive, which indicates some external energy is always required to detach the particle in either of the bulk phases.

Figure 3.12 graphically represents Equation 3.3 for the solid-water-pentane system. It can be deduced from this plot that particles like to stay at the pentane-water interface, and a specific amount of energy is needed to move them into either of the bulk phases. As exhibited, the critical three-phase contact angle is 90°. If a particle is hydrophilic (such as clay) with contact angle <90°, it is easier for a particle to go into the bulk aqueous phase. For a hydrophobic particles with contact angle >90°, particles move into the bulk pentane phase with only a very small amount of energy. The three-phase equilibrium contact angle (θ_{123}) of high rank coal particle is 106°. Therefore, the minimum free energy per unit area for detachment of a coal particle from interface into the bulk pentane phase is calculated to be 27.2 mJ/m².

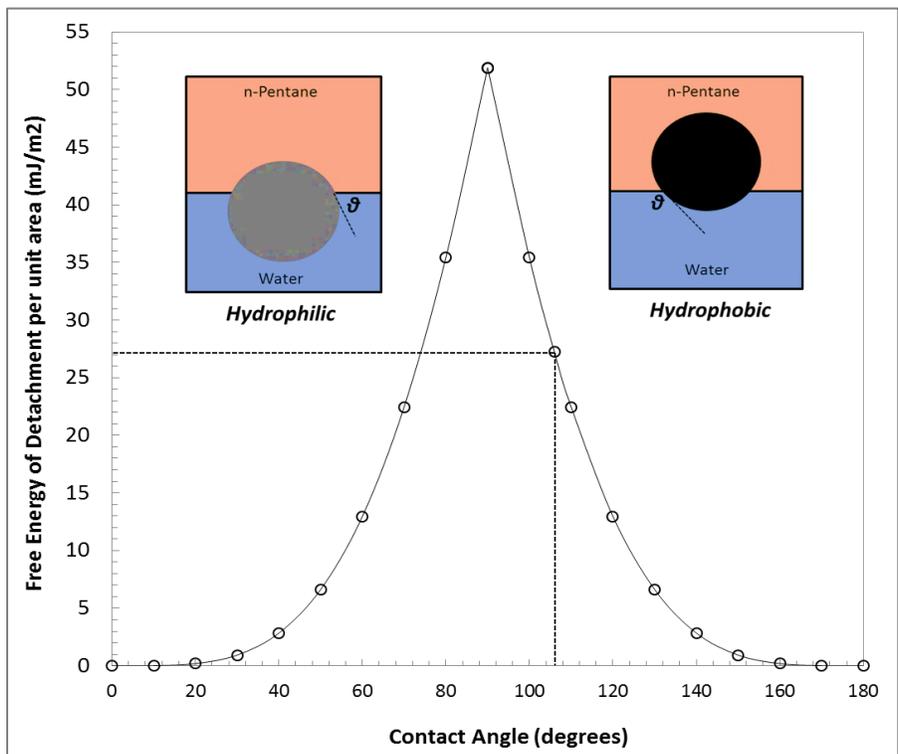


Figure 3.12 Graphical representation of free energy for detachment of a particle in pentane-water-solid system

Figure 3.13 illustrates the proposed phenomenon for dewatering of coal particles in the pentane column inside the reactor, which leads to consistent low product moisture. The phenomenon is described in four different stages showing the most likely thermodynamic states. The theory is based on the information surveyed during bench-scale testing and is very well supported by thermodynamic calculations at the three-phase interface.

State I outlined in Figure 3.13 (a) can be described as a thermodynamic equilibrium state where coal particles always like to stay at the oil-water interface. Any external energy below minimum free energy for detachment will not disturb this equilibrium and water droplet may remain attached to the coal surface.

When the external energy is equal or higher than the minimum free energy, which is 27.2 mJ/m² (calculated earlier), the equilibrium will be disturbed and the water droplet will be detached from the hydrophobic coal surface, as shown in Figure 3.13 (b) as State II. Once the water droplet is removed from the coal surface by providing enough energy, the released water droplet can have two thermodynamically probable options. First, it can attach back to any of the newly exposed coal surfaces generated during de-agglomeration, as the free energy for

attachment will be negative (in this case $\Delta G_{attach}/\Delta A = -27.2 \text{ mJ/m}^2$), which makes it thermodynamically possible. Second, the fine size water droplet can find another released water droplet and coalesce together to form a bigger droplet, as State III depicted in Figure 3.13 (c). The free energy per unit area ($\Delta G_{cohesion}/\Delta A = -103.8 \text{ mJ/m}^2$) for cohesion of two water droplets in pentane is calculated from Equation 3.5.

$$\frac{\Delta G_{cohesion}}{\Delta A} = -2\gamma_{23} \quad [3.5]$$

Since the latter case has higher negative free energy, the coalescence process of water is thermodynamically more spontaneous and naturally favorable. Consequently, micron-size water droplets quickly combine to form bigger drops, which eventually sink into the aqueous phase, as described in State IV in Figure 3.13(d). This phenomenon also helps to explain why a water column below the pentane column in the reactor can be beneficial for moisture separation. Large water droplets find it easier to cross the oil-water interface and be completely removed from the active part of the reactor.

The free energy for the cohesion of water droplets also indicates that the separation process should work most efficiently in a specific range on external energy. Too little energy ($E < \Delta G_{detach}$) will not displace the moisture associated on the coal surface that always likes to stay in a three-phase equilibrium state. Too much energy ($E > \Delta G_{cohesion}$) can prohibit the water coalescence process and may also break the existing droplets into much smaller droplets that remain in suspension in the bulk pentane phase, which may eventually end up in the final product.

As mentioned earlier, the proposed theory for the process is a perspective of what is observed during the laboratory-scale batch testing, but is very well corroborated by thermodynamic calculations. From a theoretical standpoint, it can be understood that the hydrodynamic energy density within the pentane column plays an important role in moisture reduction during dispersion. Two conclusions can be made from this study, which are critical in designing the reactor:

- The reactor should promote the water coalescence mechanism in addition to de-agglomeration and homogenization mechanism of coal particles.
- To completely remove the moisture (<1%) and achieve a dry coal product, the process works efficiently only if a specific range of external energy is provided.

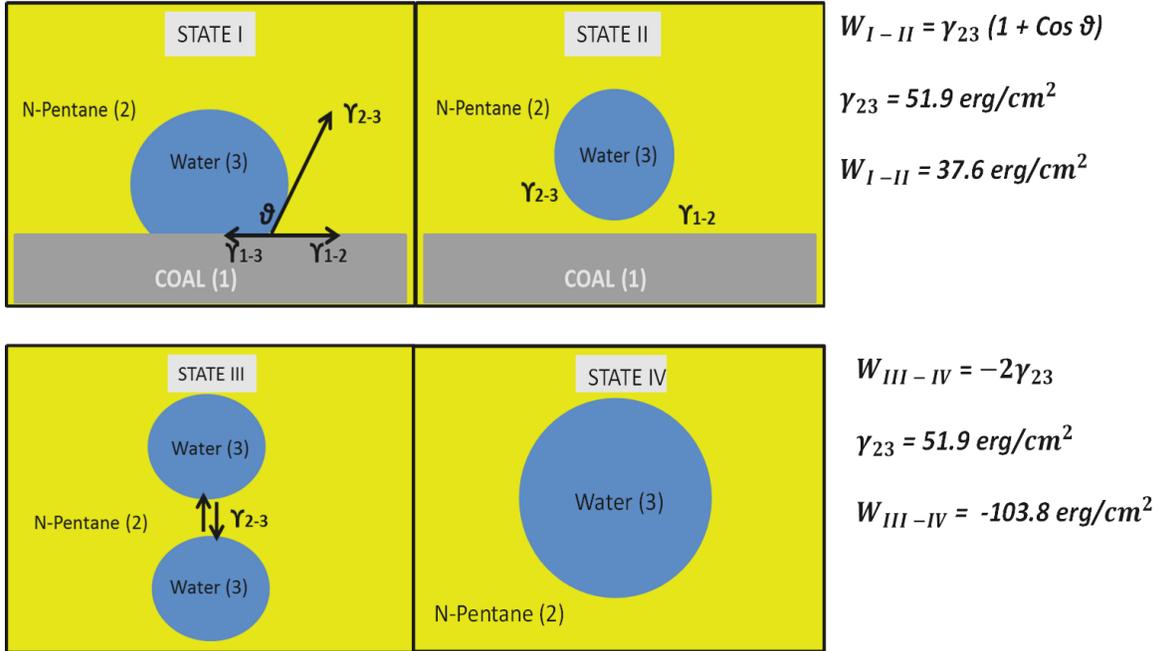


Figure 3.13 Schematic showing behavior of released water droplets from the coal agglomerates in liquid pentane column (a) State I (b) State II (c) State III (d) State IV

The calculated free energies are theoretical values, which cannot be easily verified, but these literature values provide some insight into how the process works. It is now necessary to provide scientific evidence, which supports the conclusions from proposed theory.

3.6.1 Investigation for Water Coalescence Mechanism

The coalescence mechanism of small water droplets released during the de-agglomeration process into larger water droplets is understood thermodynamically. To support the theory, a simple investigation was conducted using fluorescein, which is only soluble with water. Agglomerates were prepared with fluorescein mixed into ultrafine coal slurry and screened. The testing apparatus includes a glass beaker filled with liquid pentane and a dispersion device. The agglomerates, in small batches, were then poured constantly into the pentane bath in the beaker equipped with a mixer agitating at a low speed (80 RPM). To investigate, a video file was recorded for the complete experiment and analyzed.

Figure 3.14 shows still images from the recorded video in an incremental order of time. At 30 seconds, agglomerates were poured from the top and quickly started dispersing in pentane as illustrated in Figure 3.14(a) and 3.14(b). After 2 minutes, signs of fluorescein dyed water,

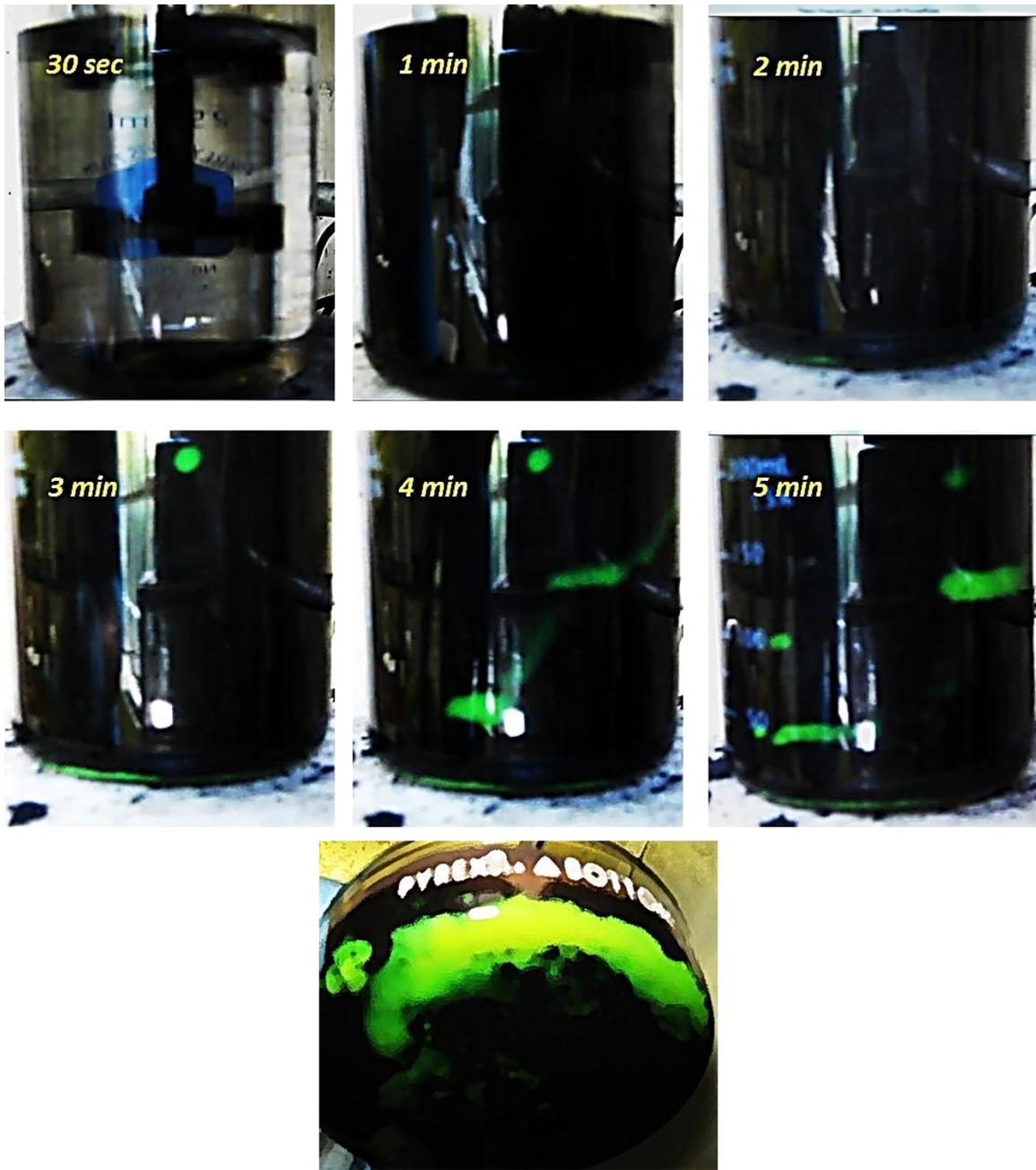


Figure 3.14 Stills from video-graphic investigation depicting coalescence mechanism of water in de-agglomeration process after (a) 30 seconds (b) 1 minute (c) 2 minutes (d) 3 minutes (e) 4 minutes (f) 5 minutes, (g) bottom of beaker after the experiment

which was trapped in the agglomerates, started appearing at the bottom of the beaker, as can be noticed in Figure 3.14(c). After 3 minutes, a prominent thin film of water layer formed, which grows until the end of the experiment, as shown in Figures 3.14(d) – 3.14(f). The clean coal dispersed in pentane was collected quickly after the experiment and the settled water layer was

analyzed. The photograph of the bottom of the beaker, shown in Figure 3.14 (g), clearly indicates that the moisture droplets released from agglomerates eventually find themselves and coalesced into a big water globule.

3.6.2 Investigation on Energy Input for De-agglomeration

In the current version of the HHS process, vibration energy is used as an external source of energy. The newly developed vibrating mesh device creates a uniform hydrodynamic shear field in the pentane column using vibrational energy. To determine if the moisture separation process works efficiently in a specific range of energy, criteria for the vibration energy need to be defined experimentally.

From the bench-scale experimental studies, two dimensionless operating parameters related to vibration energy are considered to be critical for effective dispersion and dewatering of coal particles. The first, which is called “vibration strength” (ζ), is defined as the ratio of the vibration force to the gravitational force. Vibration strength, also called vibration number, is a widely recognized parameter (Pakowaski et. al., 1984; Daleffe et al., 2004; Levy et al., 2006; Meili et al., 2010) used to quantify vibration energy in studies of vibro-fluidized beds for drying technologies. Mathematically, vibration strength can be expressed in terms of vibrational frequency (f) and amplitude of vibrations (A) as illustrated in Equation 3.7:

$$\zeta (\omega, A) = \frac{\text{Vibrational acceleration}}{\text{Gravitational acceleration}} = \frac{A\omega^2}{g} \quad [3.6]$$

where ω is angular frequency of mechanical vibration. Since $\omega=2\pi f$, Equation 3.6 can be re-written as:

$$\zeta (f, A) = (2\pi f)^2 \frac{A}{g} \quad [3.7]$$

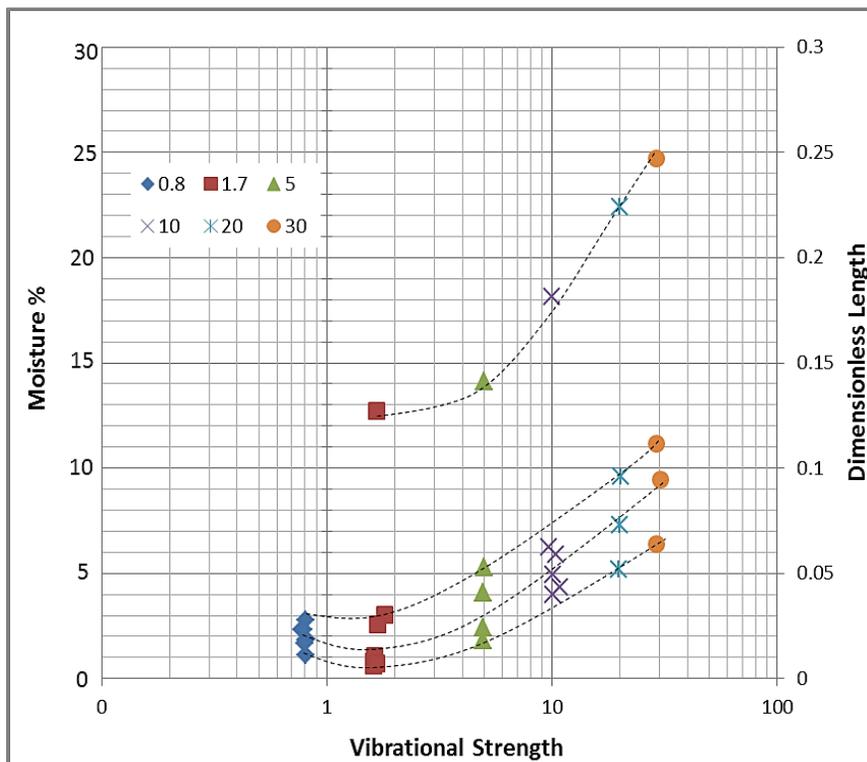


Figure 3.15 Effect of Vibration strength on product moisture

The second operating parameter is the dimensionless length, which is the ratio of vibrational amplitude (A) and the pentane column length (Z_p) in the reactor. It was observed that these parameters affect the moisture separation individually as well as in the combination with each other. The detailed description of the interactions between these parameters is provided in Chapter 4, as these criteria were critical in developing the reactor for the Proof-of-Concept (POC) pilot-scale unit.

Figure 3.15 is a semi-log plot between product moisture and the vibrational strength. The plot shows the variation in product moisture contents as a function of vibration strength for different dimensionless lengths. When low strength is applied ($\zeta < 2.5$), the process produced consistently low moisture products ($< 4\%$). When a higher strength is applied ($\zeta > 10$), the moisture in the product varied over a wide range and was controlled primarily by other parameters. The increase in moisture indicates that an excessive amount of energy may hinder the water coalescence mechanism inside the reactor. It is very evident from the data that the increased in energy may not necessarily improve the kinetics of dispersion; rather it can

substantially hamper the product quality. From engineering point of view, this information is highly vital both in terms of economics and scale-up.

3.7 Conclusions

The HHS process implements the novel concept of dewatering by displacement. The process makes use of a novel vibrating mesh reactor, which is the crux of the proposed technology. The reactor substantially improves coal quality after oil-agglomeration of ultrafine coal particles by dispersing coal particles in the oil phase and by coalescing and rejecting water droplets that would otherwise be trapped in the coal-oil agglomerates. In order to better understand the technology, several series of bench-scale tests were conducted to provide insight regarding the underlying thermodynamics and kinetics that control the system. The thermodynamic studies uncovered several important aspects of the process, including the water coalescence mechanism and the specific range of energy required for an efficient performance. Likewise, the kinetic studies assisted in determining the rates of homogenization and de-agglomeration, which directly control the behavior of particles inside the reactor. The information obtained from the thermodynamic and kinetic studies is crucial for the design of the reactor.

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CHAPTER 4 – Engineering Development of HHS Process POC Pilot Plant

4.1 Introduction

After successful bench-scale demonstration of the *Hydrophobic-Hydrophilic Separation* (HHS) process, a preliminary design for a proof-of-concept (POC) pilot plant was developed using the batch-scale testing data. Perigon, a chemical engineering design firm based in North Carolina, was consulted for review of the preliminary designs and for recommendations on process equipment and safety features for the POC plant. The construction of the POC pilot plant was started at the Department of Mining and Minerals Research Laboratory in Virginia Tech and was sponsored by Evan Energy, LLC, an investment company based in Richmond, Virginia. The POC processing unit was designed for cleaning fine coal (0.15 mm x 0) with a raw dry feed capacity of 100 pounds/hour. To take advantage of gravity flow and to minimize the pumping requirement in the POC operation, a modular type design was developed.

The construction of the pilot plant started in August 2012 and completed in June 2013. The POC pilot scale units were constructed as totally non-electric, enclosed units due to the presence of flammable hydrocarbon liquid. Power required for agitating the slurry and moving the material through the process was provided by pneumatic motors. For pumping the slurry, peristaltic pumps were utilized, which eliminated any possible leaks due to pump shaft seals. All the processing units were designed to be operated under a nitrogen blanket at a slightly elevated pressure. All the necessary safety features were incorporated in the POC pilot plant. A multi-point pentane and oxygen sensing system was installed to monitor the leaks at the agitator shaft seals, in the vent from the condenser, and near the floor around the processing unit. Ancillary electrical equipment supporting the processing unit (water heater, water chiller, nitrogen generator, compressed air supply, etc.) was located in an adjacent permanent building, while the POC plant was constructed in the open-air shed. To eliminate any possibility of static electricity due to the fluid flow, all process units and streams were grounded with multiple ground rods. In addition, a series of startup, shutdown and operating protocols were developed for a safe operation.

Shakedown testing commenced in June 2013 and was completed in August 2013. Several modifications were implemented in the POC operation during the period, which are discussed in the chapter.

4.2 Development of Process Flowsheet Diagram (PFD)

After the successful bench-scale studies a 100 lbs/hr process flowsheet for the HHS process was developed using the data obtained from the laboratory testing. The LIMN® process flowsheet software developed by David Wiseman Pty Ltd was used for balancing solids, water, and pentane flow rates under steady-state conditions. LIMN® is a Microsoft Excel-based software package, which has built in routines for process modeling.

In the proposed flowsheet, several parameters were examined including pentane losses with the discharge of solid products and losses due to pentane solubility in water. Figure 4.1 shows the balanced flowsheet designed for a clean coal product with a target moisture of 6%. In the proposed design, two new units were added in the process, which were not implemented earlier in the continuous bench-scale set-up. These units were a sieve bend to minimize water flow into the phase separator (vibrating mixer) and a clarifying thickener to minimize pentane and carbon losses.

In the developed flowsheet, the feed stream is treated with a high dosage of liquid n-pentane (25% by weight of carbon content) in a high/low shear mixing tank for agglomeration process. The agglomerated overflow from the mixer unit passes through a sieve bend where the sieve oversize material (mostly agglomerates) treated in a phase separator (later called as “vibratory mixer”), which is the key unit operation in the process. The undersize stream from the sieve bend, which mainly contains water and mineral matter, passes to a clarifying thickener. The thickener underflow is rejected from the process as waste. Any residual pentane or partially agglomerated fine coal particles that are lighter than water float as overflow from the thickener and are recycled back to the high/low-shear mixer. This additional clarifying step helps in minimizing the losses of pentane in the process.

The phase separator disperses the agglomerated coal and entrapped moisture (around 40% moisture) in pentane as described in the batch scale testing. The final target moisture was specified 6% by weight in the flowsheet to balance the water in the process streams. The phase separator overflow with 10% solids concentration (dry coal in pentane) is pumped to a hydrophobic liquid (HL) thickener. Coal particles and associated moisture settle quickly in pentane liquid because of the higher differential density between clean coal, water and pentane. It was observed during the batch testing that some amount of moisture (4-8%) in product actually facilitates coal settling in the HL thickener. The underflow of the phase separator, which mainly

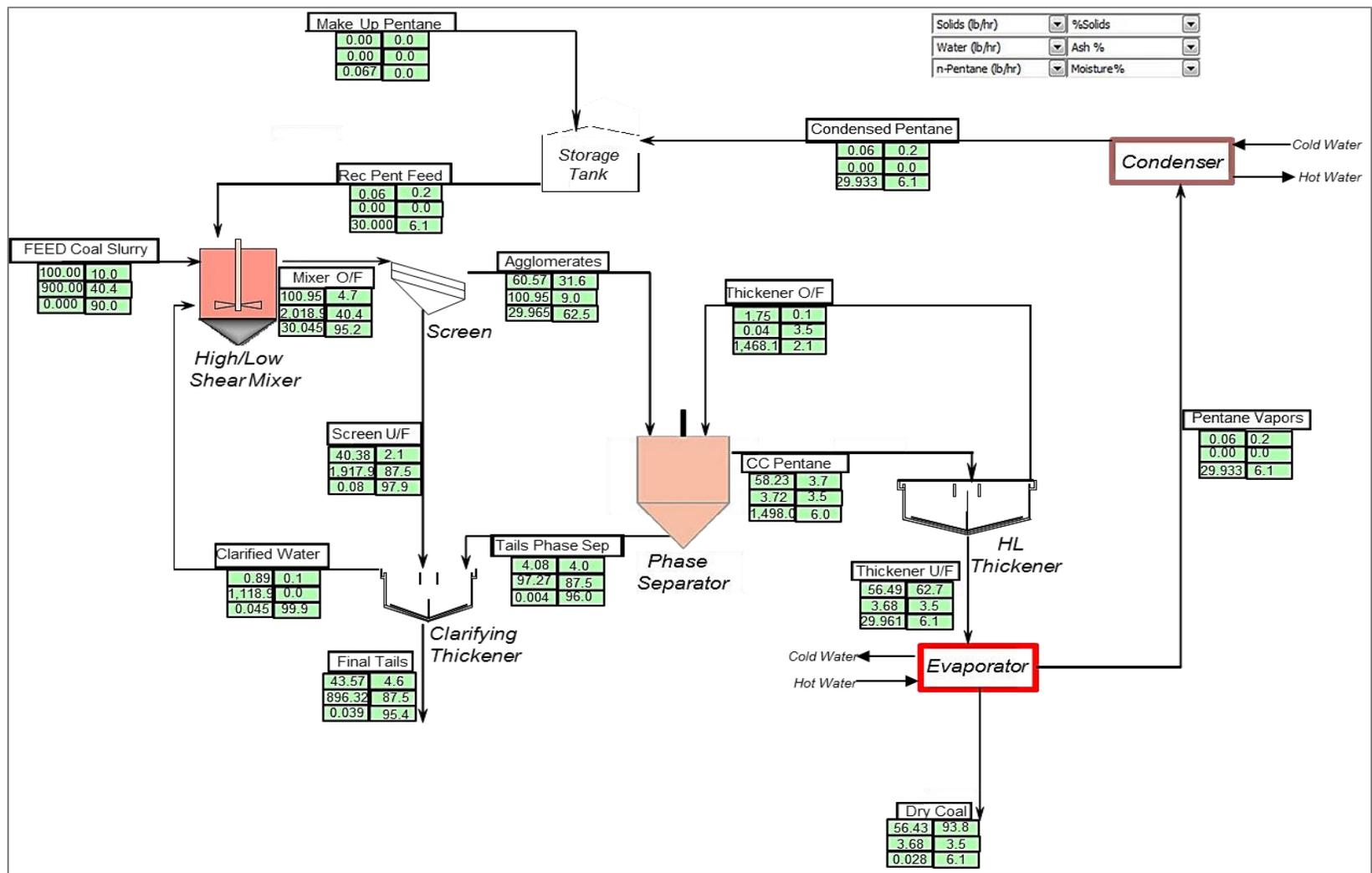


Figure 4.1 Proposed mass-balanced HHS process flow sheet for 100 lbs/hr POC pilot plant

contains water and mineral matter, is pumped into the clarifying thickener. The HL thickener is initially filled with pentane prior to operation. The supernatant from HL thickener, which may carry a small percentage of solids, is transferred back to the phase separator. This pentane recycle helps in continuous flushing of dispersed coal from the phase separator to the HL thickener. The settled coal from the HL thickener (30% solids) is pumped to a pentane recovery circuit. The pentane recovery circuit is comprised of an evaporator and a condensing unit. The condensed pentane liquid, which is pure pentane, is transferred back to the pure pentane drum. A make-up pentane stream covers any losses of pentane in the process.

The LIMN® software was used to balance the solid and liquid flow rates through the process circuit. The simulation required several thousand iterations to reach steady state. The simulation results indicated that the total loss of pentane would be approximately 0.067 lbs/hr based on pentane solubility in water and pentane absorption in coal (obtained from bench-scale tests). This loss equates to about 1.34 pounds per ton of coal processed.

The simulated flowsheet proved to be very helpful for the engineering design and development of a proof-of-concept (POC) pilot-scale plant, which is the focus of this research. The flowsheet was further modified during the scale-up and shakedown testing as new data became available, as will be discussed later in this document. Additionally, Perigon, a chemical engineering firm based in North Carolina, was consulted regarding the appropriateness of the simulated flowsheet. The consultation was primarily to review the POC design and to recommend the pentane recovery system. Moreover, Perigon assisted in identifying safety features necessary to operate the POC plant in an intrinsically safe manner.

4.3 Procedure for Development of POC Unit Operations

The primary intent to develop the POC pilot plant is to demonstrate the separation capabilities of the HHS process on a large-scale. The HHS process is unique in that the technology involves several sub-processes such as mixers, size separators, heat-exchangers, and a novel dispersion/de-agglomeration method for dewatering. The engineering development of the POC unit operations was not only limited to technical data obtained from bench-scale testing, but also on scientific and engineering judgments based on previous research in the published literature.

The novelty of the process and lack of scale-up information created a high level of uncertainty in designing the POC test circuitry. In light of this, a conservative scale-up approach was used in determining the critical dimensions and relative sizes of the POC units. In theory, this approach can be used by applying the principle of similarity for a same process step (i.e. in batch and POC). This principle involves maintaining geometric ratios and dimensionless groups (characterizing the phenomena of interest) constant at a larger scale. The phenomena involved in the HHS process are complex; therefore, it is difficult to maintain constant values for all the dimensionless groups associated with the process.

The conceptual flowsheet shown in Figure 4.1 provided crucial steady-state information, such as slurry flow rates, solids mass rates, etc., necessary for sizing of the reactors and pumps. Another prime parameter for sizing is the residence time for each process step. Although in batch-scale testing, the residence times for unit operations were significantly low, the POC units were designed conservatively with in excess capacity to provide much higher residence times. The design of over-capacity reactors was a *cautious* step taken to give flexibility in the pilot plant testing, particularly in terms of accommodating wide variations in operating parameters.

4.4 Development of Mixing Devices

Translation of mixing processes from a laboratory scale kitchen blender to the POC pilot operation was challenging. Though data is available in the literature from several thousand mixing applications, identifying an exact scale-up correlation was not possible. The oil agglomeration process involves two stages mixing. The high-shear mixing step is needed to break hydrophobic bridging oil into small droplets and facilitate the coal particle-oil contact. The low shear mixing step is needed to promote agglomerate growth.

The two most common parameters generally used for mixing scale-up are constant P/V (actual horse-power drawn by an impeller/ active volume in a tank) and constant T/V (actual impeller torque/ active volume). Unfortunately, the kitchen blender used in laboratory testing does not provide any credible information for actual power drawn or impeller torque. On the contrary, the blender did provide the information that was used to attain dynamic similitude among the four fluid forces in a mixing tank. One is the inertia force put in by the mixer and the other three are opposing forces that resist mixing. These are the viscous force, gravitational force, and the surface tension force. The ratio of the inertia force with these opposite forces

generate dimensionless quantities called Reynolds number (Equation 4.1), Froude number, and Weber number (Equation 4.2) respectively, which can be used for designing POC pilot plant mixing applications. It must be noted that Froude number is usually important only in cases where gross vortexing exist and thus can be eliminated by installing baffles in a tank in turbulent conditions (Amanullah, 2004). The Reynolds number for mixing applications is defined as:

$$Re = \frac{N\rho d^2}{60\mu} \quad [4.1]$$

where N is speed (rpm) of an impeller, ρ is the density of slurry (Kg/m^3), d is the impeller diameter (m) and μ is the slurry viscosity (N-sec/m^2). Values of Re define the flow conditions. For $Re < 100$, the flow is laminar while for $Re > 1000$, the flow is defined as turbulent. Similarly, Weber number for a mixing application can be defined as:

$$W_b = \frac{N^2\rho d^3}{3600\sigma} \quad [4.2]$$

where ' σ ' is the interfacial tension (N/m) of the hydrophobic liquid.

4.4.1 High-Shear Mixer

The 1.25 L glass jar used for high-shear mixing on the bench-scale system has a cylindrical shape and tapered-flat bottom. The internal diameter (D) of the jar was 4.5 inches with two baffles that were each 0.5 inch wide (b). A custom paddle-type two-flat-blade impeller of 1.5 inch diameter (d) was installed at the bottom. The blender's top speed (N) was up to 18,000 RPM and was adjusted using a variable-speed controller. For batch-scale testing, the high-shear mixing was conducted at 11,000-12,000 RPM for 15-20 seconds, and later the speed was lowered down for low shear mixing. Additionally, in each test 600 ml of coal slurry (6% solid) was used to make the liquid level (Z) in the blender equal to 3.5 inches above the top of the impeller. For sizing the high-shear prototype unit, the geometrical ratios such as impeller diameter/ tank diameter (d/D); baffle width/ tank diameter (b/D); and impeller diameter/ liquid level height (d/Z) were kept constant. Two baffles were also designed in the POC unit similar to the laboratory scale blender.

Of the three aforementioned dimensionless quantities for scale-up, the Weber number is theoretically the most appropriate group for high-shear mixing scale-up since the phenomenon involves dispersing hydrophobic liquid into small droplets. Additionally, Reynolds number was

evaluated to keep the same order of turbulence in the mixing system. For a similar feed type and hydrophobic oil and using Equation 4.2, one can establish the following relationship:

$$N_{HS-POC} = N_{HS-lab} \left(\frac{d_{lab}}{d_{POC}} \right)^{3/2} \quad [4.3]$$

For effective dispersion of oil droplets, a 4-inch diameter (d_{poc}) high-dispersion blade, which is very common in applications such as paint dispersion, was selected. These impellers convert the majority of the energy of the motor to shear force. These impellers have much lower power number, of the order of 0.45, but they are run at very high speed to produce desired dispersion. From Equation 4.3, a scale-up correlation is established to identify the required speed (rpm) for the POC prototype unit (illustrated in Figure 4.2). Additionally, Reynolds number at these operating speeds, calculated from Equation 4.1, shows same order of turbulent flow in laboratory scale tests ($Re_{lab} = 2.5 \times 10^5$ at 11000 RPM), as well as in the pilot-scale tests ($Re_{poc} = 4.1 \times 10^5$ at 2500 RPM).

The process flowsheet shows the slurry feed rate to the mixing units is 4.3 gallons/min. Based on the given flow rate and scale-up ratios, the high-shear mixing tank was fabricated using the specifications shown in Figure 4.3. The constructed tank provides approximately 2 minutes of residence time for high-shear mixing. Table 4.1 summarizes the scale-up ratios and calculated design parameters used for designing POC high-shear mixing unit.

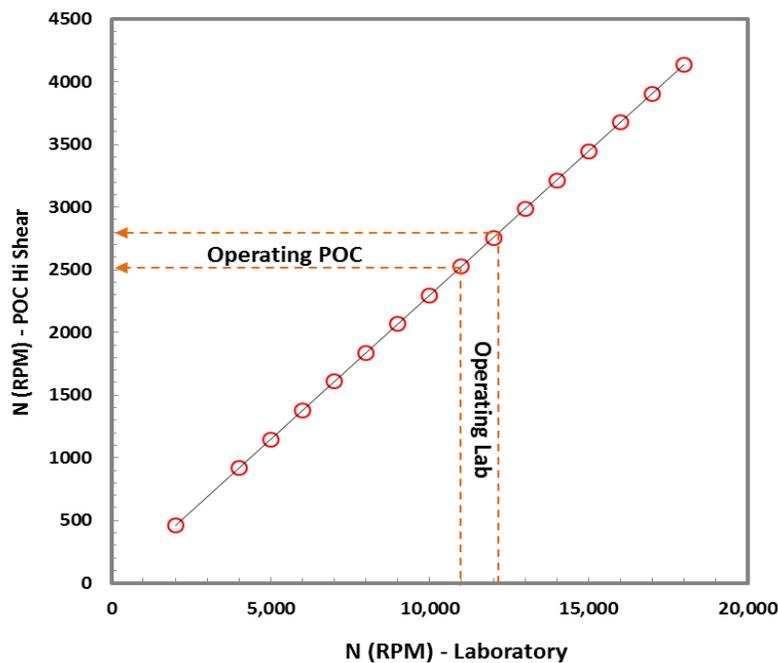


Figure 4.2 Scale-up correlation between lab-scale high-shear mixing and POC prototype.

Table 4.1 Geometric ratios and dimensionless criteria used for designing POC Hi-shear mixing unit

Parameters	Laboratory Scale	Designed Pilot Scale
Impeller diameter (d)	1.5"	4"
Tank diameter (D)	4.5"	14"
Baffle width (b)	0.5"	1.5"
Liquid level (Z)*	3.5"	9"
RPM (N)	11,000	2500
Geometrical Ratios		
d/D	0.33	0.29
b/D	0.11	0.11
d/Z	0.43	0.44
Dimensionless Quantity		
Weber number**	1.2×10^6	1.1×10^6
Reynolds Number**	2.5×10^5	4.1×10^5

*Liquid level height is calculated from the position of the impeller

**Complete data is available in Appendix B

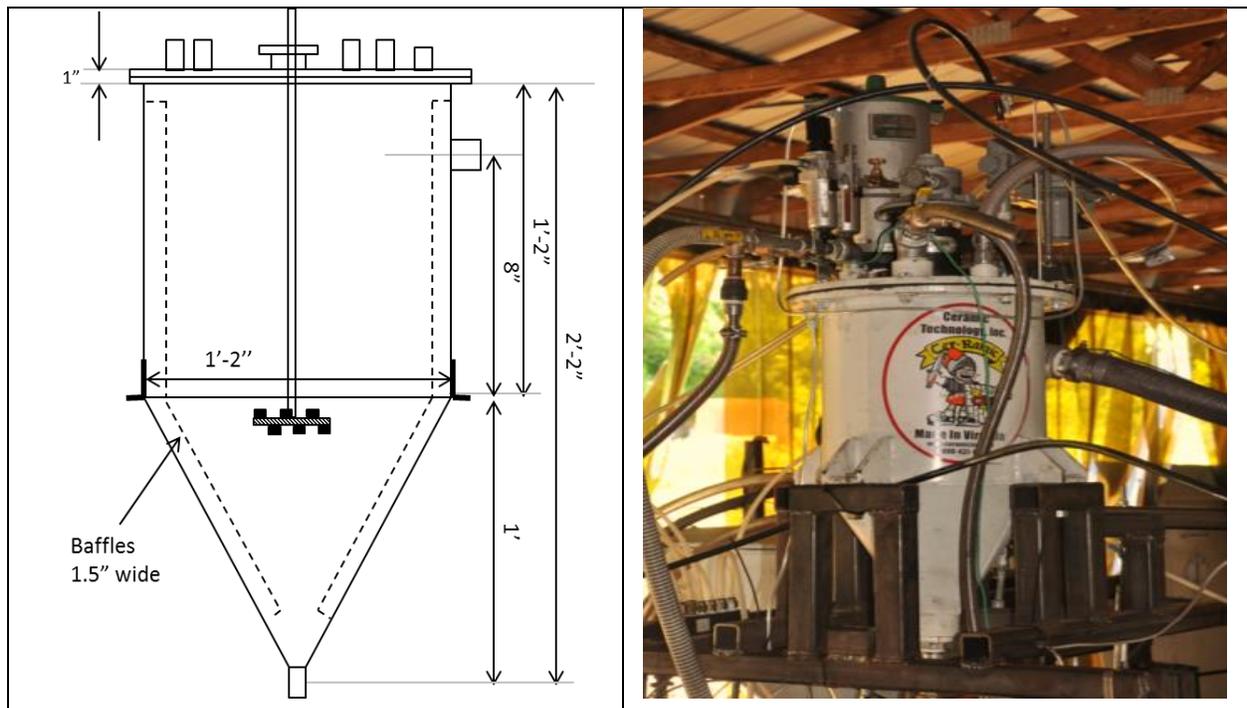


Figure 4.3 (a) Hi-shear mixing tank design (b) Constructed hi-shear tank for POC plant.

4.4.2 Low Shear Mixing

In the laboratory-scale testing, low-shear mixing was achieved by utilizing the same kitchen blender, but operated at lower speed in the range of 5,000-6,000 rpm. The sole purpose of low-shear mixing was to allow micro-agglomerates to grow, thus minimizing the carbon loss in the reject. The residence time used in the laboratory tests varied from 40 seconds to 6 minutes for agglomerate growth. The growth rate depended on the coal hydrophobicity. In the laboratory-scale testing, it was observed that some of the high-grade bituminous coals do not require low shear mixing, as they quickly grow during the high-shear mixing. Thus, the installation of low-shear tank in the POC pilot plant was a cautious step taken and added as an option to provide flexibility in terms to treating variable coal feedstocks.

Impeller operating speed required in the pilot plant for low shear mixing was set based on keeping a constant Reynolds number. From Equation 4.1, for same feed type and hydrophobic liquid, a correlation can be established to identify the needed speed as described in Equation 4.4.

$$N_{LS-POC} = N_{LS-Lab} \left(\frac{d_{LS-Lab}}{d_{LS-POC}} \right)^2 \quad [4.4]$$

An excess capacity tank was designed for low-shear mixing with multiple overflow ports, as shown in Figure 4.5(a), to generate variable residence time ranging from 6 minutes to 15 minutes at a given flow rate of 4.3 gallons/minute. For sufficient mixing in the excess volume tank, two (2) identical 5-inch diameter propellers were installed on the same shaft. Typically, in such cases, the spacing between the propellers is kept at least one impeller diameter. The bottom impeller was located 11 inches below from the lowest tank overflow port so that the geometric ratio, d/Z (impeller diameter/liquid level height) = 0.43, could be kept constant. The second impeller was installed 12 inches above the bottom impeller (greater than twice the impeller diameter). Using the correlation from Equation 4.4, operating speed was calculated to be 450-540 RPM. This speed was in the same range as the laboratory-scale unit, whose Reynolds number was in range of 1.2×10^5 to 1.4×10^5 .

The complete data for the Reynolds number and Weber number analyses are provided in Appendix B for POC development of the low- and high-shear mixers, respectively.

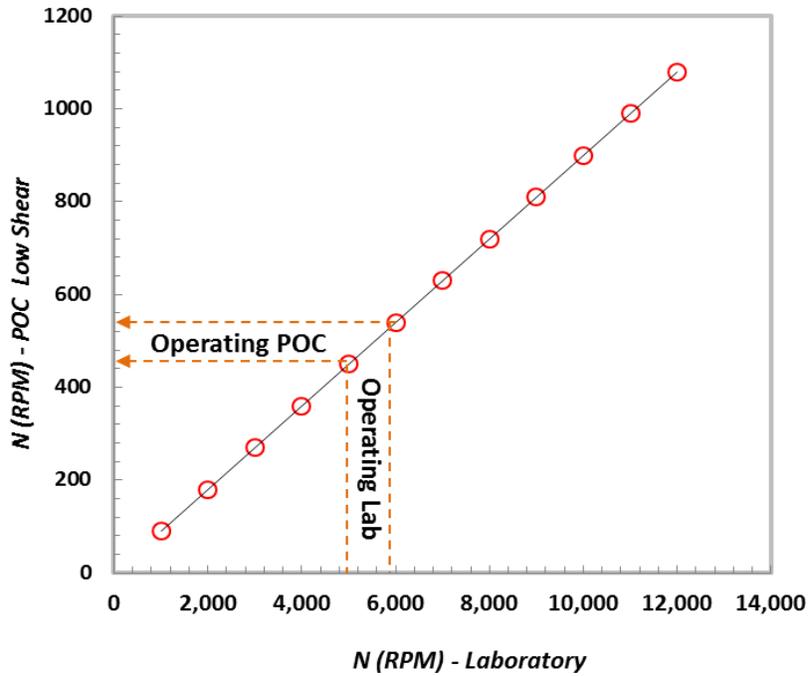


Figure 4.4 Scale-up correlation between lab-scale low-shear mixing and POC prototype.

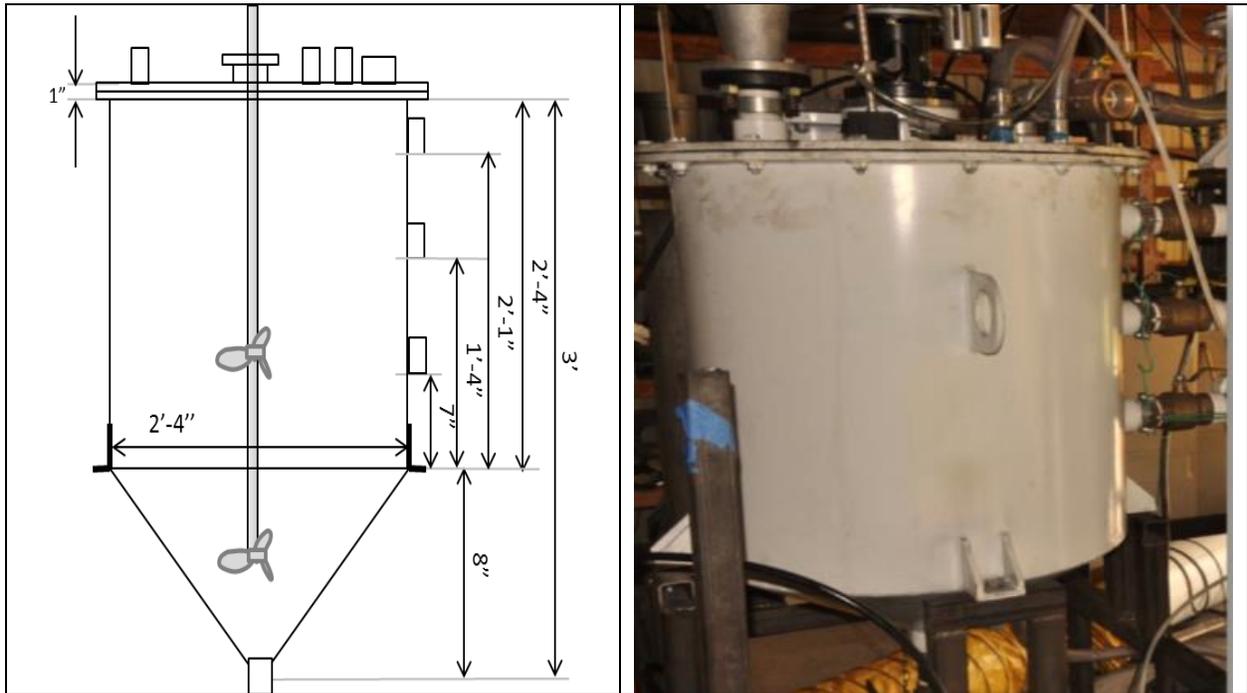


Figure 4.5 (a) Low-shear mixing tank design (b) Constructed low-shear tank for POC plant

4.5 Selection of Sieve Panel

The overflow of high/low shear mixing is a solid-oil-water system. This three-phase system is treated in a stationary curved sieve bend to separate the agglomerated coal from the dirty aqueous phase. Typically these sieve bends are sized based on material flow rate over the panel. A 1 feet x 1 feet square panel can dewater up to 100 gallons/minute (Luttrell, 2013) and removes a maximum of 45% water (Woodie, 2013).

Conn-Weld Industries donated two curved sieve screens for the POC plant, a 60 mesh and a 45 mesh wedge wire designed perpendicular to flow. The screens were 2 feet wide x 1 feet long and slightly curved with an angle of 37° (Figure 4.6a). For safety reasons, the whole system was enclosed in a custom-made stainless steel screen-box (Figure 4.6b) manufactured and donated by the Eriez Manufacturing Company. The screen-box was designed to hold up to 5 PSIG of pressure.

