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(54) **CLEANING AND DEWATERING FINE COAL**

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See application file for complete search history.

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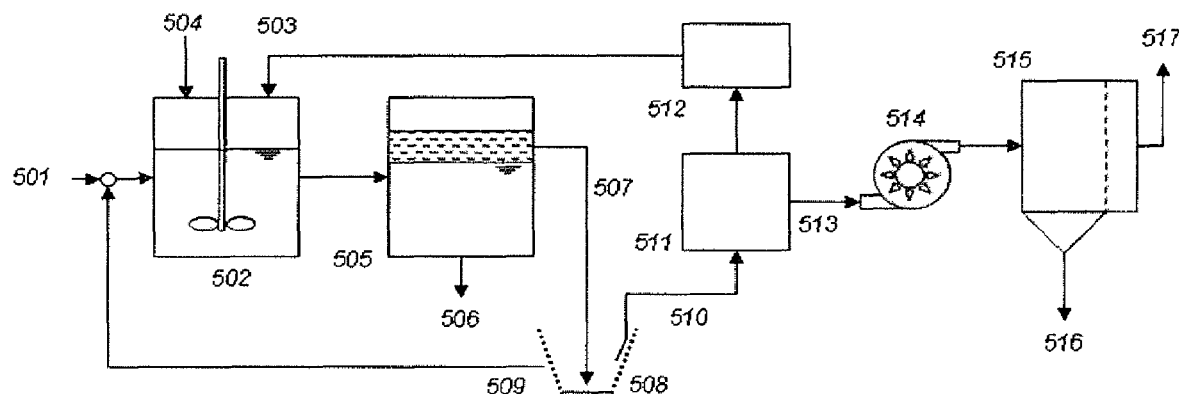
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(57) **ABSTRACT**

Fine coal is cleaned of its mineral matter impurities and dewatered by mixing the aqueous slurry containing both with a hydrophobic liquid, subjecting the mixture to a phase separation. The resulting hydrophobic liquid phase contains coal particles free of surface moisture and droplets of water stabilized by coal particles, while the aqueous phase contains the mineral matter. By separating the entrained water droplets from the coal particles mechanically, a clean coal product of substantially reduced mineral matter and moisture contents is obtained. The spent hydrophobic liquid is separated from the clean coal product and recycled. The process can also be used to separate one type of hydrophilic particles from another by selectively hydrophobizing one.

**16 Claims, 4 Drawing Sheets**



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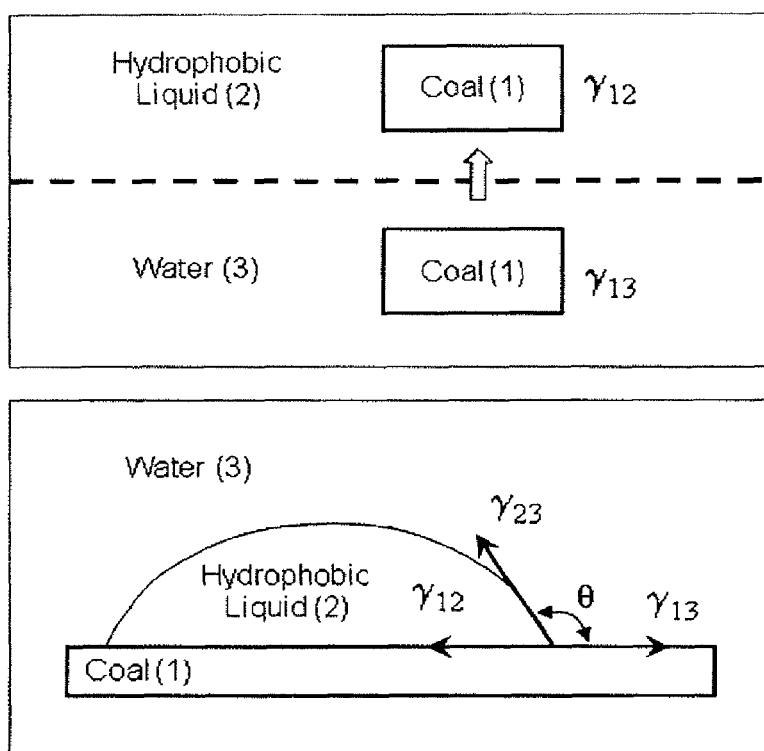


