# HYDROPHOBIC-HYDROPHILIC SEPARATION (HHS) PROCESS FOR THE RECOVERY AND DEWATERING OF ULTRAFINE COAL

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## Abstract

Flotation is regarded as the best available method of upgrading minerals and coal fines. However, its efficiency deteriorates rapidly with decreasing particle size. Further, ultrafine concentrates are difficult to be dewatered economically, forcing companies to discard part of the ultrafine materials to impoundments. To overcome these problems, a new method of separating and simultaneously dewatering ultrafine particles has been developed. Following extensive laboratory-scale test work, the process, known as hydrophobic-hydrophilic separation (HHS), has been tested successfully in continuous operations at proof-of-concept (POC)- and pilot-scale tests. The results show that the HHS process is capable of producing high quality clean coal with high recoveries and low moistures.

## Introduction

Coal preparation plants are designed with up to four parallel processing circuits for treating coarse (> 12 mm), intermediate (12x1 mm) small (1x0.15 mm), and fine (<0.15 mm) particles. The plus 0.15 mm fractions can be effectively cleaned efficiently with gravity separation methods (Wills, 2006). At present, the only commercially viable option for cleaning the finest fraction is froth flotation (Yoon et al., 1999). In flotation, air is dispersed in the form of small air bubbles in a tank in which coal fines are suspended. The small air bubbles selectively collect the hydrophobic coal particles and float to the surface, forming a froth phase which overflows into a launder. As is well known, ultrafine coal particles of less than 30-50 μm are difficult to be collected by the air bubbles, resulting in low recoveries. Furthermore, fine particle flotation suffers from low carrying capacities and poor selectivity due to entrainment problems. (Bethell et al., 2005; Luttrell et al., 2014).

In addition, the froth products containing ultrafine coal are difficult to dewater. Mechanical dewatering in general becomes inefficient with decreasing particle size due to small cake porosity and high surface area, resulting in high moistures (Hucko et al., 1988). The cost often becomes prohibitive with particles of smaller than ~45 μm (Bethell et al., 2005). Moreover, the high-moisture products are difficult to handle and incur high shipping costs and lower thermal efficiencies (Honaker et al., 2013).

Because of the issues concerning fine coal cleaning and dewatering, coal producers are often forced to discard coal fines to waste ponds. The current trend in the U.S. is to deslime fine coal prior to flotation using 15-cm (6-inch) diameter classifying cyclones to remove the bulk of the -45 μm materials (Bethell et al., 2005). A study conducted by National Research Council (NRC) reports that some 70-90 million tons of fine coal is discarded to waste impoundments every year in the U.S. The study also estimated that ~2 billion tons of fine coal has been discarded over the years, out of which 500-800 million tons are in active impoundments (Orr, 2002). These numbers must be much larger now than those reported in the NRC report. The loss of fine coal to impoundments represents not only significant losses of revenue but also environmental concerns. In principle, the finer the coal, the higher the quality of coal if it can be cleaned and dewatered economically.

In this communication, a new concept of cleaning and dewatering fine coal, known as hydrophobic-hydrophilic separation (HHS) process is presented and discussed. Following a series of laboratory tests conducted, a series of proof-of-concept (POC)-scale tests have been tested successfully at Virginia Tech. A variety of cyclone overflows and screen-bowl effluents containing less than 44 μm particles were processed to obtain clean coal products assaying less than 5% ash and 7% moisture at 50 kg/hr clean coal capacity with high coal recoveries. After the successful POC-scale test program, a pilot-plant has been designed and constructed at an operating coal preparation plant. The plant is designed to produce 1 ton/hr clean coal. This article describes the operating principles of the HHS process and presents some of the results obtained to date at the laboratory-, POC- and pilot-scale test programs.

## HHS Process

Figure 1 represents the concept of the HHS process. In Step I, a hydrophobic particle, *e.g.*, bituminous coal, placed in water phase is transferred to a hydrophobic liquid phase above. The process is spontaneous, with its free energy of transfer being negative, *i.e.*, $\Delta G_t < 0$. In Step 2, the hydrophobic particle is removed to a vapor phase. The residual hydrophobic liquid adhering to the surface is evaporated and condensed for recycling. The free energy change associated with the Step II is positive, *i.e.*, $\Delta G_e > 0$. However, the energy required for the vaporization is a fraction (14-16%) of what is required for vaporizing water in thermal drying.