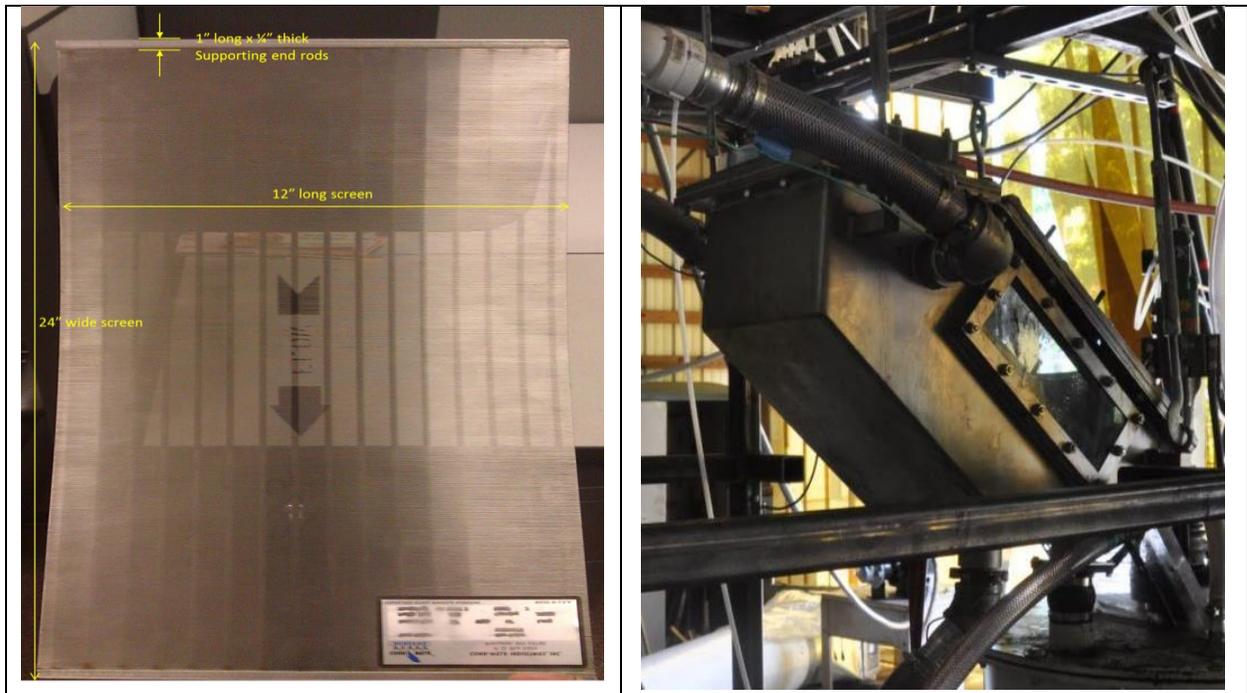


Figure 4.6 (a) Sieve panel from Conn Weld (b) Installed enclosed screen-box in POC pilot.

4.6 Development of Novel Dispersion Device

The novelty in the proposed HHS Process technology comes from the innovative de-agglomeration unit. The unit serves multiple functions involved in cleaning and dewatering fine particles. The development of the prototype reactor and scaling-up of the novel vibratory dispersion device, by far, was the most challenging task in designing the POC plant. As this step in the process is the heart of the HHS technology, successful scale up of this unit was essential.

4.6.1 Construction

The prototype POC reactor was designed as a replica to the corresponding laboratory-scale unit, but with multiple overflow ports to evaluate variable design parameters. The detailed design and constructed unit is illustrated in Figure 4.7. Two 24-inch diameter Sweco screens of aperture 165 mesh and 35 mesh with a center hole was attached to a central support shaft. The screens were separated 8 inches apart, to a single shaft to replicate the laboratory-scale dispersion device. To generate oscillatory motion, an explosion proof pneumatic vibrating saw was attached to the innovative dual-screen shaft system (shown in Figure 4.8) with a custom-made cylindrical adapter. The detailed designs are available in Appendix B. The pneumatic saw is a 1.3 HP unit that can run at variable frequencies from 0-30 Hz with a constant amplitude of 1.125 inches.

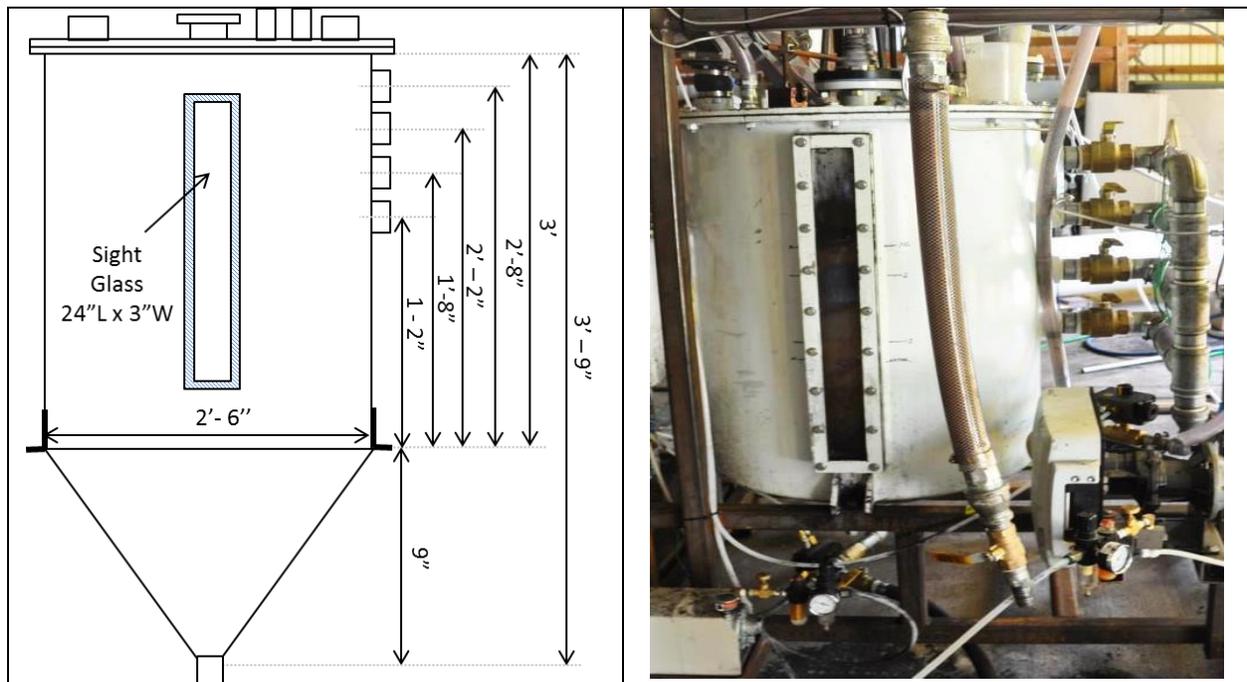


Figure 4.7 (a) Low-shear mixing tank design (b) Constructed low-shear tank for POC pilot.

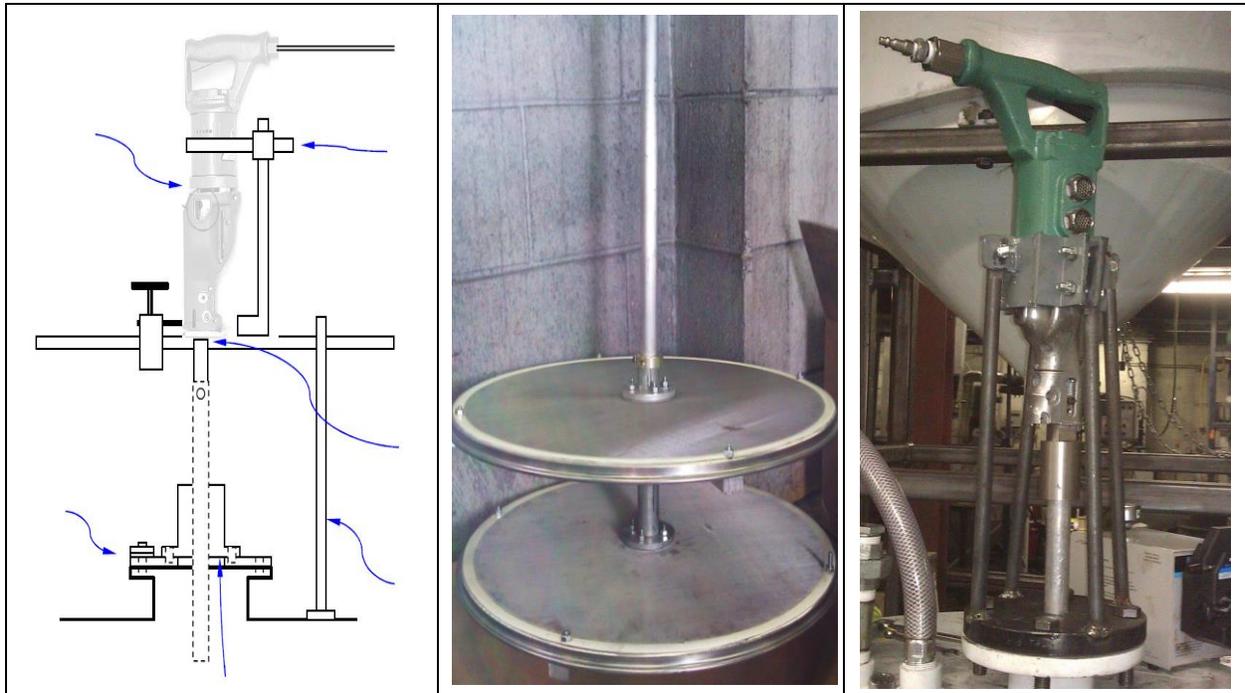


Figure 4.8 (a) *Set-up of POC mechanical vibrating device* (b) *Constructed vibrating mesh system for POC pilot* (c) *Pneumatic saw used to provide oscillations*

4.6.2 Parametric Studies and Scale up Criteria

Two dimensionless quantities were investigated at batch-scale, vibration strength and the dimensionless length. The two parameters are considered to be critical for the de-agglomeration unit to achieve a low-moisture product. Vibration strength, which relates vibration energy as a function of both frequency and amplitude, has been defined previously in Chapter 3 (Equation 3.7). The dimensionless length is defined as the ratio of the oscillation amplitude (A) to the hydrophobic liquid column height (Z_p) in the vibrating mixer. It can be described as the characteristic length traveled by a completely dispersed particle reporting to the overflow port.

In light of this, a detailed response surface two factorial (2FI) model was developed using Design Expert® software designed by Stat-Ease. The software is commonly used to locate ideal process conditions utilizing the existing data. The designed model provides a combinatorial relationship in terms of coded factors that can be used to make prediction about the response for parameters within the data range. In the coding system, high levels are coded as +1 values and low levels are coded as -1 values. The coded equation for the vibrating mixer calculated by model was found to be:

$$\% \text{ Moisture} = 10.96 + 7.30 (VS) + 9.92 (DL) + 7.24 (VS * DL) \quad [4.5]$$

Where “VS” is *vibrational strength* and “DL” is *dimensionless length*. Equation 4.5 shows that the coded values are large positive coefficients, which indicates high impact of both the parameters individually as well as in combination on final product moisture. The actual equation derived using the batch-scale data is given by:

$$\% \text{ Moisture} = 0.76 - 0.043 (VS) + 26.48 (DL) + 5.97(VS * DL) \quad [4.6]$$

Equation 4.6 with actual factors may be used (though it is not recommended due to the empirical nature of the expression) to make predictions about the moisture response for each factor. The R-squared value for the model is 0.717 and is in reasonable agreement with the adjusted R-squared value, which is 0.813, showing the model can be used to navigate within the design space. The response surface based on two-factorial combinatorial model is illustrated in Figure 4.9. It is apparent that, higher vibration strength (energy) and high dimensionless length escalate the product moisture.

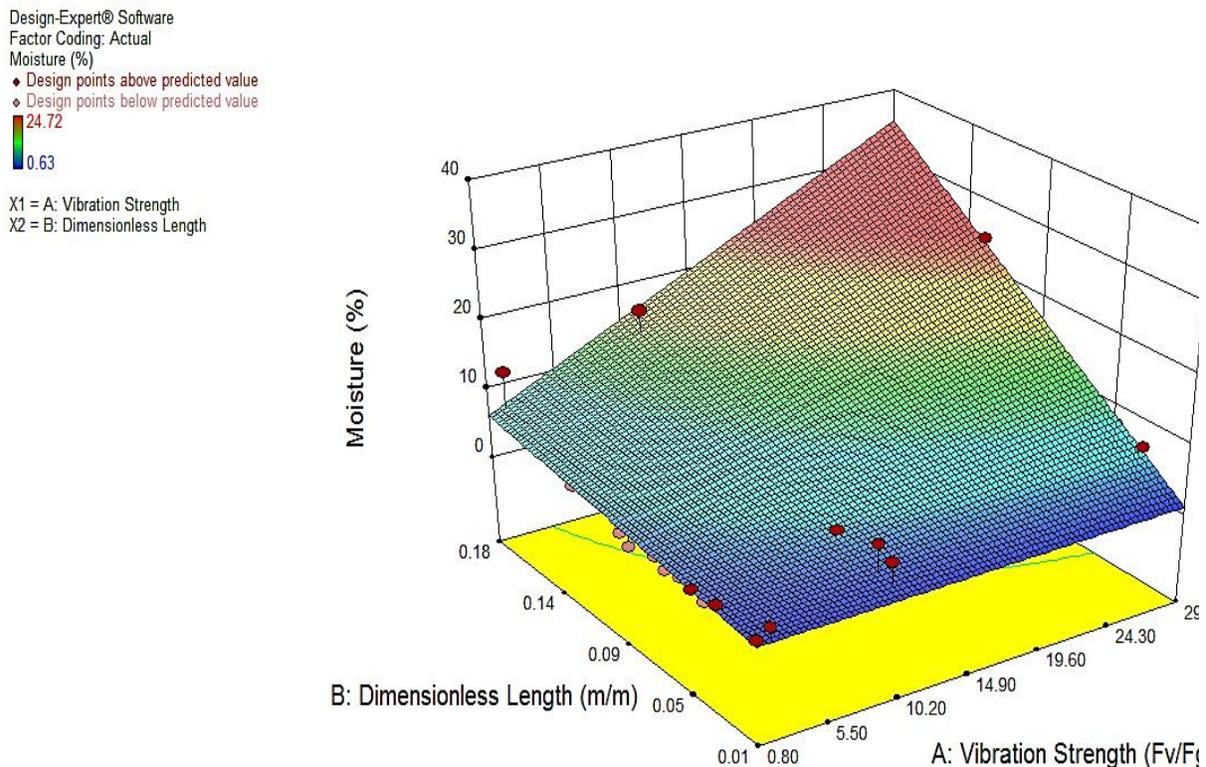


Figure 4.9 Response surface curve showing the effect of vibration strength and dimensionless length on product moisture

4.6.3 Operating Conditions for POC unit

To identify the operating conditions of POC unit, the scale-up correlation was developed to achieve same product moisture. Figure 4.10 shows the effect of variable dimensionless length (A/Z_p) on the HHS process product moisture obtained from the batch-scale unit. The experimental data clearly identify the effective dimensionless length, which is less than 0.1 for single-digit product moisture. Therefore, for fixed amplitude of 1.125 inches in the POC unit, the hydrophobic liquid column height (Z_p) was kept 11 inches. This height placed the bottom screen in the oil phase, 1-inch above the oil-water interface.

For vibration strength, Equation 3.7 establishes following scale-up criteria:

$$f_{POC} = \frac{1}{2\pi} \left(\frac{g \cdot \zeta_{Lab}}{A_{POC}} \right)^{1/2} \quad [4.7]$$

where, f_{poc} is the operational frequency of the de-agglomerator at POC pilot unit, ζ_{Lab} is the vibration strength at laboratory scale, A_{poc} is the amplitude of oscillatory frequency in the pilot unit and g is the gravity (9.81 m/sec^2). A series of experiments was conducted on the batch unit to identify an effective range of vibration strength required for consistent product moisture. Figure 4.11 shows a semi-log plot between the product moisture with respect to the vibration strength. From the plot, it is evident that the low vibration strength (<2.5) always produced consistent moisture reductions irrespective of dimensionless length. The moisture values were more inconsistent at higher vibration strengths (>10). From a thermodynamic standpoint, lower energy in the process is necessary to facilitate desirable water coalescence and to eliminate the unwanted formation of stable micro-emulsions.

Figure 4.12 provides a graphical correlation that identifies the operating frequency for the POC unit at constant vibration strength and given amplitude 1.125 inches. For low vibration strength (0.5 to 2), the required operating frequency is only in the range of 2-4 Hz. The low frequency is easy to manage and eliminated concerns over the mechanical stability of the oscillating screen-shaft structure at higher operating frequencies.

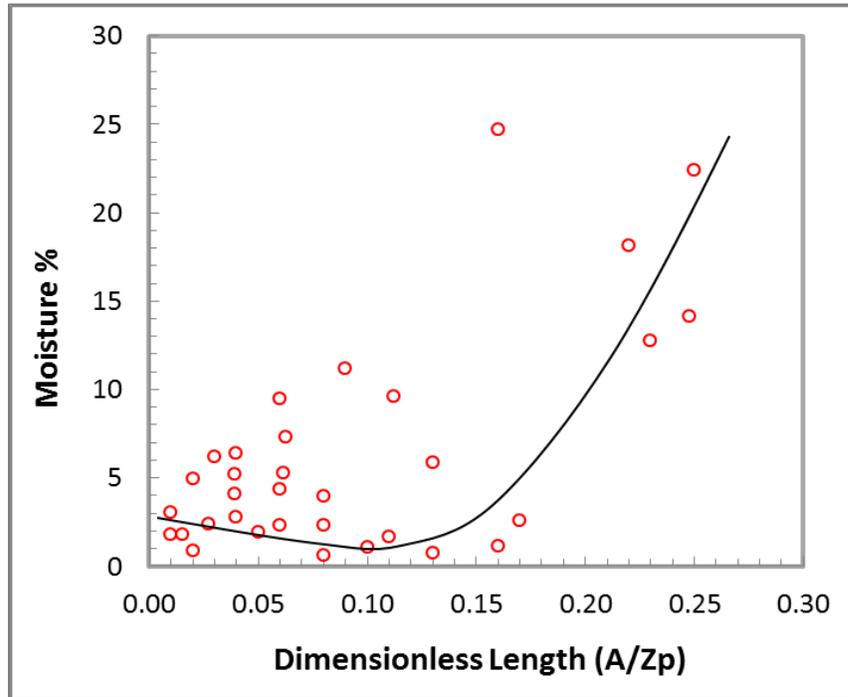


Figure 4.10 Experimental data showing effect of dimensionless length on product moisture

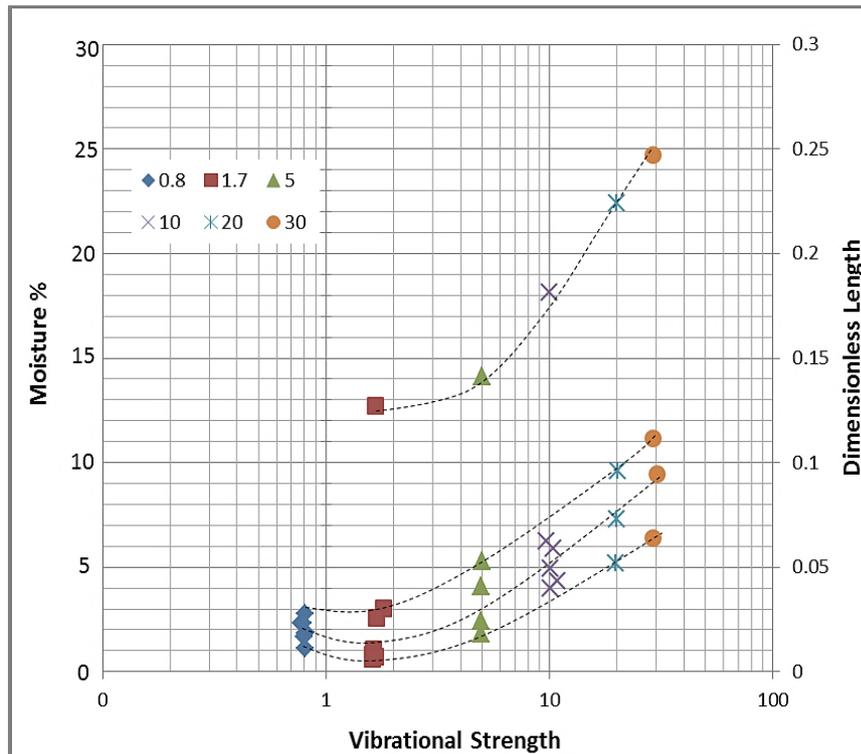


Figure 4.11 Experimental data showing the effect of vibration strength on product moisture

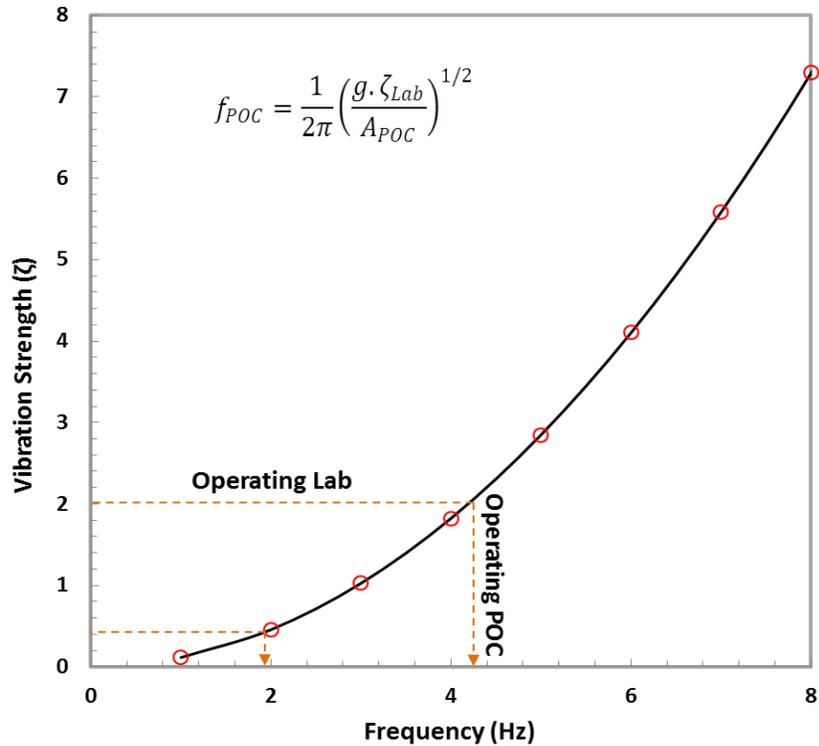


Figure 4.12 Scale-up correlation between lab-scale vibratory mixer and its POC prototype.

4.7 Development of Process Thickeners

Solid-liquid separation systems are the key part of any process involving liquid for separation. The separation can be achieved by several ways such as in settling tanks, thickeners, centrifuges etc. For the HHS process POC pilot-plant, both thickener and solid-bowl centrifuge units were initially considered for processing of the tailings and vibrating mixer overflow (pentane-in-coal product), respectively. Thickeners typically produce 15-30% solids products and have a longer residence time. Solid-bowl centrifuges can produce up to 60% solid products and are more common for recovering fine particles. Although latter can be more suitable in reducing the pentane evaporation load, the cost associated with a smaller solid-bowl centrifuge (based on a given flow rate) was 20-fold higher compared to a stationary tank. Hence, a thickener was designed to treat the process stream containing the coal-pentane product from the POC vibrating mixer unit.

4.7.1 Development of Hydrophobic Liquid Thickener

The hydrophobic liquid thickener intercepts the clean dewatered coal in the pentane liquid stream to thicken the solids and ultimately reduce the load in the evaporation step. The top

size of the particle to be treated in the pilot plant is 44 microns. A simple Stokes equation calculation for the top size coal particle suggests 9 times higher terminal velocity in pentane as compared to water (Figure 4.13). During the period of POC development and construction, settling studies of particles in pentane were not studied and, therefore, the HL thickener for the POC unit operation was designed based on an upper flow rate dictated by an approximate residence time target. Later, a detailed study for particle settling was conducted using the Coe and Clevenger method for developing a thickener model and is discussed later in this document. The process flowsheet shows approximately 5 gallons/minute pulp flow rate to achieve 30% solids from the thickener underflow at 15 minutes residence time.

An 80 gallon capacity tank was designed as shown in Figure 4.14 with a 360° circumferential overflow launder and a large 45° conical bottom. Sizing for a conventional thickener is typically based on a rise rate (i.e. gallons per minute feed per square feet of tank surface area) of 0.5 gallons/minute/feet² (Smith, 2010). For 5 gallons/minute feed rate, the required tank area should be around 10 ft², which provided a diameter of the POC unit approximately 3 feet 6 inches.

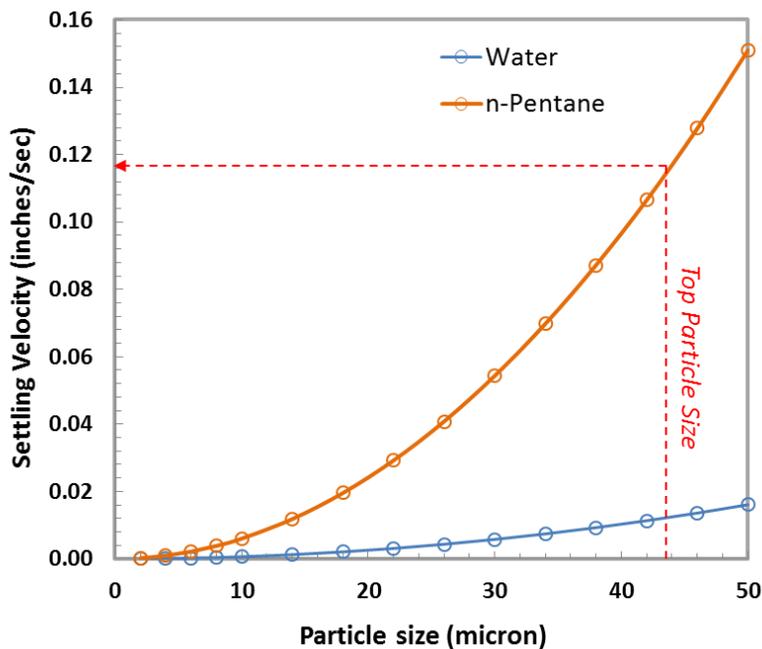


Figure 4.13 Schematics showing differences in settling velocity of particle in water and pentane using Stokes law

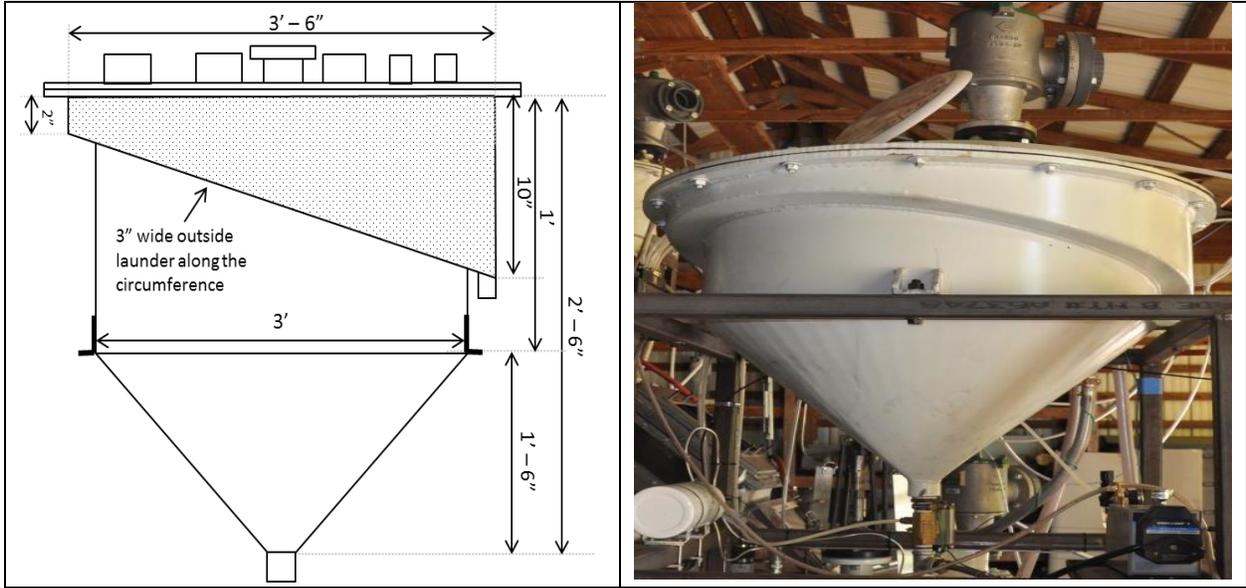


Figure 4.14 (a) Hydrophobic liquid thickener design (b) Constructed HL thickener for POC pilot plant

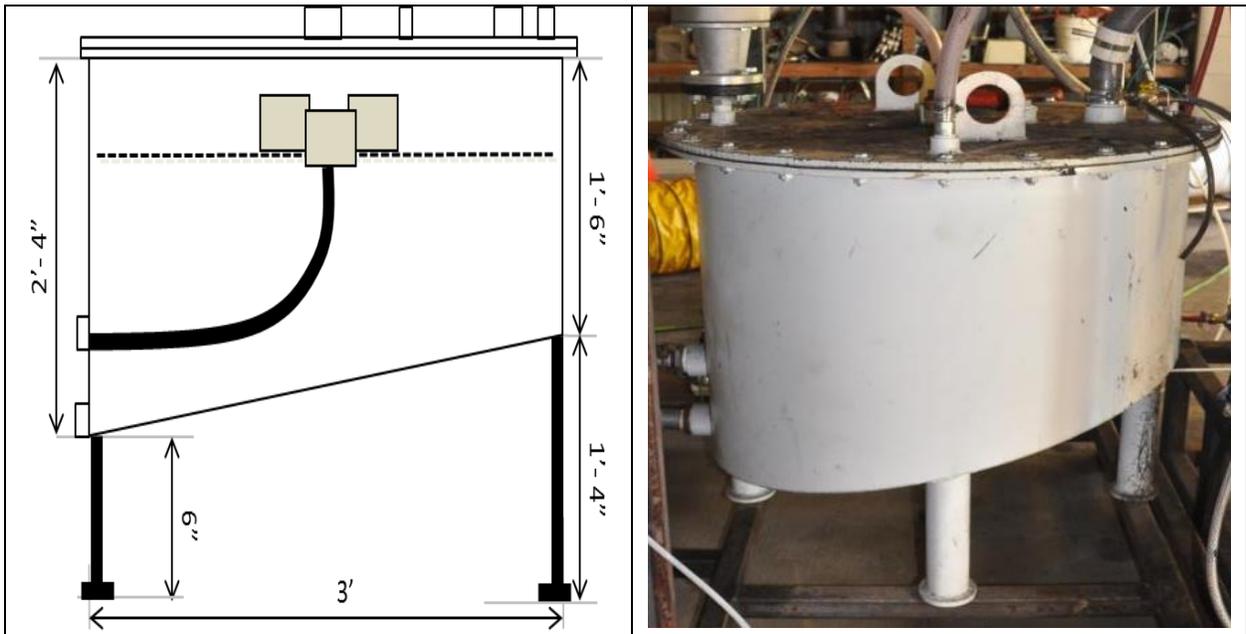


Figure 4.15 (a) Tailings thickener design with equipped oil skimmer (b) Constructed tailings thickener for POC pilot plant

4.7.2 Development of Tailings Tank

The tailings thickener was incorporated into the POC pilot plant to clarify the undersize stream from the sieve bend and the underflow stream from the vibratory mixer. The tank was custom designed (Figure 4.15) in order to accommodate a floating oil skimmer. The skimmer was used to recover and recirculate any un-agglomerated coal particles and associated pentane liquid back into the system. The recycling minimizes any carbon loss and oil consumption in the pilot plant. The process flowsheet shows approximately 4.1 gallons/minute flow rate feed; therefore, a 60 gallon tank was designed to provide 15 minutes of residence time. The diameter of the tank was calculated in a similar way as for the hydrophobic liquid thickener, and calculated to be about 3 feet. The details of the oil-skimmer are provided in Appendix B.

4.8 Selection of Heat Exchangers

The two heat exchanging systems that are required for oil recovery in the HHS process are a hydrophobic liquid evaporator and a gas condenser. Though several direct and in-direct heat dryers are available in the market, capital costs associated with these units was the main criteria in selection of the dryer for the POC plant. For this application, only in-direct heat dryers were considered. In in-direct type dryers, heat is transferred through conduction and the heating medium does not make any direct contact with the pulp that to be dried (Osborne 1988). The condenser unit was selected from off-the-shelf item from the manufacturer. The selection was based on the required surface area and required gallons/minute of condensation capacity. Additional recommendations and suggestions were considered from Perigon in making final decisions about the purchase of these units.

4.8.1 Procurement and Re-fabrication of Dryer

Several options were considered for the dryer including new and used units, as well as rental pilot-scale units. The initial cost for new units was very high and out of the allocated budget, while rental units were only available for a limited time period. Therefore, a decision was made to find a used in-direct heat exchanging dryer and to repurpose the unit as required for the process. After several searches and with a recommendation from Perigon, a twin-screw (4-inch diameter) pilot-scale Holoflight® sludge dryer was located and procured from an aftermarket equipment supplier.

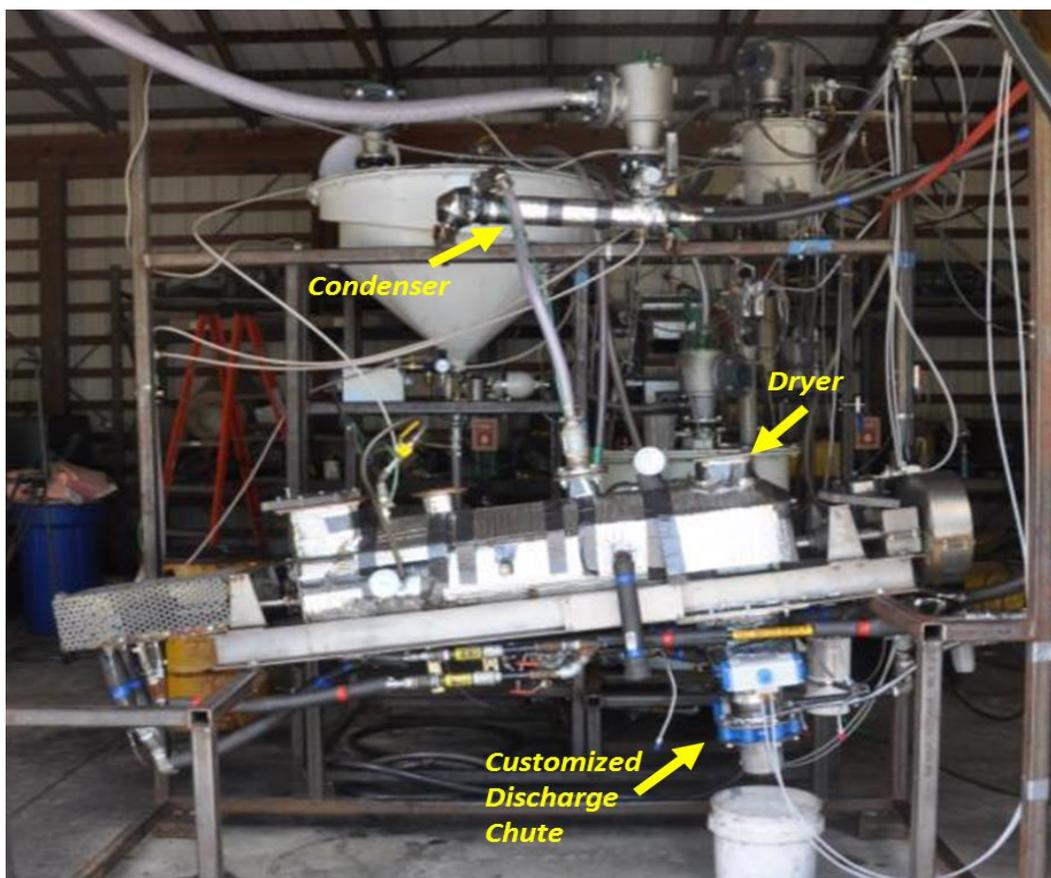


Figure 4.16 Installed pentane recovery systems in the POC pilot plant

The dryer has nominal length 4 feet with screw area 10 ft². The total volume of the unit is 1.7 ft³ with a jacket outside to circulate heating medium (Figure 4.16). The unit was designed to use thermal oil for heating at 500°C to dry sludge. However, pentane is a low volatile liquid with very low boiling point (98°F) and low specific heat of vaporization (156 BTU/lbm at STP, 153.7 BTU/lbm at 98°F) that can be evaporated with only gentle heating. For this reason, water was considered as a heating medium as it was safe and easy to handle.

The purchased dryer unit was cleaned, repaired, and refurbished as per the requirements. The modifications include installation of an explosion-proof pneumatic motor with gear-box and a custom discharge chute with a nitrogen gas chamber and two pneumatically controlled butterfly gate valves. The nitrogen chamber was added to collect dry clean coal product and to eliminate any atmospheric oxygen that could cause a safety risk. The residence time of solids in the dryer was 8-12 minutes when operating at a screw speed of 30 RPM.

Selection and Sizing of Water Heater

The temperature in the batch-scale laboratory evaporator was maintained at 120°F to drive off all the liquid pentane from the clean coal product. Similarly, the POC dryer unit was maintained at a temperature of 120°F. From the conceptual material balance flowsheet, the amount of pentane at 30% solids was found to be 128 pounds/hour. The heat capacities of pentane liquid ($C_{p-liquid}$) and pentane gas (C_{p-gas}) are 0.57 and 0.427 BTU/lbm/°F. From the given data, the specific energy required to evaporate pentane from room temperature ($T_r = 70^\circ\text{F}$) to the ambient temperature ($T_a = 120^\circ\text{F}$) was calculated from the following equation:

$$\Delta h_{Total} = C_{p-liquid}(T_b - T_r) + \Delta h_{vap}|_{T_b} + C_{p-gas}(T_a - T_b) \quad [4.8]$$

From Equation 4.8, the required specific energy is $\Delta h = 179.06$ BTU/lbm. Therefore, the power required to evaporate 128 pounds/hour pentane in the dryer was $P_{Required} = 22,942$ BTU/hour or 6725 watts. A 3500 watt household water heater with two heating elements was procured for this purpose. Typically, in the household heaters, only one element works at a time; therefore, the water heater was modified so that both heating elements could be used at the same time. This modification made it possible to provide up to a total of 7,000 watts of heat input if necessary for the POC pilot plant operation. The detailed description of the heating system can be found in the Appendix B.

4.8.2 Selection and Sizing of Condenser

A standard shell and tube heat exchanging condenser (TEMA standard) was considered for the pilot plant operation. This design is the most common condenser type used in hydrocarbon refining and other chemical processes. For sizing, the basic heat exchanger equation (Equation 4.9) was used to estimate initial area required (square feet) in condenser.

$$A_0 = \frac{Q}{U T_{LMTD}} \quad [4.9]$$

where Q is the heat load in the condenser (BTU/hr), U is the heat transfer coefficient (BTU/hr-ft²-°F) of the application, and T_{LMTD} is the log mean temperature difference and can be calculated from Equation 4.10.

$$T_{LMTD} = \frac{(T_1 - t_2) - (T_2 - t_1)}{\frac{(T_1 - t_2)}{(T_2 - t_1)}} \quad [4.10]$$

In Equation 4.10, T_1 is the inlet tube side fluid temperature (30°F), t_2 is the outlet shell side fluid temperature (70°F), T_2 is the outlet tube side fluid temperature (50°F), and t_1 is the inlet shell side fluid temperature (120°F). Therefore, from the given temperature values, $T_{LMTD} = 52.5^\circ\text{F}$. The overall heat transfer coefficient (U) for tubular condensation of organic vapors when cooling is conducted by flowing chilled water inside the tube. The heat flow is typically in the range of 50-200 BTU/hr-ft²-°F (Primo, 2010). The total heat load (Q) to the condenser, as calculated in the previous section, is 22,942 BTU/hr, therefore the initial estimated area calculated from the Equation 4.9 was found to be in the range from 2.2 – 8.7 ft².

From the available off-the-shelf units, a 7.9 ft² shell and tube condenser with a maximum rated capacity of 12 GPM was selected. The unit, which incorporated wide baffles and a four-tube side-pass configuration, was purchased and installed (Figure 4.16). The 4 pass design refers to the number of times the cooling medium in the tubes passes through the pentane vapor/liquid in the shell. A mixture of 30% propylene glycol and 70% water was used as a cooling medium with an inlet temperature 30°F, as recommended by the manufacturer.

Selection of Chiller Unit

A portable water-cooled chiller with a capacity of 1.5 tons was purchased as per the recommendation from Perigon. The unit can maintain a cooling fluid (water-glycol mixture) temperature in the range from 20-80°F and has a built in ½ HP pump, which can circulate cooling fluid at a flow up to 3.6 GPM. The detailed description can be found in the Appendix B.

4.9 Construction of POC Pilot Plant

4.9.1 Modular Design

The proposed novel technology involves three separate process “modules” combined together to achieve a low moisture product. Oil-agglomeration is a well-known process and involves high and low-shear mixing, screening, and tailings thickener as illustrated in Figure 4.1. The oil recovery circuit includes an evaporator and condenser, which are commonly used in solvent extraction processes. The phase separation process is the key component in the HHS technology and the focus of the research. Based on this, POC plant was divided into three

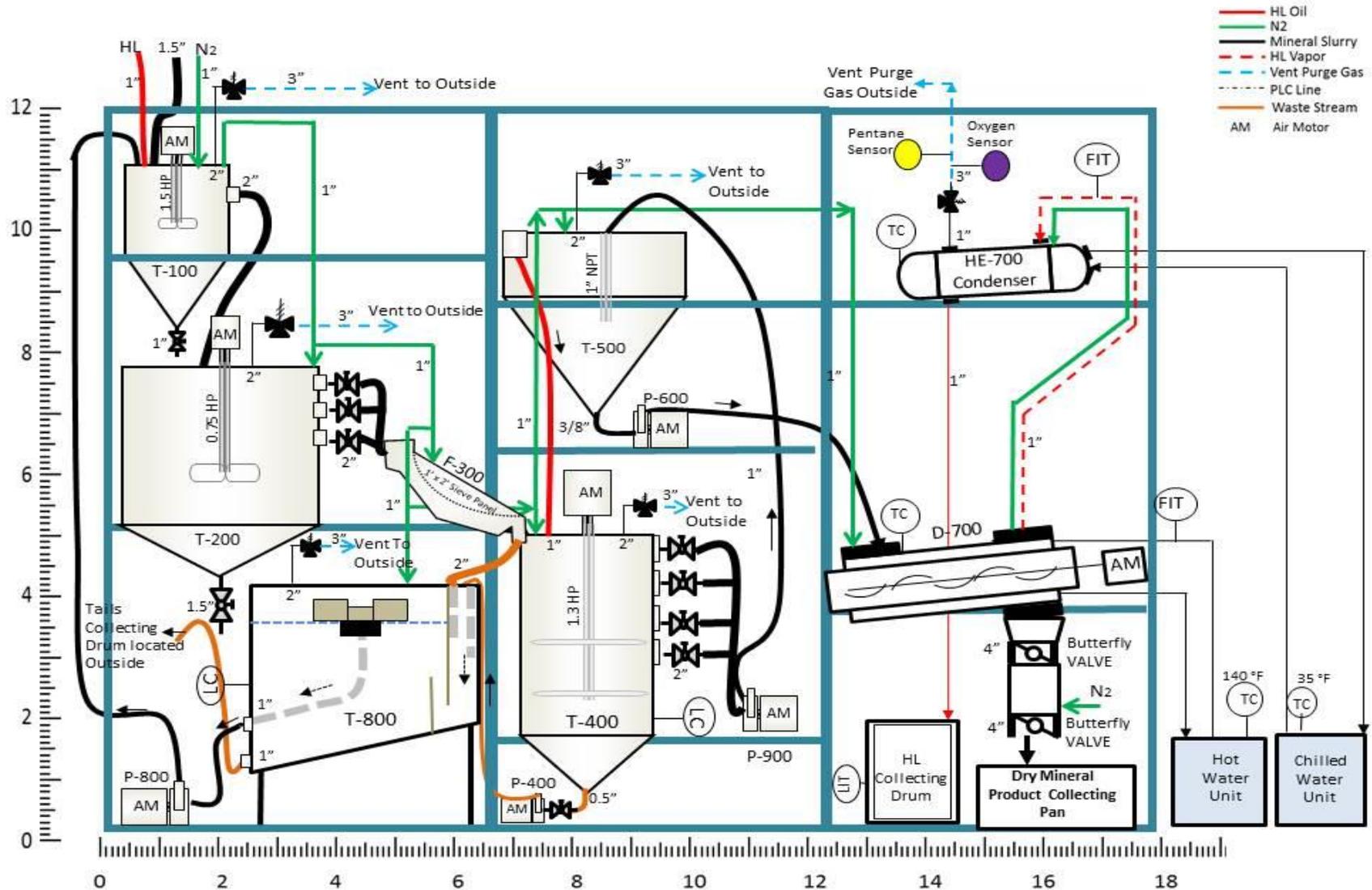


Figure 4.17 P&ID flowsheet showing modular design of POC pilot scale plant

different modules specifically for each process described above. A P&ID flowsheet was designed as described in Figure 4.17.

Module #1 is an oil agglomeration process, where fine coal slurry mixed with a small dosage of pentane in a high-shear mixing tank (T-100). Due to high-shear mixing, the pentane liquid breaks into small droplets, which adhere to fine coal particles and cause them to start coagulating. These micro-agglomerates float on the top of the slurry and are transferred to a low-shear mixing tank (T-200) by gravity flow. The low-shear mixing tank has a long retention time, which helps tiny agglomerates to grow. Since only coal is hydrophobic in nature, it only takes part in the agglomeration process, leaving behind water and mineral matter from the slurry.

The low-shear tank overflow, which carries coarser agglomerates, is passed to a stationary curved sieve bend (F-300) to separate these agglomerates from water and clay. The oversized coal agglomerates from the sieve bend are transferred to a phase separation process in Module #2. The underflow of water and clay is transferred to a classifying thickener (T-800), which is equipped with a traditional floating oil skimmer inside the tank. In the thickener (T-800), any un-agglomerated fine coal particles and absorbed pentane reporting in the sieve underflow will float on top of water due to its lower density. The skimmer is set to continuously pump (P-800) the top layer from the classifying thickener back to the high-shear mixing tank.

In Module #2, the coal agglomerates are dispersed in the vibrating mixer (or de-agglomerator) reactor (T-400). These agglomerates contain considerable water that is bridged between the coagulated oil-coated fine coal particles. The vibrating mixer disperses these agglomerates in pentane using mechanical vibration energy inside the reactor. The small water drops bridged within the agglomerates are displaced from the coal surfaces and quickly coalesce with other small water drops. The coalescence eventually leads to the formation of large water droplets, which is a thermodynamically favorable process. These larger droplets grow in mass and start settling. The droplets eventually cross the pentane-water interface and enter the submerged aqueous phase inside the reactor. The water column inside the reactor is constantly maintained by pumping (P-400) this extra amount of water to the classifying thickener in Module#1. The dispersed low moisture clean coal in pentane is pumped (P-900) to the HL thickener (T-500) for settling ultrafine particles. The settled coal from the HL thickener is pumped (P-600) to Module #3 in the oil-recovery circuit. The overflow from T-500, which is

mostly pentane with a very low solids concentration, is transferred back to the de-agglomeration reactor for continuous flushing of the dispersed coal.