Figure 1

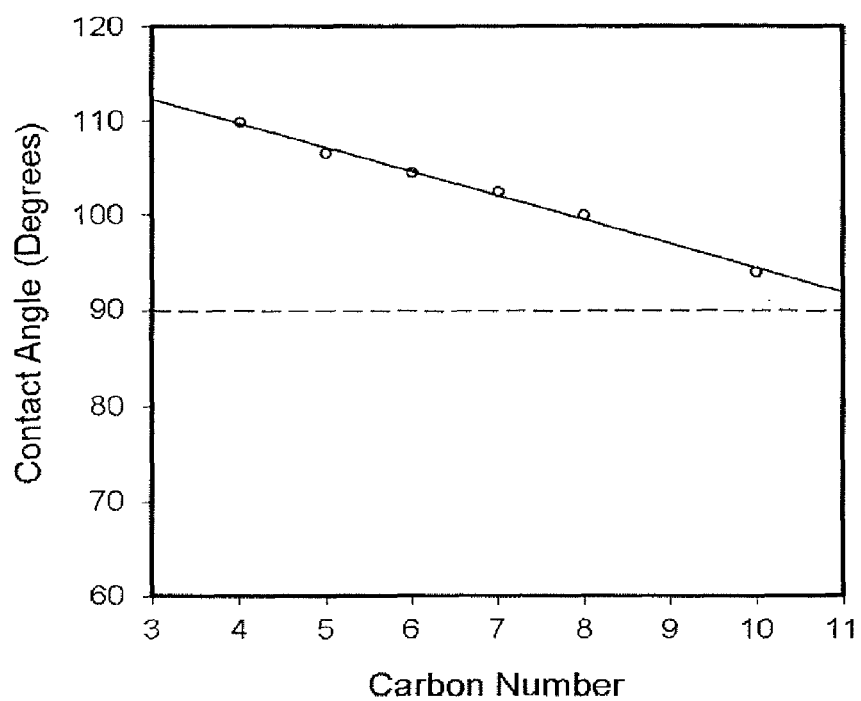


Figure 2

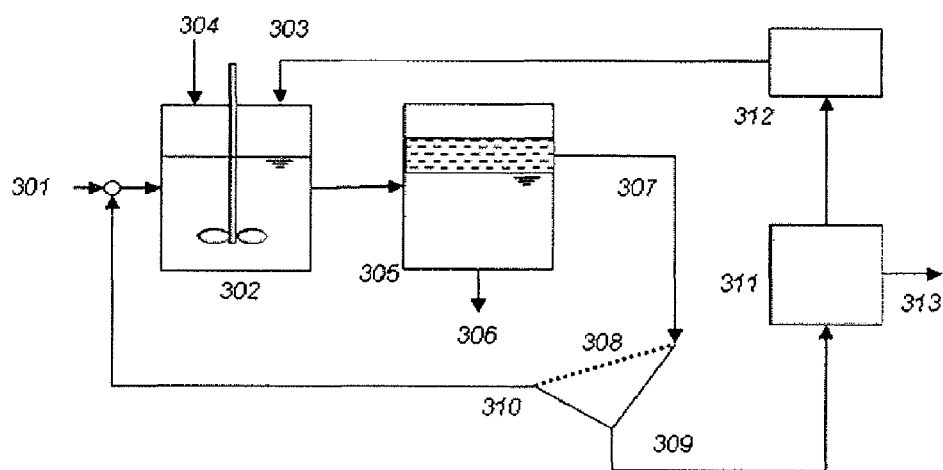


Figure 3

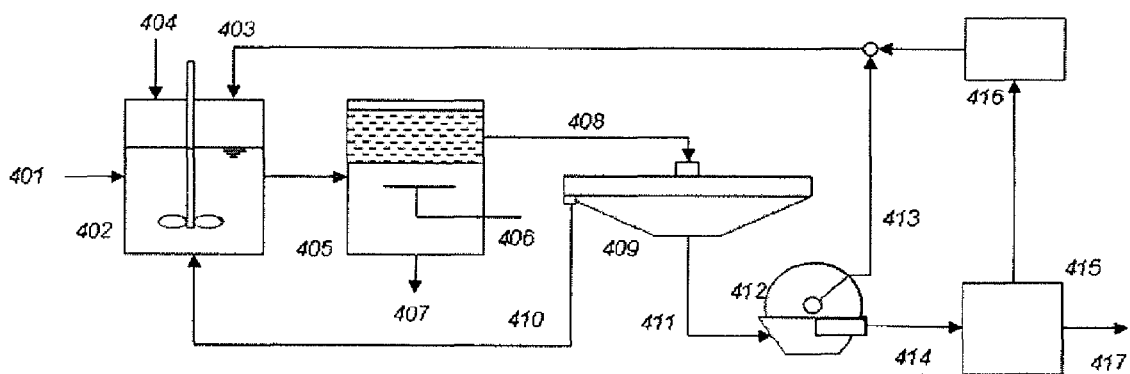


Figure 4

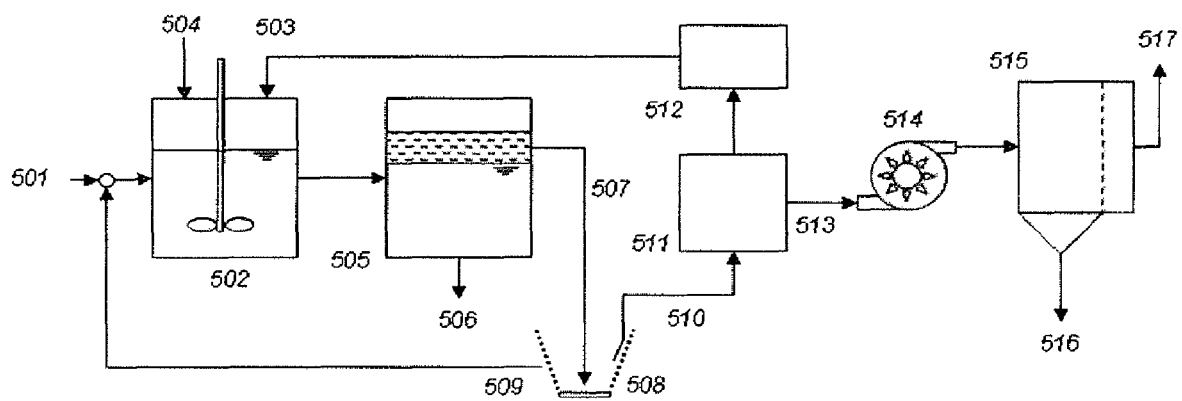


Figure 5

**CLEANING AND DEWATERING FINE COAL****CROSS-REFERENCE TO RELATED APPLICATIONS**

This application is a divisional application of U.S. Non-provisional application Ser. No. 13/576,067, which is a national stage completion of PCT/US2011/023161 filed on Jan. 31, 2011, which claims the benefit of U.S. Provisional Application No. 61/300,270, filed on Feb. 1, 2010, the disclosures of which are incorporated herein by reference.

**STATEMENT OF GOVERNMENT INTEREST**

This invention was made with government support under Grant No. DE-FC26-05NT42457 awarded by the US Department of Energy. The government has certain rights in the invention.