Step I of the HHS process is similar to the two-liquid flotation process, which has been shown to be superior to flotation for the recovery of ultrafine particles (Mellgren and Shergold, 1966; Lai and Fuerstenau, 1968; Shergold, 1976). In two-liquid flotation, hydrophobic particles are collected by oil, while in flotation hydrophobic particles are collected by air. For an air bubble to collect hydrophobic particles suspended in water with a finite water contact angle ($\theta_W$), it is necessary that wetting tension ($\gamma_{SV}$-$\gamma_{SW}$) be lower than the surface tension of water ($\gamma_{WV}$), where the subscripts S, W, and V represent solid, water, and vapor phases, respectively. For an oil droplet to collect a hydrophobic particle with an oil contact angle $\theta_O$, it is likewise necessary that the wetting tension ($\gamma_{SO}$-$\gamma_{SW}$) be lower than the surface tension of water ($\gamma_{WV}$). In general, $\gamma_{SO} < \gamma_{SV}$. It follows, therefore, that $\theta_W < \theta_O$.

Figure 2 shows the contact angles ($\theta_O$) of n-alkanes with n = 4-10 on a bituminous coal in water. As shown, the contact angles are in the range of 94 to 110°, which are well beyond the values obtainable with air bubbles. The captive bubble contact angles ($\theta_W$) of the U.S. bituminous coals are ~65° (Aplan, 1984). Thermodynamically, it would, therefore, be easier to collect hydrophobic particles with oil droplets than with air bubbles. Kinetically, oil-particle attachment should be faster than bubble-particle attachment. For an air bubble to attach on a surface, it must overcome the repulsive van der Waals force, which should slow down the process. On the contrary, the van der Waals forces in the wetting films formed between oil droplets and hydrophobic surfaces are attractive, which should lead to faster collection efficiencies.

The hydrophobic particles transferred to the hydrophobic liquid phase should be free of surface moisture. If hydrophilic particles are suspended in the

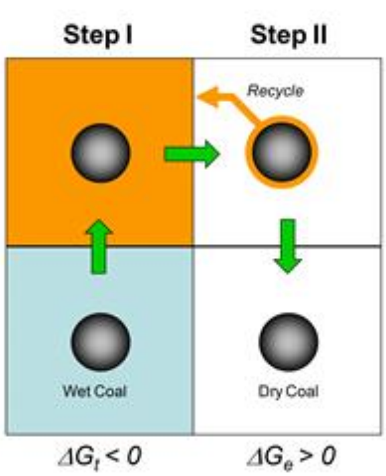


**Figure 1:** Steps involved in the HHS process.

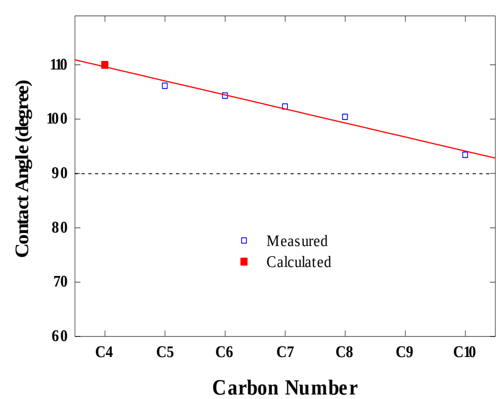


**Figure 2**: Contact angles of *n*-alkanes in water on a bituminous coal in water.

same aqueous phase, they will stay behind and will not enter the organic phase. Therefore, the two liquid flotation process described above can achieve both recovery and dewatering of hydrophobic particles. For cleaning coal fines, the process can be used to separate hydrophobic particles from hydrophilic minerals and at the same time dewater the clean coal product. For obvious reasons, the process is referred to as hydrophobic-hydrophilic separation (HHS).

## Experimental

### *Bench-Scale Tests*

*Procedure:* Testing of the HHS process was initially carried out using a semi-continuous bench-scale circuit (Figure 3). For these tests, a sample of ultrafine coal from a 15 cm (6-inch) desliming cyclone overflow was procured from a processing facility. The sample contained 6-8% solids by weight. Table 1 shows the sample characteristics on dry basis (db). The average heat content of the sample was 5,994 Btu/lb (db). The particles in the slurry were exceptionally fine with about 85% of the particles smaller than 30 μm.

In each test, coal slurry is fed to a reactor, to which a volume of hydrophobic liquid (a short-chain alkane) is added and agitated for mixing. The agitated slurry overflows continuously to an upgrading unit, called Morganizer, in which the water-in-oil emulsions stabilized by hydrophobic coal particles, or the coal agglomerates in which water droplets are entrapped, are mechanically destabilized so that the particles are liberated from the water droplets. The droplets of water separated from coal settle to the bottom of the Morganizer along with the hydrophilic mineral matter and are discharged.

The coal particles, liberated from water droplets and mineral matter and dispersed in oil phase, overflows to a column cell, in which coal particles settle to the bottom and the oil free of coal particles exits the column as an overflow and is recycled. The settled coal-in-oil sludge is fed to a hydrocarbon stripper, in which the light hydrocarbon oil is vaporized, condensed, and recycled. Most of the work was conducted using pentane whose boiling point is 36.1°C.