In Module #3, the low moisture fine coal product with pentane from T-500 reports to the evaporation/dryer unit (D-700). The dryer is heated with hot water and continuously maintained at a temperature of 110-120°F. The liquid pentane vaporizes quickly in the dryer, leaving behind the low moisture fine coal product. The pentane vapors are re-condensed into a liquid phase in the condenser unit (HE-700). The condensed pentane is free of solids and, therefore, passed back into pentane barrels (HL collecting drum) for reuse into the process. The low moisture clean coal product is collected at the discharge end of the dryer through two pneumatically-controlled butterfly gate valves. A specific pneumatically controlled instrumentation system was designed to control the sequential opening and closing of these valves.

The entire POC system was purged with 95% nitrogen during the plant operation to keep an oxygen deficient environment inside the operating units. The nitrogen is controlled with a spring-loaded pressure regulator installed at T-100 to create a small positive pressure of 3 to 5-inches of water column (w/c). Pressure vents are installed on each unit in Module #1 and Module #2 and set at 7-inches of w/c to eliminate any build-up of pentane vapor inside the units. The pressure vent on the condenser in Module #3 acts as an emergency vent and is set at a slightly lower pressure, i.e. 5-inches of w/c. Since all the units are interconnected with nitrogen lines, the unwanted build-up of pressure in any unit opens the emergency vent first. Any release of vapors through this emergency vent is directed outside the building for safety purposes.

4.10 Selection of Auxiliary Units

Auxiliary units for the POC pilot plant include several items such as pumps, agitator drives, nitrogen generator unit, etc. Although, the selection and sizing of these items were based on operating flow rates and RPMs, safety and compatibility with pentane were also the two major criteria considered. The detailed description of the units is available in the Appendix B.

4.10.1 Selection of Pumps

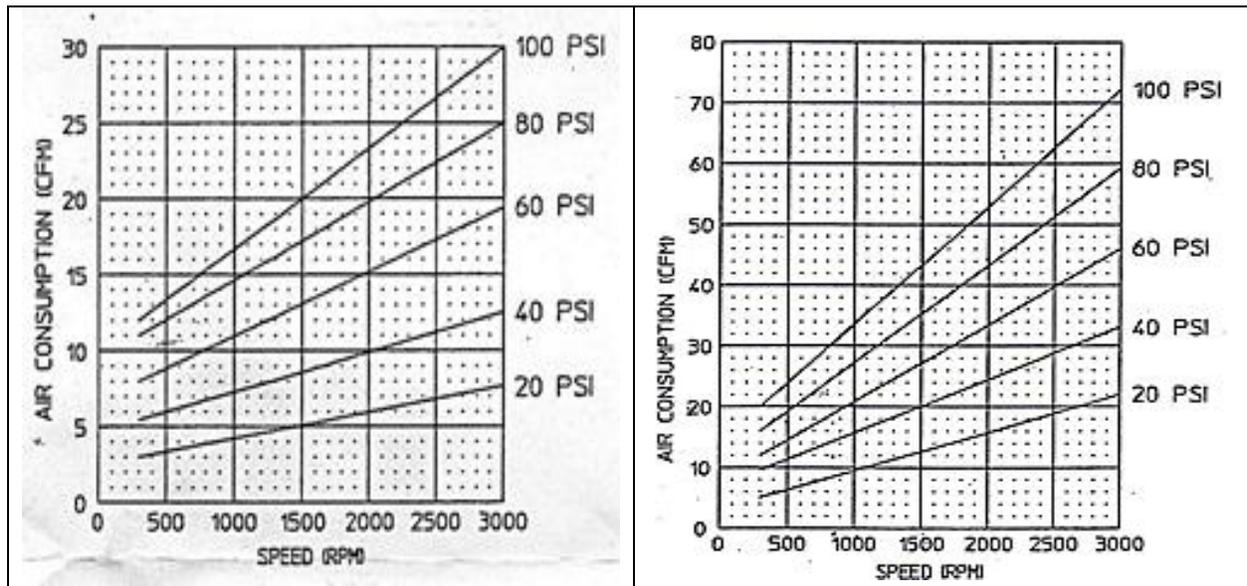
The 100 pounds/hour raw dry feed POC pilot plant entails small operating flow rates associated with the slurry streams, therefore, peristaltic pumps were considered in the process. These pumps also eliminate any possible leaks due to pump-shaft seals. The modular design

shown in the Figure 4.17 maximizes gravity flows and minimizes the pumping requirement. The POC plant required a total of six (6) pumps including a feed slurry pump and hydrophobic liquid reagent pump. In addition, explosion-proof pneumatic motors and pentane compatible Tygon® tubing were procured for all the pumps. The detailed listing of pumps with required flow rates is provided in Table 4.2.

Table 4.2 Description of pumps used in the POC pilot scale operation

Pump Name	Flow Path		Max GPM* , Motor HP*	Required GPM
	From	Feed To		
P-100	Feed Slurry Sump	Hi-shear Mixing Tank	11, 0.75	2
P-200	Pentane Reagent	Hi-shear Mixing Tank	0.5, 0.75	0.09
P-400	Vibrating Mixer Under Flow	Tailings Thickener	2.1, 0.75	0.2
P-600	Hydrophobic Liquid Thickener Underflow	Dryer/ Oil Recovery Module	0.5, 0.75	0.48
P-800	Skimmed Tailings Thickener Overflow	Hi-shear Mixing Tank	2.1, 0.75	2.24
P-900	Vibrating Mixer Over Flow	Hydrophobic Liquid Thickener	11, 0.75	4.84

* Manufacturer Ratings



* Specifications provided by Gast Motors

Figure 4.18 Air consumption and RPM relationship at operating pressure for agitators used in (a) low-shear mixing, (b) hi-shear mixing

4.10.2 Selection of Agitators

Agitators are needed for mixing in high-shear and low-shear mixing tank, which require 2500 RPM and 500 RPM, respectively. For high-shear mixing, a 1.7 HP explosion-proof air powered motor was selected providing 0-3000 RPM, while for low-shear mixing a 0.95 HP with similar characteristics was purchased. Figure 4.18 shows the compressed air demand versus speed curves for both motors.

4.11 Safety Measures and Equipment

Because of very low boiling and flash point, pentane is listed as a Class 1A type flammable liquid, which necessitates precautionary measures in storage and handling. Also, the utilization of a Class 1A liquid at such a large scale requires permits and clearances from multiple regulatory agencies. With the proposed POC design, approximately 110 gallons of liquid pentane required in the process of which only 5.8 gallons/hour is active volume. Several measures were taken under the recommendations and safety codes from the agencies including Virginia Tech Environmental Health and Safety Department (EHS), Virginia State Fire Marshall, Virginia Fire Department, Virginia Tech University Building Officials, and Perigon during the construction and installation of POC pilot plant.

4.11.1 Installation of Safety Units

The construction and assembly of the POC plant was performed at Virginia Tech's Mining and Minerals Research Laboratory. Due to several permitting complications related to the operation the pilot-plant in a closed environment, the constructed modules were placed outside the research laboratory into an open storage shed behind the building at a distance of 60 feet away (EHS requirement) from any permanent structure. The storage area had no electrical connections and power supplies; therefore, ancillary electrical equipment supporting the processing unit (i.e., water heater, water chiller, nitrogen generator, compressed air supply, etc.) were installed inside the main building and air supply lines, water lines, and nitrogen supply lines were connected to the storage area. The brief description of additional safety units installed and steps undertaken for the safe operation of POC pilot plant are outlined below. The details of all the auxiliary units are available in Appendix B.

Nitrogen Generator

Nitrogen gas was needed for purging the POC units to eliminate any oxygen inside the operational tanks. A pilot-scale PRO-N-8 model nitrogen generator from Onsite Gas was procured for the pilot plant. The unit uses micro-sieves to remove oxygen from air and thus provides nitrogen at three purity levels at 95%, 97%, and 99%. In addition, the generator is mounted on an in-built 60 gallon receiver tank to maintain the pressure in the POC units. The nitrogen gas was supplied in 1/2" air hose to a nitrogen reservoir tank located on Module #1, which ultimately supplies nitrogen to the POC units at a regulated pressure.

Nitrogen Pressure Regulators

The whole POC system was pressurized with nitrogen at a slightly above atmospheric pressure (2.5-7" of water column). For regulating this pressure, two 3/4" Fischer type Y690AH spring loaded pad-depad pressure regulators were installed on the hi-shear mixing tank and with the nitrogen chamber below the product discharge chute at the dryer.

Pressure Vents

Enrado High Performance pressure relief valve, Model 953 and designed for 1"-7" of water column pressure, were installed on each of the five operating tanks and at the condenser. The vents on the tanks were set at 7" of water column pressure while the vent installed on the condenser was set at 5" of water column making it as an emergency vent, where any released nitrogen and pentane vapors were discharged outside the shed.

Pentane and Oxygen Sensors

Pentane gas sensors were required to detect the traces of pentane vapors, if there any, below its LEL (lower explosion limit = 1.4 % by volume) around the moving shaft outside the tanks, as well as in the near vicinity of the pilot plant area. An oxygen gas sensor was required to detect oxygen percentage inside the POC system. Typical minimum oxygen concentration (MOC) required initiating a fire with pentane vapors is 11.8% by volume (Mashuga and Crowl, 1998); therefore, during the POC operation, oxygen level was always kept below 10% by volume as a precautionary measure, by managing nitrogen gas flow rate.

A six (6) - multiport pentane (0-100% LEL) and oxygen (0-25% by volume) remote infrared gas sensing device, designed and manufactured by Conspec (Figure 4.19a), was purchased. To operate and regulate the remote sensing device, a PLC (process logic control) box, demonstrated in Figure 4.19 (b), with required ladder-logic codes and HMI (human machine interface) were developed with the assistance of in-house capabilities of the research team. The PLC box was connected with an alarm system to notify the operator, if the concentration of the pentane vapors exceeds the flammability limit. The information in detail can be found in Appendix B.

In addition, a hand-held pentane and oxygen gas sensor, Tetra model from CEA instruments, was also procured to detect any leaks around the POC pilot plant during operation.

Forced Ventilation System

An outdoor fan of diameter 2 feet was installed outside the shed with a 30 feet long flexible ventilation pipe connected to it to provide forced ventilation inside the shed such that the air flow was concurrent with the wind flowing inside the building.

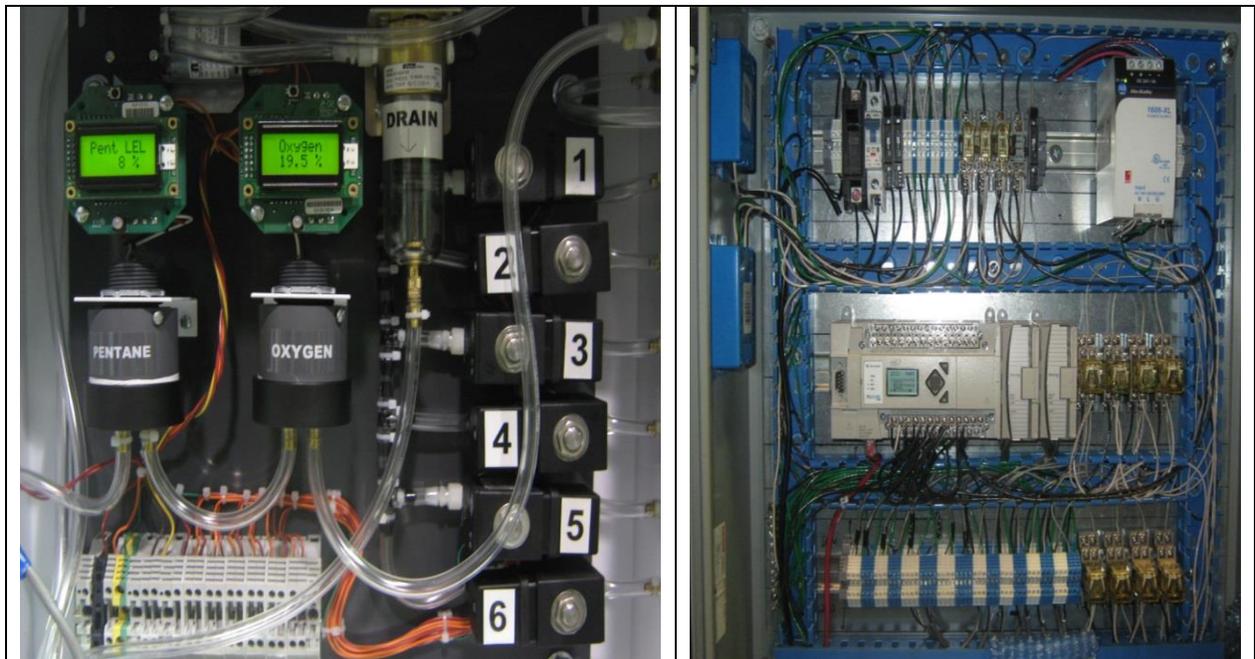


Figure 4.19 (a) Conspec multiport pentane and oxygen sensing system (b) PLC box system developed to control remote sensing device

Hazard Material (HazMat) Storage Cabinet

A rental temperature controlled storage cabinet was procured to store pentane barrels during inactive hours. The unit can accommodate up to 12 barrels and is self-equipped with an air-conditioning unit and a dry chemical based fire-suppression system.

Fire Extinguishers and Fire Suppression System

Four standard fire extinguishers were installed at each corner of the POC plant at a distance of 10 feet. In addition, each module was equipped with helon-gas based fire suppression system (very commonly used in Nascar) connected with gas transfer aluminum lines, installed at several points across the POC units, which can be more prone to a hazard.

Fail-safe and Emergency Shutoff Valves

Three fail-safe pneumatically controlled spring loaded ball valves were installed at the pentane discharge point in the tanks installed in Module # 2. In addition, manually controlled 3-way emergency ball valve was installed intercepting the air supply from the compressor to the POC pilot plant.

Spill Containment System

Spill containment barriers were installed all across the shed as per recommendation from EHS. In addition, the test site was equipped with a spill containment kit specifically designed for hydrocarbon cleaning and disposal.

Grounding Wires

The whole POC system was grounded such that each operational unit and hose connected to each other with ground wire and ultimately to the ground rods installed outside the shed, as per recommendation from state Fire Marshal to eliminate hazards caused either due to static generated from material flow or any nature activity.

Back-up Power Supply and Safety Signs

An additional gasoline based power generator was equipped to supply power (in-case of power failure) to nitrogen generator, PLC control box and other ancillary unit installed for safety

purposes. This provides enough time to shut-down the pilot plant in a safe manner, as per shutdown protocols. Safety signs were installed all around the shed as a precautionary measure for safety.

4.11.2 Safety Protocols

Prior to start-up and shake-down testing, a complete set of operational protocols were developed. These included:

- Pre-Start Checks
- Startup Procedure
- Operating Procedures
- Normal Shutdown Procedure
- Emergency Shutdown Procedure
- Emergency Spill Handling Procedure

These protocols were further reviewed by multiple regulatory agencies listed earlier. Virginia Tech personnel conducted a thorough review of state and federal regulations and applied to the POC protocols to ensure compliance prior to commencing shakedown testing. As part of the process, representatives from Virginia Tech's EHS group and the Virginia State Fire Marshal's office reviewed the POC system after construction and installation was completed. The complete protocols are listed in Appendix A.

4.12 Shakedown Testing and Modifications

After completing the review of newly constructed POC pilot plant, the VT University Building Official granted a temporary permit to use the storage shed as test site for POC pilot plant testing and evaluation. Shakedown testing of the pilot plant was conducted to identify and rectify any operational issues prior to full-scale pilot runs. Major shakedown tasks included testing and optimizing the mixing units, sieve screen, vibrating mixer, heat exchanging units, and oil-skimmer. In addition, shakedown testing assisted operators to practice start-up and shutdown protocols to run the pilot plant in an intrinsically safe manner.

Prior to adding feed coal slurry and pentane into the system, shakedown testing was started distinctively module wise with water, where each unit was tested for any possible leaks.

In addition several other items were tested such as proper functioning of ancillary units — water heater and chiller, testing nitrogen purging system and accurate detection from gas sensors, pumps operations, and testing PLC controls and HMI interface for effective operation and control of the POC pilot plant.

4.12.1 Material Procurement

For shakedown testing, a total of six barrels of screenbowl main effluent sample was procured from Consol's Buchanan preparation plant. The sample was high-grade metallurgical coal with 3.8% solids and only 7% dry ash. The top particle size (d_{90}) was found 34 micron with 98% finer than 38 micron. After each test, the feed slurry was reconstituted in the sample barrels and perfectly mixed again before charging to the POC pilot plant for next shakedown testing. Pentane was procured in bulk (3 barrels - 156 gallons; 99.5% pure) from South Hampton Resources, a supplier based in Texas.

4.12.2 Shakedown Test #1

The first shakedown testing of the POC pilot plant, utilizing coal slurry and pentane liquid, was conducted under the constant supervision of a Virginia Tech EH&S official. This included proper start-up of pilot plant, constant monitoring of gas levels, proper initial charging and handling of pentane liquid into the vibrating mixer tank and hydrophobic liquid thickener. The coal slurry was first agitated thoroughly using an electric mixer located outside the shed. The well-mixed slurry was pumped from the sample barrels at a pre-determined flow rate into the high-shear mixing tank. The pentane feed was also pumped at the same time into the high-shear tank.

Two major issues were encountered in the testing. First, during the period of the initial charge of the pentane and the slurry transferred into the system, only a small amount of vapors condensed in to the pentane-receiving column, which was unusual because the condenser was flooded with pentane liquid. An additional by-pass vent line was installed from the condenser to the pentane-receiving column, which eliminated the vapor lock in the receiver column and allowed the liquid pentane to flow to the receiver column. The condenser appeared to be working efficiently with the modified arrangement. Second, after few minutes of POC operation, just when agglomerates begin to detect over the sieve bend, the laboratory air compressor (rated 50

CFM at 100 PSI) failed to maintain the air pressure needed to operate all the pneumatic drives. This caused ultimately the shutdown of the pilot plant. No samples were collected during the first shakedown testing. To eliminate the issue, a 185 CFM diesel powered portable air compressor was rented and installed in the further testing.

4.12.3 Shakedown Test #2

Similar procedures were followed in the start-up of the pilot plant. The two major issues were encountered during the operation. First, because of the small flow rate from the low-shear mixing tank, the sieve screen was quickly blinded and agglomerates appeared to be stick on the top of the screen. With only a small amount of agglomerates overflowing from the screen, the plant was continued to run in a hope to collect a product sample. The second issue encountered was all the air supply lines were flooded with condensed water. This flooding is believed to be due to the high humidity in the atmospheric air utilized by the air compressor. To eliminate any damage to the pneumatic motors, the plant was shut down before any sample could be collected.

To rectify the first issue, several major modifications were conducted in the screen box. The feed port for the screen was re-located at the back of the box (initially there were two feed ports on the side of the screen-box) just opposite to the low-shear tank overflow port to streamline the fluid flow. Two wash-water lines were also installed inside the completely enclosed screen box with additional pneumatic rapper from outside, below the box. In addition, as the screen area was much larger for the given flow rate, almost $2/3$ of the area was covered by a thin sheet (1/4") of Teflon™. Although this caused some extra amount of dirty water reported in the overflow of the screen, the sheet facilitated smooth flow of agglomerates into the vibrating mixer.

The second issue was resolved by installing a small water collecting tank (high pressure rated) between the air compressor and air supply line. This did not completely eliminate the problem but resolved flooding of condensed water in to the air-supply lines. Any residual moisture in compressed air was trapped by water-filters installed before the pneumatic motors.

4.12.4 Shakedown Test #3

The third shakedown test also experienced problems. When all the units appeared to be working well, the peristaltic pump tube of P-900 burst, which led to emergency shutdown. Emergency spill procedures were followed to clean the pentane spill. The spilled material was

collected and disposed carefully. As no spare pump tube was available during the time of the test, the plant was ultimately shut down without collecting any sample.

4.12.5 Shakedown Test #4 and 5

A common problem was encountered during shakedown test 4 and 5: the dryer was observed to be flooded with water. The presence of unwanted water ultimately affected the final product moisture. Two main causes were identified for the aforementioned problems. First, during the plant operation, water vapors generated inside the processing units were carried by nitrogen gas through inter-connected nitrogen lines to the dryer (green dotted lines). It was visibly noticed that the water vapors fogged the sight-windows of the dryer, which ultimately condensed into large water droplets during the long operating period. To eliminate this issue, nitrogen lines connected to the dryer were re-routed (blue dotted lines) and connected directly to the condenser unit so as to by-pass the dryer, as outlined in Figure 4.20(a).

The second reason for water reporting to the dryer was related to the control of the pentane-water interface level inside the vibrating mixer unit. For an efficient separation, the interface level must be below the bottom most oscillating screen. In POC system, this level is

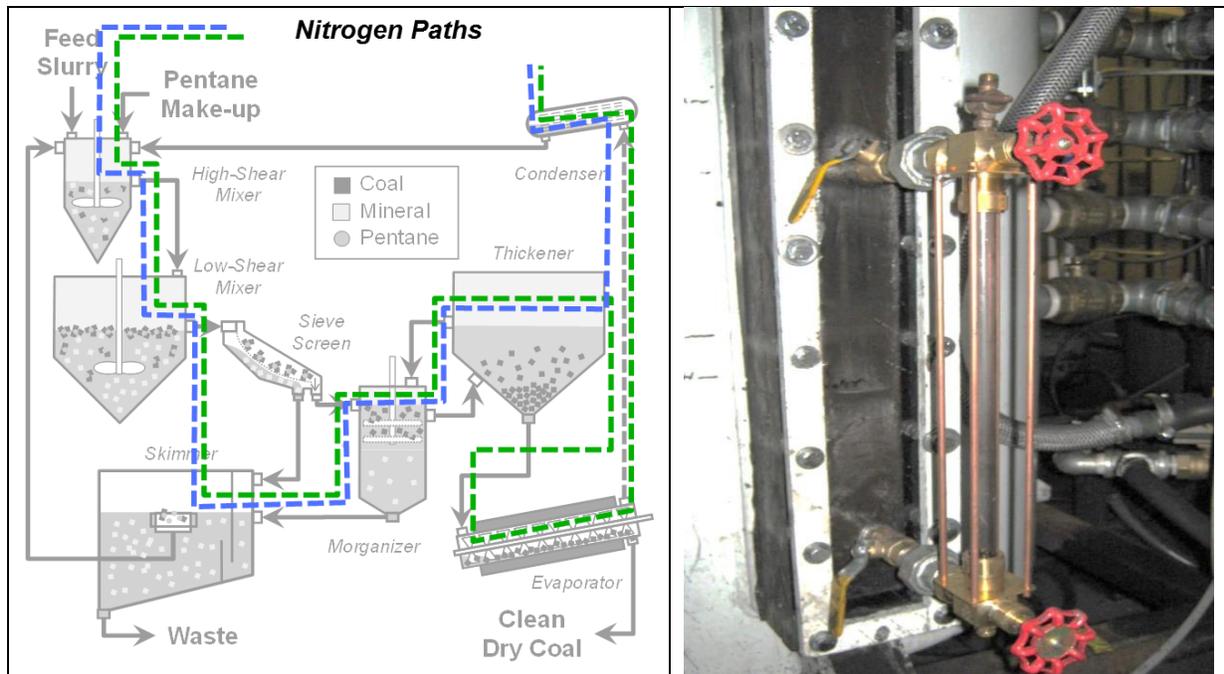


Figure 4.20 (a) Schematic showing re-routed nitrogen path in the POC system (b) Image of additional sight glass to monitor oil-water interface in vibrating mixer

Table 4.3 Shakedown test 4 and 5 assays obtained from POC pilot plant

Test Number	Feed		Product		Tails
	%Solids	Ash%	% Moisture	Ash%	
<i>Shakedown 4</i>	3.8	7.0	20.2	2.1	NOT COLLECTED
			21.4	2.2	
<i>Shakedown 5</i>			5.4	2.0	

monitored visually through the sight window installed in the tank and controlled manually by adjusting the vibrating mixer underflow pump.

In shakedown test #4, the sight glass (made with 1” thick Plexiglas) was completely smudged with coal-oil mixture, thus it was almost impossible for the operator to locate the interface level. When the water level rose to more than the marked limit, it passed to the overflow stream, which ultimately flooded the dryer. Two clean coal product samples were collected before the plant shutdown, but without a tailings sample. The results from this test are shown in Table 4.3.

To resolve the issue, prior to shakedown test #5, the sight window was equipped with a float (painted fluorescent) made of oak wood. The oak wood has a specific gravity of 0.78, which is in between pentane liquid (0.62 SG) and water (1.00 SG). The system worked for several minutes, but the float was also quickly coated with coal-oil mixture, making it impossible to monitor the interface level. Because of the high possibility of the dryer flooding again with process water, the POC plant was shut down before steady-state could be achieved. Only one clean coal product sample was collected in this test and again without a tailings sample. The results are shown in Table 4.3.

Though there were several hiccups in shakedown tests #4 and #5, the preliminary results obtained (as outlined in Table 4.3) were very promising. The high moisture obtained in test #4 was significantly reduced to a single digit in the test run #5, demonstrating that the HHS process can drop moistures to levels only provided by thermal dryers. In addition, the product ash (~2%), (similar values as achieved in the bench-scale system) showed the excellent cleaning capability of the process on a large-scale. Unfortunately, the reject samples in both the tests could not be collected because of untimed shutdown.

The setbacks in pilot-scale testing caused by the inability of the operator to monitor the interface level was finally overcome by installing an additional sight glass level, as shown in Figure 4.19(b). The glass level was positioned such that the top port was located in the middle of pentane column and the bottom port was located in the middle of aqueous phase. The system was tested in the next shakedown test, which showed the sight glass level worked very well for monitoring the interface level, although the Plexiglas window smudged again.

4.12.6 Shakedown Test # 6

Shakedown test #6 was conducted with the same feed sample used in previous tests. The pilot plant was run for few hours until all the reconstituted feed was consumed. A total of two sets of sample were collected in a gap of 30 minutes of operation and the results are summarized in Table 4.4. The 97% of carbon recovery in the product from the HHS process indicates almost all the combustible was recovered from the feed.

Even though no major operational issues were encountered during shakedown test #6, a couple of minor issues were observed. Therefore, some modifications were made in the pilot plant to avoid these issues in the full POC pilot-scale testing. First, it was hard for an operator to move feed from one barrel to another in every 15-20 minutes and simultaneously operate the plant. This issue also introduced inconsistency into the feed quality to the pilot plant. To rectify this problem, a 480 gallon feed sump was installed outside the shed with an electric mixer. The feed sump can accommodate up to seven (7) barrels of feed slurry easily. Second, it was observed that a substantial amount of pentane was condensing and pooling in the nitrogen chamber installed below the dryer discharge chute, thus reporting in the final coal product, which was a loss. To address this issue, a water heating jacket (by-pass copper tubing from hot water lines) was installed all around the chamber. The whole system was insulated to maintain a hot environment inside the chamber. This kept the pentane in a vapor form in the chamber allowed the vapor to be carried by flowing nitrogen to the condenser.

Table 4.4 Shakedown test 6 assays obtained from HHS process POC pilot plant

Test Number	Feed		Product		Tails	Combustible Recovery %	% Ash Rejection
	%Solids	Ash%	% Moisture	Ash%	Ash%		
<i>Shakedown 6</i>	3.8	7.0	4.2	2.1	64.0	97.0	71.8
			3.8	2.1	64.8	97.1	71.9

4.13 Conclusions

The proof-of-concept (POC) pilot plant for the novel HHS process was constructed in an intrinsically safe manner under a constant monitoring of multiple regulatory agencies. The primary motivation to develop the POC plant was to demonstrate the thermodynamic concept of dewatering-by-displacement at a large scale. After the completion of construction, shakedown testing was conducted on the newly developed POC system. Several necessary modifications were made during the shakedown testing to streamline the pilot plant operation.

The preliminary data obtained from newly engineered HHS process POC pilot plant tested with a screenbowl main effluent sample showed encouraging results and proved this revolutionary concept at a large scale. The data shown in Table 4.4 elucidate the separation capabilities of the process in terms of producing a high quality premium coal product from a currently discarded stream. The consistency in producing low-moisture and low-ash product from the shakedown testing signified an efficient operation of the pilot plant in achieving the primary goal. The pilot-scale testing was moved to next stage where different coal feed stocks were evaluated to obtain critical data needed to develop a full-scale demonstration unit.

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CHAPTER 5 – Pilot-Scale Testing and Evaluation of HHS Process

5.1 Introduction

The coal waste impoundments are considered a permanent disposal sites. According to a 2002 National Research Council report, 70-90 million tons/year of fine coal refuse discarded to impoundments due to the lack of appropriate separation technologies (Orr, 2002). Unfortunately, these so-called “waste” impoundments are unexploited energy resources that could not be recovered by existing commercial technologies and are, therefore, discarded. Researchers from Virginia Tech have developed a new process called “*Hydrophobic-Hydrophilic Separation*” (HHS) based on a thermodynamic concept of dewatering-by-displacement. In the concept, the surface properties of hydrophobic coal are exploited with hydrophobic liquid for the size fraction (150 microns x 0) where differential gravity is ineffective for separation. Bench-scale system for the proposed technology was developed and tested, which showed promise in removing both mineral matter and water simultaneously from these fine coal discarded streams. Therefore, a successful commercialization for the HHS process will help the mining industry in recovering the amount of coal that is currently discarded in impoundments as well as generating a substantial increase in revenue.

In light of this, Evan Energy LLC., an investment company based in Richmond-VA, has sponsored to construct a Proof-of-Concept (POC) pilot plant in Virginia Tech, which can demonstrate the capabilities of HHS process on a larger-scale. The construction of the pilot plant of rated capacity 100 pounds/hour feed was completed in Spring 2013. Shakedown testing commenced in June 2013 and was completed in August 2013 with the necessary modifications. Preliminary test results from shakedown testing obtained from Buchanan’s screenbowl main effluent sample tested on the newly engineered POC pilot plant were highly encouraging. Though the real challenge is to evaluate the pilot plant with variety of feeds, particularly high ash feed, on a large-scale. This chapter details the pilot scale test program, the test results and the performance evaluation of the HHS process POC pilot plant.

5.2 Samples Procurement

A total of three different samples were procured for the evaluation of POC pilot-scale plant from three Appalachian coalfields regions. The details of each sample and site descriptions

are discussed in the following sections. All these coal preparation plants are considered as the potential sites for installation of the first HHS process next scale demonstration plant in future.

5.2.1 Samples from Lone Mountain

Lone Mountain processing facility is owned by Arch Coal and can be the first probable site for the installation of the first HHS process demonstration plant. The facility is located in the heart of Central Appalachia coalfields, Lee County, in South West Virginia. The preparation plant produces premium quality steam coal product at a production rate of 1200 tons/hour and equipped with typical size-size separators, dense-media gravity separators and fine coal flotation circuit. The flotation feed is first deslimed by multiple banks of 6.5-inch diameter classifying cyclone. The cyclone underflow (typically 150 x 44 microns) is treated in flotation circuit while the cyclone overflow (below 44 microns) is discarded, because of several obvious reasons mentioned earlier in the document. At present, the processing facility is suffering a loss of approximately 74 tons/hour solids in this ultrafine waste stream (Lone Mountain, 2013), which has ash in the range of 55-60%. A total of two batches of sample were procured during the pilot-plant testing. The first batch of sample (Sample A) was used for first three pilot test runs (pilot test #1-3). Whereas the second batch of sample (Sample B) was tested in pilot test #4, which was specifically conducted for an external laboratory, based in Beckley, West Virginia, to collect and analyze samples around each intermediate unit operation involved in the POC pilot plant for a detailed evaluation.

Sample A

For the first three pilot-scale test runs, a total of five (5) barrels of the deslime cyclone overflow raw coal sample was procured from the facility. The percent solid in the sample was recorded 7.3% with an ash of 55.7%. The size distribution of the raw coal sample, as illustrated in Figure 5.1, indicates particle top size (d_{90}) 44 microns (size where 10% material is retained).

Sample B

For pilot test #4, a total of six (6) barrels of the deslime cyclone overflow raw coal sample was procured from the preparation plant. The percent solid in the sample was 7.8% with an ash of 60.5%. The size distribution of the raw coal sample is exhibited in Figure 5.2, which indicates particle top size (d_{90}) approximately 38 microns.

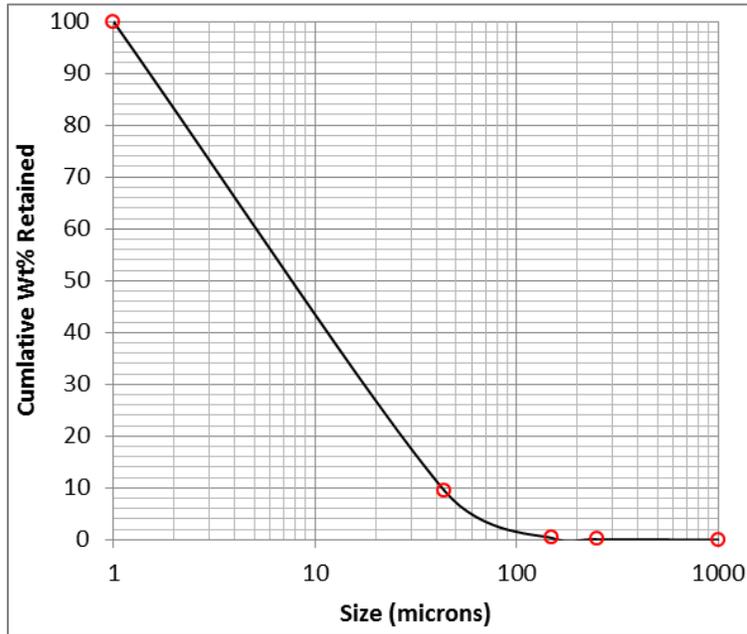


Figure 5.1 Size distribution curve for Lone Mountain feed sample 'A'

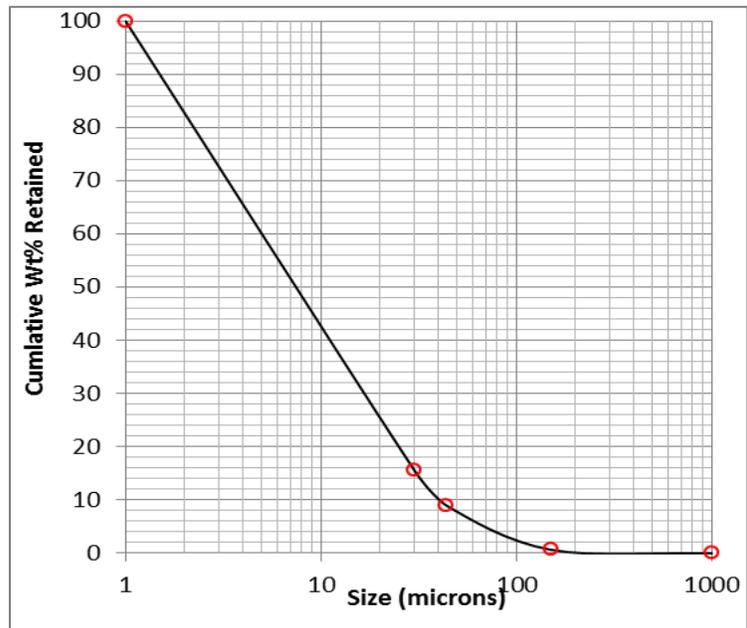


Figure 5.2 Size distribution curve for Lone Mountain feed sample 'B'

5.2.2 Sample from Leer Preparation Plant

The Leer Complex is located in Taylor County, West Virginia and owned by Arch Coal. All the mined coal is processed through a newly constructed 1,400 ton-per-hour preparation plant and can be another potential site for installation of the first HHS process demonstration unit. The preparation plant is equipped with two stage dense-medium cyclone circuit for coarse coal

washing. The fine coal cleaning circuit implements reflux classifiers and column flotation for recovering combustible material. Prior treating the fine coal from flotation circuit, the feed is de-slimed using bank of 6-inch classifying cyclone, which cuts at 45 microns. The deslime cyclone overflow (size below 45 microns) is discarded to the plant thickener because of high percentage of clays (Chafin et al., 2012).

A total of seven (7) barrels of 6-inch de-slime cyclone overflow raw coal sample were procured from Arch's Leer preparation plant. A percent solid in the sample was recorded 3.8% with a high ash of 60.5%. The size distribution of the raw coal sample, as shown in Figure 5.3, indicates particle top size (d_{90}) approximately 55 microns.

5.2.3 Sample from Sentinel Preparation Plant

The Sentinel processing plant facility is located in Barbour County, West Virginia and also owned by Arch Coal. Mining operations extract coal from the Clarion coal seam. Coal from the Sentinel mining complex is processed through 615 tons/hour preparation plant. The plant is well equipped with heavy media vessel and cyclones for coarse coal processing while spiral gravity concentrator and conventional flotation cells for fine coal processing (Coal Age, 2013). The flotation product is dewatered with screen-bowl centrifugal dryer. The centrifuge main effluent, which carries typically 50% ultrafine coal particles (-325 mesh) of the flotation concentrate, is discarded into the plant thickener.

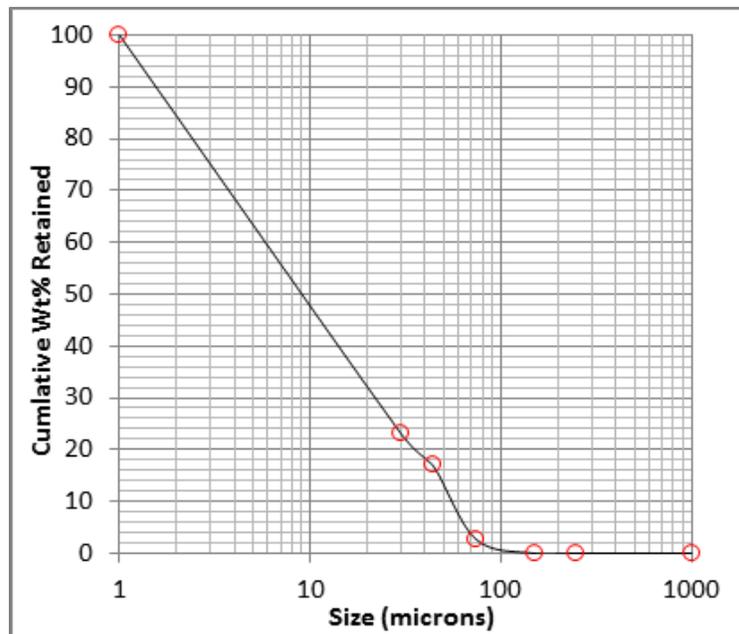


Figure 5.3 Size distribution curve for Leer plant feed sample

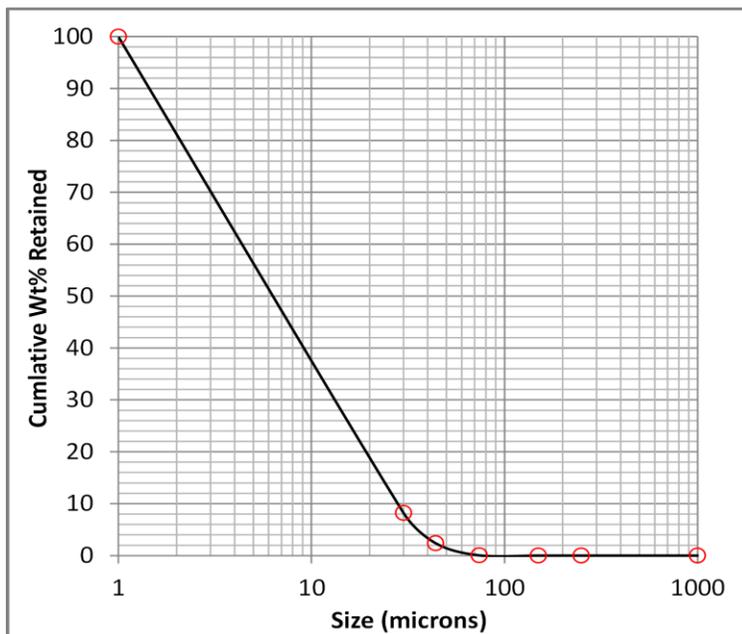


Figure 5.4 Size distribution curve for Sentinel plant feed sample

A total of seven (7) barrels of screenbowl main effluent was procured from Arch’s Sentinel preparation plant. A percent solid in the sample was recorded 4.5% with an ash of 28.5%. The size distribution of the raw coal sample, as illustrated in Figure 5.4, indicates particle top size (d_{90}) approximately 29 microns.

5.3 POC Pilot-Scale Test Results

Similar start-up, safety measures and operating protocols were followed as described in Appendix A. Prior to the test, the coal feed slurry to the pilot plant was prepared in a newly installed sump and mixed well before charging at a pre-determined flowrate of 2 gallons/minute. In each test run, at least one set of samples was collected (feed, product and reject) for analysis. In order to determine pentane loss associated with clean-coal, the product samples were collected in sealed plastic bags and opened at the time of analysis.

Two major modifications were performed during the course of full pilot-scale plant runs to gain detailed material balance as well as to investigate key POC units, which are needed for in-depth evaluation of the HHS process POC operation. These modifications are listed below:

- After pilot test #3, a total of 13 sample locations (showed in Figure 6.12) were identified, and sample ports (3-way ball valves) were installed on these intermediate process streams to collect samples from each unit operation.

- After pilot test #5, the vibrating mixer tank, the key unit operation in the process, was re-designed and replaced with a very low-volume tank.

The POC pilot test results are discussed in the following sub-sections individually for each test.

5.3.1 Pilot Test #1

Pilot-scale testing was started utilizing the first batch (Sample A) of de-slime cyclone overflow sample procured from Lone Mountain plant facility. The fresh sample feed (as-received) from the preparation plant was used in the first test and recovered back for the later test runs after analyzing samples. A total of three product and tails samples were collected at a fix interval of 30 minutes. The direct data obtained from the pilot-test is outlined in Table 5.1. The consistency in low ash clean coal product and high reject ash indicates excellent cleaning capabilities of the HHS process even for high-feed ash tested on the POC unit. In addition, single-digit product moisture values indicated the potential in this innovative dewatering method involved in the HHS process.

From the analyzed assay values, performance parameters such as combustible recovery, ash rejection and sulfur rejection were determined. The HHS Process POC pilot plant system was able to recover up to 86% carbon and rejected impressively more than 98% ash (mineral matter) from the discarded deslime cyclone overflow feed sample of Lone Mountain. On the contrary, the sulfur rejection was only 9%. The low sulfur rejection is expected because most of the sulfur is in organic form, which is also hydrophobic in nature and, therefore, recovered with the clean coal product. The complete assessment is discussed later in the chapter. In later tests, sulfur was not analyzed (except pilot test #4) as a parameter for performance evaluation.

Table 5.1 Pilot Test #1 samples assay from the HHS process POC plant

Test Number	Feed			Product				Reject	
	% Solids	Dry Ash %	Dry Sulfur %	Pounds/hour	% Moisture	Dry Ash %	Dry Sulfur %	Dry Ash %	Dry Sulfur %
<i>Pilot Test #1</i>	7.3	55.7	0.4	1.8	4.6	2.2	0.63	89.4	0.06
				2.6	5.3	2.5		89.8	
				5.4	8.5	2.5		89.3	

5.3.2 Pilot Test #2 and #3

After collecting enough samples required for analysis from pilot test #1, the tails and clean coal product of the Lone Mountain cyclone overflow feed sample was re-constituted and mixed well to utilize in pilot test #2 and similarly later on for pilot test #3. A total of two product and reject samples were collected in both the test and analyzed. In addition, as anticipated that the feed characteristics will change, feed samples were collected in each test run. The complete set of assays is illustrated in Table 5.2.

The feed to POC plant deteriorated after each test run. Even with a higher feed ash, the HHS process pilot plant produced consistently low-ash and low-moisture product with exceptionally high reject ash. Even though, the assay values for product and reject are very similar to pilot test #1, the increase in feed ash has decreased combustible recovery to a range from 69 to 73%. On the other hand, the ash rejection was still reported as high as 98.8%. The complete evaluation is discussed later in the chapter.

5.3.3 Pilot Test #4

The second fresh batch of cyclone overflow sample (Sample B) from Lone Mountain was procured and used in pilot test #4, which was conducted primarily for Precision Laboratory, located in Beckley, West Virginia. The laboratory analyzed the samples collected from pre-defined sample points located in each intermediate process streams around the POC pilot plant. In addition, the pentane loss associated with clean coal product was also determined by the laboratory. The complete data obtained from the test is instrumental in development of the next-scale 1 metric ton/hour HHS process demonstration plant. The feed, product and reject assays are outlined in Table 5.3. The detailed description with sample assays from the intermediate streams is discussed in Chapter 6.

Table 5.2 Pilot Test #2 and #3 samples assays from the HHS process POC plant

Test Number	Feed		Product		Reject Ash %
	%Solids	Ash%	% Moisture	Ash%	
<i>Pilot Test #2</i>	7.8	66.2	5.9	3.3	86.0
			5.2	3.3	86.1
<i>Pilot Test #3</i>	8.6	67.5	6.8	3.8	88.3
			9.6	3.6	86.9

Table 5.3 Pilot Test #4 samples assay from the HHS process POC plant

Test Number	Feed			Product				Reject	
	%Solids	Dry Ash %	Dry Sulfur %	Pounds/hour	Air-Vented % Moisture	Dry Ash %	Dry Sulfur %	Dry Ash %	Dry Sulfur %
Pilot Test #4	7.8	60.5	0.3	2.8	12.5	2.7	0.64	90.6	0.04
	4.5	77.3	0.13	5.7	9.8	2.7	0.66	88.7	0.04

NOTE: The samples were collected and analyzed by Precision Laboratory, West Virginia.

During the test run, two sets of samples were collected from each sample point. After collecting the first set of samples, the feed to the pilot plant appeared to be low in the feed sump, and therefore could not be nixed properly by sump agitator. This can be noticed in the second feed sample characteristics outlined in Table 5.3. Nevertheless, the plant continued to run until the feed sump was emptied and second set of sample was collected.

The low-product ash reported by Precision Laboratory from both the samples, as well as from previous pilot test runs, clearly indicates the coal cleaning capabilities of the HHS process are independent of the feed ash. In addition, the tail ash was reported as high as 90.6%. From the assay analysis, performance parameters were evaluated, which showed the plant recovered 84.4% combustibles with ash rejection 98.5% from the first set of sample. The inconsistent feed for second sample affected the performance, as the combustible recovery was only 56.8% with ash rejection 99.5%. Due to inconsistency in the feed, only the first set of samples was used later in development of process flowsheet (discussed in Chapter 6) for 1 metric ton/hour demonstration plant.

Another purpose for conducting the pilot test #4 was to determine the pentane loss associated with the clean coal product. The pounds/ton losses reported by the external laboratory for both the samples were 26 and 148 respectively. Even for the first sample, the loss was very high. In addition, the product moisture disclosed by the lab was also slightly higher as compared to previous pilot test runs. After communicating with the lab, it was found that the samples were vented for pentane vapors in open atmosphere overnight in humid conditions. The humidity is expected to increase sample moisture and bring irregularities in the reported analysis. In later tests, attempts were made to determine the exact amount of pentane and moisture in clean coal product using thermo-gravimetric and gas chromatography analysis.

5.3.4 Pilot Test #5 and #6

After successful testing with Lone Mountain samples, pilot test #5 was conducted with the fresh feed procured from Leer's deslime cyclone overflow stream, while pilot test #6 was conducted with the re-constituted feed from the same sample. Prior to the pilot test #6, a major modification was conducted, which was replacing the old vibrating mixer unit with a reduced-volume vibrating mixer. The details of this investigation are discussed in later sections. Standard operational protocols were followed for the pilot test #5. Only one set of samples was collected in the pilot run and the direct data obtained from the tests are outlined in Table 5.4. The low-ash results elucidate the high performance of HHS process with this type of coal feed. Furthermore, the combustible recovery calculated was 79.7% with the ash rejection 97.5%.