**FIELD OF INVENTION**

The instant invention pertains to methods of cleaning fine coal of its impurities in aqueous media and removing the process water from both the clean coal and refuse products to the levels that can usually be achieved by thermal drying.

**BACKGROUND OF INVENTION**

Coal is an organic material that is burned to produce heat for power generation and for industrial and domestic applications. It has inclusions of mineral matter and may contain undesirable elements such as sulfur and mercury. Coal combustion produces large amounts of ash and fugitive dusts that need to be handled properly. Therefore, run-of-the-mine coal is cleaned of the mineral matter before utilization, which also helps increase combustion efficiencies and thereby reduces CO<sub>2</sub> emissions. In general, coarse coal (50×0.15 mm) can be cleaned efficiently by exploiting the specific gravity differences between the coal and mineral matter, while fine coal (approximately 0.15 mm and smaller) is cleaned by froth flotation.

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 via a mechanism known as hydrophobic interaction. The clean coal product reporting to the froth phase is substantially free of mineral matter but contains a large amount of water. Wet coal is difficult to handle and incurs high shipping costs and lower combustion efficiencies. Therefore, the clean coal product is dewatered using various devices such as cyclones, thickeners, filters, centrifuges, and/or thermal dryers. In general, the cost of dewatering increases with decreasing particle size and can become prohibitive with ultrafine particles, e.g., finer than 44 μm. In such cases, coal producers are forced to discard them. Large amounts of fine coal have been discarded to numerous impoundments worldwide, creating environmental concerns.

Many investigators explored alternative methods of cleaning fine coal, of which selective agglomeration received much attention. In this process, which is also referred to as oil agglomeration or spherical agglomeration, oil is added to an aqueous suspension while being agitated.

Under conditions of high-shear agitation, the oil breaks up into small droplets, collide with coal particles, spread on the surface, form pendular bridges between different coal particles, and produce agglomerates. Nicol, et al. (U.S. Pat. No. 4,209,301) found, that adding oil in the form of unstable oil-in-water emulsions can produce agglomerates without intense agitation. The agglomerates formed by these processes are usually large enough to be separated from the mineral matter dispersed in water by simple screening. Further, selective agglomeration gives lower-moisture products and higher coal recoveries than froth flotation. On the other hand, it suffers from high dosages of oil.

The amounts of oil used in the selective agglomeration process are typically in the range of 5 to 30% by weight of feed coal (S. C. Tsai, in *Fundamentals of Coal Beneficiation and Utilization*, Elsevier, 1982, p. 335). At low dosages, agglomerates have void spaces in between the particles constituting agglomerates that are filled-up with water, in which fine mineral matter, e.g., clay, is dispersed, which in turn makes it difficult to obtain low moisture- and low-ash products. Attempts were made to overcome this problem by using sufficiently large amounts of oil so that the void spaces are filled-up with oil and thereby minimize the entrapment of fine mineral matter. Capes et al. (*Powder Technology*, vol. 40, 1984, pp. 43-52) found indeed that the moisture contents were in excess of 50% by weight when the amount of oil used was less than 5%. By increasing the oil dosage to 35%, the moisture contents were substantially reduced to the range of 17-18%.

Keller et al. (*Colloids and Surfaces*, vol. 22, 1987, pp. 37-50) increased the dosages of oil to 55-56% by volume to fill up the void spaces more completely, which practically eliminated the entrapment problem and produced super-clean coal containing less than 1-2% ash. However, the moisture contents remained high. Keller (Canadian Patent No. 1,198,704) obtained 40% moisture products using fluorinated hydrocarbons as agglomerants. Depending on the types 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 et al., *Coal Preparation*, vol. 8, 1990, pp.1-17).

Smith, et al. (U.S. Pat. No. 4,244,699) and Keller (U.S. Pat. No. 4,248,698; Canadian Patent No. 1,198,704) used fluorinated hydrocarbon oils with low boiling points (40-159° F.) so that the spent agglomerants can be readily recovered and be recycled. These reagents are known to have undesirable effect on the atmospheric ozone layer. Therefore, Keller (U.S. Pat. No. 4,484,928) and Keller, et al. (U.S. Pat. No. 4,770,766) disclosed methods of using short chain hydrocarbons, e.g., 2-methyl butane, pentane, and heptanes as agglomerants. These reagents also have relatively low boiling points, allowing them to be recycled.

Being able to recycle an agglomerant would be a significant step toward eliminating the barrier to commercialization of the selective agglomeration process. Another way to achieve this goal would be to substantially reduce the amount of the oils used. Capes (in *Challenges in Mineral Processing*, ed. by K. V. S. Sastry and M. C. Fuerstenau, Society of Mining Engineers, Inc., 1989, pp. 237-251) developed the low-oil agglomeration process, in which the smaller agglomerates (<1 mm) foamed at low dosages of oil (0.5-5%) are separated from mineral matter by flotation rather than by screening. Similarly, Wheelock et al., (U.S. Pat. No. 6,632,258) developed a method of selectively agglomerating coal using microscopic gas bubbles to limit the oil consumption to 0.3-3% by weight of coal.

Chang et al. (U.S. Pat. No. 4,613,429) disclosed a method of cleaning fine coal of mineral matter by selective transport of particles across the water/liquid carbon dioxide interface. The liquid CO<sub>2</sub> can be recycled. A report shows that the clean coal products obtained using this liquid carbon dioxide (LICADO) process contained 5-15% moisture after filtration (Cooper et al., Proceedings of the 25th Intersociety Energy Conversion Engineering Conference, 1990, August 12-17, 1990, pp. 137-142).