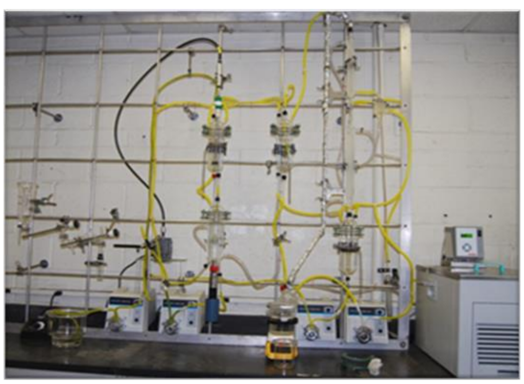

**Figure 3:** Bench-scale HHS process.

**Table 1**: Size-by-size analysis of feed sample.

| Size (mm) | Cumulative Feed Data (db) | | |
|---|---|---|---|
| | Mass (% ) | Ash (%) | Sulfur (%) |
| +0.15 | 0.67 | 3.67 | 0.74 |
| + 0.044 | 8.97 | 3.73 | 0.75 |
| + 0.030 | 15.66 | 6.25 | 0.72 |
| - 0.030 | 100.00 | 60.5 | 0.30 |

**Table 2:** Bench-scale results

| Clean Coal Product | | | Refuse Ash (%) | Comb Rec. (%) |
|---|---|---|---|---|
| Moist. (%) | Ash (%) | Heat (Btu/lb) | | |
| 2.73 | 4.55 | 14090 | 89.74 | 82.98 |
| 1.42 | 4.76 | 14248 | 89.51 | 82.57 |
| 2.21 | 3.72 | 14288 | 90.20 | 83.75 |
| 2.08 | 4.34 | 14215 | 89.86 | 83.18 |
| 3.05 | 4.25 | 14087 | 89.89 | 83.22 |
| 1.82 | 3.40 | 14393 | 90.05 | 83.44 |

*Results:* The results of the laboratory-scale tests are shown in Table 2. As shown, the HHS process reduced the ash content from 65% to 3.4-4.8% with moistures in the range of 1.4-3.1%. With a range of refuse ash of 89-90%, one obtains combustible recoveries of ~83%. Due to the low moisture and low ash contents, the heating values of the clean coal products were >14,000 Btu/lb on an as-received basis. These results show that the HHS process can produce premium fuels from waste products such as desliming cyclones and screen-bowl effluents. The products may also have application as high-value products such as carbon feedstock, pulverized coal injection (PCI), direct reduction, *etc*.

### *POC-Scale Tests*

Based on the successful bench-scale testing, a proof-of-concept (POC) test unit was constructed at Virginia Tech, as shown in Figure 4. For a given test, 6-7 drums of ultrafine (-44 μm) refuse was brought to the facility and homogenized in a 480 gallon sump prior to feeding the POC unit at a 2 gallons per minute (GPM) feed rate.

The feed slurry was contacted with a hydrophobic liquid (pentane in the present work) in two stages of mixing at different intensity levels to obtain agglomerates (or Pickering in-oil emulsions). The agglomerates/emulsions were separated from the

**Figure 4**: POC plant for the HHS process.

aqueous phase and fed to a Morganizer, in which the agglomerates/emulsions are fully dispersed. When fully dispersed, the water droplets and the mineral matter dispersed in them are liberated from coal. The hydrophobic particles dispersed in the hydrophobic liquid was allowed to overflow to a thickener for solid/liquid separation. It was found that the ultrafine coal particles settle fast in an organic (pentane) phase.

The thickener underflow was fed to a pentane recovery system, which consisted of a Holoflight® dual screw dryer operating at 60 °C and a condenser. The spent pentane, including the thickener overflow and the condenser discharge, was returned to the mixing tank, where the feed slurry made its first contact with pentane. The dry coal stripped of the hydrophobic liquid was discharged to the product hopper after passing through a series of two gas-locks.

Table 3 shows the results of the POC-sale tests conducted on different bituminous coals from eastern U.S. They included desliming cyclone overflows and screen-bowl effluents. The former assayed 53.6 to 67.5% ash, which were reduced to 3.4 to 3.9% ash with the product moistures in the range of 3.5 to 8.5%. The combustible recoveries were 79.7 and 86%, which may appear low. However, the ash rejections were 97.5 and 98.3%, demonstrating that the HHS process is highly efficient. Ash rejections represent % ash reporting to tails.