For moisture studies, thermo-gravimetric analysis was conducted on clean coal product sample at 50°C until all the liquids (pentane and water) are removed and combined weight loss is reported in Table 5.4. This is because the initial method used for moisture determination in the tests, prior to pilot test #4, involved preheating of the clean coal sample at 40°C for a 6-8 minutes in the oven to remove the traces of pentane and then conduct the moisture analysis at 105°C. It is observed that the method has several issues, which are discussed in the next section. To eliminate any irregularities with analysis, combined weight loss is reported from pilot test #5.

5.3.5 Pilot Test #7

Pilot test #7 was conducted with the fresh screenbowl main effluent sample procured from Sentinel preparation plant. Similar to the pilot test #6, the small vibrating mixer unit was used in this pilot-test. Three sets of sample were collected in the pilot run and the direct data obtained for the best set from the test are outlined in Table 5.5. The low-ash results further confirm the high performance of HHS process with this type of coal feed. Moreover, the combustible recovery calculated was 90.8% with the ash rejection 86.8%. In addition, an investigation was conducted during the pilot test #7 to study the effect of high dosage of frother concentration in the feed on the pilot plant performance. The details are discussed later in the chapter.

Table 5.4 Pilot Test #5 and #6 samples assays from the HHS process POC plant

Test Number	Feed		Product		Reject Ash%
	%Solid	Ash%	Combined Weight % Loss	Ash%	
<i>Pilot Test #5</i>	3.8	53.0	8.5	3.4	84.4
<i>Pilot Test #6</i>	3.5	50.9	14.0	3.3	85.7

Table 5.5 Pilot Test #7 sample assay from the HHS process POC plant

Test Number	Feed		Product		Reject Ash%
	%Solids	Ash%	Combined Weight % Loss	Ash%	
<i>Pilot Test #7</i>	4.5	28.5	16.6	5.5	78.9

5.4 Method for Moisture Determination

To determine the moisture in the final product obtained from the POC pilot plant, a gravimetric method was established, which is based on several assumptions. It must be noted that there is no standard method available to exactly determine volatile fractions (pentane and water) in a coal-water-pentane mixture. In this method, the sample was first exposed at 40°C for a pre-determined time. After the time period, initial sample weight was noted and the sample was reheated in an oven at 105°C for 1 hour and the final sample weight was recorded. The difference in the weight yielded the weight percent loss, which was considered as percent moisture in the sample.

To identify the pre-determined time for pentane evaporation, an investigation was conducted. Synthetic samples were prepared with known weights of pentane, water, and dry coal powder. A moisture balance (manufactured by A&D, Model MF-50) was set at 50°C (which is the lowest temperature that can be set on the equipment) and connected with a computer. Each synthetic sample was heated isothermally at the set temperature inside the moisture balance chamber and percent weight loss was plotted with time as exhibited in Figure 5.5. The graph shows two evaporation rates with a sharp elbow at approximately a percent weight loss very close to the known initial weight percent of pentane in the synthetic samples. All the experiments conducted with different weight percent of pentane and water showed the time for the inflection point at approximately 4 minutes.

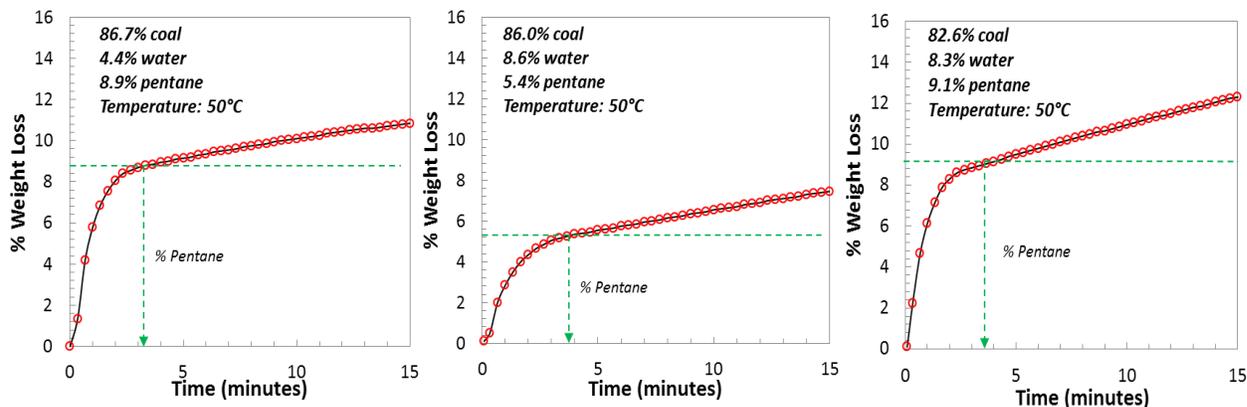


Figure 5.5 Synthetic samples weight loss curves with time

Therefore, the evaporation time for pentane was identified at the inflection point, and the time was generalized for POC product samples. The POC samples were first exposed at 40°C in an oven for 6-8 minutes (time increased because of lower temperature) prior to conduct moisture analysis. This method was not ideal because some moisture will also evaporate at this temperature, and there is a possibility that some percentage of pentane will be left in the POC test run samples. However, the method was expected to provide a fair estimation of moisture in the clean coal product. Several assumptions were made to generalize this gravimetric method to use for determination of moisture in POC test samples:

- Evaporation of pentane was independent of surface area exposed at higher temperature.
- All the pentane was evaporated in 4 minutes from the sample irrespective of its weight percentage in the sample.
- There was no absorption of pentane with coal.
- Pentane was easily available for evaporation from the coal surface.

The method was abandoned after pilot test #4, as sample characteristics that obtained from POC dryer unit and the synthetic sample was observed to be different. Because of the helical motion of the Holoflite® screw dryer used in the pilot plant, the clean coal product obtained was conglomerated into coal balls (illustrated in Figure 5.6) instead as a fine powder. In contrast with synthetic samples results, the weight % loss versus time curve for the POC sample did not showed a similar sharp elbow (illustrated in Figure 5.7), rather showed a blunt curve when tested. The blunt curve indicates that some portion of pentane and water may be trapped in the conglomerated coal sample. Similar curves were obtained for all the samples received from

the POC dryer unit. The initial method developed with synthetic samples was not suitable with the POC test samples for moisture determination and, therefore, the method was abolished.

There may be multiple reasons but three possible reasons are discussed here. First, generally evaporation of a liquid can be considered as the movement of molecules from the surface into the vapor phase. Pentane like other hydrocarbons is (almost) insoluble in water. In pentane-water system, pentane floats on the top of water surface. Typically, in low concentrations, pentane makes a very thin layer, covering the entire water surface. Previous studies (Smith, 2008) conducted with synthetic samples showed evaporation of pentane differs with varying conditions. Smith (2008) further revealed that for water-pentane mixture only, pentane molecules evaporate much quicker as pentane does not like water. On the contrary, in pentane-coal system pentane likes coal and, therefore, tends to stay longer when heated. The second reason could be that the coal is a bad conductor for heat transfer. Since the POC product coal is conglomerated, the rate of evaporation is very slow and therefore it is hard to identify any distinction between rate of evaporation of moisture and pentane. The third reason could be that the POC samples may have a very minor percentage of pentane and all the liquid is moisture only. The synthetic tests were conducted at high percentages of pentane (5-9%), which provide a sharp elbow in the weight loss curve as described in Figure 5.5.



Figure 5.6 Conglomerated dry coal product obtained from POC dryer unit

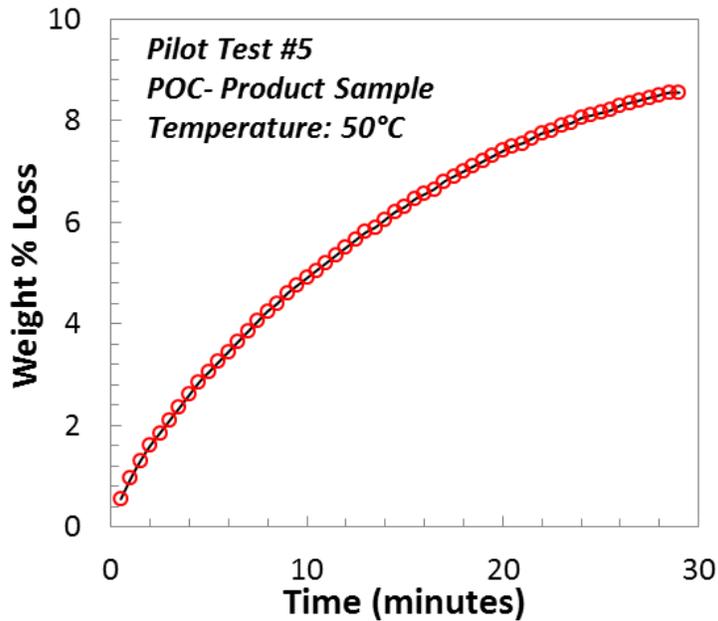


Figure 5.7 Weight loss curve for sample collected in POC pilot test #5

Due to this complexity and in absence of a viable method, a combined weight % loss (moisture and pentane) was reported from pilot test #5. Further attempts were made using gas chromatography analysis to estimate the amount of pentane in these samples. Once pentane is determined, moisture can be recalculated knowing the total weight percent of liquids in the clean coal sample.

5.5 POC Performance Assessment

The direct data obtained from the HHS process pilot-scale plant has proved that combined cleaning and dewatering for ultrafine coal can be achieved in a single process using the concept of hydrophobic displacement. The consistent low-moisture and low-ash clean coal products were obtained from three different type of coal samples tested on the POC pilot plant. Crucial investigations were conducted during the pilot test runs, such as testing vibrating mixer with small residence time impact of skimming, effect of feed size distribution, effect of excessive frother in feed and pentane absorption analysis. These investigations were necessary to collect information for designing the next-scale demonstration unit. The following section discusses these investigations in detail in addition with a general performance assessment of the POC pilot plant.

5.5.1 Separation Efficiency

Separation efficiency, which is defined as the recovery of the desired material and rejection of unwanted material in the clean coal product, is a performance indicator for any process. The separation efficiency curves are commonly used to determine optimum conditions of the process for certain type of feed. These curves normalize any variation in the feed to provide optimum conditions. Table 5.6 outlines complete set of data for each pilot-test with their separation efficiencies.

In shakedown test # 6, conducted with Buchanan screenbowl main effluent, almost all the carbon (97% from feed) was recovered with substantial amount of ash also rejected (72% from feed) using the novel process. The ash rejection was relatively high considering the feed ash was only 7%.

The pilot test conducted with deslime cyclone overflow feed (Pilot test #1 to #6) also produced enviable performance with the POC plant. The fresh feed from Lone Mountain (pilot test #1 and #4) provided carbon recoveries as high as 86% with ash rejection unexceptionally high (> 98%). Similar results were demonstrated with Leer deslime cyclone overflow feed. One of the main reasons to discard minus 44 micron raw feed using 6-inch deslime cyclone in the preparation plants is that it carries large amount of clay material. It is apparent that HHS process can easily remove this clay material and produce premium quality sellable product from this ultrafine raw coal stream.

Pilot test #7 test results, conducted with Sentinel screenbowl main effluent, are in compliance with other feeds tested on POC plant. The high combustible recoveries with relative high ash rejection further corroborate the outstanding performance of the HHS process with ultrafine coal slurries.

A batch scale system typically depicts a plug flow system, which indicates optimum performance level of any process that can be achieved. The POC plant was developed with several engineering assumptions based on bench-scale testing surveys. The separation efficiencies obtained from POC pilot test results are in good agreement with the HHS process bench-scale system, exhibiting the excellent performance of HHS process pilot plant. Figure 5.8 illustrates the comparison between the batch and pilot-scale separation efficiencies.

Table 5.6 Complete pilot-scale test data obtained from the HHS process POC plant

Test Number	Feed	Product		Reject	Combustible Recovery%	%Ash Rejection	Separation Efficiency
		% Moisture	Ash%				
Shakedown #6	7.0	4.2	2.1	64.0	97.0	71.8	68.8
		3.8	2.1	64.8	97.1	71.9	69.0
Pilot Test #1	55.7	4.6	2.2	89.4	85.3	98.4	83.7
		5.3	2.5	89.8	86.0	98.3	84.3
		8.5	2.5	89.3	85.2	98.3	83.5
Pilot Test #2	66.2	5.9	3.3	86.0	68.6	98.8	67.4
		5.2	3.3	86.1	68.8	98.8	67.6
Pilot Test #3	67.5	6.8	3.8	88.3	72.9	98.6	71.5
		9.6	3.6	86.9	69.2	98.8	68.0
Pilot Test #4	60.5	12.5	2.7	90.6	84.4	98.5	82.9
	77.3	9.8	2.7	88.7	56.8	99.5	56.3
Pilot Test #5	53.0	8.5*	3.4	84.4	79.7	97.5	77.2
Pilot Test #6	50.9	14.0*	3.3	85.7	83.2	97.3	80.5
		14.5*	3.2	78.7	72.6	97.7	70.3
Pilot Test #7	28.5	16.6*	5.5	78.9	90.8	86.8	77.6
	29.1	12.9*	5.0	82.2	92.2	88.3	80.5

* Combined percentage of moisture and pentane is reported.

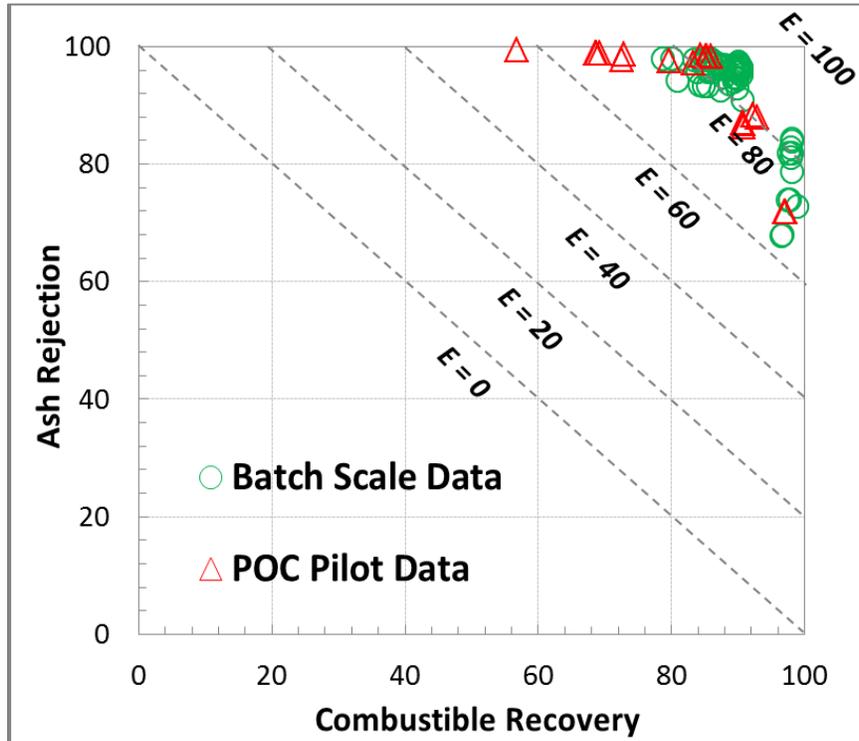


Figure 5.8 Performance comparisons between HHS process batch scale and pilot scale data

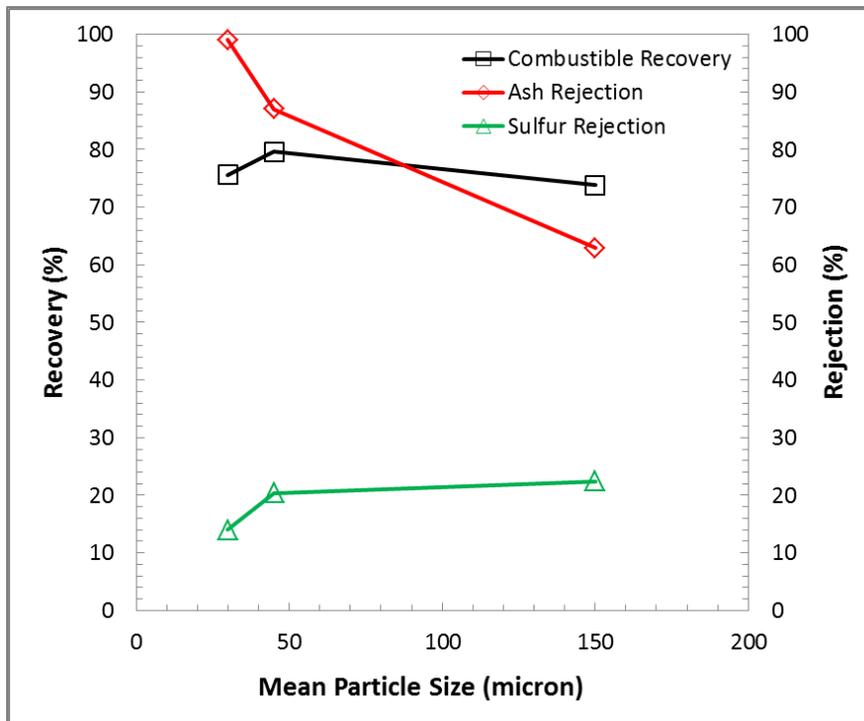


Figure 5.9 Performance evaluation of POC pilot plant with particle size

5.5.2 Particle Size Effect – Lone Mountain

In pilot test #4, conducted with Lone Mountain deslime cyclone overflow feed, the collected samples (feed, product and tails) were screened at three size fractions. These fractions were generated using sieves of aperture 60 mesh, 100 mesh, 325 mesh, and 500 mesh to investigate the performance of the process with particle size. Figure 5.9 shows the recovery and rejection plot with geometric mean size of the particles. The process performance is escalated for particles below 75 microns, however, as the particle size increases, both combustible recovery and ash rejection is decreased. Furthermore, the process is inefficient to separate organic sulfur from the feed. This is because the organic sulfur is hydrophobic in nature.

5.5.3 Effect of Re-designed Vibrating Mixer

A new vibrating mixer unit, with significant volume reduction ($1/6^{\text{th}}$ of old unit), was installed by replacing the old vibrating mixer in the POC pilot plant (Figure 5.10). As compared to other unit operations in the pilot plant, the vibrating mixer is the most unknown unit in the process. The sole purpose of this investigation was to evaluate the plant performance by reducing the volume of pentane in the unit, but keeping the same design parameters (cylindrical reactor with conical bottom) and flow rates. This helped to determine if the scale-up of next-stage unit needed to be volume based or not. The complete comparison between old and new vibrating mixer is outlined in Table 5.7.

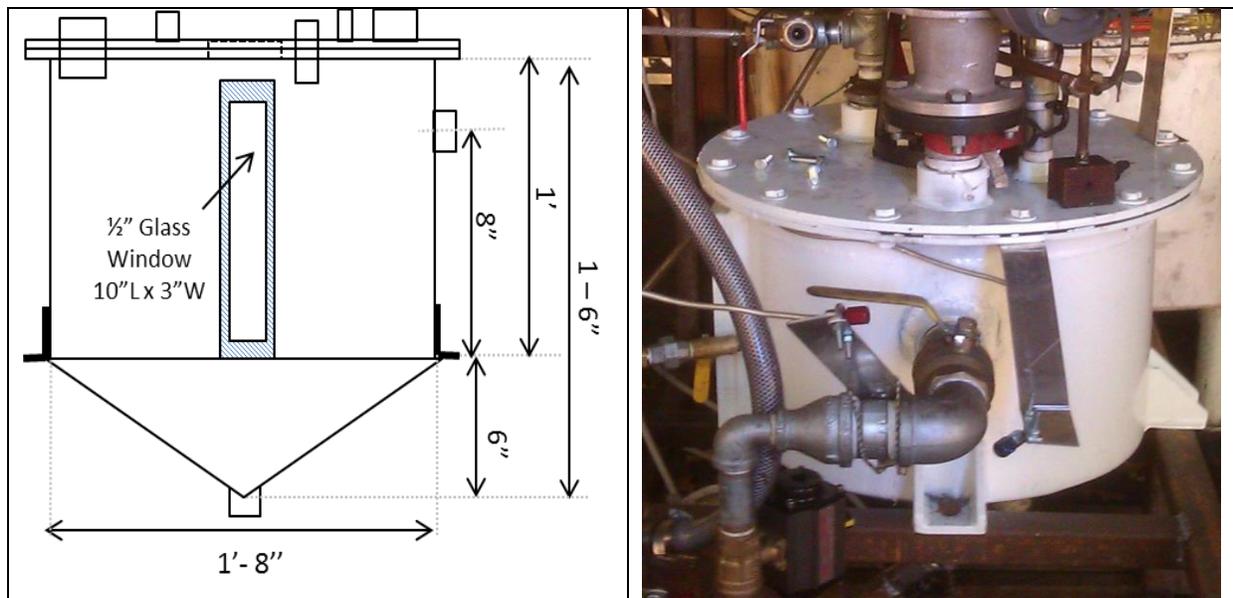


Figure 5.10 New reduced volume vibrating mixer tank design and constructed unit

Table 5.7 Design changes between old and new vibrating mixer unit

	<i>Old-Vibrating Mixer</i>	<i>New Vibrating Mixer</i>
Total Tank Volume	120 gallons	20 gallons
Volume – <i>Aqueous Phase</i>	53 gallons	2.2 gallons
Volume – <i>Pentane Column</i>	35 gallons	10 gallons
Total Flow In	5.04 gallons	5.04 gallons
Residence Time	~7 minutes	~2 minutes
Sweco Screens Diameter	24” (165 mesh & 35 mesh)	18” (165 mesh & 35 mesh)
Operating Frequency, Amplitude	2.5 Hz, 1.125”	2.5 Hz, 1.125”

At a given process flow rate of 5.04 gallons/minute to the unit, the residence time in the process significantly reduced from 7 minutes to 2 minutes. An additional advantage with smaller unit was handling a lower volume of pentane (10 gallons as compared to 35 gallons) in the vibrating mixer. Pilot test #5 and #6 were conducted with old and new vibrating mixer respectively with the same feed sample obtained from Leer de-slime cyclone overflow.

Results (outlined in the Table 5.4) obtained from pilot test #5 and #6 clearly indicates that there is no significant difference in cleaning aspect of the process. The product ashes only differ by 0.1% and reject ashes by 1.3%. In addition, the combustible recovery calculated for pilot test #6 improved to 83.2% as compared to 79.7%, with an ash rejection 97.3%. This signifies that

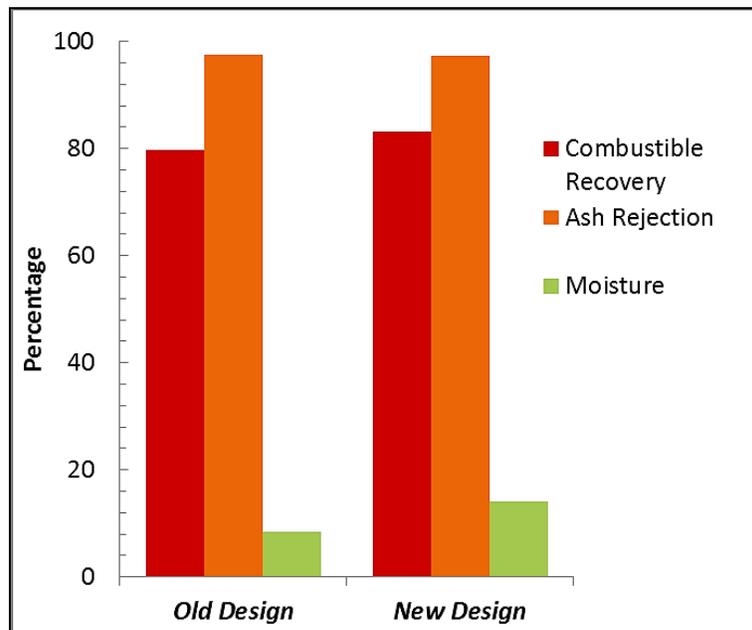


Figure 5.11 Performance comparison of two vibrating mixer unit tested in POC pilot plant

the process scale-up might not be volume-based but on screen area-based. The moisture varies by 5.5 percentage points, which may be due to the misplacement of water droplets in the product. The performance comparison between the old and new design is illustrated in Figure 5.11.

5.5.4 Effect of Oil Skimmer

The pilot test #6 was also conducted to unravel the impact of oil-skimmer on the POC plant performance. After collecting the first sample in usual operating conditions, the oil-skimming pump (P-800) was deactivated, and the plant continued to run for another 30 minutes. The second set of samples (product and reject) were collected and analyzed. Figure 5.12 exhibits comparison of combustible recovery and ash rejection between the two sets of sample. With skimmer in operation, there was no effect on ash rejection (97.3% as compared to 97.7%), whereas, the combustible recovery improved significantly by 10.6% as outlined in Figure 5.12. Clearly, the investigation showed implementation of oil-skimmer was necessary in the POC pilot system to achieve better performance from the process. The direct data obtained from the analysis is exhibited in Table 5.8.

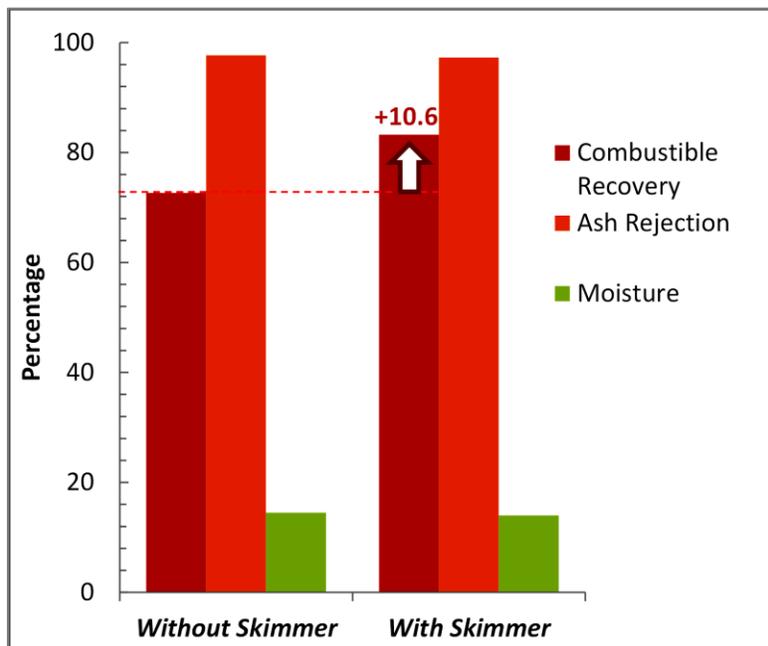


Figure 5.12 Performance comparisons of POC plant with and without skimmer in operation

Table 5.8 Pilot scale test data showing the effect of skimming on POC performance

Pilot Test #6	Feed		Product		Tails Ash %	Combustible Recovery%	% Ash Rejection
	%Solid	Ash %	Combined Weight % Loss	Ash %			
<i>With Skimmer</i>	3.5	50.9	14.0	3.3	85.7	83.2	97.3
<i>Without Skimmer</i>			14.5	3.2	78.7	72.6	97.7

5.5.5 Effect of High Frother Dosage

Typical concentration of an alcohol-based frother used in the conventional flotation process is 15 ppm (Kohmuench et al., 2010). After collecting first set of sample in the pilot test #7, a high dosage of frother (30 PPM of MCHM type) was added into the feed sump and conditioned for 20 minutes. The investigation was conducted to evaluate the effect of residual frother present in the in-plant streams of screenbowl main effluent. The pilot plant was operated for another hour and the second set of sample was collected and analyzed. The direct data obtained from the test is illustrated in Table 5.9. It is apparent from Figure 5.13 that there is no significant effect of high dosage of frother on the POC pilot-plant performance.

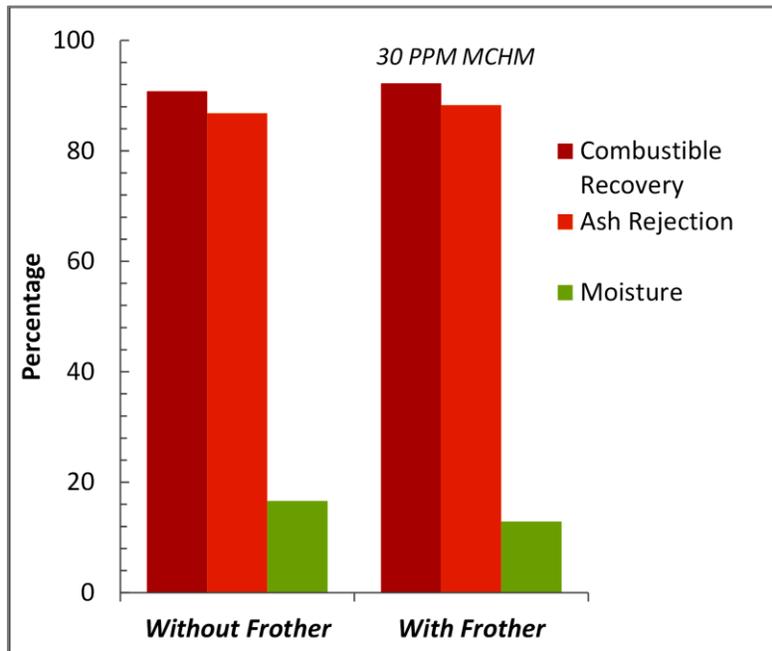


Figure 5.13 Performance comparisons of POC pilot-plant with and without frother

Table 5.9 Pilot-scale test data comparison between with and without high dosage of frother

Pilot Test #7	Feed		Product		Tails Ash%	Combustible Recovery%	% Ash Rejection
	%Solid	Ash%	% Moisture	Ash%			
<i>Without Frother</i>	4.5	28.5	16.6	5.5	78.9	90.8	86.8
<i>With Frother 30 PPM</i>	4.6	29.1	12.9	5.0	82.2	92.2	88.3

5.5.6 Estimation of Pentane Loss - Gas Chromatography Analysis

Gas chromatographic (GC) analysis was conducted with Leer product sample collected from HHS process POC pilot plant. Several individual samples of weight 100 mg in special sealed glass vials (25 ml) were prepared. Each vial was heated at 50°C for 30 minutes and it was assumed that all the pentane would be evaporated in the headspace inside the vial. Then, a 1.5 ml sample was collected from the headspace and injected into a “flame ionization detector” type GC system. The reported analysis was used to calculate pentane lbs/ton loss in the coal samples (illustrated in Figure 5.14). The data indicates that on an average at least 0.182% pentane is absorbed in the POC coal samples, which is equivalent to 3.64 lbs/t of clean coal product.

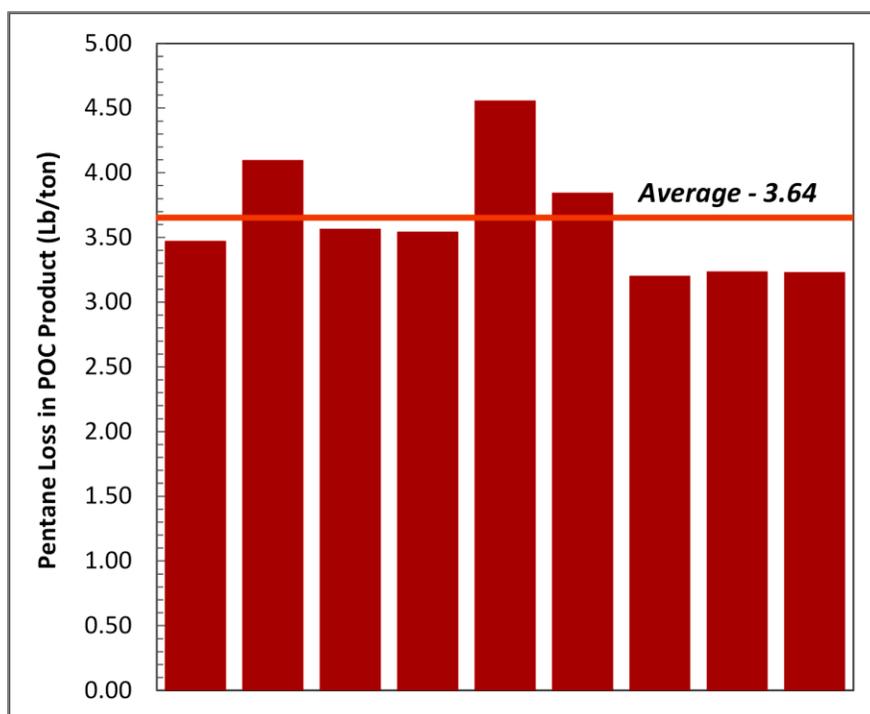


Figure 5.14 Gas chromatography analyses for Leer clean coal sample obtained from HHS process POC pilot plant

The details of the investigation and the final report for the analysis are attached in Appendix D. It is worth mentioning that the theoretical model (as described in Chapter 2) predicted 3.97 lbs/ton of pentane loss in vapor trapped in the void spaces of bulk coal powder.

5.6 Conclusions

The primary goal of developing a Proof-of-Concept (POC) pilot-plant, to demonstrate the HHS process on a larger scale, was successfully achieved. The POC test results with four types of coal were found to be in good agreement with the previous data obtained using a bench-scale system. With consistent low-ash and low-moisture products, the POC test data showed for the first time that the theoretical concept of dewatering by displacement could be engineered and continuously operated for ultrafine coal recovery. The HHS process is a transformative technology that is expected to be beneficial to the industry both in terms of increasing revenue generation and reducing environmental impacts by producing energy resources from currently discarded coal streams and existing coal impoundments.

Originally, a detailed and complete parametric study of the pilot-scale plant was planned. However, the winter weather conditions stalled the POC testing program. Nonetheless, the POC pilot operation provided crucial design information needed for the development of a next-scale demonstration plant.

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CHAPTER 6 - Modeling and Economic Analyses of HHS Process

6.1 Introduction

Modern coal processing plants incorporate as many as four separate cleaning circuits for treating coarse (plus 2 inches), intermediate (2 inch x 1 mm), small (1 x 0.15 mm) and fine (0.15 x 0.044 mm) size fractions of feed coal. The ultrafine particles below 44 microns are often discarded due to low recoveries, poor dewatering performance and high cost. To address this problem, researchers at Virginia Tech have developed the *Hydrophobic – Hydrophilic Separation* (HHS) process to more efficiently remove ash and water from these ultrafine streams in a cost effective manner. Bench-scale tests conducted in the current work have successfully demonstrated that the HHS process simultaneously clean and dewater ultrafine coal streams, which are currently discarded in many existing coal preparation plants. The bench-scale tests consistently showed moisture and ash levels in final product below 10% with variable types of coal feedstocks. In light of this, a Proof-of-Concept (POC) plant was successfully designed, constructed and tested in the current work. The consistent low-moisture low-ash coal products obtained from POC plant further demonstrated that the technology could be commercialized at a larger production rate.

Data obtained from bench and POC-scale testing of the HHS process provided critical engineering information for the development of a next-scale demonstration unit. However, the HHS process is an advanced separation technology that incorporates several complex sub-processes such as oil-agglomeration, solid-liquid separation, oil-recovery process and the innovative de-agglomeration process using vibrating mesh device. Therefore, successfully simulating each unit operation using reliable models would be of great benefit in designing and improving each processing unit.

The chapter presents the results of several bench-scale studies conducted to develop mathematical models for each unit operation. The models were then incorporated into the LIMN® flowsheet simulator, which is a powerful Microsoft Excel-based software package. The resulting simulation package can be used to predict the performance of each unit operation in the HHS process even before actually running the testing equipment. In the current work, this process-engineering tool has been used to develop a 1 metric ton per hour (1 t/hr) process flowsheet for the HHS process. The flowsheet for the 1 t/hr demonstration plant was based on

data obtained in the POC plant using coal samples from the Lone Mountain preparation plant. The models were incorporated in the flowsheet simulator to provide preliminary design specifications for the plant. Furthermore, economic evaluations of the HHS process were conducted for Lone Mountain facility and for the Buchanan preparation plant. The economic evaluations examined potential increases in productivity and direct revenue generation that may be realized by implementing the HHS technology in these existing fine coal cleaning circuits.

6.2 Model for Mixing Operation

Oil-agglomeration, which is the first step of the HHS process, utilizes both high and low-shear mixing. Mixing is itself a complex process involving several dimensionless quantities, which are application specific. Until it is explored, it is unknown which quantity can be used for scale up. On the bench-scale system, mixing was achieved using a standard kitchen blender, which could not provide crucial data for scale-up. The POC system was designed overcautiously with excess volume (residence time) to deal with uncertainties created by a lack of scale-up data. Therefore, to identify the governing criteria and develop an accurate model for the agglomeration step in the HHS process, a detailed investigation was conducted on a batch-scale.

In POC-scale testing, it was determined that the loss of pentane associated with coal is substantially higher as compared to water in the tails. Any unrecovered coal particle in the HHS process reject will also carry pentane coated on its surface, which ultimately is a loss. This loss is a key economic driver in the process. Therefore, attempts were made to determine optimum mixing conditions and scale-up factors that provide minimal carbon loss in the agglomeration tails. To evaluate mixer performance, a parameter called *ash recovery ratio* (ARR) was used, which is defined as the ratio of tails ash to feed ash. The ratio was studied with different mixing parameters such as impeller RPM, impeller diameter, specific power input, and mixing time.

6.2.1 Experimentation and Results

Figure 6.1 illustrates the setup used to conduct the mixing studies. The apparatus includes a mixing device with an in-built feature of measuring torque (in N-cm). The speed can be controlled from 60 to 2000. The device is connected with a mixing shaft with impeller at the end. Two types of impellers, each of different diameters (1, 2, and 3 inches) were evaluated.

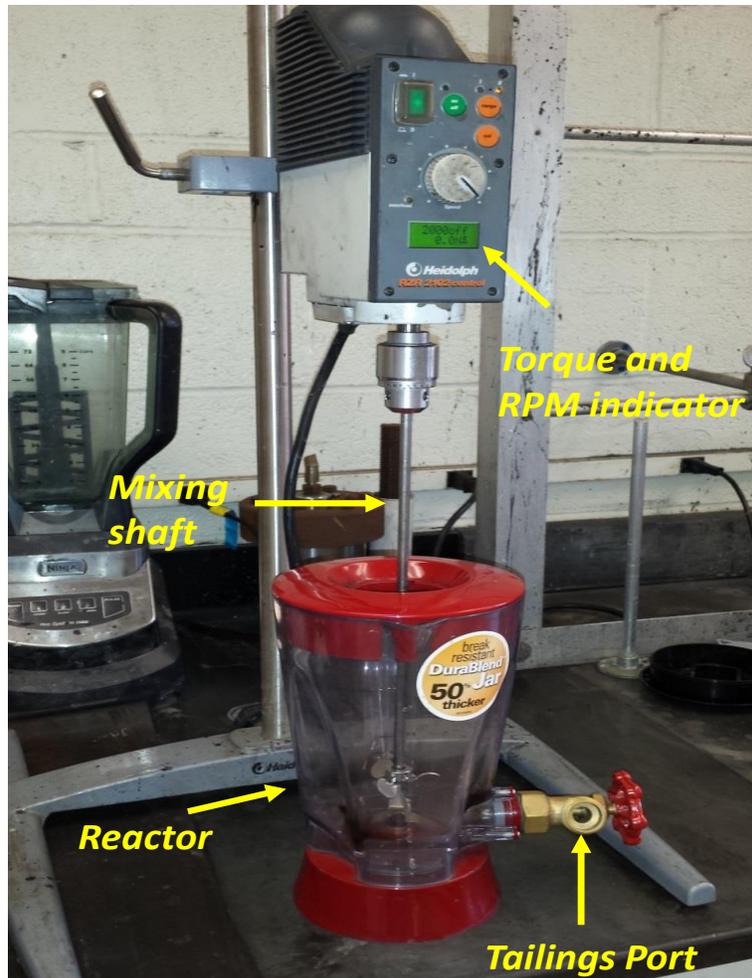


Figure 6.1 Bench-scale apparatus used for agglomeration studies

The first was a laboratory propeller, which has low intensity and high pumping number. The second was a high-dispersion blade, which has high intensity and a very low pumping number. The internal diameter of the reactor at the location of impeller was held constant at 4 inches of depth. Furthermore, a port was installed at the bottom of the reactor to withdraw high-ash tails after agglomeration.

The mixing tests were carried out at variable time periods and RPMs for each impeller using a high-rank bituminous coal sample (as-received 4.5% solids) procured from the Leer facility. Pentane was used as the agglomerating agent. After each test, the agglomeration process was terminated and the torque values were recorded. The reactor was then kept stationary for 30 seconds. During this time, the phase separation was visible where all the agglomerated coal floated on the top of dirty aqueous phase. After an additional 30 seconds, all of the tails collected

from the tailings port were collected and analyzed. The agglomerates that remained in the reactor were not collected or analyzed.

Figure 6.2 shows the direct data obtained during the investigations at different impeller diameter (d)/reactor diameter (D) ratio, which is also considered as another critical parameter. A higher ash-recovery ratio indicates that a higher tails ash was achieved in the test. At d/D ratio = 0.5, the tail ash recovery was reported maximum at 2,000 RPM and 4 minutes. As anticipated, the ash-recovery ratio improves with increasing residence time except in case of d/D = 0.75 with high RPM, where the ratio is highest at 15 seconds and then decreases with time. It was observed that, at extremely high specific energy and increasing mixing time, agglomerates formed very quickly but soon broke into smaller size aggregates. This may be due to excessive shearing effect per unit volume inside the system.

Figures 6.3 and 6.4 illustrates several plots showing the effect of impeller tip speed (feet/second), power/volume (KW/m³), d/D ratios and residence time on the tailings ash for both types of impeller respectively. The trends with tip speed in both the cases (Figure 6.3a; Figure 6.4a) indicate an optimum condition for the given reactor geometry, which is approximately 17 feet/sec, to achieve the highest reject ash. The tip speed is a direct indication of shear intensity provided to the system, showing it is one of the prime factors affecting the process. Therefore, tip speed must be considered for the scale up of this unit operation in the HHS process.

On the contrary, in case of propeller power/volume curve (Figure 6.3c) does not produce a significant correlation with ash ratio, though it appears to improve with increasing power. This may be due to the fact that propeller type impellers have high pumping number (0.5), while high-shear blades have low pumping number (0.26), where trend is more significant (Figure 6.4c). Residence time defines the reactor volume needed in any process. Figure 6.3e depicts significant information for designing the agglomeration unit for the HHS process. At high impeller speed and d/D ratio, substantial reject ash is achieved at very short mixing time with propeller type blade. However, the effect is different with high-shear blade (Figure 6.4e). It was observed that the former type impeller created vortex and were excellent for mixing while the latter was only good for dispersion only. From the trends, it is evident that propellers are good for agglomerates growth while high-shear blade can be used prior to agglomeration for dispersion of pentane liquid and coal-oil contact in the ultrafine coal slurry for a very short residence time.