Yoon et al. (U.S. Pat. No. 5,459,786) disclosed a method of dewatering fine coal using recyclable non-polar liquids. The dewatering is achieved by allowing the liquids to displace surface moisture. Yoon reports that the process of dewatering by displacement (DBD) is capable of achieving the same or better level of moisture reduction than the nal drying at substantially lower energy costs, but does not show the removal of mineral matter from coal.

### SUMMARY OF INVENTION

It is an object of the invention to provide a method of cleaning fine coal suspended in water of its mineral matter and simultaneously dewatering the clean coal product by displacing the water adhering to the surface of coal with, a hydrophobic liquid. It is also an object to remove the water entrapped in between the fine particles by subjecting the particulate material to a high-shear agitation in a gaseous phase. In this invention, fine coal refers to coal containing particles mostly smaller than 1 mm in diameter, but the most significant benefits of this invention can be realized with fine coal containing particles less than 0.25 mm.

According to the invention, a hydrophobic liquid is added to an aqueous medium, in which fine coal is dispersed, and the suspension (or slurry) is agitated. Addition of the hydrophobic liquid can take place when the suspension (or slurry) is being agitated. The hydrophobic liquid is chosen so that its contact angle on the coal surface, as measured through the aqueous phase, is larger than 90°. 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. The amount of the hydrophobic liquid to be added should be large enough so that all of the recoverable coal particles can be engulfed (or immersed) into the hydrophobic liquid phase. The coal particles engulfed into the hydrophobic liquid phase are essentially dry because the water in contact with the hydrophobic surface is displaced spontaneously by the hydrophobic liquid during the process of engulfment. However, the dewatering by displacement (DBD) process has a problem in that significant amounts of the process water can be entrained into the organic phase in the fowl of water drops stabilized by hydrophobic coal particles. It is well known that particles with contact angles larger than 90° stabilize water drops in oil phase forming a water-in-oil emulsion (Binks, Current Opinion in Colloid and Interface Science, vol 7, 2002, pp. 21-41). It has been found that much of the water entrained into the hydrophobic liquid phase is present as large globules.

As noted by Keller et al. (Coal Preparation, vol. 8, 1990, pp. 1-17), large globules of water are also formed in conventional oil agglomeration processes, in which the amounts of oil added to aqueous slurry of fine coal are in the range of 5 to 56% by volume (a similar range may be used in the practice of the instant invention; however, other ranges might be used, e.g., 5 to 56% by weight, more than 20% by volume or weight, less than 20% by volume or weight, etc). Obviously, the water-in-oil emulsions are still being formed

during oil agglomeration processes, which may be an explanation for the high moistures of the clean coal products obtained from these processes.

The hydrophobic liquid containing dry coal particles and entrained water as water-in-oil emulsion is phase-separated from the aqueous phase containing hydrophilic mineral matter. In one embodiment of the present invention, the hydrophobic liquid is transferred to a size-size separator, such as screen, classifier, and/or cyclone, to remove the globules of water from the dry coal particles. The smaller size fraction (e.g., screen underflow) consists of the dry coal particles, while the larger size fraction (e.g., screen overflow) consists of the water globules stabilized by coal particles. If the dry coal yield is low, depending on the efficiency of the size-size separation and the size of coal, the larger size fraction can be re-dispersed in water and subjected to another set of agitation and screening to recover additional coal. In a continuous operation, the larger size fraction may be returned to the feed stream to allow the misplaced coal particles to have another opportunity to be recovered. In this embodiment, the larger globules of water can be readily removed. It would be difficult, however, to remove the smaller droplets stabilized by finer coal particles using the currently available size-size separation technologies, making it difficult to obtain effectively dry coal particles containing less than 1% moisture. If such low moistures are not desired, one can increase the cut size of the size-size separation step, e.g., by increasing the screen aperture, to obtain higher moistures, e.g., 5 to 10% by weight. The clean coal product which is now substantially free of mineral matter and surface moisture may then be subjected to a process, in which a small amount of residual hydrophobic liquid is recovered and recycled.

In another embodiment, the water droplets (or globules) are broken up using an appropriate mechanical means such as ultrasonic vibration so that the hydrophobic coal particles are detached from the water droplets (or globules) and dispersed in the hydrophobic liquid. The organic liquid phase in which the coal particles are dispersed is separated from the aqueous phase in which hydrophilic mineral matter is dispersed, and then subjected to appropriate solid-liquid separation means such as settling, filtration and/or centrifugation. The recovered hydrophobic liquid is recycled. The small amount of the hydrophobic liquid that may be adhering onto the surface of the hydrophobic particles (or solids) obtained from the solid-liquid separation step is also recovered and recycled using processes that may involve vaporization and condensation.

In still another embodiment, the hydrophobic liquid, in which dry coal and water globules are dispersed, is subjected to a solid-liquid separation using a centrifuge, filter, roller press, or other suitable separator. In this embodiment, the water-in-oil emulsions become smaller in size by expression and drainage, leaving only very small droplets of water trapped in between particles. In the instant invention, the entrapped interstitial water is released by disturbing the cake structure, in which the small droplets are entrapped, by high-shear agitation. The tiny water droplets may vaporize or exit the system. Thus, a combination of the solid-liquid separation involving expression and drainage and the additional step involving high-shear agitation allows the moisture contents to be reduced to less than 8% by weight, the levels that can usually be achieved by thermal drying. The extent of the moisture reduction can be achieved by controlling the process of high-shear agitation in terms of agitation intensity, duration, and devices employed.