The ash content of the screen-bowl effluents was much lower (7.0 to 13.7% range) as they were effluents from clean coal dewatering centrifuges. With these low-ash feeds, the ash rejection was in the range of 63.0 to 73.9%, and the tailings ash ranged from 64.8 to 79.4%, both of which appeared to indicate poor separation efficiencies. However, the combustible recovery was in the range of 96.7 to 97.7%, demonstrating that the HHS process is a highly efficient separation process even for low ash feeds. It is particularly noteworthy that the moistures of the clean coal products were 2.1 to 5.0% range, despite the fact that the %solids of the feeds were ~3% or ~97% moisture.

The results of the POC-scale tests showed that the HHS process is a highly efficient process for both minerals and surface moisture. Furthermore, the process removes both impurities simultaneously. The separation efficiencies were so high that there was no need to do scavenging and cleaning operations as is usually the case with flotation. The results obtained from a single-stage HHS process were superior to multiple stages of flotation, followed by costly thermal dewatering.

The POC unit tested in the present work yielded typically 25 to 55 kg/hr of clean tons, depending on the ash and solids content of the feed.

***Pilot-Scale Tests***

A pilot-scale facility with a design capacity of 2.5 t/hr of dry solids was next constructed and installed at an operating coal preparation plant in Central

**Table 3:** POC-scale results for the HHS process.

| Location and Sample Source | Feed Ash (%wt) | Product (%wt) | | Refuse Ash (%wt) | Combustible Recovery (%wt) | Ash Rejection (%wt) |
|---|---|---|---|---|---|---|
| | | Moisture | Ash | | | |
| Eastern KY Deslime Cyclone OF | 55.7 | 5.3 | 2.5 | 89.8 | 86.0 | 98.3 |
| Southern WV Deslime Cyclone OF | 53.0 | 8.5 | 3.4 | 84.4 | 79.7 | 97.5 |
| Northern WV Screen Bowl Effluent | 13.7 | 4.9 | 5.0 | 76.3 | 96.7 | 68.0 |
| SW Virginia Screen Bowl Effluent | 7.0 | 3.8 | 2.1 | 64.8 | 97.1 | 72.3 |
| Southern WV Screen Bowl Effluent | 10.7 | 3.8 | 3.1 | 79.4 | 97.7 | 73.9 |

**Figure 5:** Dry clean coal in a product hopper.

Appalachia. The basic design is the same as the POC-scale test facility constructed at Virginia Tech. The pilot-plant is currently undergoing shake-down testing. Preliminary data obtained to date shows that the POC-scale tests were duplicated at the pilot scale.

The feed to the pilot plant is a classifying cyclone overflow with ash content of 56-60%. The clean coal products assayed typically 3.8-4.7% ash and 5.3-12.2% moisture. The average heat content of the clean coal is 13,709 Btu/lb (as-received). It is anticipated that the results will improve further when the shakedown testing is completed, and all of the operational variables for the process are fully optimized. Figure 5 shows a 'dry' clean coal product obtained from the pilot plant.

## Discussion

Froth flotation is regarded as the best available separation process for upgrading coal and mineral fines. However, its efficacy deteriorates rapidly with decreasing particle size, requiring long retention times and multiple stages of cleaning and scavenging operations. Furthermore, flotation concentrates are wet; therefore, a series of dewatering steps are usually required to produce salable products. The cost of dewatering can often be prohibitive for cleaning and dewatering ultrafine coal. Therefore, many companies often discard them to impoundments.

It has been shown in the present work that the hydrophobic-hydrophilic separation (HHS) process can be used to recover coal from the ultrafine refuse that is currently being discarded. The quality of the clean coal products are superior to the clean coal produced at coarser particle sizes in coal preparation plants. The reason for this is due to the fact that mineral liberation improves with decreasing particle size. In effect, the finer the coal, the higher the coal quality. The quality of the products are so high that they may be marketed as specialty fuels, feedstocks for activated carbon, *etc*.

The HHS process has also been tested for upgrading minerals. The laboratory-scale testes conducted to date produced encouraging results.

## Conclusions

A novel separation process known as hydrophobic-hydrophilic separation (HHS) has been developed. The new process has been tested successfully for cleaning and dewatering of ultrafine coal refuse at three different scales, *i.e*., bench-, proof-of-concept (POC)-, and pilot-scales. The results obtained at POC-scale tests are essentially the same as obtained from bench-scale continuous tests. The pilot-scale testing, which is still underway, also produces similar results.

The test results show that the HHS process can produce clean coal containing less than 5% ash and moisture. In general, the product quality improves with finer coal due to improved mineral liberation. Also, the product moisture is independent of particle size as the HHS process is designed to remove surface moisture by displacement. The results obtained at pilot-scale tests produced a practically dry product.

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