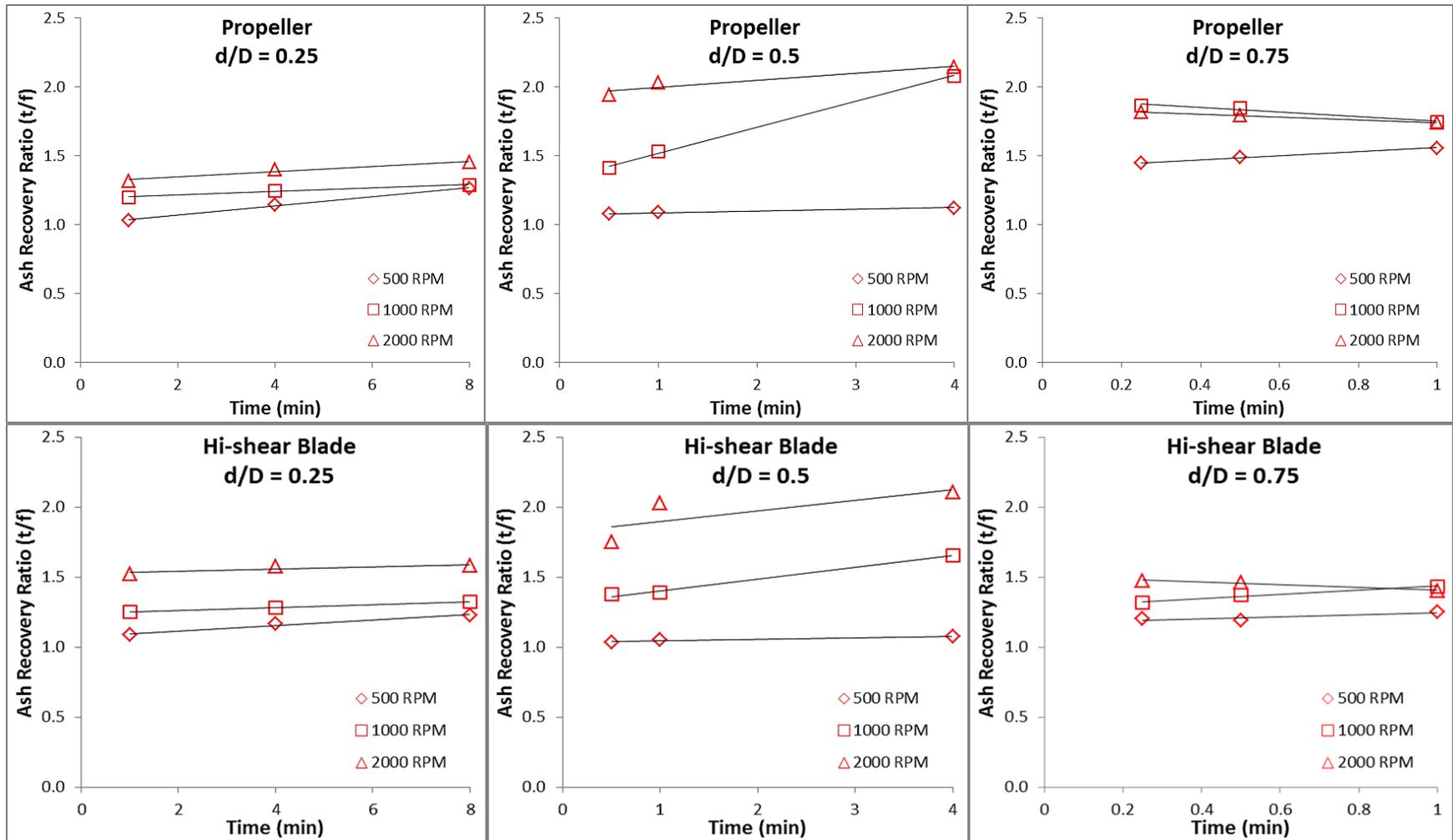


Figure 6.2 Experimental data showing trends of ash-recovery ratio with time at different mixing conditions

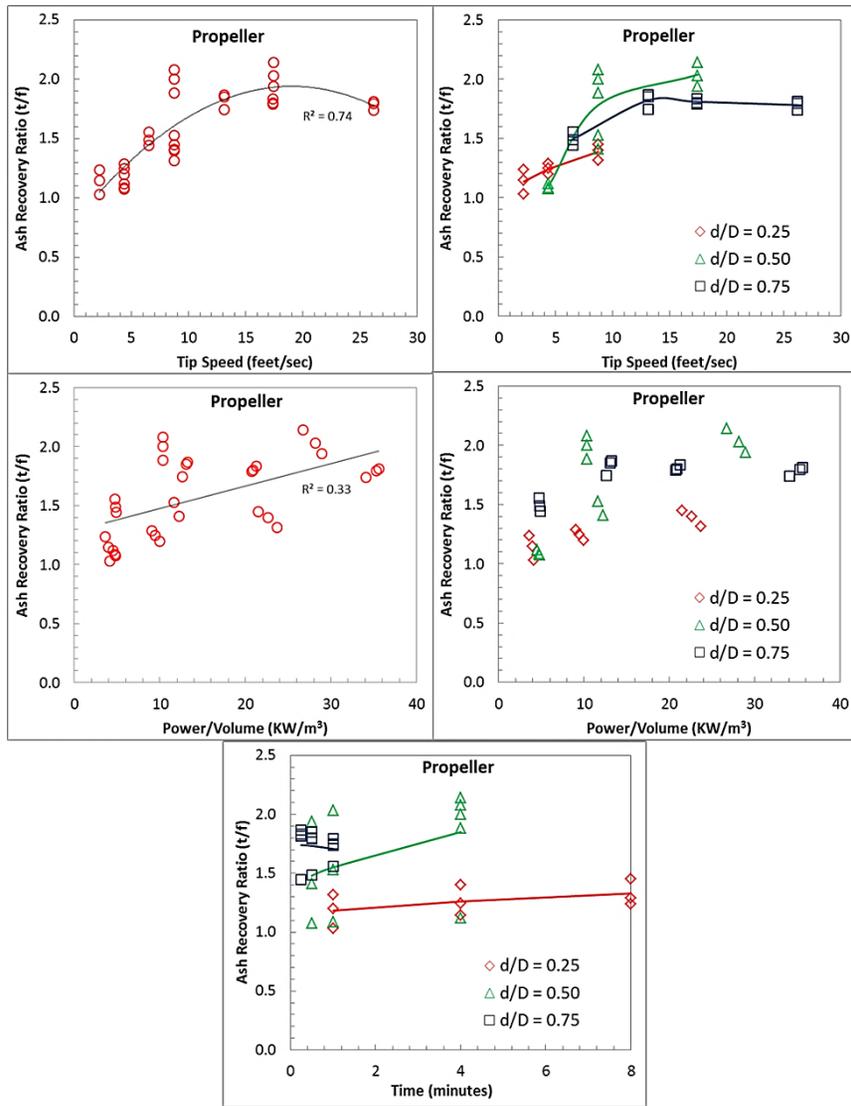


Figure 6.3 Trends of ash-recovery ratio with (a)& (b) tip speed, (c)& (d) power per unit volume and (e) time for propeller type impeller

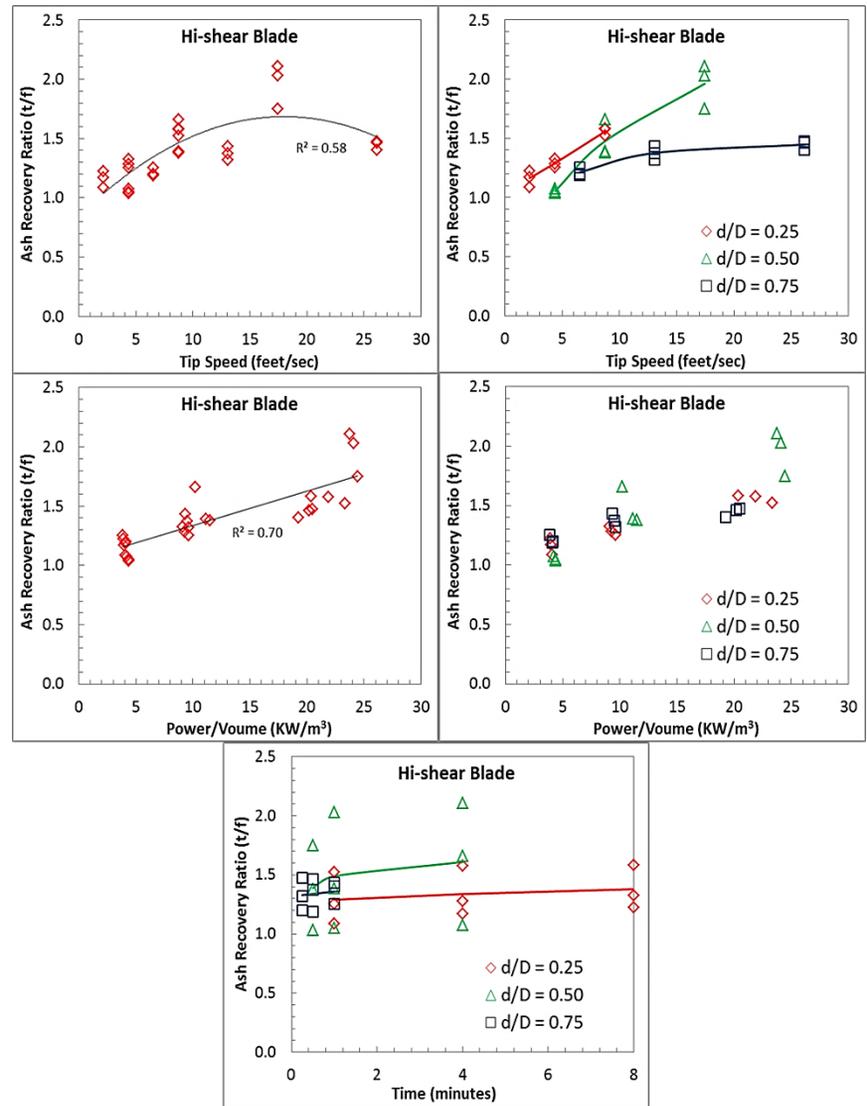


Figure 6.4 Trends of ash-recovery ratio with (a)& (b) tip speed, (c) & (d) power per unit volume and (e) time for hi-shear blade type impeller

It is important to mention that the trends are expected to vary once the geometric ratios are changed. Similar studies may be required to identify optimum conditions for a specific type of reactor geometry. The detailed data for the investigation is listed in Appendix D.

6.2.2 Model Development

For modeling purposes, the ash recovery ratio was normalized with maximum possible ash percentage, which is 100%. Indirectly, the normalized ash-recovery ratio can also be defined as the ratio of carbon in the reject relative to the feed, which is $(100-t)/(100-f)$. Where, t and f are respective reject and feed ash percentages. The model was developed using the test data obtained from propeller type impeller, because it was identified from batch-scale studies that these types of impellers would be better for the agglomeration step.

Figure 6.5 illustrates the different normalized ash ratio plots at a given d/D ratio with time. The model is developed with an assumption that the reactor is a plug flow system. In addition, the normalized ash ratio curves does not close in the given time period, therefore a correction factor (α) is used. A model equation for normalized ash ratio (NAR) using the rate constant (k) and correction factor (α) for the plug flow reactor can be expressed as:

$$NAR_{predicted} = (1 - \alpha) * e^{-kt} + \alpha \quad [6.1]$$

The fitting parameters k and α is calculated for the best model fit for each RPM and each d/D ratio as shown in Tables 6.1 and 6.2. These parameters are further correlated as a function of tip speed and specific power. The details are outlined in Appendix D.

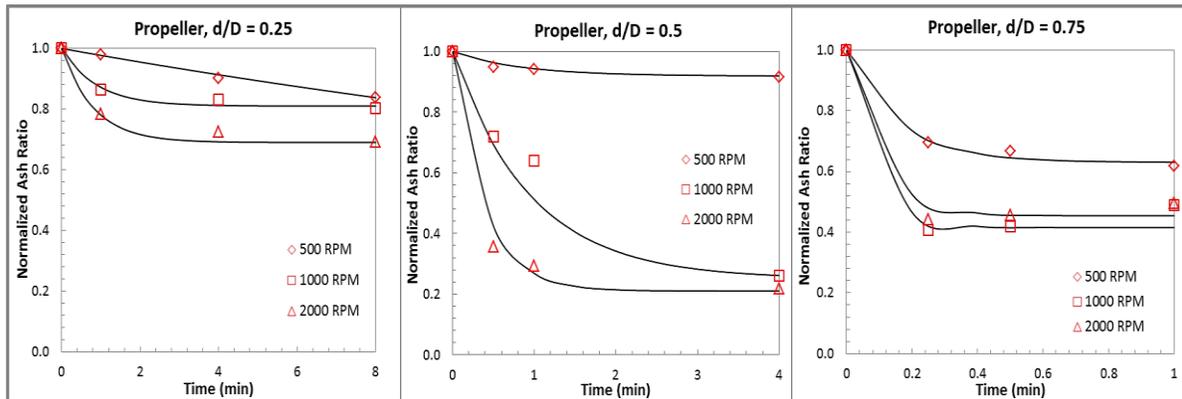


Figure 6.5 Model fitting for agglomeration studies conducted with propeller type impeller

Table 6.1 Response matrix for fitting rate constant (k) at variable RPM and d/D ratio

		RPM			
		k	500	1000	2000
d/D	0.25	0.035	1.12	1.23	
	0.5	1.2	1.05	2.6	
	0.75	6.3	10.2	12.2	

Table 6.2 Response matrix for fitting correction factor (α) at variable RPM and d/D ratio

		RPM			
		α	500	1000	2000
d/D	0.25	0.33	0.81	0.69	
	0.5	0.919	0.25	0.21	
	0.75	0.63	0.454	0.415	

The model equation for rate constant (k) was calculated empirically ($R^2 = 0.99$) in terms of tip speed (TS) in *meter/second* as described in Equation 6.2. Similarly, empirical equations for the correction factor (α) were determined as a function of tip speed in *meter/sec* and specific power (SP) in KW/m^3 for individual d/D ratio ($R^2 = 0.82$), as shown in Equation 6.3.

$$\begin{aligned}
 k &= 1.004 * \ln(TS) + 0.572 && \text{for } \frac{d}{D} \leq 0.5 \\
 k &= 4.256 * \ln(TS) + 3.68 && \text{for } \frac{d}{D} > 0.5
 \end{aligned}
 \tag{6.2}$$

$$\begin{aligned}
 \alpha &= TS^{-0.898} * SP^{0.082} && \text{for } \frac{d}{D} = 0.25 \\
 \alpha &= TS^{-2.86} * SP^{0.437} && \text{for } \frac{d}{D} = 0.5 \\
 \alpha &= TS^{-1.755} * SP^{0.429} && \text{for } \frac{d}{D} = 0.75
 \end{aligned}
 \tag{6.3}$$

6.2.3 Discussion

The investigation on oil-agglomeration with ultrafine coal and pentane provided useful information that can assist the designing units for the demonstration plant. The data shows that tip speed is an important criterion in the HHS process agglomeration step and can be used for scale-up process. The low-intensity and high-pumping propeller type impellers assist agglomeration growth process. While the high-shear blade is good for dispersion of immiscible

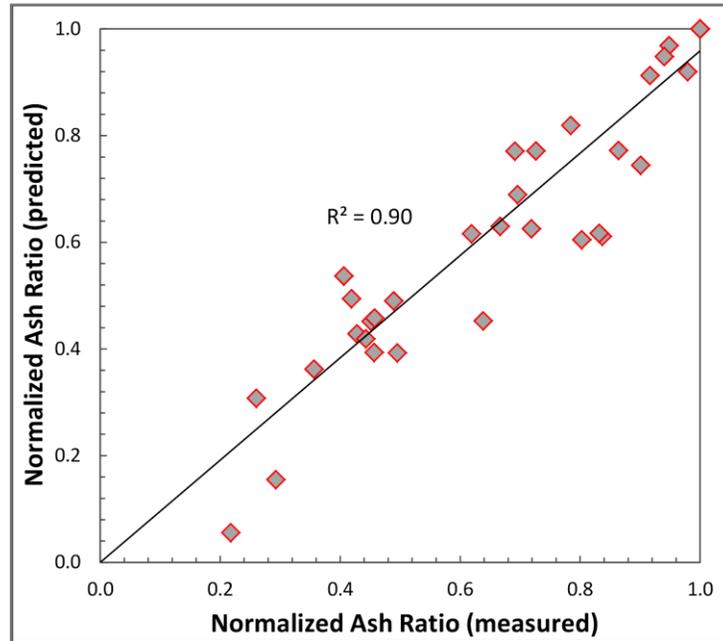


Figure 6.6 Correlation between measured and predicted values of normalized ash ratio

liquid in coal slurry. For high-dispersion blades, very low residence time will be preferred. Additionally, a high reject ash is achievable at a high impeller speed and high d/D ratio at a very short retention time.

The developed model is fairly accurate ($R^2 = 0.9$) and found a discrete function for specific d/D ratio, which is a best fit using the available experimental data. Figure 6.6 illustrates the correlation between experimentally measured and predicted values from empirical model of normalized ash ratio.

6.3 Model for Vibrating Mixer

The vibrating mixer unit is equipped with a novel oscillatory mesh device that facilitates three important mechanisms necessary for achieving low-moistures and high recoveries. These are de-agglomeration (breaking of agglomerates), homogenization (keep particles in suspension) and water coalescence. The combination of the first two is dispersion mechanism. The kinetic study was conducted on batch-scale vibrating mixer and was discussed in Chapter 3. In the investigation, the rate of homogenization ($K_h = 0.36 \text{ min}^{-1}$) in the reactor was determined using dry coal powder, while the rate of dispersion ($K_d = 0.25 \text{ min}^{-1}$) was identified using the same procedure but with spherical coal agglomerates. Therefore, the difference in rates defined the

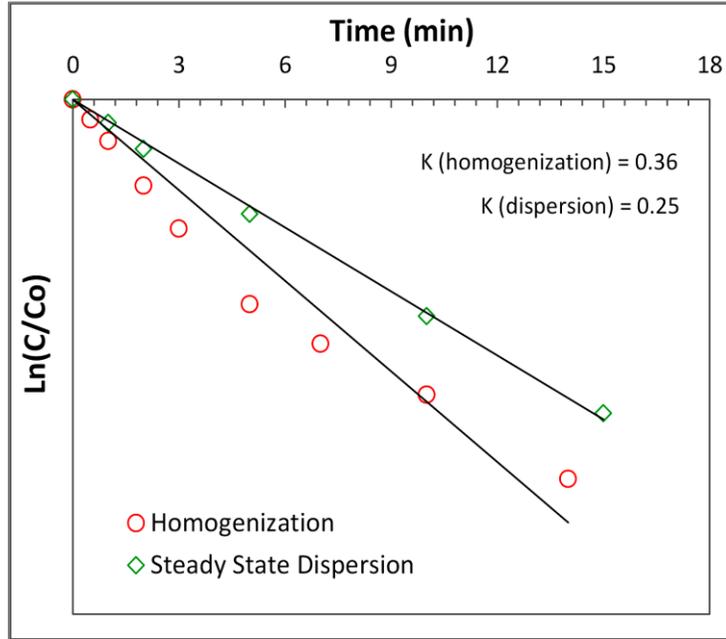


Figure 6.7 Semi-log concentration plots for mechanisms involved in vibrating mixer

rate of de-agglomeration or breakage ($K_b = K_d - K_h = 0.11 \text{ min}^{-1}$). The investigation indicated that the agglomerate dispersion mechanism follows a first order rate when operating under steady state conditions. Figure 6.7 illustrates the semi-log concentration plot with time showing the rates of dispersion and homogenization mechanism.

From the dispersion rate data, a simple kinetic rate model can be defined for the concentration in the reactor as a function of time, as described in Equation 6.4. The experimentally measured data and predicted values fit excellent correlation with a coefficient of determination (R^2) equals to 0.9976 and are outlined in Table 6.3.

$$C(t)_{\text{reactor}} = C_0 * e^{-0.25t} \quad [6.4]$$

Furthermore, the relationship between the rate constant and time can be analyzed for reactor modeling using the Levenspiel equation (described in Equation 6.5), which is appropriate for first-order kinetic processes. The relationship provides recovery as a function of the dimensionless Peclet number and the dimensionless product of mean residence time of particles and the process rate constant (Levenspiel, 1999). Peclet number is a mixing intensity indicator used to study transport phenomena of particles in fluids. The Peclet number is zero for perfectly mixed reactors and infinite for plug-flow reactors.

Table 6.3 Measured and predicted values correlation for vibrating mixer

Time (minutes)	C/Co (in Reactor)	
	Measured	Predicted
0	1.00	1.00
1	0.76	0.78
2	0.56	0.61
5	0.26	0.29
10	0.08	0.08
15	0.03	0.02

$$\frac{C}{C_o} = \frac{4Ae^{(P_e/2)}}{(1+A)^2 e^{(AP_e/2)} - (1-A)^2 e^{(-AP_e/2)}} \quad [6.5]$$

$$A = \sqrt{1 + 4K\tau/P_e}$$

From the experimental kinetics data, the mean residence time (τ) can be calculated using Equation 6.6, which was found to be *4.45 minutes*. Similarly, the Peclet number can be estimated using its relationship with dimensionless variance (σ^2) as described in Equation 6.7. The Peclet number for the reactor was calculated approximately *0.93*, which indicates the vibrating mixer is close to a well-mixed reactor.

$$\tau = \frac{\sum tC\Delta t}{\sum C\Delta t} \quad [6.6]$$

$$\sigma^2 = \frac{\sum t^2 C\Delta t}{\tau^2 \sum C\Delta t} - 1 = 2\left(\frac{1}{P_e} - \frac{1-e^{-P_e}}{P_e^2}\right) \quad [6.7]$$

6.4 Model for Regent Thickener

In the novel HHS process, the thickening of suspended ultrafine clean coal particles in pentane from the vibrating mixer is a very important step, particularly in designing the heat exchanger units. Higher thickener underflow solids will reduce the liquid pentane load that has to be evaporated in the dryer. The force of gravity concentrates the suspended particles in the thickener. Therefore, to properly apply gravitational sedimentation in identifying the right size thickener, both basic and applied theory must be considered.

Several popular studies conducted previously by Coe and Clevenger (1916) and Kynch (1952) utilize batch-scale settling data in determining the unit area ($m^2/\text{ton}/\text{hour}$) required in industrial scale thickeners. These studies were established to quantify the settling of particles in water as a carrier liquid. For the HHS process, similar settling data was generated utilizing ultra-fine clean coal particles (below 34 microns, 2% ash) in pentane as a carrier liquid.

Bench-scale tests were performed in 1-L graduated cylinder at different percent solids in liquid pentane and the interface height was recorded with time. The settling rate data obtained from the investigation is available in Appendix D. In the HHS process, the thickener feed contained a low percent solids ranging from 1 – 10%. Therefore, settling curves between interfacial heights and settling time was generated only for low percent solids, as shown in Figure 6.8. In the batch settling tests, for an initial solid concentration of C_o (Kg/m^3) and height of interface at $t=0$ of H_o , the total solids mass in the measuring cylinder can be defined as $C_o H_o A$. If the time taken for all the solids to settle past a layer of concentration “C” is “ t_u ” then $C_o H_o A / t_u$ represents the amount of solids can be brought through the concentration layer per unit time. The method is widely recognized as the Oltmann method, which relies on identifying the compression point (inflexion point) of the settling interface. The time “ t_u ” is defined when the compression is believed to begin.

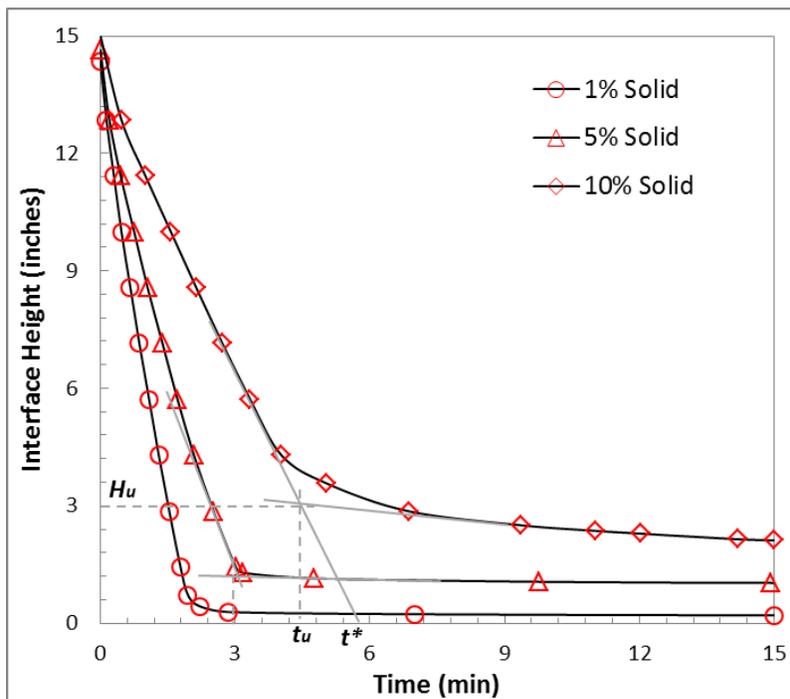


Figure 6.8 Bench-scale settling data for ultrafine coal particles in liquid pentane

The Oltmann procedure (Dahlstrom, 2003) was followed in developing the thickener model to determine the unit area required for the thickener. For 1 ton/hour of dry solid, the required unit area for thickener based on the Oltmann procedure will be:

$$U.A. = \frac{t_u}{C_0 H_0} \quad [6.8]$$

From material balance one can deduct the following relationship:

$$C_u H_u = C_0 H_0 \quad [6.9]$$

At low percent solids, the settling rate curve follows first-order kinetics with two rate constants, one before the compression point (considered as free settling) and one after the compression point (considered as hindered settling). Time “ t_u ” can be expressed in terms of t^* , which is the time intercepted corresponding to the first settling rate, as described in the Figure 6.8.

$$t_u = t^* \left(\frac{C_u - C_0}{C_u} \right) \quad [6.10]$$

From the recorded settling data, time t^* was correlated empirically in terms of feed % solids (%S) as:

$$t^*(minutes) = 0.54 e^{0.2 (\%S)} \quad [6.11]$$

The concentration ratio outlined in Equation 6.10 can be re-written in terms of percent solids where %UF is the underflow solids percentage at time “ t_u ” and the feed percent solids (%S) replaces C_0 . In addition, considering the specific gravity of solids of 1.25 SG and pentane of 0.626 SG, C_0 can be described in terms of feed percent solids (%S) as shown below:

$$C_0 = 6.62 (\%S) - 0.73 \quad [6.12]$$

By incorporating Equations 6.9 – 6.12 into Equation 6.8, the unit area can be described in terms of feed percent solids (%S), initial height (H_0 in meters) and underflow percent solids (%UF) as:

$$U.A. (m^2/ton/hour) = \frac{9 e^{0.2 (\%S)}}{(6.62 \%S - 0.73) H_0} \left(\frac{\%UF - \%S}{\%UF} \right) \quad [6.13]$$

In the current work, Equation 6.13 was used to develop a dual model, a design model, and a simulation model in the LIMN® software. The models were used to estimate the unit area for the desired underflow percent solids and to determine the thickener underflow percent solids for a given thickener unit area, respectively. An image of the developed model is illustrated in Figure 6.9. The detail analyses for the settling rate can be found in Appendix D.

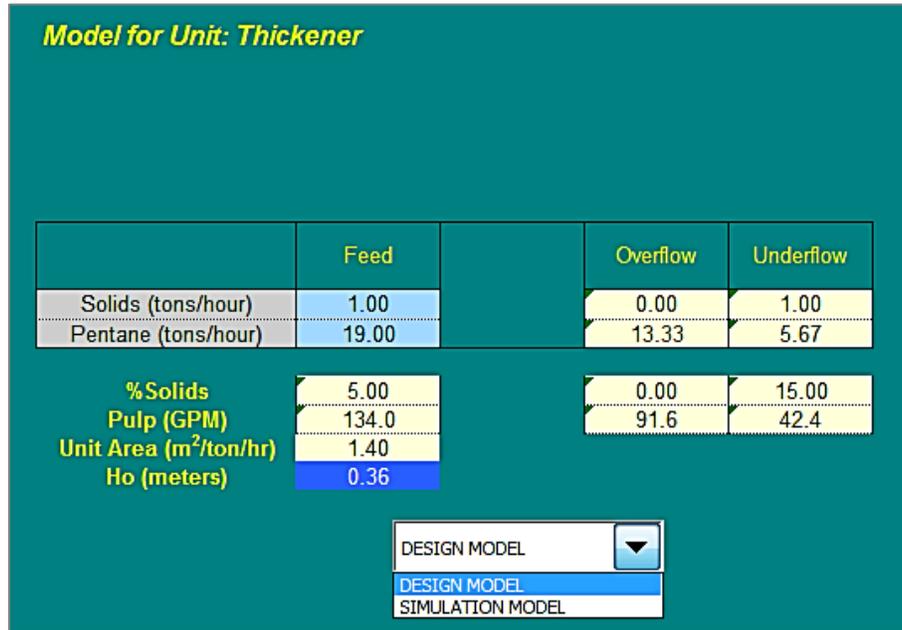


Figure 6.9 Pentane thickener dual model developed in LIMN® software

Considering the particle size, the settling rate of ultrafine coal solids in pentane was observed to be very high. The unexpectedly high rate may be because particles do not carry any electrostatic repulsive force when suspended in a non-polar liquid. Therefore, the remaining attractive force naturally coagulates the ultrafine particles, which increases the settling rate.

6.5 Model for Reagent Dryer

A basic pentane evaporation model was developed in LIMN® based on the bench-scale data reported in Chapter 2. The thermo-gravimetric experiments were conducted with known amounts of ultrafine coal mixed with known amounts of liquid pentane in sealed vials. Each vial was exposed to an isothermal environment at different temperatures, and the weight loss was recorded with time. Figure 6.10 shows plots of concentration ratios (C/C_0) with time at each temperature. The evaporation of pentane for each temperature closely follows an exponential relationship with time with R^2 values ranging from 0.89 to 0.93, and can be best fit using the following equation:

$$C_{Lb/ton}|_{time=t} = A * C_{Lb/ton}|_{t=0} * e^{-B*t} \quad [6.14]$$

In Figure 6.10, the red circles indicate the batch-scale experimental data while the predicted values from the empirical equation is shown with a black line.

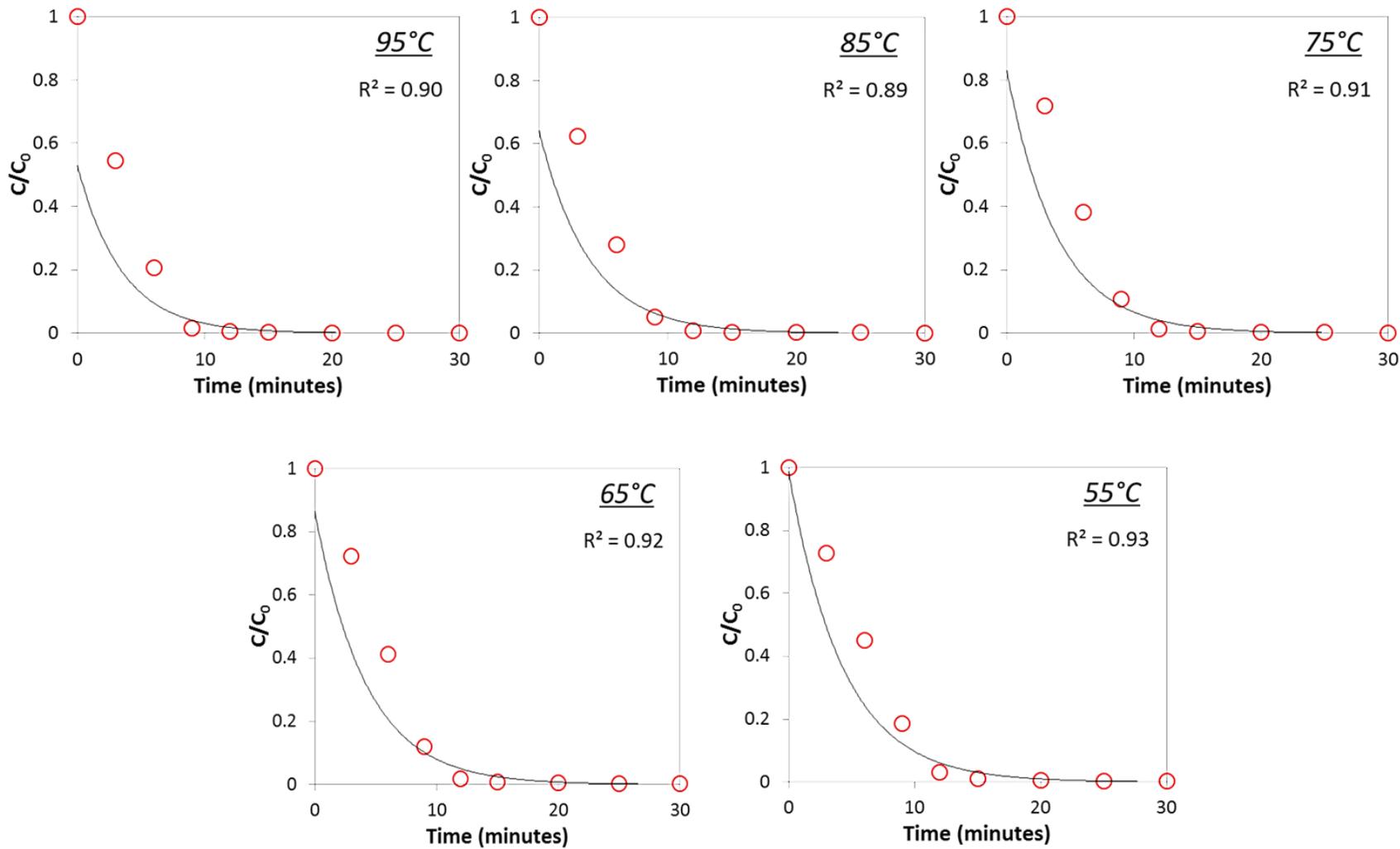


Figure 6.10 Pentane loss rate plots associated with clean coal product at various temperatures

The two fitting parameters, A and B , which are dependent on temperature (θ) in °C, were calculated empirically from the bench-scale data. The input parameters in the model are initial pentane load, which can be calculated from thickener underflow percent solids and temperature. The detailed analysis for the modeling correlation and direct data obtained from the investigation can be found in Appendix D.

$$A = -0.011 * \theta + 1.628 \quad [6.15]$$

$$B = 0.168 * e^{0.005 * \theta} \quad [6.16]$$

The abovementioned model was utilized to develop a simulator within the LIMN® flowsheet software (illustrated in Figure 6.11). The model generates pentane loss curves associated with coal at various temperatures ranging from 55-95°C. The model provides data points on a simulated curve that shows the level of pentane loss as a percentage at a given residence time. The data points can be used to determine the pentane losses in pounds/ton of coal for heating the coal-pentane pulp under isothermal conditions.

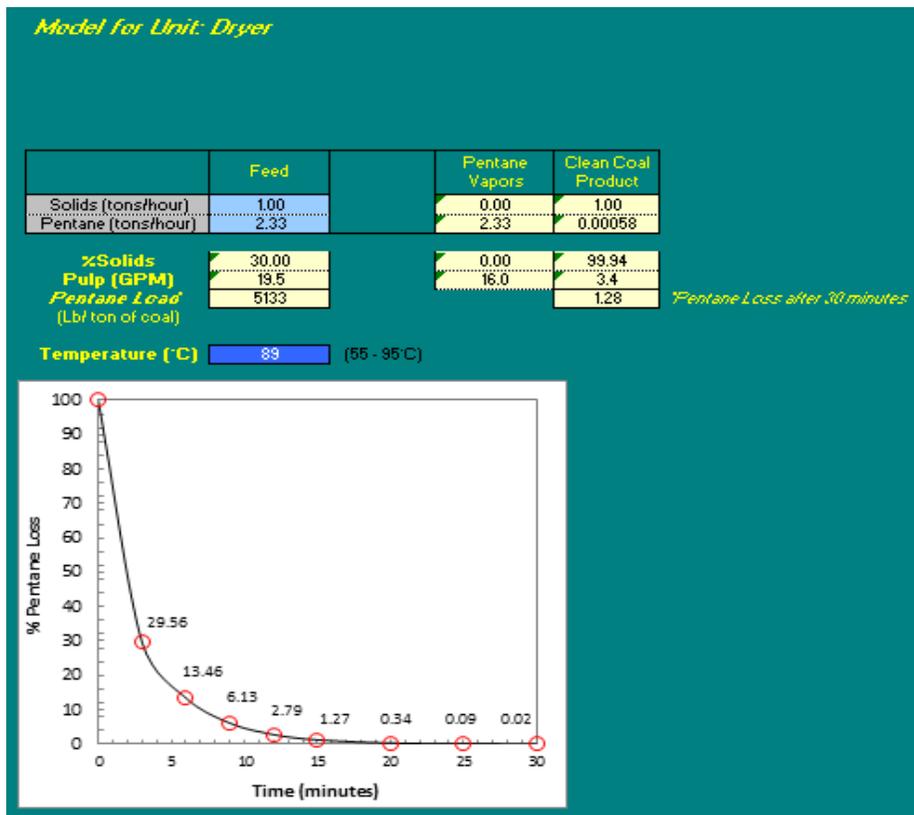


Figure 6.11 Pentane absorption simulator designed in the LIMN® software

It must be noted that the model is based on bench-scale experimental data and is expected to vary depending on the heat transfer coefficient of the drying technology. Industrial dryers have a high heat transfer coefficient as compared to the bench-scale system and therefore, an appropriate dryer-condenser system is expected to reduce the loss of pentane as compared to what is predicted with the proposed model.

6.6 Development of 1-Metric ton Plant Flowsheet

In pilot scale test #4, conducted with Lone Mountain deslime cyclone overflow feed, various samples were collected from intermediate sample streams in addition with regular feed, product and tail samples. Figure 6.12 shows the simplified flow diagram indicating the sample points across the POC pilot plant. The data obtained during the test was utilized in the development of a flowsheet for a 1 metric ton per hour demonstration plant (Table 6.4). The LIMN® processing software was used to design the material and heat balance flowsheet, which shows the steady-state flows necessary to specify and design each unit operation. Figure 6.13 shows the newly drafted flowsheet used as the first-step for the prototype demonstration plant.

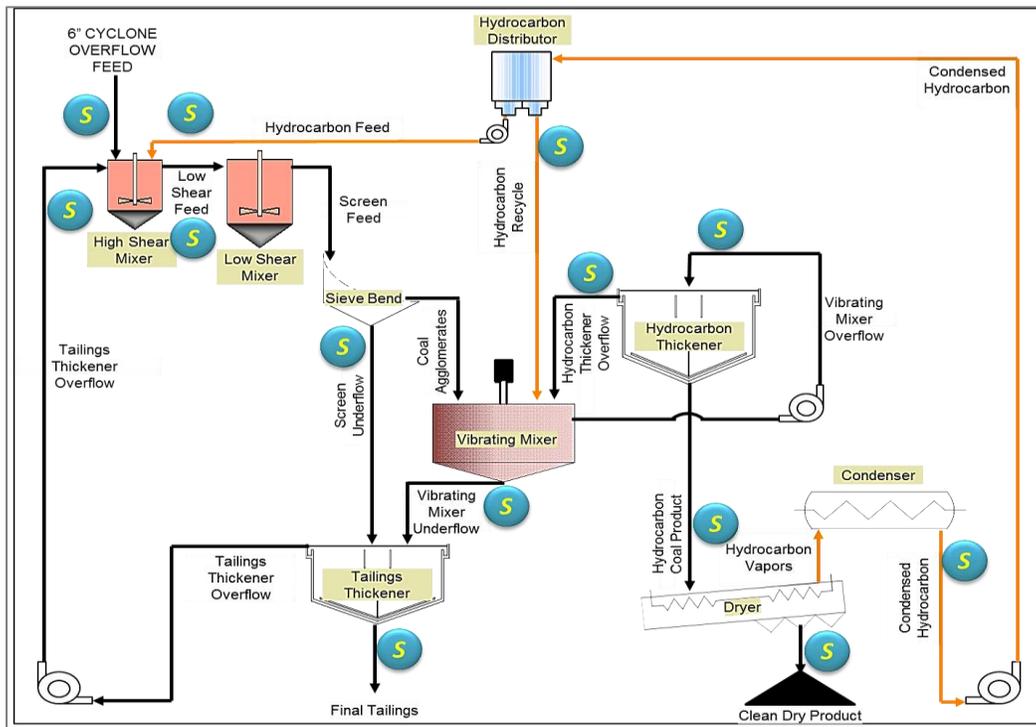


Figure 6.12 Schematics showing sample points across the POC pilot plant

Table 6.4 Direct data obtained from POC pilot scale plant at various sample points

		<i>Sample 1</i>	<i>Sample 2</i>
Feed	Ash%	60.5	77.3
	%Solids	7.8	4.5
	%Sulfur	0.3	0.13
<i>Hi-Shear O/F Ash%</i>		41.4	68.8
<i>Sieve Screen U/F Ash%</i>		83.2	73.6
<i>Vibrating Mixer U/F Ash%</i>		90.7	83.3
<i>Vibrating Mixer O/F Ash%</i>		1.9	2.1
<i>HL Thickener U/F Ash%</i>		2.8	2.4
<i>Skimmer Ash%</i>		78.6	74.9
Product	Ash%	2.7	2.7
	%Moisture	12.5	9.8
	%Sulfur	0.64	0.66
Reject	Ash%	90.6	88.7
	%Sulfur	0.04	0.04

The major difference between the existing POC design and the proposed demonstration plant is the replacement of sieve-bend with a stationary tank called as ‘*phase separator*’. The phase separator allows the newly formed agglomerates to float on the top of dirty aqueous phase, which will be skimmed from the top of the tank to the vibrating mixer. This modification is proposed because of reasons listed below:

- To eliminate maintenance associated with sieve bend.
- The screen allows undersize micro-agglomerate to pass to the tailings tank, while the phase separator will transfer all coal mass floating on the top to the vibrating mixer tank, thus minimizing the carbon and pentane losses.

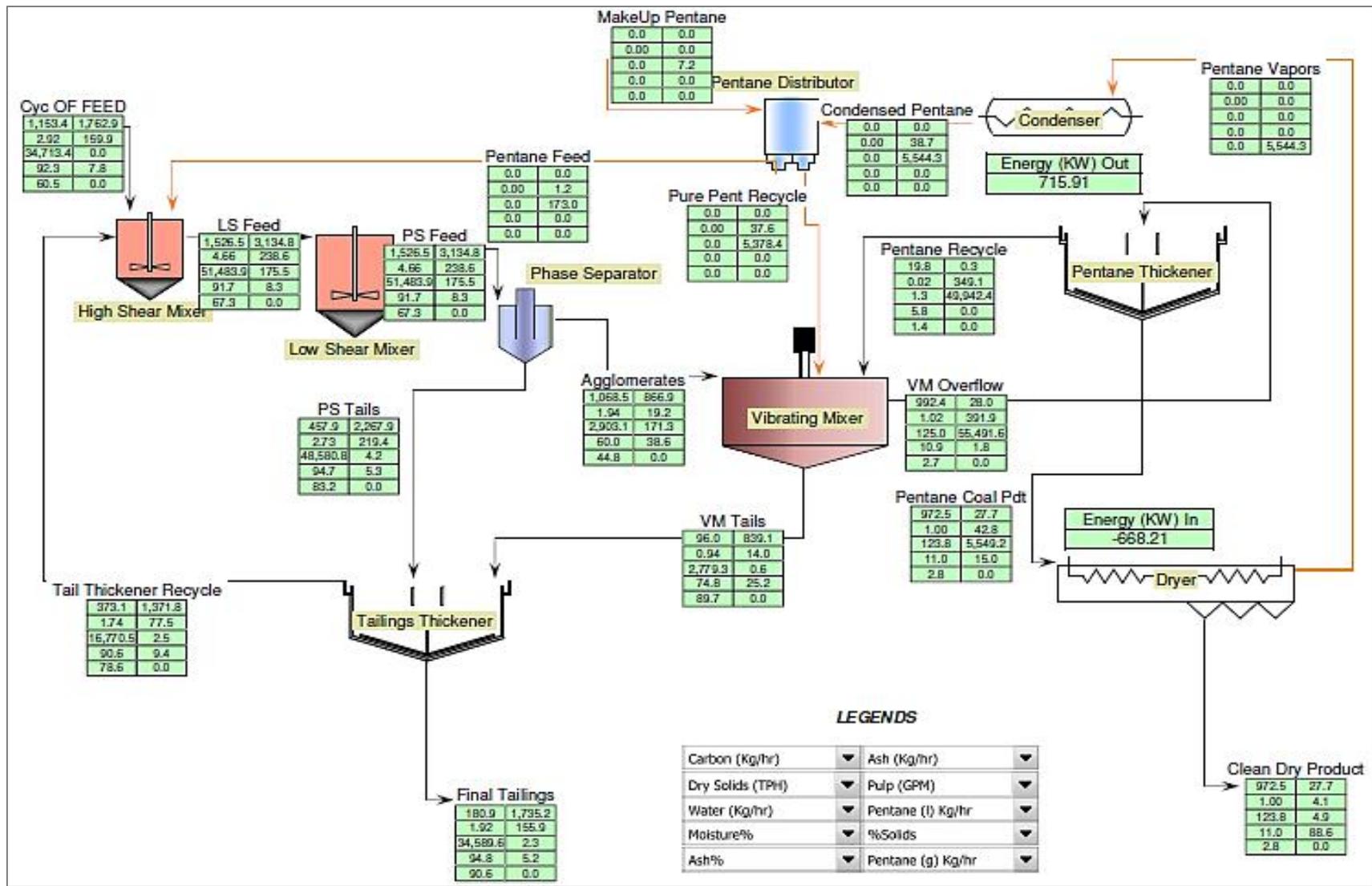
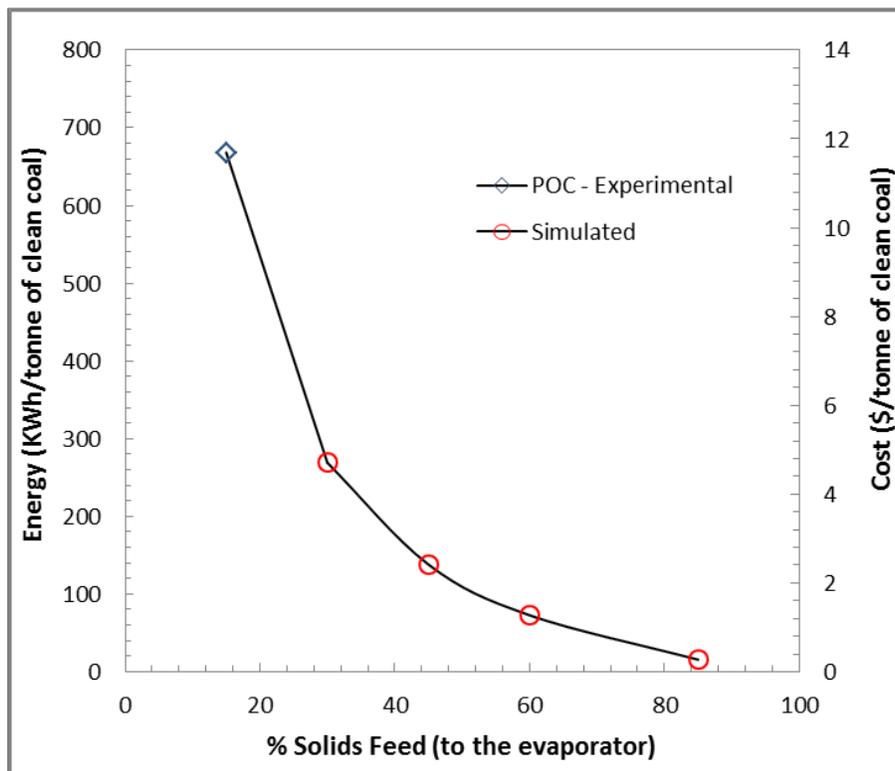


Figure 6.13 Preliminary mass-heat balance process flowsheet for 1 metric ton/hour clean coal HHS process demonstration plant

6.6.1 Thermal Energy Requirements

The newly drafted 1 metric ton HHS process flowsheet indicates that a high amount of energy will be required for evaporation and condensation of pentane. This high value is because the hydrocarbon thickener underflow stream was only 15% solids by weight during the pilot test #4. At this low value, the pentane load to the dryer would be very high. It is important to note that the energy requirement can be reduced by increasing the solids concentration in thickener underflow stream using an appropriate solid-liquid separation device, such as a solid-bowl centrifuge. Fortunately, during pilot test #7, the thickener underflow concentration was observed to be as high as 45.3% from the same static thickener. This higher value would substantially reduce pentane losses. Due to high discrepancies in percent solids in the thickener underflow stream, the process flowsheet was simulated at various solids concentration in the thickener underflow stream to predict energy requirements (Kwh/ton) and associated cost (\$/ton) for pentane loads to the dryer (Figure 6.14). This analysis provides critical information for the design the heat exchanging system for the 1 metric ton demonstration plant.



Note:- Cost estimation is based on natural gas price \$5.50/MMBTU

Figure 6.14 Prediction of thermal energy requirement for dryer and associated cost relative to thickener underflow solids

6.7 Projected Economics of the HHS Process

Prior to economic analysis of any process for coal, it is necessary to address the market value of this commodity. Typically the payments in the coal market are reported on a per MMBTU basis, which is the heat content of the as-received product. The following assessment is made with the current electric power generation fuel cost, which is \$2.36 per MM BTU (EIA, 2014), and \$5.84 per MM BTU or \$135 per ton (EIA, 2012) for premium coking coal.

Appalachian mined coals are typically high-rank bituminous type with an average heat value of 15,000 BTU/lb (dry ash-free basis). The existing preparation plants in this region produce coal for either the coking and steam coal markets, depending on the seam characteristics. However, the very fine coal, due to its high moisture content, is often discarded. The newly developed HHS process can produce premium quality coal product from these discarded ultrafine streams. This premium quality product can be blended for either of the abovementioned markets, thus providing revenue generation for coal producers.

6.7.1 Revenue Assessment from POC Data

As an example, in the existing Lone Mountain facility, the discarded raw coal deslime cyclone overflow is 74 tons solids/hour (Lone Mountain, 2013). With an ash content of 60.5% (dry basis), as recorded in pilot test #4, 29.23 tons/hour ($74 \times 0.395 = 29.23$) of combustible material is lost in this stream. The HHS process POC pilot scale data demonstrated that 84.4% carbon could be recovered with 2.7% ash and 12.5% moisture. The heat content of the as-received product is 12,333 BTU/lb ($15,000 \text{ BTU/lb} \times 0.975 \times 0.875 = 12333 \text{ BTU/lb}$). The total carbon produced per hour is 54,373 pounds ($29.23 \text{ ton/hour} \times 0.844 \times 2204 \text{ lb/ton} = 54,373 \text{ lb/hr}$). Therefore, the total heat value recovered per hour is 671 MM BTU ($12,333 \text{ BTU/lb} \times 55,606 \text{ lb/hour} = 671 \text{ MM BTU/hour}$). If this high quality product is sold to the coking coal market, the annual gross revenue generation for the coal producer will be \$23.5 million ($29.23 \text{ ton/hour} \times \$135/\text{ton} \times 6000 \text{ hour/year} = \$23.5 \text{ million/year}$). Similarly, if the HHS process product blended with utility coal, the annual gross revenue generation will be \$9.5 million at the current market price ($671 \text{ MM BTU/hour} \times \$2.36/\text{MMBTU} \times 6000 \text{ hour/year} = \9.5 million/year).

A similar assessment can be conducted for the low-ash screenbowl main effluent stream. POC pilot test conducted with Buchanan samples showed as high as 97.1% combustible recovery

with product ash 2.1% and moisture 3.8%. The facility is discarding this stream at a flow rate of 450 gallons/minute (Meenan, 2014). At 3.8% solids and 7% feed ash, total combustible loss is 8,110 lb/hour (450 gallon/min x 8.5 lb/gallon x 0.038 x 0.93 x 60 min/hour). The heat value of the HHS process as-received product will be 14,123 BTU/lb (15000 BTU/lb x 0.979 x 0.962 = 14123). Therefore, total heat content generated per hour is 115 MM BTU (8,110 lb/hour x 14,123 BTU/lb) and the producer will gain \$3.3 million/year (4.1 ton/hour x \$135/ton x 6000 hour/year = \$3.3 million/year) gross revenue, if the product is sold to the coking coal market. Similarly, if the product is blended with utility coal, the annual gross revenue generation will be \$1.6 million (115 MM BTU/hour x \$2.36/MMBTU x 6000 hour/year = \$1.6 million/year).