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The hydrophobic liquids used in most of the embodiments of the instant invention are recovered and recycled. Bulk of the liquid is recovered without involving phase changes, while only the small amount of the residual hydrophobic liquid adhering onto the surface of hydrophobic particles (e.g., coal) is recovered by vaporization and condensation. If the liquid has a boiling point below the ambient, much of the processing steps described above are carried out in pressurized reactors. In this case, the small amount of the residual hydrophobic liquid can be recovered in gaseous form by pressure release, which is subsequently converted back to liquid before returning to the circuit. If the boiling point is above the ambient, the hydrophobic liquid is recovered by evaporation. Thermodynamically, the energy required to vaporize and condense the recyclable hydrophobic liquids disclosed in the instant invention is substantially less than that required to vaporize water from the surface of coal particles,

It has been found that the high-shear dewatering (HSD) process can also be used for the clean coal product obtained by a process not involving the DBD or oil agglomeration process described in the instant invention, e.g., flotation. It is necessary, however, that the clean coal product be dewatered by filtration, centrifugation or any other method to produce a cake in which small droplets of water are trapped in between the coal particles. The HSD process can also be used to remove the water from a filter cake formed by hydrophilic particles such as silica and clay.

It is, therefore, an object of the invention to remove inorganic mineral matter from fine coal and simultaneously remove water from the product using a hydrophobic liquid. The invention may be practiced with different types of coal including without limitation bituminous coal, anthracite, and subbituminous coal.

It is another object of this invention to further reduce the moisture of clean coal product to the extent that they can be dried without using excessive heat.

It is still another object of the invention to further reduce the moisture of the particulate materials obtained using dewatering methods such as filtration, centrifugation, or expression, by subjecting them to high-shear agitation.

It is still another object to recover the spent hydrophobic liquid for recycling purposes.

#### DESCRIPTION OF THE DRAWINGS

These and other objects of the invention will be fully understood from the following description of the invention in reference to the figures attached hereto.

FIG. 1 illustrates the concept of dewatering by displacement for coal.

FIG. 2 is a graph showing the contact angles of n-alkane hydrophobic liquids on the surface of a hydrophobic coal immersed in water.

FIG. 3 is a schematic representation of one embodiment for the present invention.

FIG. 4 is a schematic representation of another embodiment of the present invention.

FIG. 5 is a schematic representation of still another embodiment of the present invention.

#### DETAILED DESCRIPTION

Two hydrophobic entities in an aqueous environment are attracted to each other. This is a phenomenon known as hydrophobic interaction. Thus, with reference to FIG. 1a, when a hydrophobic coal particle 1 encounters a hydrocar-

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bon liquid 2 in water 3, the latter can spread on the surface, or the former can be engulfed into the latter, during the course of which the water molecules on the surface are displaced by the hydrophobic liquid.

The process of dewatering by displacement (DBD) may be depicted schematically by FIGS. 1a and 1b. The change in Gibbs free energy per unit area ( $dG/dA$ ) associated with the process is given by the following relationship,

$$dG/dA = \gamma_{12} - \gamma_{13} \quad [1]$$

where  $\gamma_{12}$  and  $\gamma_{13}$  are the interfacial tensions at the coal/hydrophobic liquid and coal/water interfaces, respectively. For the displacement process to be spontaneous,  $dG/dA$  must be less than zero.

FIG. 1b shows the contact angle ( $\theta$ ) measured through the aqueous phase of a hydrophobic liquid placed on a coal surface in water. At the three-phase contact, one can apply the Young's equation:

$$\gamma_{12} - \gamma_{13} = \gamma_{23} \cos \theta \quad [2]$$

in which  $\gamma_{23}$  is the interfacial tension between water and hydrophobic liquid. By combining these two equations, one obtains the following relationship:

$$dG/dA = \gamma_{23} \cos \theta < 0 \quad [3]$$

for the spontaneous displacement (dewatering) of water from the surface of coal. According to this relation, the free energy change becomes negative when  $\theta > 90^\circ$ .

We measured the contact angles of n-alkanes on the polished surface of a bituminous coal sample from the Moss No. 3 coal preparation plant, Virginia. As shown in FIG. 2, the contact angles increased with decreasing chain length, and the contact angles were larger than  $90^\circ$ . Thus, all of the n-alkanes used for the contact angle measurements can be used to displace the water from the coal surface. That the contact angle increased with decreasing hydrocarbon chain length suggests that the shorter chain n-alkanes would be a better hydrophobic liquid to be used to displace the water from the coal surface. An added advantage of using a shorter-chain n-alkane is that they can more readily be recycled than the longer chain homologues due to their lower boiling point. One can also use liquid carbon dioxide, which is a well-known hydrophobic liquid.

The process described above can be used to simultaneously remove both the mineral matter and water from the coal particles dispersed in water. However, it has not been previously recognized that the process has an inherent problem of entrapping water into the clean coal products, as is the case with the selective agglomeration (or oil agglomeration) processes. We have already discussed two mechanisms of entrapping water: one is the entrapment of water in the void spaces formed between the particles constituting agglomerates, and the other is the formation of water-in-oil emulsions. The former may be addressed by using larger amounts of oil as suggested by Keller et al. (Colloids and Surfaces, vol. 22, 1987, pp. 37-50), while the latter can be addressed as disclosed in the present invention.

It is well known that colloidal particles with contact angles ( $\theta$ ), measured through the aqueous phase, that are close to  $90^\circ$  can readily adsorb at an oil-water interface and produce oil-in-water or water-in-oil emulsions (Kinks, Current Opinion in Colloid and Interface Science, vol. 7, 2002, pp. 21-41). For spherical particles, water-in-oil emulsions are formed when  $\theta > 90^\circ$ , while oil-in-water emulsions are formed when  $\theta < 90^\circ$ . The energy ( $E$ ) required to detach a

spherical particle of radius  $r$  from an oil/water interface, whose interfacial tension is  $\gamma_{23}$ , is given by

$$E = \pi r^2 \gamma_{23} (1 \pm \cos \theta) \quad [4]$$

The sign in the bracket is negative for the removal of particles into aqueous phase and positive for removal into oil phase. Eq. [4] suggests that if  $\theta$  is slightly less than  $90^\circ$ , the particles will be held at the oil/water interface and stabilize oil-in-water emulsions. If  $\theta$  is slightly above  $90^\circ$ , however, the particles will be held at the interface forming water-in-oil emulsions. In this regard, it is not surprising that Keller et al. (Coal Preparation, vo. 8, 1990, pp. 1-17) reported the observation of "massive water globules", which was responsible for the high moisture contents of the clean coal products obtained from the selective agglomeration process. This was probably one of the reasons that Keller et al. explored the possibility of using the clean coal products as feedstock for coal-water slurry manufacture.