6.7.2 Generalized Revenue Model

A generalized revenue model is developed to identify the minimum size of production plant profitable to the coal producers. At present, a detailed economic analysis cannot be possible due to lack of cost data; therefore, considerable assumptions are made into the model.

The annual gross return can be calculated as a function of clean coal tons produced. It is assumed that the HHS product coal has specifications 10% moisture and 3% ash. Therefore, the as-received heat value of the product will be 15000 x (1 – 0.1) x (1 – 0.03), which is 13095 MM BTU/ lb. For 4800 operating hours in a year (300 days, 2 shifts of 8 hours each), the gross return from an ‘X’ ton/hour plant will be:

$$\text{Annual Gross Return}_x \left(\frac{\$}{\text{year}} \right) = (V * 13095 * 2204 * 4800 * 10^{-6}) * X \quad [6.17]$$

Where, V is the coal value in \$/MM BTU, which varies with the type of market.

The investment and the front cost are divided in three parts: capital cost, operating and maintenance cost, and personnel cost. These costs are discussed individually in the following sub-sections.

Capital Cost

Capital cost may be sub-divided into two portions: fixed cost and ramp-up cost. The fixed capital cost is required to construct the plant and procure its ancillary units, whereas the latter is necessary to bring the plant into full production. Let’s assume, the fixed capital cost for 1 metric-ton plant is ‘C_i’. Usually, the installation cost is approximately 10% of the fixed capital cost

(Osborne, 1988). Therefore, the total capital cost for a 1 metric-ton plant is ' $1.1 C_i$ '. To predict capital cost for ' X ' ton/hour plant, the sixth-tenths rule is applied (Osborne, 1988). Furthermore, this capital cost will be distributed over the plant life (assumed here 10 years) resulting, in this case, in a depreciation rate 10%. A straight-line depreciation is assumed with no salvage value. Therefore, annual capital cost for ' X ' ton/hour plant can be simply described as illustrated in Equation 6.18.

$$\text{Annual Capital Cost}_x \left(\frac{\$}{\text{year}} \right) = 0.11 C_i * \left(\frac{X}{1} \right)^{0.6} \quad [6.18]$$

Power, Operating Supplies and Maintenance Cost

Three major operating and maintenance costs are considered: electrical costs, a reagent costs, and annual maintenance cost. Annual power costs are usually determined by (Osborne, 1988):

$$\text{Cost } (\$/\text{year}) = \text{Connected power (KW)} \times \text{hours/year} \times \text{Equipment-utilization factor} \times \$/\text{KW-hr}$$

For 1 metric-ton plant, connected power is assumed to be 300KW and equipment-utilization factor is 0.75. The current price for electricity in the United States is \$0.12 per kilowatt-hour. For ' X ' ton/hour plant, the sixth-tenths rule is applied to predict the electrical cost for large production plants. Therefore, annual electrical consumption cost is:

$$\text{Annual Electrical Cost}_x \left(\frac{\$}{\text{year}} \right) = 300 * 4800 * 0.75 * 0.12 * \left(\frac{X}{1} \right)^{0.6} = 129600 * \left(\frac{X}{1} \right)^{0.6} \quad [6.19]$$

Reagent cost is distributed in two portions: fixed cost and reagent-loss cost. Considering the reagent is recovered and recycled, the fixed reagent cost is required at the start of production. The annual fixed reagent cost is divided over the plant life, assuming straight-line depreciation. Any reagent loss during the production will be needed to compensate by procuring new reagent, which is the reagent-loss cost. The 1 metric-ton/hour flowsheet, illustrated in Figure 6.13, shows approximately 500 gallon of reagent will be needed for this capacity. It is assumed that the reagent requirement will linearly escalate with increase in tons/hour capacity. The approximate bulk cost for the reagent is \$1.00 per pound. Furthermore, a conservative percentage of reagent loss is assumed, which is 0.5% (11.02 pounds/metric-ton) of clean coal produced. Therefore, the annual reagent cost for ' X ' ton/hour plant operated for 4800 hours/year can be described from the following:

$$\text{Annual Reagent Cost}_x \left(\frac{\$}{\text{year}} \right) = 52896 * X + 258.5 * X = 53154.5 * X \quad [6.20]$$

With no data available for maintenance cost, it is assumed to be 15% of the total annual capital cost for the production unit. Therefore, from the above analysis, the total annual O&M cost for 'X' ton/hour plant is:

$$\text{Annual O\&M Cost}_x \left(\frac{\$}{\text{year}} \right) = 129600 * \left(\frac{X}{1} \right)^{0.6} + 53154.5 * X + 0.0165 C_i * \left(\frac{X}{1} \right)^{0.6} \quad [6.21]$$

Personnel Cost (Labor Cost)

Typically in a coal production plant requires a manager, a plant supervisor and operators. For small production units (<120 tons/hours), one manager and one supervisor would be enough for monitoring the plant (or even multiple plants); however, number of operators may vary with the production scale as well as amount of instrumentation implemented in the plant. It is a discreet function with the production scale, because one person/shift can operate a 5 ton/hour unit as well as 25 ton/hour unit. It is assumed that one operator/shift will be added after every 25 ton/hour module in a fully instrumented plant. This is described in detail in Table 6.5.

The average annual base salary for one person is assumed \$80,000. With 50% benefit, the average cost per person is \$120,000. Therefore, the annual labor cost can simply be calculated:

$$\text{Annual Labor Cost}_x \left(\frac{\$}{\text{year}} \right) = \frac{\text{Annual Salary}}{\text{Labor}} * (\text{No. of Labor in 'X' tph plant}) \quad [6.22]$$

From the above economic analysis, the annual net revenue can be determined by subtracting Equation 6.17 from Equation 6.18, Equation 6.21 and Equation 6.22, which will be shared by involved parties.

Furthermore, to identify a profitable production unit in the current market situation, the return on investment (ROI) was determined before taxes. The return on investment can be defined as a measure of revenue generated from the process relative to the total amount of investment required to produce that gross-revenue. Therefore, from the above economic analysis:

Table 6.5 Minimum labor required in one fully instrumented production unit

	<i>Production Scale (tons/hour clean coal)</i>			
	1-20	25-50	55-75	80-100
Shifts/day	2	2	2	2
Manager	1	1	1	1
Supervisor	1	1	1	1
Operator/shift	1	2	3	4
Total labor	4	6	8	10

Table 6.6 Process economic analyses at various clean coal ton/hour modules

<i>ton/hour unit</i>	1	5	10	15	30	60	100
	<i>Return on Investment (without taxes)</i>						
Coking Coal	(0.393)	0.526	1.108	1.503	2.166	2.98	3.648
Utility Coal	(0.755)	(0.383)	(0.148)	0.012	0.280	0.608	0.878

$$Return\ on\ Investment(ROI) = \frac{Equations\ ([6.17] - [6.18] - [6.21] - [6.22])}{Equations\ ([6.18] + [6.21] + [6.22])} \quad [6.23]$$

In the model, the only unknown parameter is fixed capital cost ‘*C_i*’ for 1 metric-ton/hour plant. At this point, it is not available; therefore it is assumed to be \$2,000,000 to analyze the process economics. Table 6.6 outlines the return on investments without taxes obtained from the model for both coking and utility coal market at different HHS process tons/hour modules based on the aforementioned parameters. The values indicated in ‘red’ depict loss.

Clearly, a 5 ton/hour unit will be profitable for producing coking coal; whereas, at least 15 ton/hour unit will be required to gain any revenue from the process for the utility market. Furthermore, the HHS process will be highly beneficial for the coking coal market. A 60 ton/hour module used to process coking coal can roughly generate 298% gross revenue gain for both the coal producers and investors. The complete spreadsheet for the economic analysis can be found in Appendix D.

6.8 Conclusions

Bench-scale agglomeration studies were conducted with a low-intensity (propeller) and high-intensity (high-dispersion blade) under various mixing conditions and time depicted impeller tip speed (shear effect) can be used as a scale-up criterion for agglomeration units. Using experimental data, an empirical model was developed, which is highly sensitive with the

d/D (impeller diameter/tank diameter) ratio. Therefore, this reactor geometric ratio must be considered in designing larger scale units.

A kinetic model developed for vibrating mixer shows that the dispersion mechanism follows a first-order rate. The model can be used to determine solid concentrations with time for the process streams leaving the unit. In addition, settling data for ultrafine coal particles in pure pentane assisted in developing a dual model for the hydrophobic liquid thickener. The model can predict the required unit area and thickener underflow solid concentrations needed to design the thickener. A pentane loss model, which was based on bench-scale test studies, was also developed to predict pentane consumption at a given residence time and temperature. However, it is highly recommended that dryer manufacturers be consulted for pentane loss estimation.

Finally, a revenue model was developed based on current coal values and projected initial costs. As anticipated, the model predicted substantial profits for large production plants. In addition, due to increasing personnel cost per ton of coal produced, it is recommended that any full-scale HHS production units be fully automated to minimize this cost.

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CHAPTER 7 Conclusions and Recommendations

7.1 Summary of the Research

This research involves the development of an innovative technology called the *Hydrophobic-Hydrophilic Separation* (HHS) process. The process can simultaneously recover and dewater the ultrafine (44 microns x 0) coal fraction. Existing preparation plants currently discard this size fraction, because there are no commercial technologies that can provide high recovery and low moisture for ultrafine coal. Although the particles in ultrafine streams are well liberated and can produce a low-ash product, they carry high surface moisture for the obvious reason: the smaller the particle size, the higher the surface area.

The foundation of the innovative technology is the novel thermodynamic concept of dewatering-by-displacement (DBD). The DBD concept is based on a naturally occurring phenomenon, which makes the process thermodynamically favorable. Using this concept, surface moisture on a hydrophobic particle can be reduced to a level that can only otherwise be achieved by thermal dryers. In the current research work, the HHS process has been successfully demonstrated on a bench-scale system as well as on a proof-of-concept (POC) pilot-scale plant.

In the initial phase of the research, several HHS-process bench-scale systems were constructed to achieve drying and cleaning of ultrafine particles. The gist of the innovative technology is the effective dispersion of agglomerates in liquid pentane. For this purpose, a low-energy mechanical vibrating mesh device was developed. The device can be scaled-up as compared to the initially used ultrasonic probe. Several batch-scale tests conducted with various coal feedstocks using the innovative mechanical vibrating mesh device have shown that consistent low-moisture (0.7 – 10%) and high combustibles recovery (>85%) can be achieved from the HHS process. The successful testing with a bench-scale vibrating mesh device provided the needed results to develop the technology on a pilot-scale. Alternative methods were also tested for dispersion of agglomerates. These methods can also be engineered to produce a similar quality clean coal product as achieved using the vibrating mesh device.

To understand the separation mechanism in the HHS process, several fundamental studies were conducted. The thermodynamic studies exhibit that the novel dispersion step is a complex process. It has been identified that the performance of the process is governed by three mechanisms: breakage of coal-agglomerates, suspension of particles in pentane column, and

coalescence of released water droplets. The thermodynamic study also indicated that the process is efficient in a specific range of external energy provided to the system for dispersion. At a very low energy level the agglomerates will not disperse effectively in the pentane column. In contrast, providing excessive energy in the system may hinder the water coalescence mechanism. Additionally, it was observed during experimentation that an excessive energy sometimes led to the formation of stable micro-emulsions in the reactor, which resulted in high product moisture from HHS process. To determine breakage and dispersion rate, kinetic studies were conducted. The batch-scale kinetic studies for the vibrating mixer revealed that the breaking of agglomerates in pentane column with a vibrating mesh device is a slow process. Furthermore, the kinetics of novel dispersion step can be described as a first-order rate process.

A proof-of-concept (POC) pilot-scale plant with a rated feed capacity of 100 pound/hour of raw dry feed for the HHS process was constructed at the Virginia Tech Mining and Minerals Research Laboratory. The primary intent was to demonstrate the capabilities of the HHS process on a larger scale. The POC units were designed conservatively to provide flexibility in testing various coal feedstock and to accommodate unknown factors that might hinder the testing program. Several safety features were implemented in the newly constructed plant under constant monitoring of multiple regulatory agencies. Necessary modifications were made during the shakedown testing to rectify any operational issues prior to run the pilot-scale test program.

The POC pilot-scale test results successfully demonstrated that low-moisture and high separation efficiency can be obtained consistently from the discarded ultrafine (44 microns x 0) streams by using the HHS process. Testing with low ash feed samples, such as screen bowl main effluent, moisture in the range of 4 – 16% and carbon recovery as high as 97% were achieved. Similar results were obtained when high-ash feed samples, such as deslime cyclone overflow, were tested in the POC system. Here, moisture was reported in the range of 5 – 14% with combustible recovery as high as 86%. The performance measuring index, i.e. separation efficiency (E), obtained from the HHS process POC plant was reported as high as 83.4%. Furthermore, the separation efficiencies are in good agreement with the results obtained with HHS process bench-scale system.

During the pilot-scale test program several parameters were evaluated. These studies indicate that the HHS process is robust. The technology is able to process raw coal samples from various sources with wide range of feed ash. Additionally, POC testing shows that the

technology can also process chemically treated ultrafine streams as-received from a preparation plant. The findings from the investigations are listed below:

- The POC pilot-scale test data indicate that the cleaning capability of the HHS process is independent of feed ash. A 7% feed ash sample produced 2.1% ash product while a 77.3% feed ash sample produced 2.7% ash product.
- The performance of the process depends on the particle size. This is because smaller particles are well liberated and the surface forces are more prominent in ultrafine size fraction; therefore, separation is higher for the fraction. The finer the particles the better the separation.
- Efforts were made to reduce the volume of pentane required in the system by replacing the high volume vibrating mixer unit (120 gallons) with a very low volume unit (19 gallons). The comparative study indicates that there is no significant effect on the product quality by using a small volume reactor.
- To determine the effect of residual frother in the screen bowl main effluent streams, POC performance was evaluated with a feed dosed with excessive frother (30 ppm). The results from the investigation showed no detrimental effect on the performance of the HHS process POC pilot-plant.
- Finally, the critical economic factor, i.e. the loss of pentane associated with clean coal product, was analyzed. The loss was determined using the gas chromatographic (GC) technique. The analysis showed that at least 3.6 pounds of pentane per ton of clean coal (0.18%) were lost with the HHS process POC product. This estimated loss is in support with the results obtained from the batch-scale pentane absorption rate study (3.75 lb/ton after 30 minutes), as well as with the theoretical analysis (3.97 lb/ton). Although the detail pentane recovery study can only be conducted at a production scale, preliminary results obtained from the three different methods predict a pentane loss of less than 4 pounds per ton of HHS product.

To identify scaling-up criteria for each unit operation involved in the HHS process, several batch-scale investigations were conducted. Using the experimental data obtained from the investigations, empirical models and simulators were developed. Following are the findings that can be significant in designing the next-scale HHS process prototype plant:

- The batch-scale agglomeration study revealed that for high/low shear mixer, the tip speed is one of the primary scale-up criteria that must be considered. High reject ash is achievable using high impeller speed with short residence time and high d/D (impeller diameter/ tank diameter) ratio.
- For the vibrating mixer, a rate model can very well define the dispersion mechanism.
- Settling rate investigation of ultrafine coal in pentane exhibited a high settling velocity of the particles before they enter into a compression zone. The study was conducted with variable solid concentration in the feed. The results indicate that 28-45% solid concentration in thickener underflow can be achieved in less than 4 minutes retention time. Based on the data a dual simulator/model on LIMN® was developed. The model can predict underflow concentration at a given thickener geometry and residence time. The model can also identify the required unit area of the thickener to achieve desired underflow concentration.
- A 1 metric-ton per hour clean coal process flowsheet was drafted on LIMN® using the data and information obtained in this research. The flowsheet was further simulated at variable thickener underflow solid concentration. The simulations provide information that can assist in identifying the heat-exchanging system for the next-stage HHS process prototype plant.

Finally, an economic assessment of the HHS process was conducted and a revenue model was developed. At the current coal market value the model showed that a 5 ton/hour clean coal production unit will be profitable to process coking coal while at least a 15 ton/hour unit will be required to process utility coal to gain revenue. Moreover, two conclusions can be made from the economic assessment:

- The process shows promise to be very profitable for the producers, if implemented in a high tons/hour processing facility.
- The economic assessment was conducted considering the plant will be fully instrumented. The additional high labor cost may decrease the revenue generation significantly.

The HHS process is a transformative technology. The novel process produces a premium quality coal product from currently discarded ultrafine streams. The high quality coal will provide an incremental value to the coal producers at no additional mining cost. A successful

commercialization of the HHS process will be instrumental for the industry, because with the innovative technology all the ultrafine coal from run-of-mine feed can be recovered at low cost. In addition to revenue generation, environmental issues, such as blackwater pollution, can be reduced significantly.

7.2 Future Recommendations

In view of the results and conclusions of the experimental work included in this dissertation, some recommendations regarding potential future investigation are provided below:

- The newly engineered POC pilot plant has been successful in achieving the goal of low-moisture product with high carbon recovery. The batch-scale investigation for agglomeration showed that shear effect (impeller tip speed) is a primary parameter to obtaining high reject ash. The shearing effect can also be achieved by using In-Line mixers, which have very low footprint and no moving parts. Therefore, it is recommended to study In-Line or dynamic mixers on POC pilot plant for agglomeration of ultrafine coal slurry. A successful operation will reduce the footprint of production units as well as reduce the operating and maintenance cost associated with this unit operation.
- Throughout the research, attempts were made to determine the exact amount of moisture and pentane in the HHS product. Due to lack of any established method, the pentane loss can only be estimated/ predicted on the basis of several assumptions. In light of this, it is highly recommended to establish a method for an accurate measurement of pentane loss associated with HHS clean coal product. This is a critical parameter in defining the economics of the novel process.
- Despite a large number of batch scale tests conducted on the newly developed vibrating mesh device to identify the parameters, a detailed parametric study is suggested. To gain further knowledge and improve the design for the novel dispersion device, a CFD study is also recommended. These detailed investigations can be significant for the successful development of the HHS process production plants in future.
- The vibrating mesh design has been very successful for effective dispersion of agglomerates, which is the requirement in the process. Due to the oscillating structure and novel design, it may be expensive to fabricate such a device on a larger scale.

Therefore, it is recommended to test alternative existing methods that can provide similar coal quality. Some examples of these alternatives, which are well established in industries, are air-pulsated jigging mechanism, dispersion with Rushton-type impellers at low speed, vibrating trays, etc.

- The POC pilot plant described in the research has been tested with in-plant discarded streams. In 2002, report published by National Research Council suggests that there is at least 2 billion tons of fine coal lying on abandoned coal impoundments. Recovering coal from these ponds will be beneficial for the environment as well as for the producers. It is recommended to test various pond tailing samples on a POC plant to demonstrate that the proposed method can be useful in recovering carbon from these abandoned resources.
- The flotation feed samples tested on the bench-scale system showed very encouraging results. To further corroborate this, it is recommended to conduct detailed investigations on various flotation feed samples on the POC pilot plant, to demonstrate that the HHS process can be beneficial for fine coal feed (150 x 44 microns).
- The unique concept of hydrophobic displacement exploits the high affinity of the hydrophobic particles in water with a hydrophobic liquid for separation. Coal is a low-price commodity. The HHS process may be used to recover ultrafine particles in other mineral industries that are currently discarded due to limited technology. For example, the common practice in phosphate processing is to discard fine particles (below 100 microns). Similarly, in copper processing, typical discard size is 10-15 microns. The HHS process can be beneficial to recover ultrafine value product from these discarded streams. Hence, it is suggested to investigate the HHS process for other minerals.

APPENDIX A. POC PROTOCOLS

**Pilot-Scale Fine Coal Cleaning and Dewatering Processing
Unit**

Proof-of-Concept Process Evaluation Research Project

**Department of Mining and Minerals Engineering
Minerals and Coal Research Laboratory
800 Plantation Road**

OPERATIONAL PROTOCOLS

**Pre-Start Checks
Startup Procedure
Operating Procedures
Normal Shutdown Procedure
Emergency Shutdown Procedure
Emergency Spill Handling Procedure**

April 8, 2013

Revisions – April 10, 2013, June 10, 2013

Pre-Start Checks

- Processing Plant Area
 - Ensure that the fire extinguishers are readily available around the area.
 - Ensure the back door to the Research Laboratory is open to provide access to the process control.
 - Ensure the gate is open to provide access from the highway to the processing unit and storage area.
 - Personnel operating the processing unit or entering the area must wear flame retardant and/or 100% cotton clothing.
 - Cell phones are prohibited within 25 feet of the processing unit.

- Processing Unit
 - All pipe hoses are connected properly and securely.
 - All nitrogen lines are connected properly and securely.
 - All air supply lines are securely connected.
 - All ground wires are securely connected –
 - Hose connections
 - Tanks
 - Modular frames
 - Earth ground
 - All guards are in place around the moving equipment.
 - Visually check all shaft seals for wear, damage, and other conditions that may result in leaks.
 - Temperature sensors operating properly.
 - Flow meters operating properly.
 - All emergency vents are intact and set at 7” of water column pressure.
 - Drain valves closed on Tank-100 and Tank-200.
 - Discharge valve closed on Tank-800.
 - Agitator shafts secure on drives for Tank-100, Tank-200, and Tank-400.

- Nitrogen Generator
 - Nitrogen generator operating properly - check for system faults, alarms.
 - Operating pressure at nitrogen generator receiver/supply tank at 80-100 psi.
 - Pressure at POC regulator set at 20 psi for the nitrogen purge regulators to purge complete process.

- Compressed Air Supply
 - Compressed air supply operating at normal pressure, 120 psi.
 - Air supply pressure properly set at 80 psi at the POC manifold.

- Process Control System
 - Control system powered up, operating properly.
 - Pentane and oxygen sensing system powered up, operating properly.
 - Tubing to all sensors connected and with intakes at proper locations.
 - Ensure the pentane vapor levels from all six points indicated on the PLC control system are 0.75% or less (Lower Explosive Limit {LEL} = 1.5%).
 - Ensure the oxygen level in the condenser purge stream indicated on the PLC control system is less 5.0%.

PROCESS START UP PROCEDURE

1) Ancillary Equipment

- Turn the power switch on for the processing area ventilation fan.
- Turn circuit breakers ON for water heater and chiller.
- Water chiller:
 - Turn power switch ON for chiller.
 - Check temperature control, set at 35 degrees F.
 - Check for proper water flow to condenser.
- Water heater:
 - Turn power switch ON for water heater.
 - Check temperature control, set at 140 degrees F.
 - Turn power switch ON for circulating pump.
 - Check for proper water flow to dryer.
- Compressed Air Supply
 - Air supply pressure properly set at 80 psi at the POC manifold.
 - Set agitators at speed (RPM) required for processing conditions.
 - Set pumps at flow rate (GPM) required for processing conditions.
 - Set dryer screw at speed (RPM) required for processing conditions.
 - Shut off the air supply to agitator drives and pump drives.
- Monitor pentane and oxygen levels on the PLC control system.

2) Charging Processing Unit

- Check pentane and oxygen levels to ensure nitrogen gas has purged the entire system.
- Charge Tank-400 and Tank-800 to required level with fresh water.
- Move two barrels of pentane liquid from the storage cabinets to POC plant.
- Connect ground wire and charging hose and fittings to the pentane barrel.
- OPEN pentane charging valve, CLOSE Tank-400 discharge valves.
- OPEN air valve to operate Pump-900.
- Pump pentane to charge Tank-500 to the overflow weir.
- Continue pumping until the overflow of T-500 charges pentane in Tank-400 to the required level.
- CLOSE air valve to Pump-900.
- CLOSE the pentane charging valve.
- Remove the charging hose and fittings from the barrel.

- Disconnect the ground wire from the barrel.
- Move the barrels back to the storage cabinets.
- Move the third barrel of pentane liquid from the storage cabinet to the POC plant.
- Connect the ground wire and hose and fittings from the barrel to Pump-200.
- Move the recovered liquid pentane receiving barrel (HL Collecting Barrel) from the storage locker to the POC plant.
- Connect the ground wire and hose and fittings from the Condenser (HE-700) to the pentane barrel.
- Monitor the pentane vapors and oxygen on PLC control system.
- Monitor the temperature sensors on the water lines to and from the Dryer and Condenser.
- OPEN the desired overflow port valve on T-200 and CLOSE valves for other ports.
- OPEN the desired overflow port valve on T-400 and CLOSE valves for other ports.
- Place the dried product collecting pan below the Dryer (D-700) discharge port.

POC – OPERATING PROCEDURE

1) Set Process Feed and Reagent Rates, Start Agitators

- OPEN air valve to start Pump-100 for mineral slurry feed (mineral/water mixture) to Tank-100 and set at required GPM.
- OPEN air valve to start Pump-200 for pentane reagent feed to Tank-100 and set at required GPM.
- OPEN air valve to start Agitator-100 (on T-100) and set at required speed.
- When mineral slurry/pentane mixture begins overflowing to Tank-200, OPEN air valve to start Agitator-200 (on T-200) and set at required speed.
- Monitor Screen Box (F-300) through sight glass windows for mineral slurry/pentane mixture flow from T-200.
- Monitor the pentane vapors and oxygen levels on PLC control system.

2) Balance Flows through Process

- As slurry levels approach proper operating levels in Tank-400 and Tank-800:
 - OPEN air valve to start Pump-800 and set at required speed.
 - OPEN air valve to start Agitator on Tank-400 and set at frequency.
 - OPEN air valve to start Pump-400 and set at required speed.
 - OPEN air valve to start Pump-800 and set at required speed.
 - OPEN air valve to start Pump-900 and set at required speed.
- Monitor Tank-400 level and maintain level by controlling Pump-400 flow to Tank-800.
- Monitor level Tank-800 and maintain level by controlling elevation of tails discharge hose.
- Allow sufficient time for product to settle in Tank-500, then OPEN air valve to start Pump-600 and set at required speed.
- OPEN air valve to start Dryer Screws (D-700) and set at required speed.
- Allow sufficient time for dried product to begin discharging from Dryer (D-700), then activate timed cycling of the product discharge air-locking valves.
- Collect the dried mineral product in the collecting pan at the Dryer (D-700) discharge port.
- Monitor the pentane vapors and oxygen levels on the PLC control system.
- Monitor the liquid level in the condensed pentane barrel (HL Collecting Barrel).

POC – SHUTDOWN PROCEDURE

1) Clear Material from Processing Unit

- CLOSE air valve to stop Pump-100 (mineral slurry feed pump).
- CLOSE air valve to stop Pump-200 (pentane reagent feed pump).
- CLOSE air valve to stop Pump-800.
- Connect fresh water supply to Pump-100 inlet, OPEN air valve to start pump and flush inlet, pump, and discharge tubing completely with water.
- Remove the pentane reagent feed hose and fittings from the barrel.
- Disconnect the ground wire from the pentane barrel.
- Move the pentane barrel to the storage cabinet.
- Connect fresh water supply to Pump-200 inlet, OPEN air valve to start pump and flush inlet, pump, and discharge tubing completely with water.
- OPEN the drain valve slightly on Tank-800 to start transferring residual tails to tails collecting barrel.
- Continue operating Pump-100 to completely flush all residual pentane and mineral solids from Tank-100, Tank-200, Screen Box (F-300), and Tank-800.
- CLOSE the air valves to stop Pump-100, Pump-200, Agitator-100, and Agitator-200.
- OPEN the drain valves on Tank-100 and Tank-200 to drain the water into an empty barrel.
- Move two (empty) barrels of from the storage cabinets to POC plant.
- Connect ground wire and transfer hose and fittings to the pentane barrel.
- OPEN pentane charging valve.
- OPEN air valve to start Pump-900.
- OPEN Tank-400 discharge valves to completely remove any residual pentane.
- CLOSE air valve to stop Pump-900.
- CLOSE the pentane charging valve.
- Remove the charging hose and fittings from the barrel.
- CLOSE air valve to stop Pump-600.
- Connect transfer hose and fittings from Pump-600 to the pentane barrel.
- OPEN air valve to start Pump-600.
- Completely remove any residual pentane from Tank-500.
- CLOSE air valve to stop Pump-600.
- Remove the charging hose and fittings from the barrel.
- Disconnect the ground wire from the barrel.

- Move the pentane barrels back to the storage cabinets.
- Connect fresh water supply to Tank-400, completely fill tank with fresh water.
- OPEN air valve to start Pump-900, fill Tank-500 to overflowing.
- OPEN air valve to start Pump-400, transfer rinse water to Tank-800.
- Continue to add fresh water to Tank-400, pumping to Tank-500, and transferring to Tank-800 until mineral solids are cleared from tanks.
- CLOSE fresh water valve to stop flow to Tank-400.
- OPEN air valve to start Pump-600.
- Pump residual rinse water from Tank-500 to a barrel, then CLOSE air valve to stop Pump-600.
- Operate Pump-400 to remove the water from Tank-400, then CLOSE air valve to stop Pump-400.
- Monitor the condensed liquid tubing at the condenser liquid discharge port to determine when all the pentane from the system has been transferred to the pentane barrel (HL Collecting Barrel).
- Remove the hose and fittings from the barrel.
- Disconnect the ground wire from the barrel.
- Move the pentane barrel back to the storage cabinets.
- Operate the air-lock valve system on the Dryer (D-700) until all the dried mineral has been discharged from the Dryer.
- CLOSE the air valve to stop the Dryer Screws.
- Deactivate the automatic timed cycling of the Dryer discharge valves, then CLOSE both valves.
- OPEN the drain valve on Tank-800, drain all the water to a barrel to collect all the tails from the test session.
- Monitor the pentane vapors and oxygen levels on the PLC control system.

2) Ancillary Equipment

- Water chiller:
 - Turn power switch OFF for chiller.
- Water heater:
 - Turn power switch OFF for circulating pump.
 - Turn power switch OFF for water heater.
- Compressed Air Supply
 - Shut off the air supply to POC processing unit.
- Maintain the nitrogen blanket pressure on the whole POC system.

EMERGENCY SHUTDOWN PROCEDURE

Emergency shutdown procedure must be followed in the following events:

- 1) Any leaks in the hoses, pipe fittings, nitrogen lines, or air supply lines.
- 2) If the pentane sensor indicates pentane vapor levels approaching the lower explosive limit (LEL).
- 3) If the oxygen sensor indicates sufficient levels to create a potential explosive atmosphere.
- 4) Faults or failures with any mechanical moving devices (Agitators, Dryer Screws, Pumps)
- 5) Faults or failure of the nitrogen generator unit.
- 6) Electrical power outage.
- 7) Spill of pentane at the POC test area.
- 8) Any personal injury.

POC – Emergency Shutdown Procedures:

- CLOSE compressed air supply valve to stop all Pumps, Agitators, and Dryer Screw.
- CLOSE any manual valve required to stop, prevent, and/or isolate a spill condition.
- Institute the “Emergency Spill Handling Procedure”.
- Monitor the pentane vapors and oxygen levels on the PLC control system.
- Provide additional ventilation in the area of the spill if a spill occurs.
- As soon as safely possible, remove the pentane from the processing unit and clear the processing unit per the procedures under “POC – SHUTDOWN PROCEDURE” above.

Additional Requirements:

- Case 5 – Nitrogen Generator Malfunction
 - Monitor the pressure in the nitrogen generator supply tank.
 - Connect a backup nitrogen bottle to the nitrogen supply valve at the nitrogen generator.
 - Proceed with removal of the pentane from the processing unit and clear the processing unit per the procedures under “POC – SHUTDOWN PROCEDURE” above.

- Case 6 – Power Failure
 - Contact University Facilities to report the power failure and to request the expected period for the outage.
 - Monitor the pressure in the nitrogen generator supply tank.
 - Start the backup power generator.
 - Connect the process control system (includes the pentane and oxygen sensors system), the nitrogen generator, and the ventilation fan to the backup power generator.
 - Proceed with removal of the pentane from the processing unit and clear the processing unit per the procedures under “POC – SHUTDOWN PROCEDURE” above.

- Case 7 – Spill of Pentane and/or Mineral Slurry
 - Provide additional ventilation in the area of the spill.
 - Institute the “Emergency Spill Handling Procedure”.

- Case 8 – Personnel Injury
 - CALL 911.
 - Render assistance until medical aid arrives.

Emergency Spill Handling Procedure

In the event of a minor spill of pentane (less than 1 gallon) and mineral slurry:

- Follow the Emergency Shutdown procedures to stop the POC processing.
- Use spark-proof tools and intrinsically safe equipment when responding to any spill involving pentane.
- Follow the hazard information from the MSDS for the pentane:
 - Keep sources of ignition and hot metal surfaces isolated from the spill to a distance of at least 30'
 - Use safety glasses, chemical goggles, or face shields
 - Use impermeable gloves to avoid pentane liquid from irritating the skin
- Utilize the emergency spill kit to contain the liquids within the area of the POC plant and recover as much of the pentane as possible. Pentane must be absorbed and containerized as quickly as possible to minimize vapor generation.
- Ensure continuous ventilation with fresh air in the area of the spill. Do not direct ventilation air towards any potential source of ignition.
- If possible, isolate the pentane for recovery –
 - Pump as much of the pentane as possible into a storage container
 - Place the storage container in the storage cabinet
 - Use absorbent material from the spill kit to absorb residual amounts of liquid
- Pump the mineral slurry into storage containers with open tops.
- Sweep and clean the floor with the fresh water.
- Collect the dirty water in open top containers.
- Test the slurry and dirty water containers for residual pentane vapors.
- If pentane vapors are present at the top of the storage containers, place the containers in an open well-ventilated area to dissipate the vapors.
- Operate the ventilation fan located near the test site to remove any residual vapors from the POC plant area.
- Keep fire extinguishers readily available.
- When the pentane vapors has dissipated from the slurry and dirty water containers, move the containers to the research lab and follow the normal waste disposal procedures.

In the event of a major spill of pentane (more than 1 gallon) and mineral slurry:

- Follow the Emergency Shutdown procedures to stop the POC processing unit.
- As possible, spread absorbent pads across the spill to minimize vapor generation.
- Immediately evacuate the POC test site area.
- Call the Virginia Tech Environmental Health and Safety (after normal office hours, call the Virginia Tech Police Department):
 - Specify large spill of pentane, estimate amount of spill
 - Specify exact location of spill (800 Plantation Road, storage shed behind laboratory)
 - Follow all instructions from the Environmental Health and Safety or Police Department
 - Prevent entry into the area of the spill until the emergency response team arrive and take charge.
 - Designate one person to immediately go to the driveway entrance on Plantation Road to inform the emergency response team of the emergency situation and actions instituted.
- Operate the ventilation fan located near the test site to remove as much vapor as possible from the POC plant area.
- Keep fire extinguishers readily available.
- Assist the emergency response team as instructed.
- When the emergency response team has cleared the area, proceed to clean up the mineral slurry from the area.
- Pump the mineral slurry into storage containers with open tops.
- Sweep and clean the floor with the fresh water.
- Collect the dirty water in open top containers.
- Test the slurry and dirty water containers for residual pentane vapors.
- If pentane vapors are present at the top of the storage containers, place the containers in an open well-ventilated area to dissipate the vapors.
- Operate the ventilation fan located near the test site to remove any residual vapors from the POC plant area.
- When the pentane vapors has dissipated from the slurry and dirty water containers, move the containers to the research lab and follow the normal waste disposal procedures.

In the event of mineral slurry only spill:

- Follow the Emergency Shutdown procedures to stop the POC processing.
- Utilize the emergency spill kit to contain the mineral slurry within the area of the POC plant.
- Pump the mineral slurry into storage containers with open tops.
- Sweep and clean the floor with the fresh water.
- Collect the dirty water in open top containers.
- Test the slurry and dirty water containers for residual pentane vapors.
- If pentane vapors are present at the top of the storage containers, place the containers in an open well-ventilated area to dissipate the vapors.
- Operate the ventilation fan located near the test site to remove any residual vapors from the POC plant area.
- When the pentane vapors has dissipated from the slurry and dirty water containers, move the containers to the research lab and follow the normal waste disposal procedures.

EMERGENCY CONTACT NUMBERS

Virginia Tech Environment Health and Safety Services - 540 231-3600

Virginia Tech Police - 911

540 231-6411

APPENDIX B. POC PILOT PLANT DESIGNS

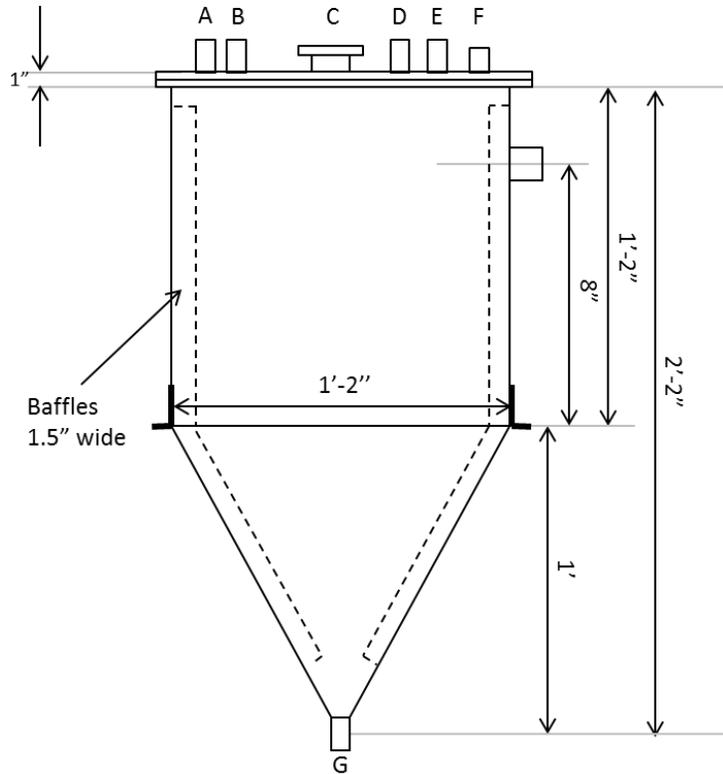
B.1 Detailed POC Tanks Design

Table B.1 Data for development of POC mixing devices

$\sigma = 0.0519 \text{ N/m}$ $D (\text{Batch}) = 1.5 \text{ inches}$ 0.0378 $D (\text{POC}) = 4 \text{ inches}$ 0.1008 $\rho = 1026 \text{ Kg/m}^3$				$\sigma = 0.0519 \text{ N/m}$ $D (\text{Batch}) = 1.5 \text{ inches}$ 0.0378 $D (\text{POC}) = 5 \text{ inches}$ 0.126 $\rho = 1026 \text{ Kg/m}^3$			
Hi-Shear Mixing				Low-Shear Mixing			
Batch		POC Unit		Batch		POC Unit	
N (RPM)	Weber No.	N (RPM)	Weber No.	N (RPM)	Reynold No.	N (RPM)	Reynold No.
2000	1186	100	56	2000	46268	200	51409
4000	4744	300	506	4000	92536	400	102818
6000	10675	600	2024	5000	115670	600	154227
8000	18977	1000	5623	6000	138804	800	205636
9000	24018	1300	9503	7000	161939	1000	257045
10000	29652	1500	12651	8000	185073	1200	308454
11000	35879	1800	18218	9000	208207	1400	359863
12000	42699	2000	22492	10000	231341	1600	411272
13000	50112	2300	29745	11000	254475	1800	462681
14000	58118	2500	35143	12000	277609	2000	514091
15000	66717	2700	40991	13000	300743	2200	565500
16000	75909	3000	50606	14000	323877	2400	616909
17000	85694			15000	347011	2600	668318
18000	96072			16000	370145	2800	719727

TANK -100

Cylindrical with conical bottom

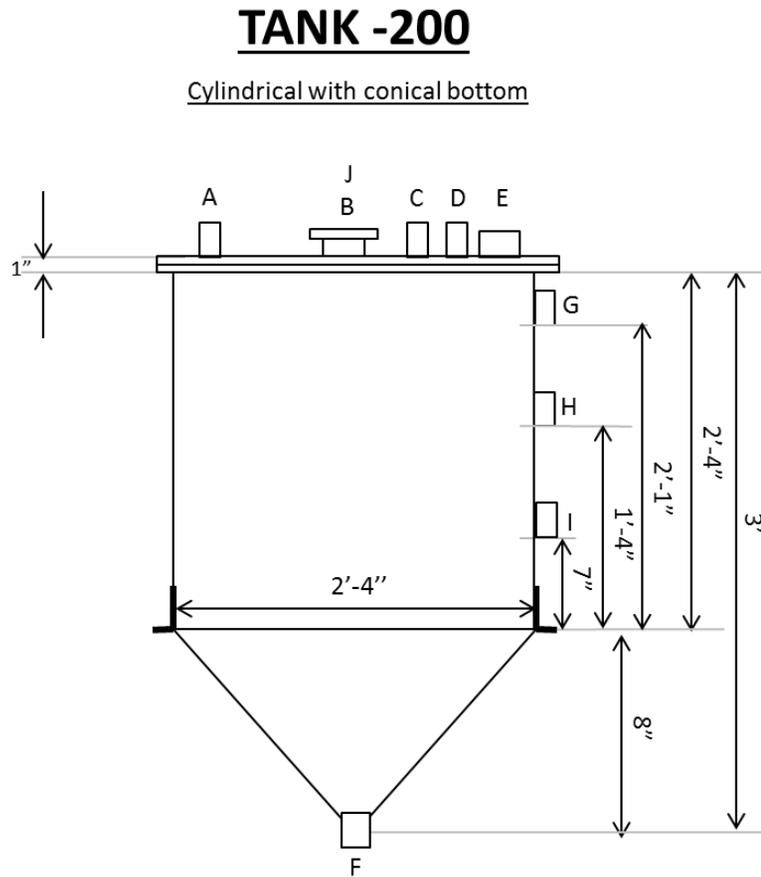


NOZZLE SCHEDULE					
			NOZZLE FLG.		
ID	Size, in	Size, mm	Rating	Type	Matl.
A	1.5	38	3000#	Screwed	Forg CS
B	1	25	3000#	Screwed	Forg CS
C	3	76	150#	Flanged	CS
D	1	25	3000#	Screwed	Forg CS
E	1	25	3000#	Screwed	Forg CS
F	1	25	3000#	Screwed	Forg CS
G	2	51	3000#	Screwed	Forg CS

DESIGN DATA	
Design Condition	2.5 psig at 120 Deg F
Operating Condition	1 psig at Deg F
Thickness	0.25 inches (Vendor to confirm)
Bolt Specifications	SA 193-B7
Nuts	SA-194-2H
Paint	Epoxy coating only on outside CS surfaces

NOTES	
1. Cover must be GASKETED fit.	
2. Cover bolt holes shall straddle 0 and 180 deg centerline or its parallel U.O.N	
3. Two (2) Baffles 1.5" wide inside on the sides, 6" above from conical bottom.	

Figure B.1 Detailed design of POC hi-shear mixing tank



NOZZLE SCHEDULE					
			NOZZLE FLG.		
ID	Size, in	Size, mm	Rating	Type	Matl.
A	2	51	3000#	Screwed	Forg CS
B	3	76	150#	Flanged	CS
C	1	25	3000#	Screwed	Forg CS
D	1	25	3000#	Screwed	Forg CS
E	2	51	3000#	Screwed	Forg CS
F	1.5	38	3000#	Screwed	Forg CS
G	2	51	3000#	Screwed	Forg CS
H	2	51	3000#	Screwed	Forg CS
I	2	51	3000#	Screwed	Forg CS
J	4	102	150#	Flanged	CS

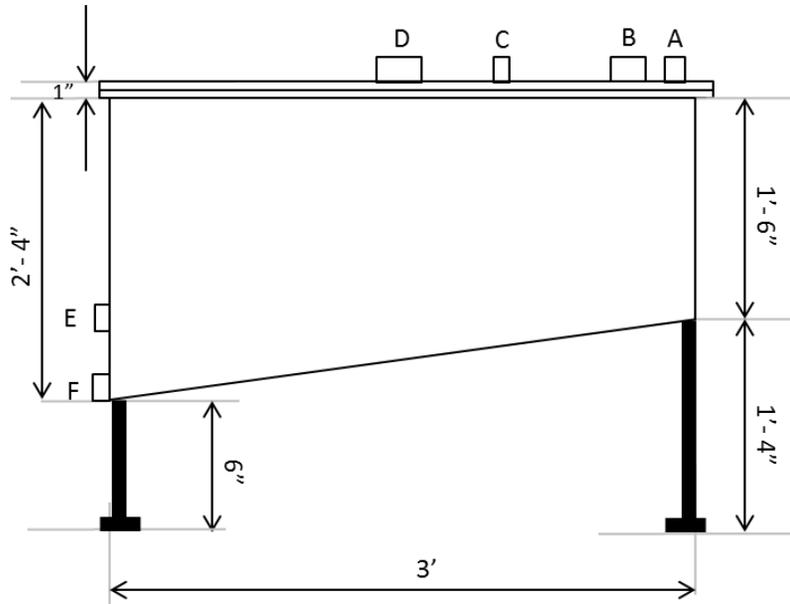
DESIGN DATA	
Design Condition	2.5 psig at 120 Deg F
Operating Condition	1 psig at Deg F
Thickness	0.25 inches (Vendor to confirm)
Bolt Specifications	SA 193-B7
Nuts	SA-194-2H
Paint	Epoxy coating only on outside CS surfaces

NOTES	
1. Cover must be GASKETED fit.	
2. Cover bolt holes shall straddle 0 and 180 deg centerline or its parallel U.O.N	

Figure B.2 Detailed design of POC low-shear mixing tank

TANK -800

Rectangular with V - shape bottom

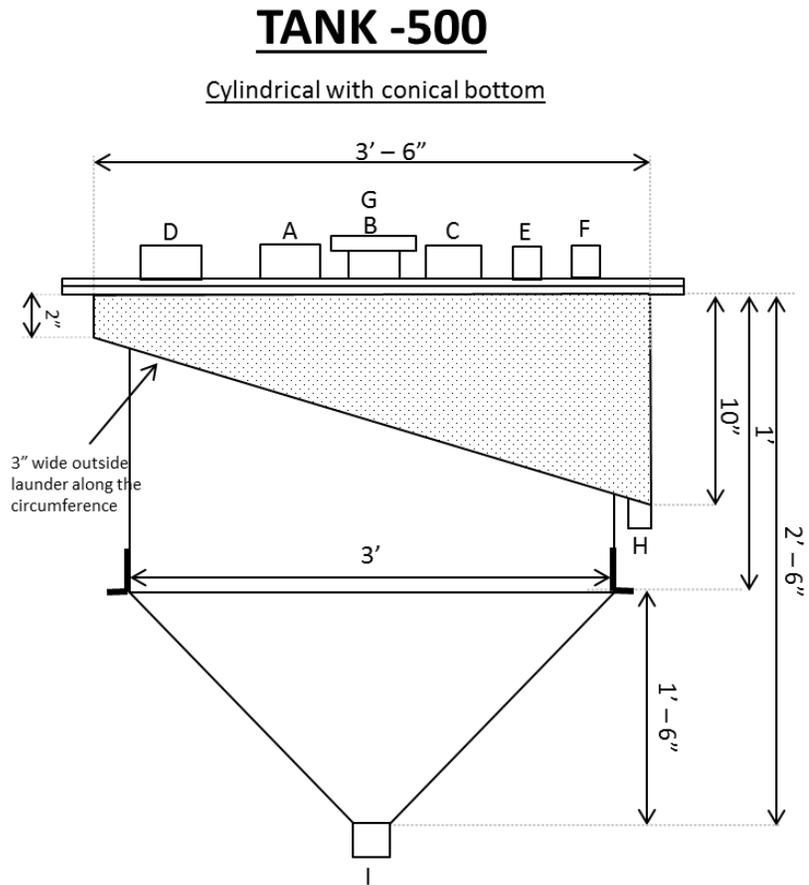


NOZZLE SCHEDULE					
			NOZZLE FLG.		
ID	Size, in	Size, mm	Rating	Type	Matl.
A	1	25	3000#	Screwed	Forg CS
B	2	51	3000#	Screwed	Forg CS
C	1	25	3000#	Screwed	Forg CS
D	2	51	3000#	Screwed	Forg CS
E	2	51	3000#	Screwed	Forg CS
F	2	51	3000#	Screwed	Forg CS

DESIGN DATA	
Dimensions	3' Length x 2' Width; Height (2' 10") from the floor
Design Condition	2.5 psig at 120 Deg F
Operating Condition	1 psig at Deg F
Thickness	0.25 inches (Vendor to confirm)
Bolt Specifications	SA 193-B7
Nuts	SA-194-2H
Paint	Epoxy coating only on outside CS surfaces

NOTES	
1. Cover must be GASKETED fit.	
2. Cover bolt holes shall straddle 0 and 180 deg centerline or its parallel U.O.N	

Figure B.3 Detailed design of POC skimmer (tailings) tank

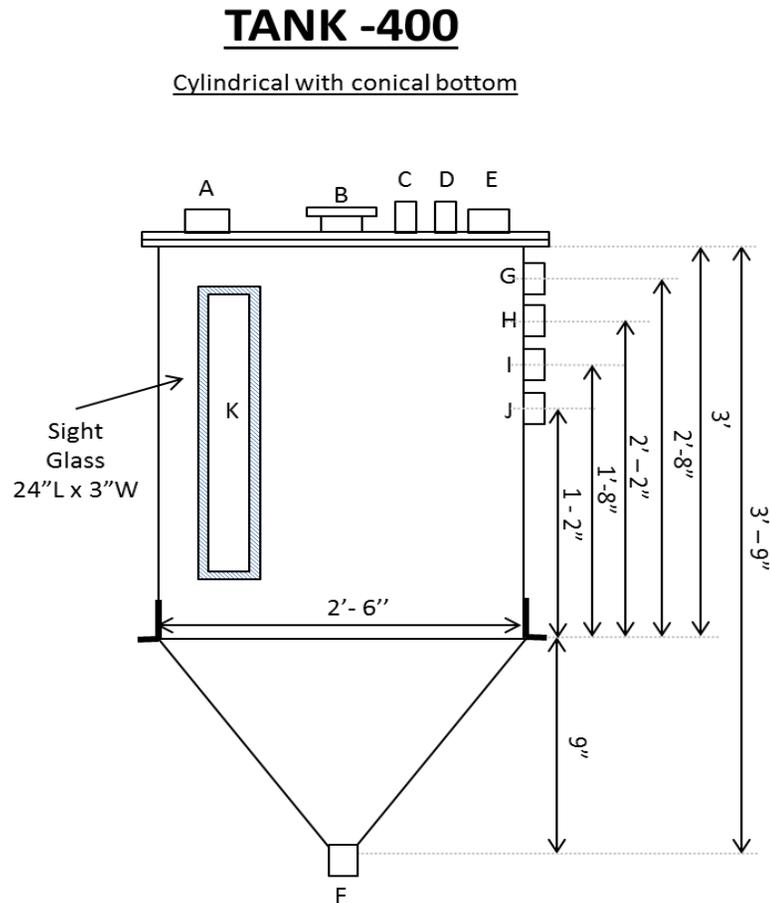


NOZZLE SCHEDULE						Notes
ID	Size, in	Size, mm	Rating	Type	Matl.	
A	2	51	3000#	Screwed	Forg CS	Next to "B"
B	3	76	150#	Flanged	CS	At Center
C	2	51	3000#	Screwed	Forg CS	Next to "B"
D	2	51	3000#	Screwed	Forg CS	
E	1	25	3000#	Screwed	Forg CS	
F	1	25	3000#	Screwed	Forg CS	
G	4	102	150#	Flanged	CS	Sight Glass
H	2	51	3000#	Screwed	Forg CS	
I	1.5	38	3000#	Screwed	Forg CS	

DESIGN DATA	
Design Condition	2.5 psig at 120 Deg F
Operating Condition	1 psig at Deg F
Thickness	0.25 inches (Vendor to confirm)
Bolt Specifications	SA 193-B7
Nuts	SA-194-2H
Paint	Epoxy coating only on outside CS surfaces

NOTES
1. Cover must be GASKETED fit.
2. Cover bolt holes shall straddle 0 and 180 deg centerline or its parallel U.O.N
3. Coupling required in all the screwed ports (to allow connection inside the tanks)

Figure B.4 Detailed design of POC hydrophobic liquid thickener tank

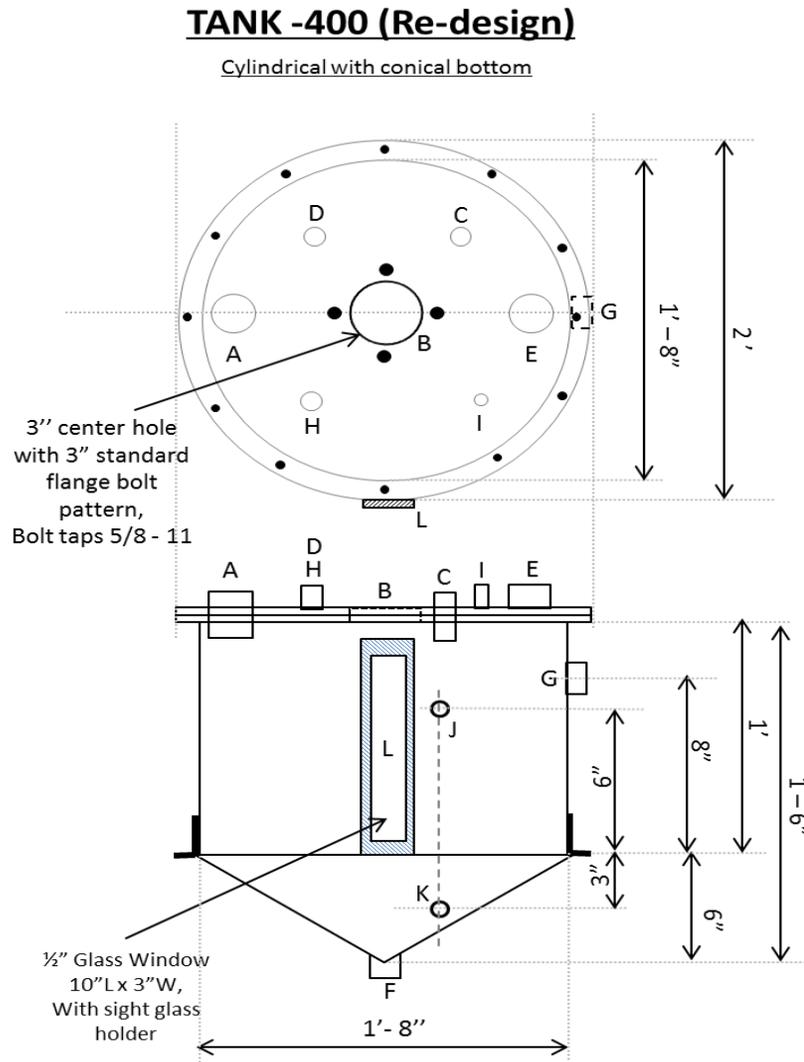


NOZZLE SCHEDULE					
			NOZZLE FLG.		
ID	Size, in	Size, mm	Rating	Type	Matl.
A	2	51	3000#	Screwed	Forg CS
B	2.5	64	150#	Flanged	CS
C	1	25	3000#	Screwed	Forg CS
D	1	25	3000#	Screwed	Forg CS
E	2	51	3000#	Screwed	Forg CS
F	1.5	38	3000#	Screwed	Forg CS
G	2	51	3000#	Screwed	Forg CS
H	2	51	3000#	Screwed	Forg CS
I	2	51	3000#	Screwed	Forg CS
J	2	51	3000#	Screwed	Forg CS
K	24	605	Special	Special	CS

DESIGN DATA	
Design Condition	2.5 psig at 120 Deg F
Operating Condition	1 psig at Deg F
Thickness	0.25 inches (Vendor to confirm)
Bolt Specifications	SA 193-B7
Nuts	SA-194-2H
Paint	Epoxy coating only on outside CS surfaces

NOTES	
1. Cover must be GASKETED fit.	
2. Cover bolt holes shall straddle 0 and 180 deg centerline or its parallel U.O.N	
3. Coupling required in all the screwed ports (to allow connection inside the tanks)	

Figure B.5 Detailed design of POC (OLD) vibrating mixer tank



NOZZLE SCHEDULE					
			NOZZLE FLG.		
ID	Size, in	Size, mm	Rating	Type Coupling)	Matl.
A	2	51	3000#	Screwed (Full)	Forg CS
B	3	76	---	Center Hole	---
C	1	25	3000#	Screwed (Full)	Forg CS
D	1	25	3000#	Screwed (Half)	Forg CS
E	2	51	3000#	Screwed (Half)	Forg CS
F	1	25	3000#	Screwed (half)	Forg CS
G	2	51	3000#	Screwed (half)	Forg CS
H	2	51	3000#	Screwed (half)	Forg CS
I	1/2	12.5	3000#	Screwed (half)	Forg CS
J	1/2	12.5	3000#	Screwed (half)	Forg CS
K	1/2	12.5	3000#	Screwed (half)	Forg CS
L	10" X 3"	252 X 75	Special	Glass Window	CS

DESIGN DATA	
Design Condition	2.5 psig at 120 Deg F
Operating Condition	1 psig at Deg F
Thickness	0.25 inches (Vendor to confirm)
Bolt Specifications	SA 193-B7
Nuts	SA-194-2H
Paint	Epoxy coating only on outside CS surfaces

NOTES	
1.	Cover must be GASKETED fit.
2.	Cover bolt holes shall straddle 0 and 180 deg centerline or its parallel U.O.N
3.	All holes for bolt connections must be drilled.
4.	Coupling required in all the screwed ports.

Figure B.6 Detailed design of POC (NEW) vibrating mixer tank

B.2 Vibrating Mixer Set-up and Assembly

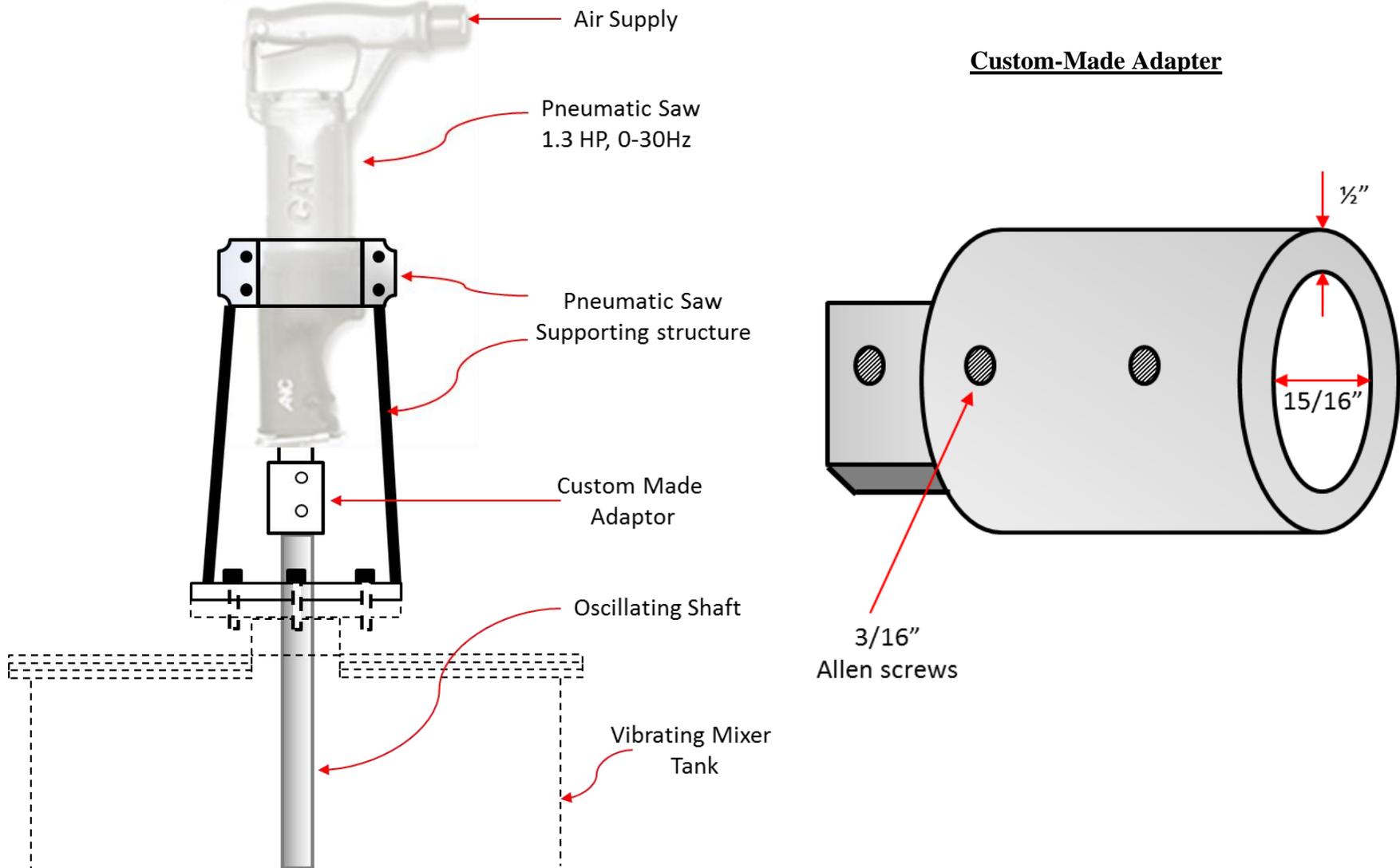


Figure B.7 Detailed design of POC novel vibrating mixing device (a) set-up (b) custom-made adapter

Vibrating Mixing Device – POC Design

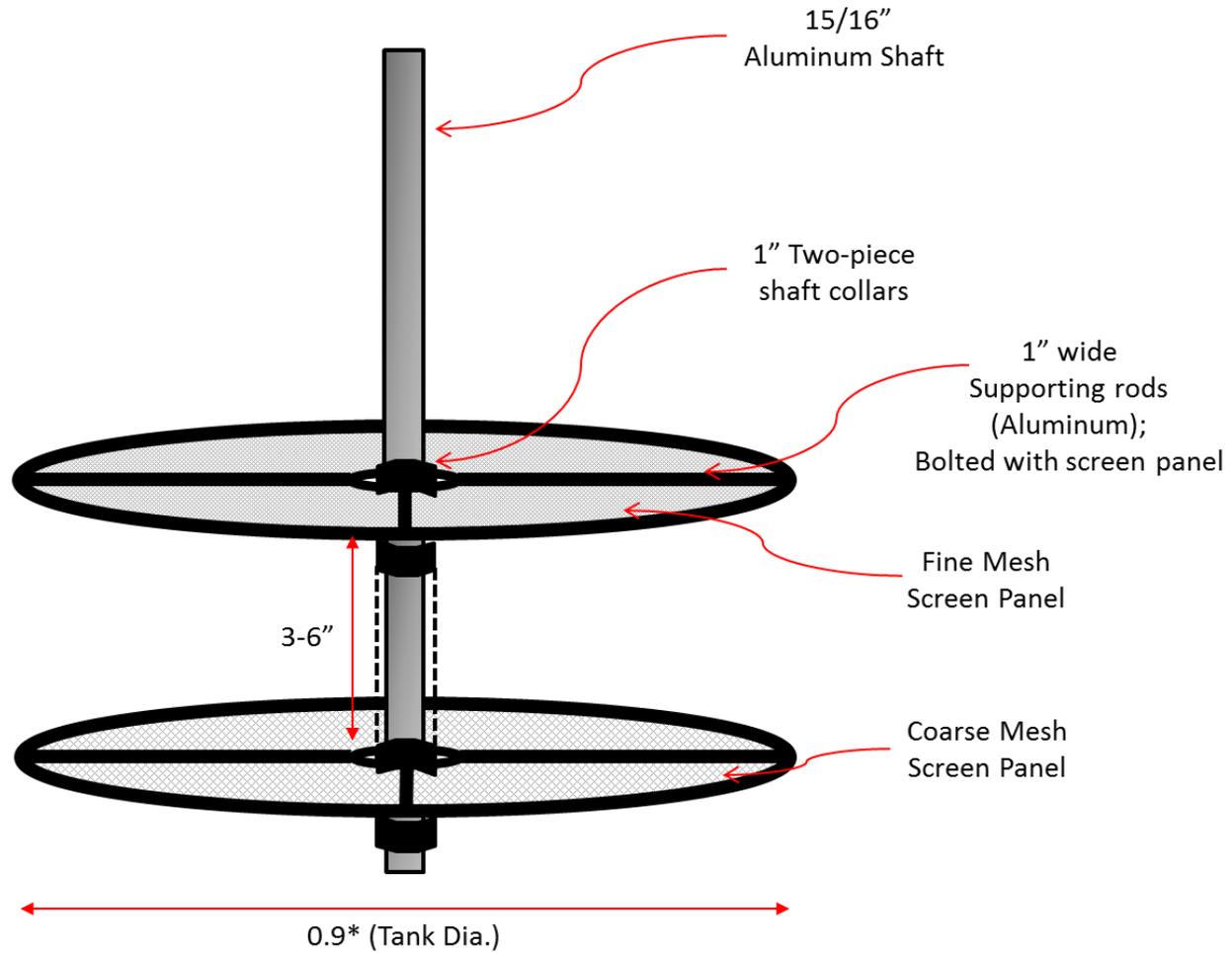


Figure B.8 POC novel vibrating mixing device mesh assembly

B.3 Ancillary Units for POC Pilot Plant



Figure B.9 Pilot-scale nitrogen gas generator for POC operation

Nitrogen Generator

- PRO N-8 Model from OnSite Gas System, Inc.
- In-built 60 gallon nitrogen gas receiving tank
- Three levels of nitrogen purity: 95%, 97%, and 99%.
- Two molecular sieve beds, captures oxygen molecules from the air and allows the nitrogen molecules to pass.
- While one sieve bed generates nitrogen, the other is purged of oxygen.
- The nitrogen exits the sieve bed and flows into the receiving tank for storage and use.



Figure B.10 Water-heater and Chiller unit for POC operation

Water Heater

- Whirlpool household water heater, capacity 40 gallon
- Two heating elements, maximum water temperature 140°F
- 3750 Watts (operating) for each element, modified so that both element can be used at the same time.
- Energy factor 0.92
- Connected with a centrifugal pump with variable speed controller.

Water Chiller

- Portable chiller, Model: M1-1.5A from Advantage Engineering
- Capacity 1.5 tons, each ton is equivalent to 12000 BTU/hr
- Air-cooled condenser, 1.5 HP compressor
- 70/30 water-propylene glycol mixture as a cooling fluid
- In-built pump rated to 3.6 GPM, ½ motor and 60 psi pressure
- Operating temperature: 30°F

Table B.2 Types of pumps utilized in the POC pilot plant



Masterflex B/T Air-Powered Pump (Cole Parmer)

- Peristaltic pump (0.55 to 11.1 GPM)
- Used for **P-100, P-900**
- $\frac{3}{4}$ HP motor, Variable speed (35 to 321 RPM)
- Compressed Air: 24 CFM at 100 PSI
- Rapid-load pump head
- Tygon E-LFL pump tubing



Masterflex I/P Air-Powered Pump System (Cole Parmer)

- Peristaltic pump (1.2 to 8.0 LPM)
- Used for **P-400, P-800**
- $\frac{3}{4}$ HP motor, Variable speed (100 to 650 RPM)
- Easy-load pump head
- Tygon E-LFL pump tubing



Masterflex L/S Air-Powered Pump System (Cole Parmer)

- Peristaltic pump (0.17 to 1.7 LPM)
- Used for **P-200, P-600**
- $\frac{3}{4}$ HP motor, Variable speed (60 to 600 RPM)
- Easy-load II pump head
- Tygon C-Flex pump tubing

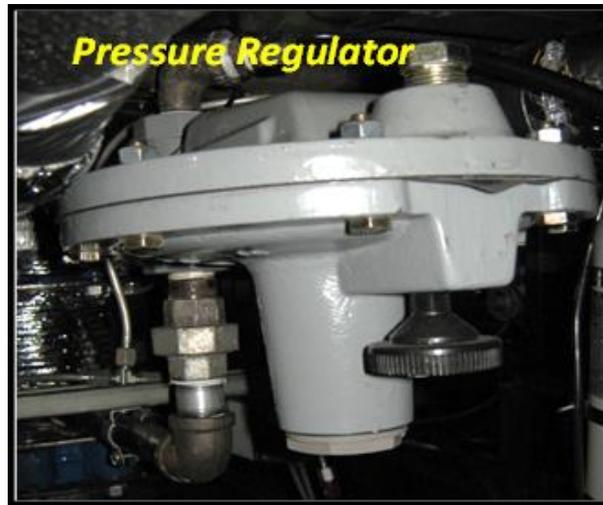


Figure B.11 (a) Nitrogen pressure regulators (b) Pressure release vent

Nitrogen Pressure Regulators

- Y690A Series gas blanketing regulators manufactured by Emerson
- Regulate nitrogen in the range from 2.5" to 7" of water column
- Orifice size 1/8", spring loaded
- Inlet pressure 40 psi provided 672 SCFH of nitrogen in the system for purging

Pressure Vents

- Model: ENARDO Series 953
- Pressure settling range: 1" to 7" of water column
- Housing material: Aluminum
- Teflon Seals, Advanced composite thermoplastic materials for seat
- Stainless steel pallets, weight equivalent to 2" of water column

POC Spill Containment Evaluation

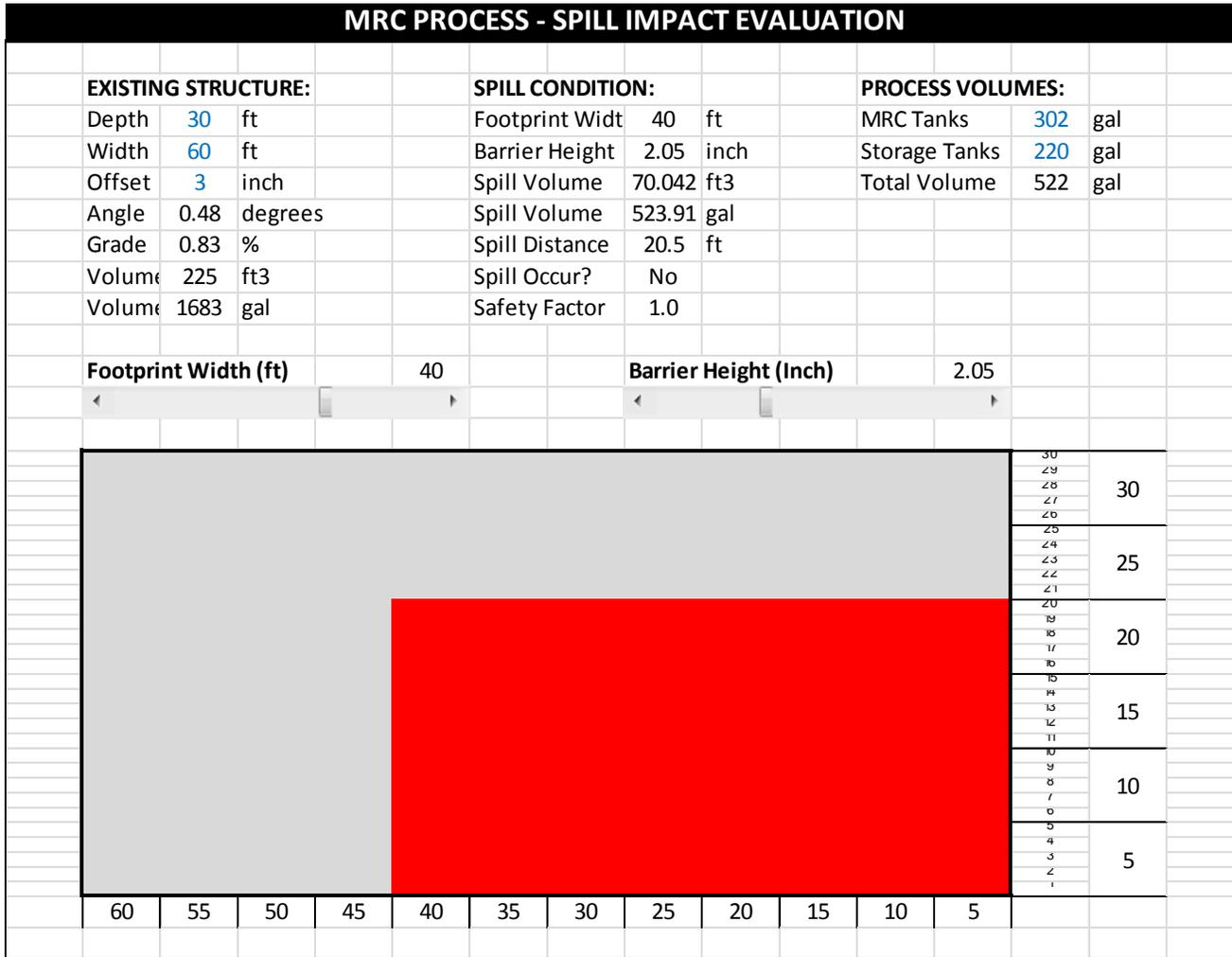


Figure B.12 Spill containment analysis for POC pilot plant test site

CONSPEC Pentane/Oxygen Remote Sensor Box (24 Volts DC Power Supply)

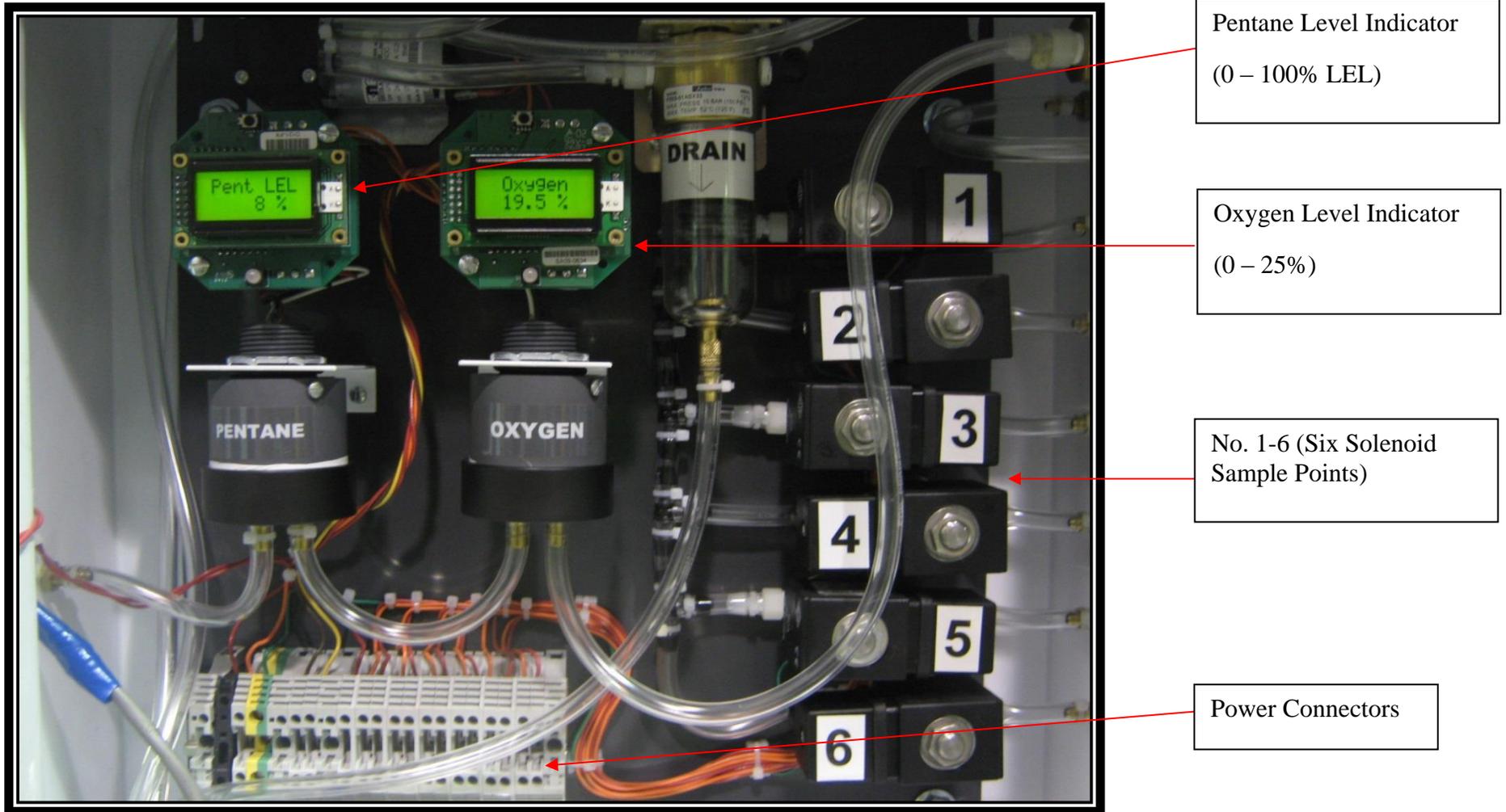


Figure B.13 Conspec multi-port remote sensing device

OIL SKIMMER (Courtesy: Megator Corporation)

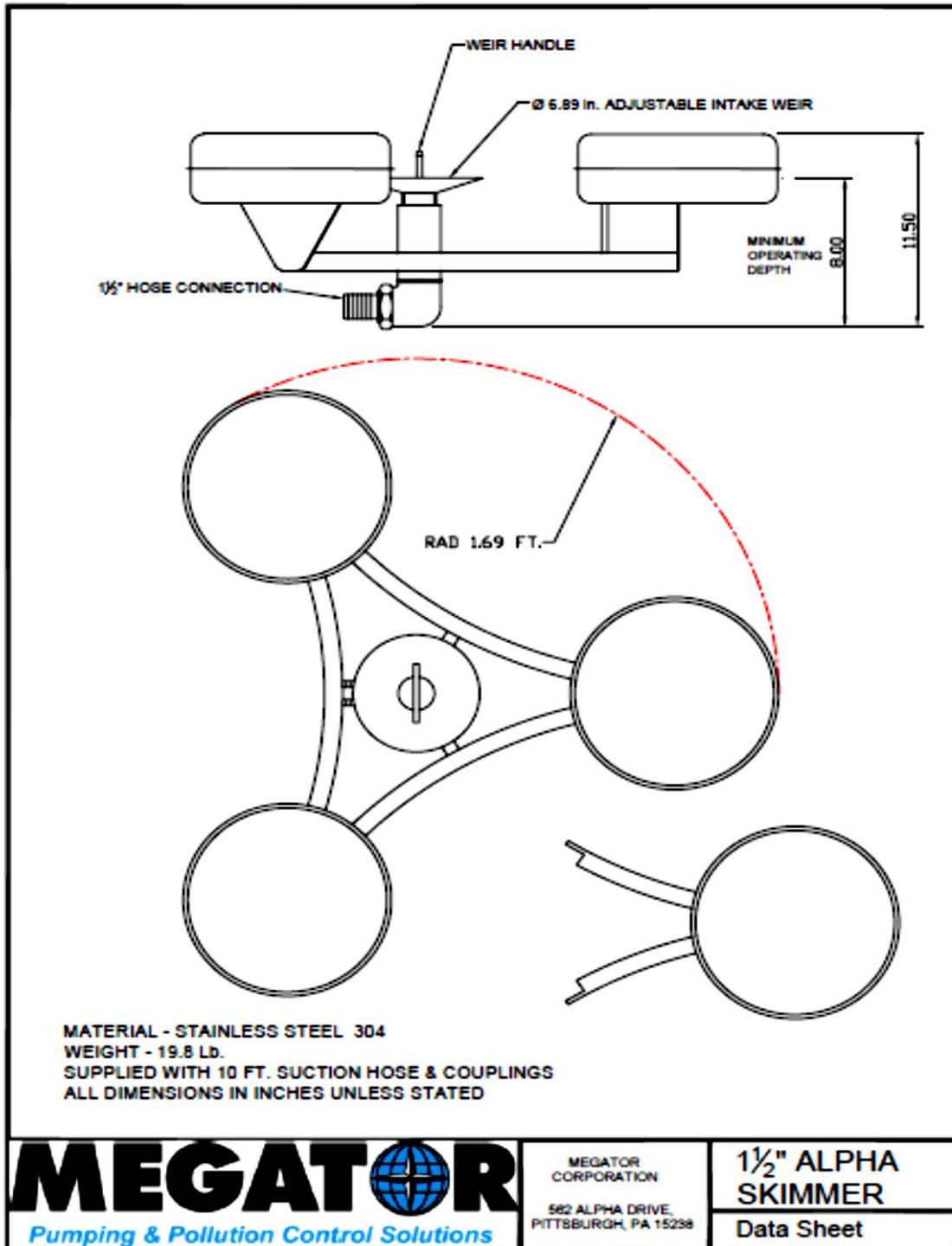
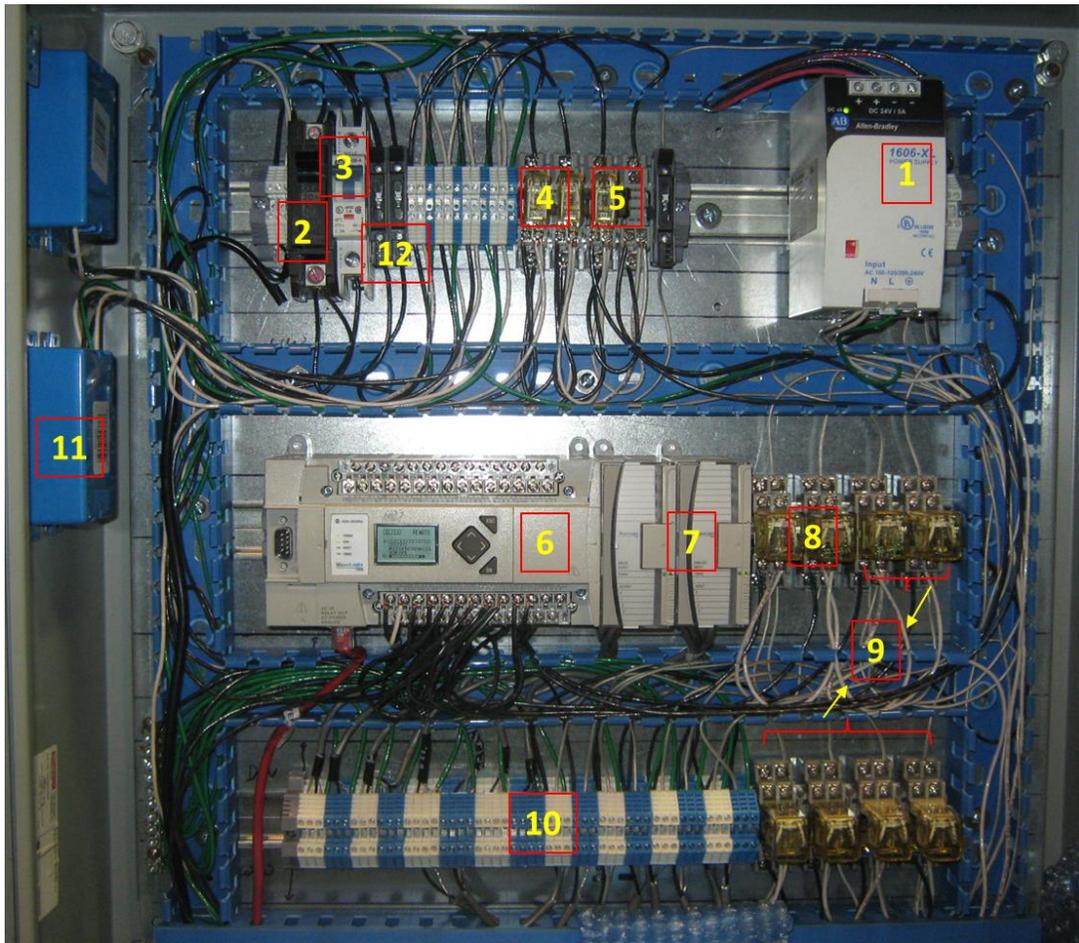


Figure B.14 Drawing of oil-skimmer used in POC unit operation

APPENDIX C. PLC INSTRUMENTATION

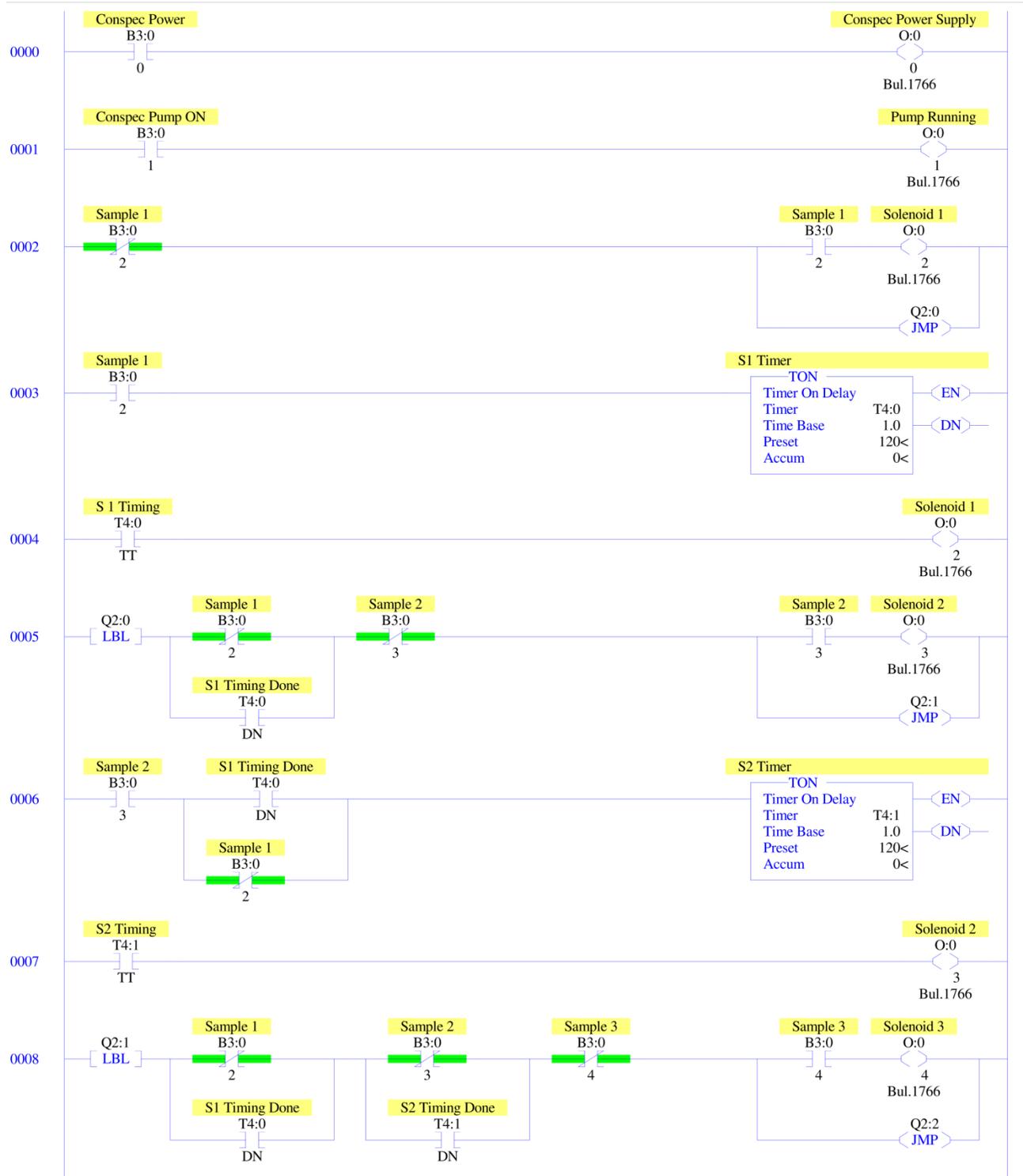
C.1 PLC CONTROL BOX

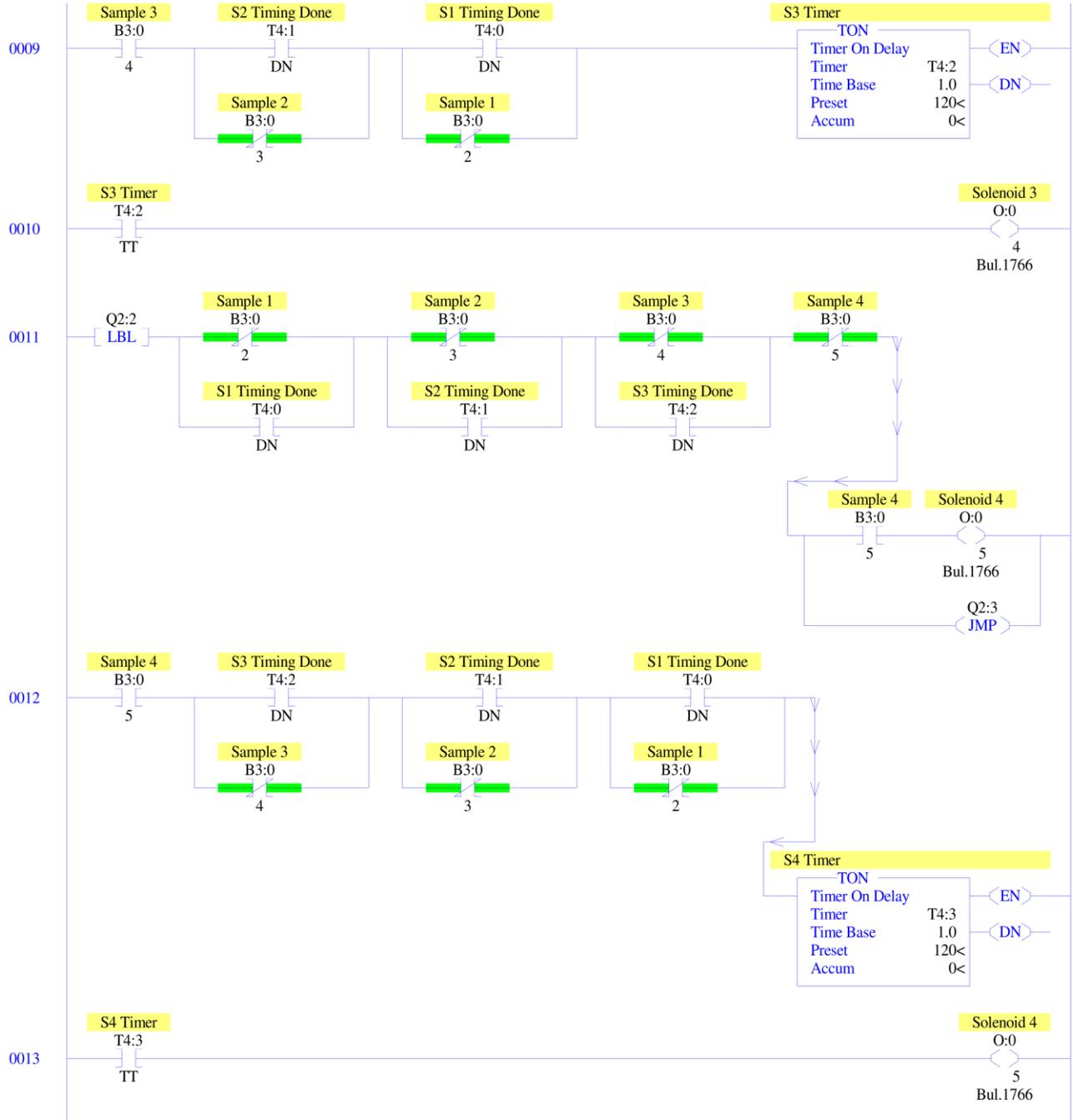


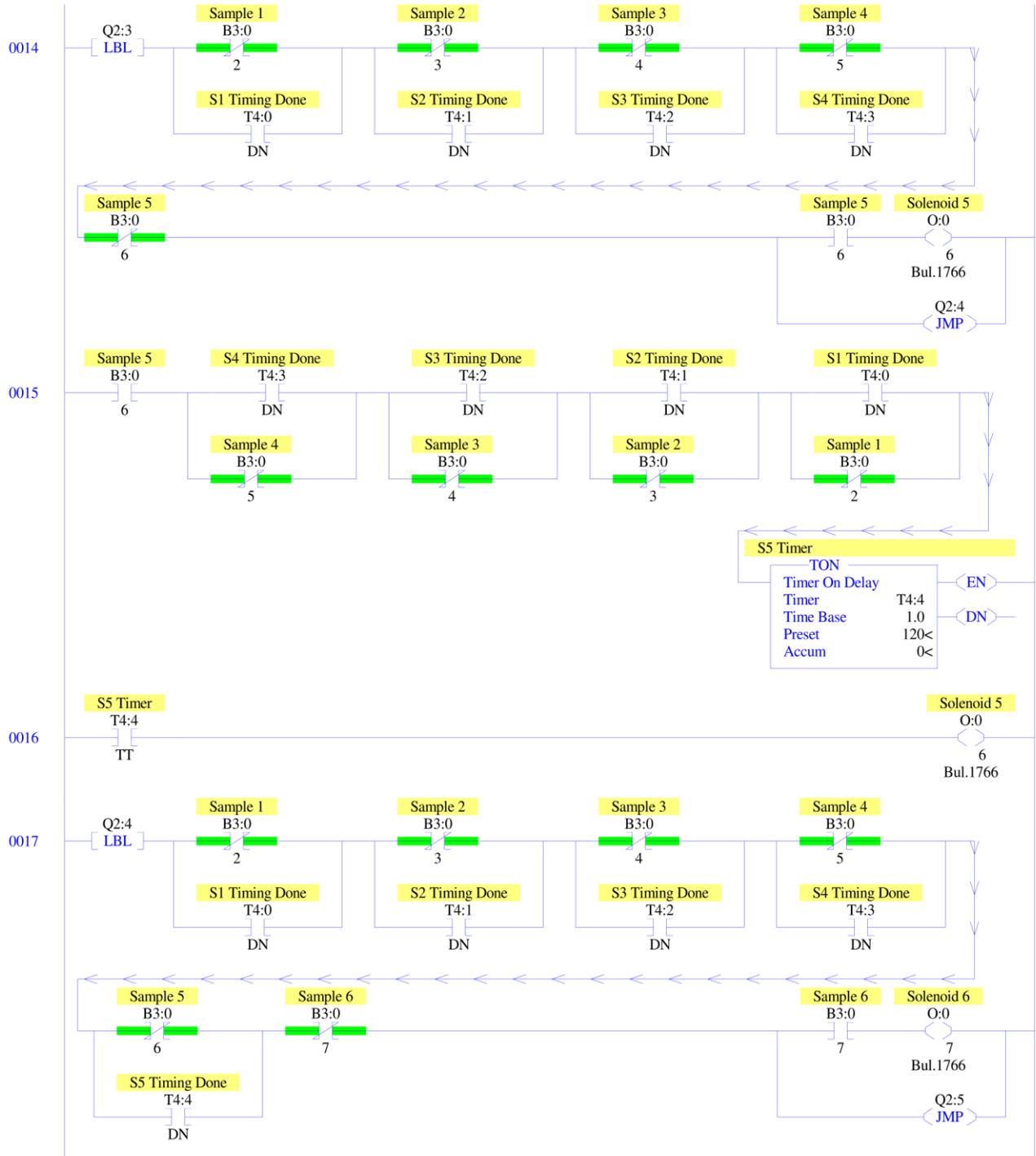
1	24 Volts DC Power Supply	7	Analog Output/Input
2	Main Switch Breaker	8	Relays (2) Conspec Power & Pump
3	PLC Box Breaker	9	Relays (6) Solenoid Sample Points
4	Relays (2) Discharge Valves	10	Power Connectors
5	Relays (2) Alarm System	11	110 Volts AC Power Supply
6	Allen-Bradley 1400 MicroLogix	12	(3) Fuses