Eq. [4] suggests also that if coal particles have a high contact angle, the detachment energy ( $E$ ) becomes small and hence they remain dispersed in oil phase. As shown in FIG. 2,  $\theta$  increases with decreasing carbon number of n-alkanes; therefore, a shorter chain n-alkane would work better in the DBD process disclosed in the present invention. On the other hand, the particles (e.g., clay) whose contact angles are well below  $90^\circ$ , they will remain dispersed in aqueous phase. Further, the DBD process should work better with finer particles in the feed, because according to Eq. [4] smaller coal particles should be more readily dispersed in the hydrophobic liquid phase than coarser particles.

Binks et al. (Langmuir, vol. 17, 2001, p. 4708) suggested that Janus particles, i.e., bifacial particles consisting of hydrophilic and hydrophobic surfaces, should improve the stability of the emulsions stabilized by "solid surfactants". Glaser et al. (Langmuir, vol. 22, 2006, p. 5227) showed actually that Janus particles reduce the tension (or excess free energy) at the water/oil interfaces substantially and thereby create favorable conditions for the formation of stable water-in-oil emulsions. Therefore, for cleaning a run-of-the-mine fine coal containing significant amounts of Janus particles (or composite particles), it would be difficult to avoid the formation of water-in-oil emulsions, with a consequence of high moisture products.

Due to the presence of the entrained water, the clean coal products obtained in conventional oil agglomeration processes exhibit high moisture contents, typically in the range of 30-55% by weight. In the instant invention, methods of removing the entrained water have been developed so that the moisture can be readily reduced to substantially lower levels. In one embodiment, the globules of water are removed using a size-size separation method selected from those including but not limited to screens, classifiers, and cyclones. These methods can remove the globules of water that are considerably larger than coal particles.

In another embodiment, the water drops stabilized by hydrophobic coal particles are broken up by appropriate mechanical means such as ultrasonic vibrator, magnetic vibrator, grid vibrator, etc., so that the coal particles are dispersed in the hydrophobic liquid, while the water drops free of coal particles drain into the aqueous phase. The organic phase in which coal particles are dispersed are then phase separated from the aqueous phase in which mineral matter is dispersed. The former is subjected to appropriate solid-liquid separation, while the latter is drained off. The hydrophobic liquid recovered from the solid-liquid separation step is recycled. The clean coal particles obtained from the solid/liquid separation step are substantially free of

surface moisture. However, a small amount of the hydrophobic liquid may be present on the coal surface, in which case the coal particles may be subjected to a negative pressure or gentle heating to recover the residual hydrophobic liquid as vapor, which is subsequently condensed back to a liquid phase and recycled.

In still another embodiment, the drops (or globules) of water are removed using a solid-liquid separation method selected from those including but not limited to filters, centrifuges, and presses. It is believed that much of the entrained water globules are expressed and/or drained during the solid-liquid separation process, leaving behind only the interstitial water droplets entrapped in between the particles constituting a filter cake. The filter cake is then subjected to a high-shear agitation to dislodge the entrapped water droplets from surrounding coal particles and release them to the vapor phase in which they can readily vaporize due to the large surface-to-volume ratio and higher vapor pressure due to large radius of curvature. Some of the released water droplets may exit the system into the atmosphere.

The process of cleaning coal by selective agglomeration requires high-intensity agitation. Nicol et al. (U.S. Pat. No. 4,209,301) stated that high-speed stirrers capable of providing greater than 10,000 r.p.m. are needed to observe phase inversion, i.e., completion of coal agglomerates. It was shown also that the phase inversion is observed after 8 minutes of agitation at 6,000 r.p.m., while it takes 18 minutes at 3,000 r.p.m. In contrast, in the present invention, neither high-speed agitation nor long periods of agitation is necessary. A gentle agitation is usually sufficient, although high energy input in the form of strong agitation or long agitation time has no harmful effect.

FIG. 3 shows an example of the first embodiment of the instant invention. Coal slurry **301** is fed to a mixing tank **302**, along with a hydrophobic liquid **303** recovered downstream and a small amount of make-up hydrophobic liquid **304**. In the mixing tank **302**, the hydrophobic liquid is broken to small droplets, which in turn undergo hydrophobic interactions with coal particles. The mixed slurry is transferred to a phase separator **305**, in which hydrophobic liquid and water are phase-separated. When a sufficient amount of hydrophobic liquid is used, the coal particles are engulfed into the liquid phase, while mineral matter is left behind in the aqueous phase. The latter **306** containing mineral matter is removed as reject, and the former **307** containing both the coal particles free of surface moisture and the globules of water stabilized by coal particles overflows onto a size-size separator (e.g., screen) **308**. The hydrophobic liquid and the coal particles dispersed in it report to the smaller size fraction **309**, i.e., underflow. The coal particles dispersed in the hydrophobic liquid is practically free of surface moisture due to the dewatering (or drying) by displacement (DBD) mechanism depicted in FIG. 1. On the other hand, the globules of water formed and entrained into the hydrophobic liquid phase during mixing **302** and phase separation **305** report to the larger size fraction **310**, i.e., overflow. The overflow stream **310** is returned to the mixing tank **302** to give the misplaced coal particles another opportunity to be recovered to the underflow stream **309** of the size-size separator **308**. The underflow stream **309** consists of clean coal particles and the spent hydrophobic liquid. If the amount of hydrophobic liquid **303**, **304** used in this embodiment is small relative to the amount of the coal in the feed stream **301**, as in oil agglomeration, the underflow **309** would consist mainly of coal particles and a relatively small amount spent hydrophobic liquid adhering to the coal sur-

face. In this case, the underflow **309**, is fed directly to the hydrophobic liquid recovery system **311**, where the spent hydrophobic liquid is recovered by vaporization, and subsequently transformed to liquid **303** by means of a compressor and/or condenser **312** before being returned to the mixer **302**. The solid **313** leaving the hydrophobic liquid recovery system **311** represents the clean coal product with low moisture. The coal recovery and the moisture content of the product coal would vary depending on the efficiency of the size-size separator **308** and the size distribution of the water droplets stabilized by coal particles. For the case of using screen for size-size separation, the use of multiple-deck screens may be useful to control coal recovery and product moisture. If the amount of the hydrophobic liquid reporting to the underflow **309** is small or the cost of the liquid is not insurmountable, one may bypass the recovery system **311**, **312**. When using a large amount of a hydrophobic liquid, it may be separated from the coal present in the underflow stream **309** by solid-liquid separation before feeding the underflow stream **309** to the recovery system **310**, **311**.

FIG. 4 shows another embodiment of the present invention, in which the amount of the hydrophobic liquid used is large. The front end is the same as in FIG. 3 in that coal slurry **401** is mixed **402** with the hydrophobic liquid recovered downstream **403** and added as a make-up source **404**. A novel feature of this embodiment is that the water droplets (or globules) stabilized by coal particles are broken up in the phase separator **405** by means of an appropriate mechanical means **406** (e.g. sonic or magnetic vibrator), so that the coal particles are more fully dispersed in the hydrophobic liquid phase. The aqueous phase containing mineral matter is removed as reject **407**. The overflow **408** from the phase separator **405** is directed to a settler (e.g., thickener) **409**, in which coal particles settle to the bottom and the hydrophobic liquid is recovered as overflow **410** and returned to the mixer **402**. The settled material **411** is then subjected to another type of solid-liquid separation (e.g., filtration) **412**, with the separated liquid (or filtrate) **413** being returned to the mixer **402**. The dry coal product **414** is then subjected to the hydrophobic liquid recovery system **415**, **416** to recover the small amount of the residual hydrophobic liquid adhering to the surface of coal in the same manner as in FIG. 3. The exit stream **417** from the recovery system **415** represents a low-ash and low-moisture clean coal product.

FIG. 5 represents still another embodiment of the instant invention. The front end of the process is the same as the first and second embodiments shown in FIGS. 3 and 4, where coal slurry **501** is fed to a mixing tank **502** which receives hydrophobic liquid recovered downstream **503** and added as a make-up source **504**. The mixture is fed to a phase separator **505**, in which the hydrophobic liquid containing coal and the aqueous phase containing mineral matter are phase separated. The latter is removed as reject **506**, while the former **507** is fed to a solid-liquid separator **508** (e.g., centrifuge), where much of the spent hydrophobic liquid recovered as underflow **509** is returned to the mixer **502**. The overflow **510** containing coal particles, a small amount of residual hydrophobic liquid adhering to the coal surface, and the tiny droplets of water trapped in between coal particles is then fed to the hydrophobic liquid recovery system **511**, **512** to recover the spent hydrophobic liquid **503** for recycle. The discharge **513** from the recovery system **511** may have a desirable amount of moisture for downstream processing such as briquetting. If not, it may be subjected to a high-shear dewatering (HSD) device **514**, in which the tiny droplets of water are dislodged from coal or vaporized

quickly due to the large surface area-to-volume ratio. The exit from the HSD device **514** is fed to a dry coal collection device **515** such as bag house or cyclone, where coal particles are collected as underflow **516** and the liberated water droplets and/or water vapor **517** exit(s) the collection device. The HSD device **513** may be selected from but not limited to dynamic or static mixer, rotating fan, fluidized-bed, vibrating screen, and air jet. The HSD process can reduce the moisture of coal to less than 8%, a level that can usually be achieved by thermal drying. The moisture level can be controlled by adjusting the rate and duration of high-shear agitation. Although the HSD process works well without an external heat source, the use of heated air may facilitate the process or reduce moisture to a lower level.

It has been found that the HSD process can be used not only for drying hydrophobic coal fines but also for drying hydrophilic mineral fines (e.g., minerals in reject **306**, **407**, and **506** in FIGS. 3-5). For the latter, an aqueous suspension of mineral matter or any other hydrophilic particulate materials is dewatered first by using a conventional process, such as centrifuge, filter, or roller press, to form a filter cake, in which a small amount of water is entrapped at the void spaces formed in between the fine particles. The filter cake is then subjected to the HSD method described above.

The hydrophobic liquids that can be used for the processes described in the present invention include hydrocarbon oils, which include aliphatic and aromatic hydrocarbons whose carbon numbers are less than **18**. For the dewatering by displacement (DBD) process, shorter-chain n-alkanes and alkenes, both unbranched and branched, and cycloalkanes and cycloalkenes, with carbon numbers of less than eight may be used so that the spent hydrocarbon oils can be readily recovered and recycled. Liquid carbon dioxide is another hydrophobic liquid that can be used for the DBD process.

When using longer-chain alkanes and alkenes, recycling may be difficult. Therefore, in these instances only small amounts of the reagents are preferably used as agglomerants. The reagent costs can be reduced by using the hydrophobic liquids from unrefined petroleum sources. For the DBD process, ligroin (light naphtha), naphtha and petroleum naphtha, diesel fuel, and mixtures thereof may be used. For selective agglomeration, small amounts of kerosene and heating oils whose carbon numbers are in the range of 12-18 may be used.