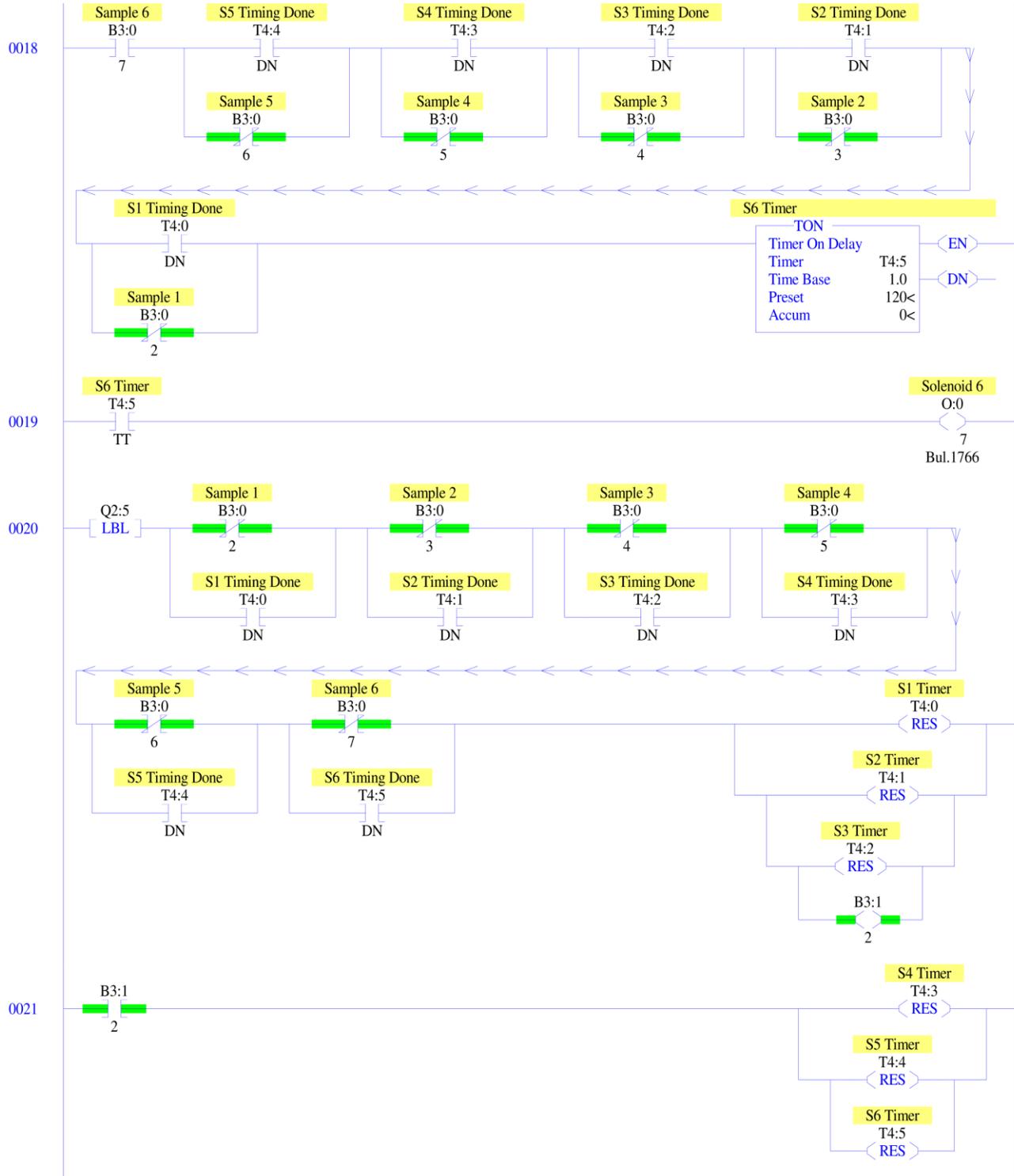
Figure C.1 PLC control box developed to operate POC pilot plant

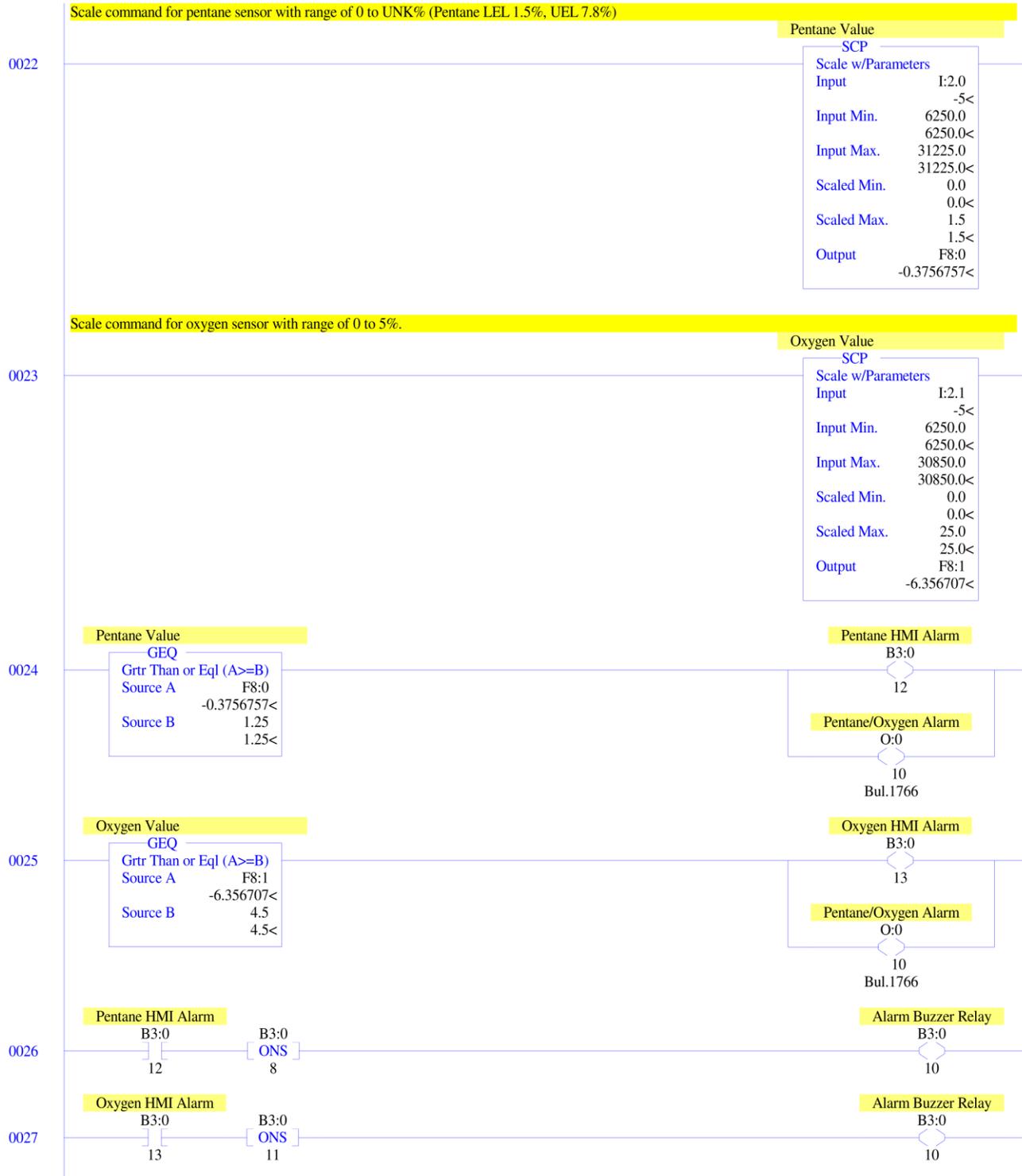
C.2 LADDER LOGIC

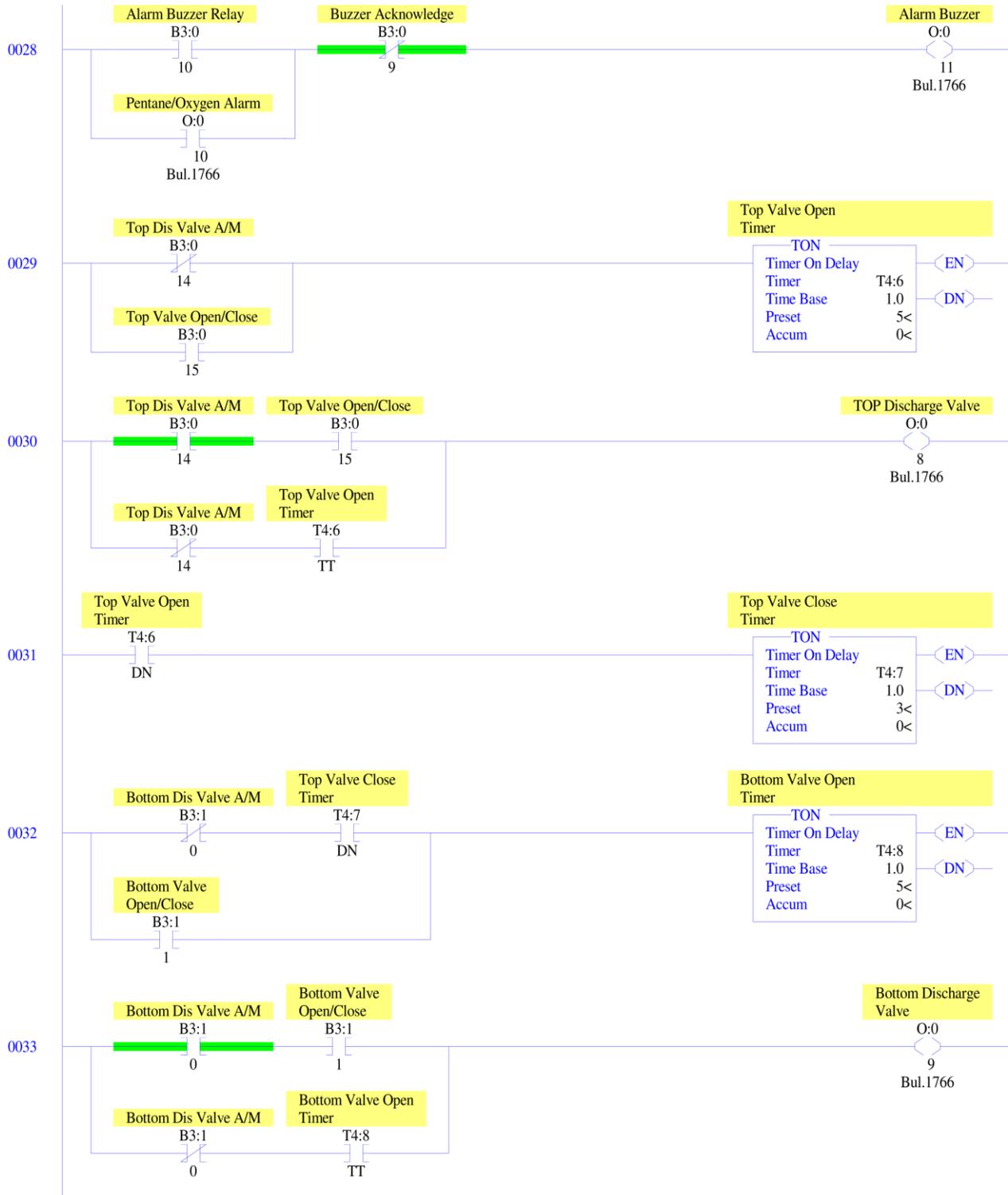


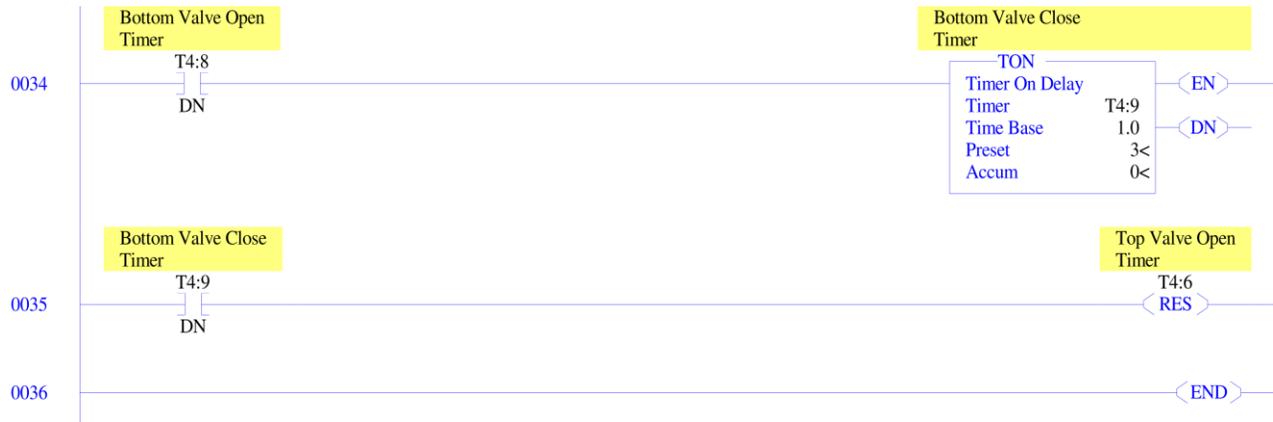




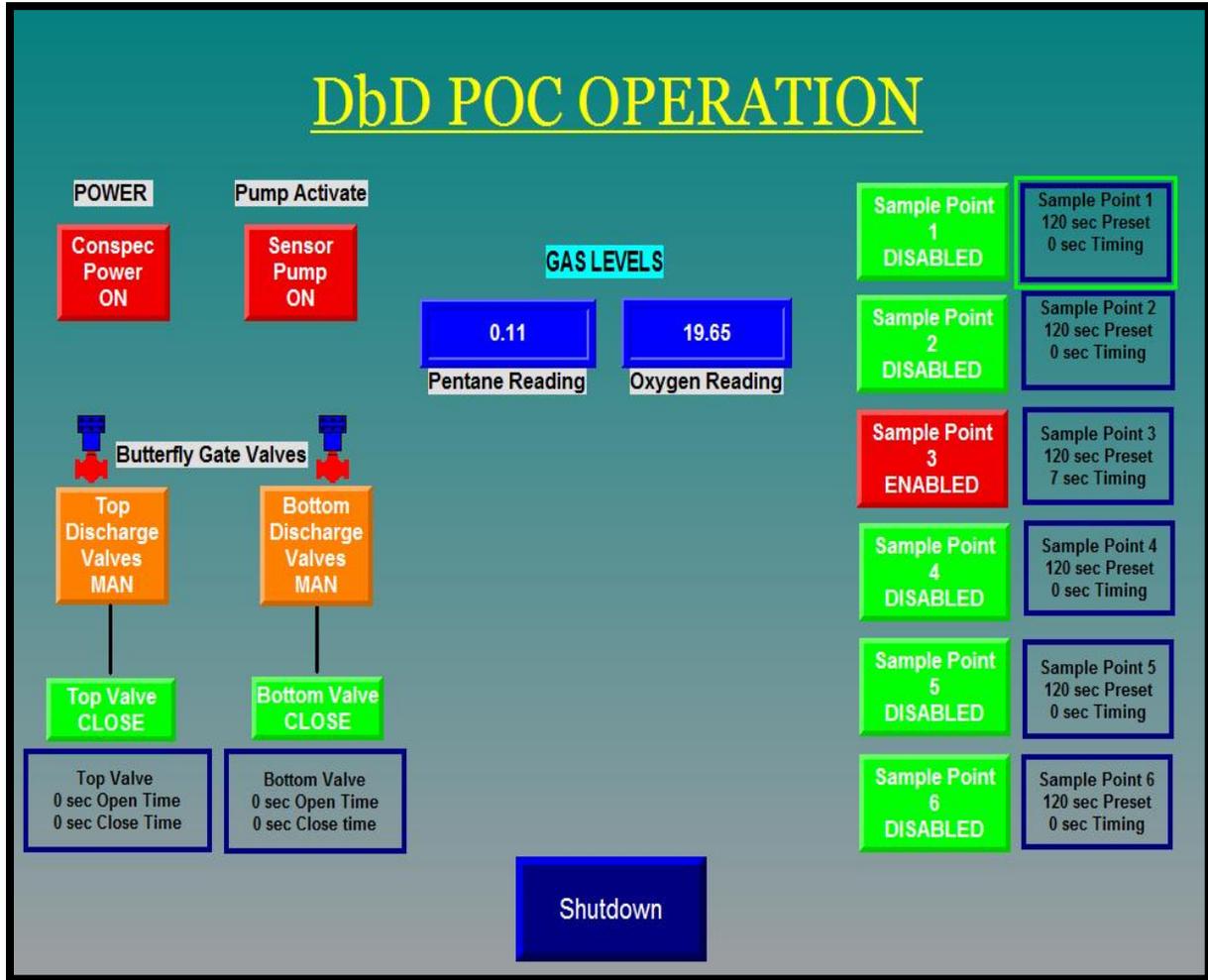








C.3 Human Machine Interface for POC Operation



<i>Switch Type</i>	<i>Function</i>
Conspec Sensor Box Power Switch	Manual On/Off
Sensor Pump Switch	Manual On/Off
Gas Level Indicators	Pentane (0 – 1.4%); Oxygen (0 – 25%)
Discharge Valves Switches	Manual/ Timer Automatic
Sample Point Switches	Timer Automatic (Manual On/Off)
Plant Shutdown Switch	Default On; Manual OFF

Figure C.2 HMI interface developed to operate POC pilot plant

APPENDIX D. DATA AND MODELING CALCULATIONS

D.1 Agglomeration Studies

Table D.1 Direct Data obtained from agglomeration studies with various propellers

ANALYSIS WITH LAB PROPELLER									
FEED:									
Ash%	40.65								
% Solids	4.5								
Slurry SG	1.026								
Volume (L)	Imp Dia (in)	RPM	Time (min)	Torque (N-cm)	Agglomerates %Moisture	Tail %Ash	Ash Recovery Ratio	Tip Speed (Feet/Sec)	Power/Vol Kw/m3
1	1	500	1	4.5	76.3	41.86	1.03	2.18	4.17
1	1	500	4	4.3	75.7	46.51	1.14	2.18	3.99
1	1	500	8	3.9	72.3	50.32	1.24	2.18	3.62
1	1	1000	1	5.4	77.8	48.72	1.20	4.36	10.01
1	1	1000	4	5.1	70.2	50.63	1.25	4.36	9.46
1	1	1000	8	4.9	68.1	52.35	1.29	4.36	9.08
1	1	2000	1	6.4	69.8	53.44	1.31	8.72	23.73
1	1	2000	4	6.1	68.1	56.89	1.40	8.72	22.62
1	1	2000	8	5.8	64.4	58.96	1.45	8.72	21.51
1	2	500	0.5	5.2	71.1	43.72	1.08	4.36	4.82
1	2	500	1	5.1	69.8	44.19	1.09	4.36	4.73
1	2	500	4	4.9	62.7	45.59	1.12	4.36	4.54
1	2	1000	0.5	6.6	59.8	57.34	1.41	8.72	12.24
1	2	1000	1	6.3	56.7	62.09	1.53	8.72	11.68
1	2	1000	4	5.6	36.6	84.56	2.08	8.72	10.38
1	2	1000	4	5.6	--	76.62	1.88	8.72	10.38
1	2	1000	4	5.6	--	81.35	2.00	8.72	10.38
1	2	2000	0.5	7.8	46.5	78.84	1.94	17.44	28.92
1	2	2000	1	7.6	45	82.61	2.03	17.44	28.18
1	2	2000	4	7.2	23.7	87.07	2.14	17.44	26.70
1.25	3	500	0.25	6.6	63.4	58.71	1.44	6.54	4.89
1.25	3	500	0.5	6.5	54.7	60.43	1.49	6.54	4.82
1.25	3	500	1	6.4	51.9	63.26	1.56	6.54	4.75
1.25	3	1000	0.25	8.9	68.5	75.88	1.87	13.08	13.20
1.25	3	1000	0.5	8.8	65.9	75.13	1.85	13.08	13.05
1.25	3	1000	1	8.5	64.8	70.96	1.75	13.08	12.61
1.25	3	1330	0.25	10.8	--	74.58	1.83	17.40	21.30
1.25	3	1330	0.5	10.6	--	73.2	1.80	17.40	20.91
1.25	3	1330	1	10.5	--	72.83	1.79	17.40	20.71
1.25	3	2000	0.25	12	54.3	73.72	1.81	26.17	35.60
1.25	3	2000	0.5	11.9	61.6	72.89	1.79	26.17	35.30
1.25	3	2000	1	11.5	63.9	70.61	1.74	26.17	34.11

Table D.2 Direct Data obtained from agglomeration studies with various hi-shear blades

ANALYSIS WITH HI-SHEAR BLADE									
FEED:									
Ash%	40.65								
% Solids	4.5								
Slurry SG	1.026								
Volume (L)	Imp Dia (in)	RPM	Time (min)	Torque (N-cm)	Agglomerates %Moisture	Tail %Ash	Ash Recovery Ratio	Tip Speed (Feet/Sec)	Power/Vol Kw/m3
1	1	500	1	4.4	72.1	44.23	1.09	2.18	4.08
1	1	500	4	4.3	68.3	47.54	1.17	2.18	3.99
1	1	500	8	4.2	64.5	49.79	1.22	2.18	3.89
1	1	1000	1	5.2	67	50.91	1.25	4.36	9.64
1	1	1000	4	5	64.7	52.08	1.28	4.36	9.27
1	1	1000	8	4.9	63.3	53.86	1.32	4.36	9.08
1	1	2000	1	6.3	63.2	61.93	1.52	8.72	23.36
1	1	2000	4	5.9	58.9	64.11	1.58	8.72	21.88
1	1	2000	8	5.5	50.3	64.25	1.58	8.72	20.39
1	2	500	0.5	4.7	62.5	42.09	1.04	4.36	4.36
1	2	500	1	4.7	62.1	42.68	1.05	4.36	4.36
1	2	500	4	4.5	58.3	43.74	1.08	4.36	4.17
1	2	1000	0.5	6.2	63.4	55.99	1.38	8.72	11.49
1	2	1000	1	6	60.2	56.41	1.39	8.72	11.12
1	2	1000	4	5.5	55.7	67.4	1.66	8.72	10.20
1	2	2000	0.5	6.6	44.2	71.12	1.75	17.44	24.47
1	2	2000	1	6.5	37.6	82.48	2.03	17.44	24.10
1	2	2000	4	6.4	33.2	85.6	2.11	17.44	23.73
1.25	3	500	0.25	5.6	65.99	48.83	1.20	6.54	4.15
1.25	3	500	0.5	5.5	65.28	48.36	1.19	6.54	4.08
1.25	3	500	1	5.2	64.21	50.9	1.25	6.54	3.86
1.25	3	1000	0.25	6.5	63.95	53.69	1.32	13.08	9.64
1.25	3	1000	0.5	6.4	64.12	55.8	1.37	13.08	9.49
1.25	3	1000	1	6.3	62.67	58.29	1.43	13.08	9.34
1.25	3	2000	0.25	6.9	60.73	59.9	1.47	26.17	20.47
1.25	3	2000	0.5	6.8	57.47	59.43	1.46	26.17	20.17
1.25	3	2000	1	6.5	55.04	57.12	1.41	26.17	19.28

D.2 Cylindrical Column Settling Data (Batch-Scale Analyses)***Table D.3 Direct Data obtained from batch-scale testing for regent thickener***

1% Solid Feed to Thickener			5% Solid Feed to Thickener			10% Solid Feed to Thickener		
Interface Height (Inches)	Time (min)	Underflow Concentration %	Interface Height (Inches)	Time (min)	Underflow Concentration %	Interface Height (Inches)	Time (min)	Underflow Concentration %
14.36	0	1.00	14.64	0	4.76	15.00	0	9.09
12.86	0.1	1.10	12.86	0.2	5.41	12.86	0.5	10.53
11.43	0.3	1.24	11.43	0.5	6.06	11.43	1.0	11.77
10.00	0.5	1.42	10.00	0.8	6.90	10.00	1.6	13.33
8.57	0.7	1.65	8.57	1.1	8.00	8.57	2.2	15.39
7.14	0.9	1.98	7.14	1.4	9.52	7.14	2.7	18.18
5.71	1.1	2.47	5.71	1.7	11.77	5.71	3.4	22.23
4.29	1.3	3.28	4.29	2.1	15.39	4.29	4.1	28.58
2.86	1.5	4.88	2.86	2.5	22.23	3.57	5.1	33.34
1.43	1.8	9.52	1.43	3.0	40.01	2.86	6.9	40.01
0.71	2.0	18.18	1.29	3.2	43.49	2.50	9.4	44.46
0.43	2.2	28.58	1.14	4.8	47.64	2.36	11.1	46.53
0.29	2.8	40.01	1.06	9.8	50.53	2.29	12.1	47.64
0.23	7.0	47.64	1.03	15	51.57	2.14	14.2	50.02
0.20	15	52.65	0.99	∞	52.99	2.11	15.0	50.53
0.16	∞	62.14				2.00	20.0	52.65
						1.98	∞	52.96

Modeling Data for Regent Thickener

1) Correlation for Equation 6.11

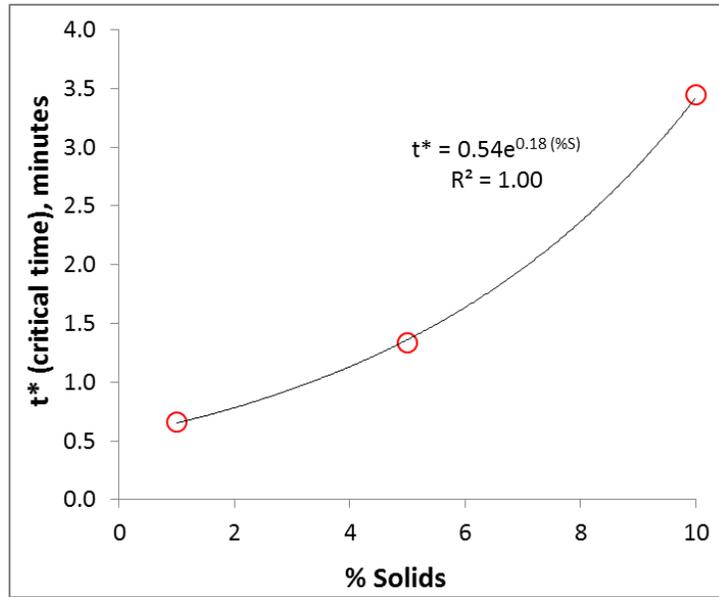


Figure D.1 Correlation between model parameter ' t^ ' and %solids feed*

2) Correlation for Equation 6.12

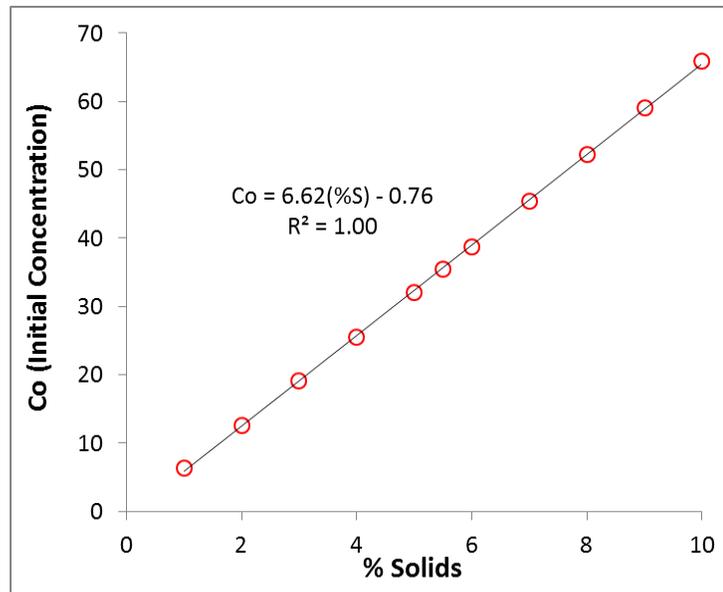


Figure D.2 Correlation between initial concentration with %solids feed

D.3 Pentane Evaporation Batch-Scale Data**Table D.4 Analyses of pentane absorption in coal at 95°C**

<i>Vail Number</i>	<i>Evaporation Time (minutes)</i>	<i>Final pentane in coal (% by weight)</i>	<i>Normalized % Pentane Absorption</i>
1	0	88.54	100.00
2	3	48.21	54.45
3	6	18.30	20.67
4	9	1.42	1.60
5	12	0.42	0.47
6	15	0.17	0.20
7	20	0.12	0.14
8	25	0.08	0.09
9	30	0.02	0.02

Table D.5 Analyses of pentane absorption in coal at 85°C

<i>Vail Number</i>	<i>Evaporation Time (minutes)</i>	<i>Final pentane in coal (% by weight)</i>	<i>Normalized % Pentane Absorption</i>
10	0	78.64	100.00
11	3	49.13	62.48
12	6	21.95	27.91
13	9	4.13	5.25
14	12	0.63	0.81
15	15	0.25	0.32
16	20	0.19	0.24
17	25	0.13	0.17
18	30	0.06	0.07

Table D.6 Analyses of pentane absorption in coal at 75°C

<i>Vail Number</i>	<i>Evaporation Time (minutes)</i>	<i>Final pentane in coal (% by weight)</i>	<i>Normalized % Pentane Absorption</i>
19	0	73.91	100.00
20	3	53.16	71.92
21	6	28.16	38.10
22	9	7.99	10.82
23	12	0.90	1.22
24	15	0.42	0.57
25	20	0.20	0.28
26	25	0.14	0.19
27	30	0.09	0.12

Table D.7 Analyses of pentane absorption in coal at 65°C

<i>Vail Number</i>	<i>Evaporation Time (minutes)</i>	<i>Final pentane in coal (% by weight)</i>	<i>Normalized % Pentane Absorption</i>
28	0	73.65	100.00
29	3	53.28	72.34
30	6	30.47	41.38
31	9	8.79	11.93
32	12	1.36	1.84
33	15	0.58	0.79
34	20	0.35	0.48
35	25	0.20	0.28
36	30	0.12	0.17

Table D.8 Analyses of pentane absorption in coal at 55°C

<i>Vail Number</i>	<i>Evaporation Time (minutes)</i>	<i>Final pentane in coal (% by weight)</i>	<i>Normalized % Pentane Absorption</i>
37	0	64.49	100.00
38	3	47.00	72.88
39	6	29.06	45.05
40	9	11.94	18.51
41	12	1.93	2.99
42	15	0.65	1.06
43	20	0.34	0.53
44	25	0.20	0.32
45	30	0.14	0.22

Modeling Correlation for Pentane Absorption

1) Correlation for Equation 6.15

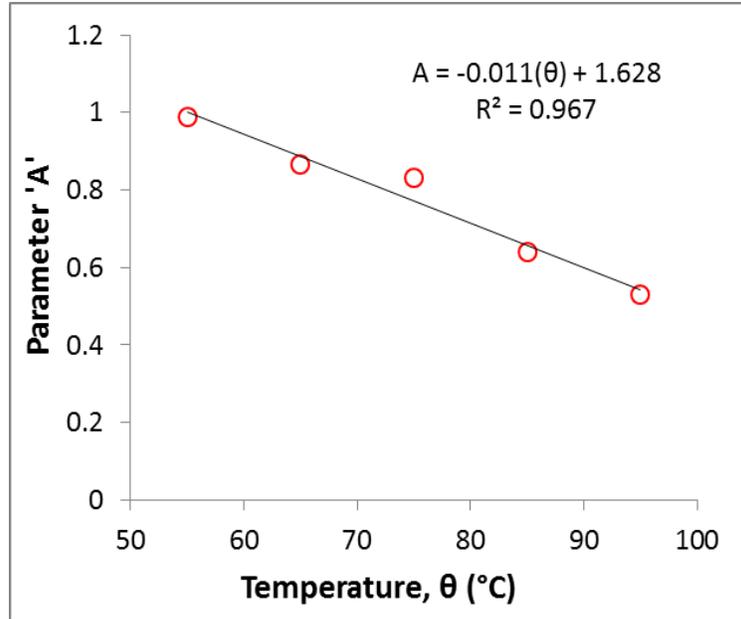


Figure D.3 Correlation between the modeling parameter 'A' and temperature

2) Correlation for Equation 6.16

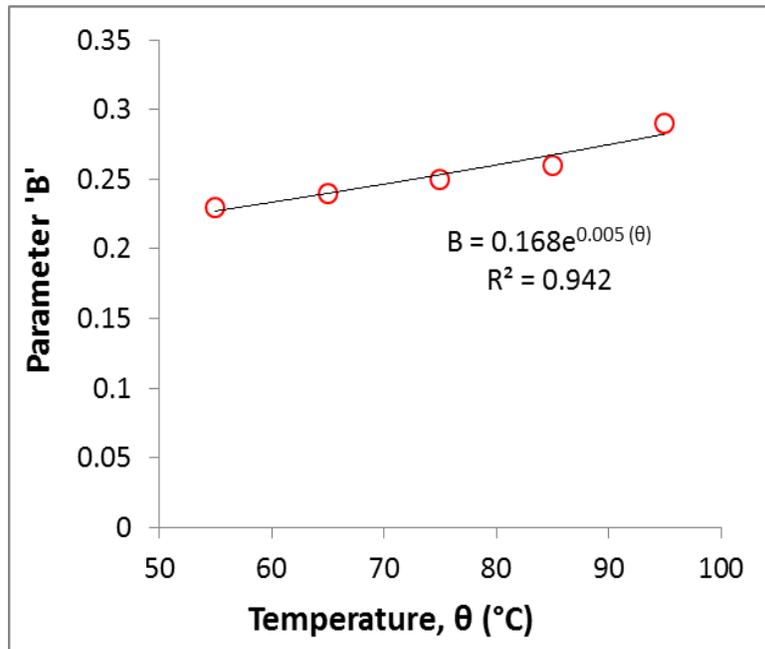


Figure D.4 Correlation between the modeling parameter 'B' and temperature

D.4 Economic Analysis – Work Sheet

COAL QUALITY SPECIFICATIONS:			OPERATING COST:		LABOR COST:					
Clean Coal		Feed Coal	Power used (KW)	300	Shifts	1-20 tph	25-50 tph	55-75 tph	80-100 tph	
DAF	As-Received		Cost/KWH (\$)	0.12	Hours/shifts	8	8	8	8	
Ash (%):	---	3.00	60.00	Load Equip Factor	0.75	Manager	1	1	1	1
Heat Value (Btu/lb):	15000	13095	420	Reagent Cost (\$/lb)	1.00	Supervisor	1	1	1	1
Moisture (%):	---	10.00	93.00	Reagent Lost (%)	0.50	Operator	1	2	3	4
COAL VALUE:			Oprt Hours/year	4800	Avg \$/Labor/year	120000	120000	120000	120000	
Coking (\$/MMBTU)	5.84		Plant Life (years)	10	Total (\$/year)	600000	840000	1080000	1320000	
Utility (\$/MMBTU)	2.36		Fixed reagent (gal/tph)	500						
			Ci (1 TPH)	2000000						

HHS PROCESS ECONOMIC ASSESSMENT

Metric tons/hour	Gross Revenue (\$/Year)		Capital Cost	O & M Cost	Labor Cost	Total Cost	NET Revenue (\$/Year)		Net Revenue Ratio	
Clean Product	Coking	Utility	\$/Year	\$/Year	\$/Year	\$/year	Coking	Utility	Coking	Utility
1	809042	326942	220000	512761	600000	1332761	(523719)	(1005819)	(0.393)	(0.755)
3	2427127	980825	425300	1047973	600000	2073274	353853	(1092448)	0.171	(0.527)
5	4045211	1634709	577836	1472957	600000	2650793	1394418	(1016085)	0.526	(0.383)
10	8090422	3269417	875836	2361311	600000	3837146	4253276	(567729)	1.108	(0.148)
15	12135633	4904126	1117062	3131060	600000	4848122	7287511	56003	1.503	0.012
20	16180844	6538834	1327519	3836527	600000	5764046	10416798	774788	1.807	0.134
25	20226055	8173543	1517703	4499644	840000	6857346	13368709	1316196	1.950	0.192
30	24271266	9808251	1693150	5131974	840000	7665124	16606142	2143127	2.166	0.280
35	28316477	11442960	1857221	5740538	840000	8437758	19878719	3005201	2.356	0.356
40	32361688	13077669	2012142	6329988	840000	9182130	23179558	3895538	2.524	0.424
45	36406899	14712377	2159485	6903605	840000	9903090	26503809	4809287	2.676	0.486
50	40452110	16347086	2300407	7463809	840000	10604216	29847894	5742869	2.815	0.542
55	44497321	17981794	2435793	8012447	1080000	11528240	32969082	6453555	2.860	0.560
60	48542532	19616503	2566335	8550968	1080000	12197304	36345229	7419199	2.980	0.608
65	52587743	21251211	2692593	9080536	1080000	12853129	39734614	8398082	3.091	0.653
70	56632954	22885920	2815020	9602103	1080000	13497123	43135831	9388797	3.196	0.696
75	60678165	24520628	2933995	10116458	1080000	14130454	46547712	10390175	3.294	0.735
80	64723376	26155337	3049837	10624267	1320000	14994105	49729272	11161232	3.317	0.744
85	68768587	27790046	3162817	11126097	1320000	15608914	53159674	12181132	3.406	0.780
90	72813798	29424754	3273167	11622434	1320000	16215601	56598197	13209153	3.490	0.815
95	76859009	31059463	3381091	12113701	1320000	16814792	60044217	14244671	3.571	0.847
100	80904220	32694171	3486765	12600269	1320000	17407034	63497186	15287137	3.648	0.878

D.5 Pentane Gas Chromatography Analyses

Identification of pentane traces in coal sample

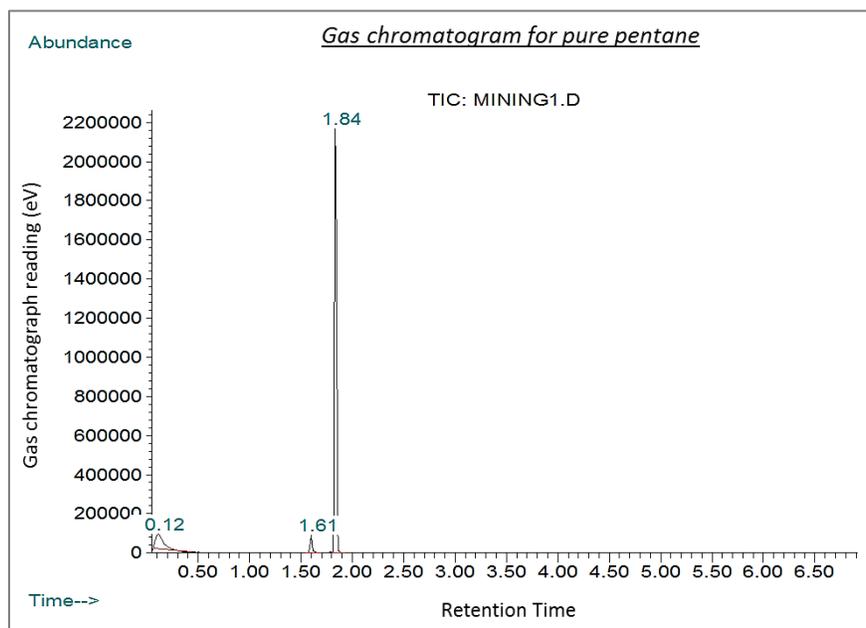


Figure D.5 Chromatogram for standard (pure pentane)

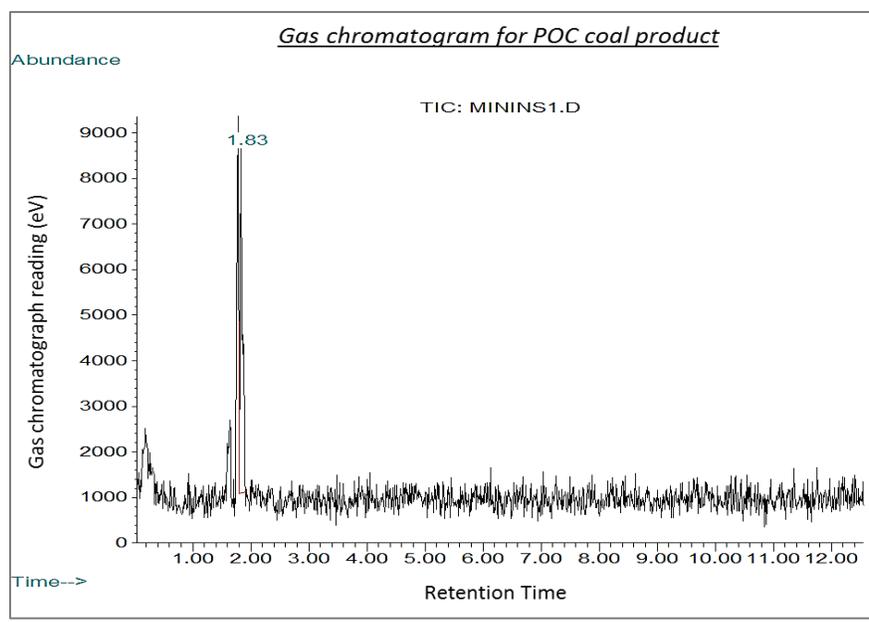


Figure D.6 Chromatogram for POC clean coal sample

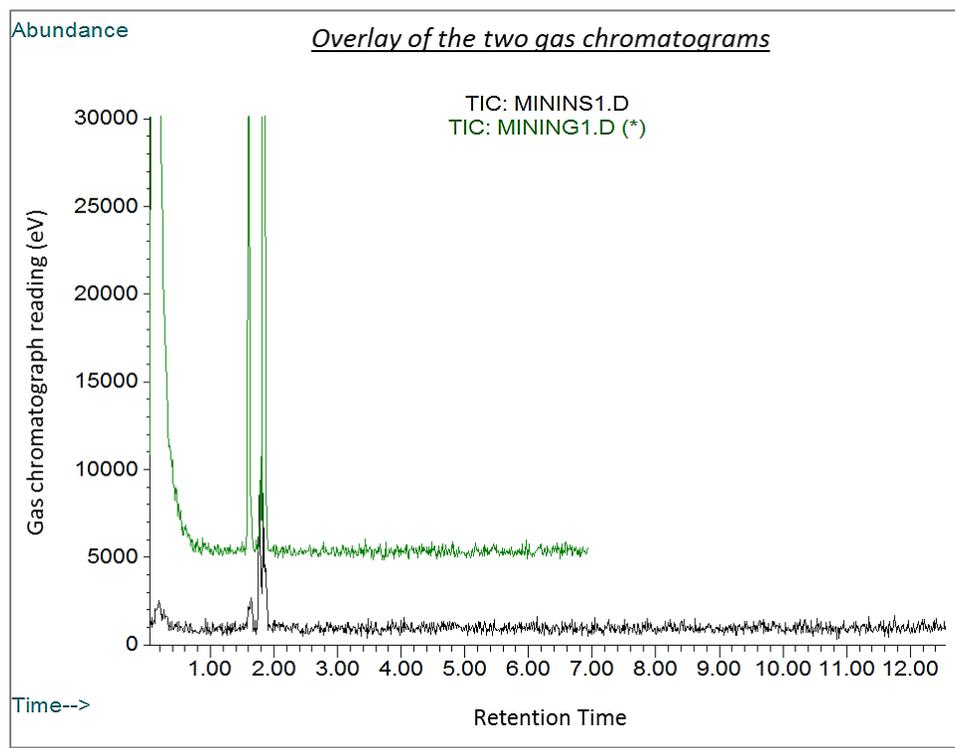


Figure D.7 Overlay of two chromatograms: standard and sample

From the preliminary gas chromatography analysis, it is evident that certain percentage of pentane is absorbed in POC clean coal product. The analysis was conducted with the assistance of Department of Chemistry at Virginia Tech. A scanned copy of the report and analysis is illustrated.

PENTANE IN COAL 10/2/13

1. Is there pentane in the coal samples? YES, both the retention times of a pure pentane standard and the HS(HeadSpace) of coal have the same retention time. Even better, The Mass Spectrum of the only peak in the HS of coal is definitely pentane.

2. How Much? At least 0.10% or 0.2% , mg/mg or lb/lb or ton/ton. Good quantitation requires two steps. Both require reliable methods of sampling pure pentane and HS of coal.

A. What is the MS detector response for pentane? IE, how much peak area does 1 ul of pure pentane generate?

Inject 1 ul of liquid pentane , assume 100 % evaporation in a 235 ml glass sample vial. This is a good assumption, no liquid is visible and we have done similar studies. We take only 1.5ml out of 235 ml and this generates 1.9×10^6 area counts.

Therefore 1ul liquid = $0.7 \text{ mg} \times 235\text{ml}/1.5\text{ml} = 110 \times 10^6$ area counts. This is our detector response factor and good data, average value of 4 injections with a relative standard deviation of 4% . This 4% proves good precision and a homogenous mixture of pentane vapors in the glass sample vial.

B. How much pentane in two samples of coal? 100 mg of coal, heated to 50C and kept at 40C. We assumed all pentane evaporated into the HS. This is not a good assumption as further analysis shows. We injected 1.5 ml of the coal HS from a 25 ml glass vial and got peak areas of 1.2×10^6 and 1.8×10^6 for the 2 coal samples, obviously not the same sample!

Therefore if all of the pentane were in the HS(ie totally vaporized, no pentane left adsorbed on the coal), we should multiple these peak areas by $25\text{ml}/1.5\text{ml}$ assuming this is 100% of the pentane. Sample A generates 17×1.2 or 20×10^6 area counts; B is $17 \times 1.8 = 30 \times 10^6$

"X" represent the mg of pentane in 100 mg of coal.

"X"mg/0.7 mg= 20×10^6 area counts/110 a.c.; $110x = 14 \text{ mg}$; $x = 0.13 \text{ mg}$ in 100mg of coal; ie 0.1%. Second sample is 0.2% pentane.



Invent the Future

GC ANALYSIS - Worksheet

<u>GC Analysis for pentane in coal processed from HHS process</u>					
Each sample weight	100	mg coal	in 25	mL vials	
Density of pentane	700	µg/µL			
<u>Standard (pure pentane)</u>			<u>POC Coal Samples</u>		
	1	µL	<u>Gas Chromatograph Readings (eV x 10⁵)</u>		
in	235	mL			
Conc.(mg/mL)	0.002979		<u>Sample No.</u>	<u>eV x 10⁵</u>	<u>µg of pentane in 100 mg of coal</u>
					<u>% Pentane in coal</u>
					<u>pentane pounds/US ton</u>
<u>Gas Chromatograph Readings (eV x 10⁵)</u>			1	312.42	173.662
For Standard			2	368.49	0.205
	154.75		3	320.83	0.178
	150.65		4	318.90	0.177
	135.56		5	410.05	0.228
	109.41		6	346.02	0.192
	124.36		7	288.16	0.160
	119.28		8	291.06	0.162
	104.69		9	290.72	0.162
	173.06				
Average	133.97				
%RSD	16.71				
<u>1.5 mL of gas head Space (100 mg coal in 25mL sample vial) injected .</u>					
	1.5	mL/injection			
from	25	mL Sample vial			
	16.67				
Therefore, in Standard 1, amount of pentane per injection					
	4.468	µg/injection of standard			