The DBD and selective agglomeration processes are ideally suited for separating hydrophobic particulate materials (e.g., high-rank coals) from hydrophilic materials (e.g., silica and clay), with the resulting hydrophobic materials having very low surface moistures. The processes as described in the instant invention can also be used for separating one-type of hydrophilic materials from another by selectively hydrophobizing one but not the other(s). For example, the processes can be used to separate copper sulfide minerals from siliceous gangue minerals by using an alkyl xanthate or a thionocarbamate as hydrophobizing agents for the sulfide minerals. Further, the DBD concept can be used for non-thermal drying of fine coal or any other particulate materials after appropriate hydrophobization.

## EXAMPLES

### Example 1

A volume of pentane was added as a hydrophobic liquid to the coal slurry placed in a 350 ml glass separatory funnel. The coal slurry was received from the Moss 3 coal prepa-

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ration plant, Virginia, at 15% solids by weight. With a stopper in place, the material in the funnel was agitated vigorously by handshaking for 4 minutes and let to stand for phase separation. Coal particles agglomerated (or were engulfed into the hydrophobic liquid) and formed a layer on top of the aqueous phase. By opening the stopcock at the bottom, the aqueous phase was removed along with the mineral matter dispersed in it. The hydrophobic liquid remaining in the funnel was agitated again for a short period of time and let to stand. It was found that large globules of water surrounded by coal particles settled at the bottom. By opening the stopcock, the water globules were removed. This procedure was repeated several times until no visible water globules could be detected. The coal sample left in the funnel was removed, and the pentane was allowed to evaporate completely before analyzing the sample for moisture content. As shown in Table 1, the clean coal product still contained 25.9% moisture, indicating that smaller droplets of water were still present in the form of a water-in-oil emulsion with hydrophobic coal particles acting as a

TABLE 1

No Screening		Screening	
	Recovery* (%)	Moisture (% wt)	
Clean Coal	94.78	25.9	Underflow
Feed	100.00		Overflow
			Feed

\*weight recovery

solid surfactant.

In another test, the clean coal product obtained in the mariner described above was screened at 60 mesh. It was found that the screen underflow assayed only 2.4% moisture, while the screen overflow assayed 58.2% moisture. This example demonstrated that the high moisture content of the clean coal product was due to the presence of the globules of water stabilized by hydrophobic coal particles, which could readily be removed by a size-size separation step to reduce the moisture content substantially.

## Example 2

Another test was conducted in the same manner as described in Example 1 on a fine coal sample (100 meshx0) from the Cardinal coal preparation plant, West Virginia. This sample was much finer than the one used in Example 1, with 80% of the material finer than 44  $\mu$ m. In this example, 800 ml of the slurry at 4.3% solids was placed in a 1 liter separatory funnel along with 200 lb/ton of pentane as a hydrophobic liquid. After agitation and settling, the aqueous phase containing mineral matter was drained off, and the pentane mixed with coal particles was left behind in the funnel. The excess pentane was allowed to evaporate, and the clean coal product analyzed for ash and moisture. As shown in Table 2, the ash content was reduced from 35.6% in the feed to 3.7% with a combustible recovery of 83.7%, but the moisture was as high as 48.7%. The high moisture content was again due to the entrainment of the water droplets stabilized by coal particles.

The procedure described above was similar to the method of dewatering disclosed by Yoon et al. (U.S. Pat. No. 5,458,786), who reported that the moisture of a Pittsburgh coal sample was reduced to 3.6% using liquid butane as hydrophobic liquid. However, the low moisture value

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reported was due to a sampling error. In U.S. Pat. No. 5,458,786, the aqueous phase was drained until the "mixture of butane and coal began to come out of the tubing". It appears now that by the time the drainage process was stopped, most of the water globules settled at the phase boundary had already been drained out. The phase boundary could not be seen because the test was conducted in copper tubing. Also, the mechanism of hydrophobic particles stabilizing water-in-oil emulsions was not known at the time. Yoon et al. failed to

TABLE 2

Product	Ash (%)	Moisture (%)	Recovery* (%)
Clean Coal	3.7	48.7	83.7
Reject	76.2	—	16.3
Feed	35.6	—	100.0

\*combustible recovery

recognize the difficulty in sampling under such circumstances.

## Example 3

The same coal sample used in Example 2 was subjected to another test under identical conditions, except that an additional step was taken to remove the entrained globules of water and obtain low moisture products. The additional step involved the use of a screen to separate the water droplets from the dry fine coal particles obtained by the DBD process depicted in FIG. 1. In this example, the clean coal product obtained using the procedure described in Example 2 was screened to obtain dry coal particles as screen underflow and water droplets as screen overflow. Initially, a 140-mesh screen was used for the separation, in which case the amount of dry coal obtained was only about 25% by weight of the feed. Therefore, the screen overflow was subjected to another stage of the DBD process, and the product was screened again to obtain additional recovery of dry coal. When using a 100 mesh screen, the recovery was significantly higher, but the moisture was also higher because smaller water droplets that passed through the larger screen. Table 3 summarizes the results obtained after several stages of screening. As shown, the moisture was reduced to 4.6%, which was substantially lower than in Example 2. Note also that the process described in this invention disclosure also produced low-ash clean coal products. Thus, the DBD process as described in the instant invention is capable of removing both mineral

TABLE 3

Product	Ash (%)	Moisture (%)	Recovery (%)
Clean Coal	3.8	4.6	75.7
Reject	68.3	—	24.3
Feed	35.6	—	100.0

matter from a fine coal slurry generated at an operating coal preparation plant and the entrained water from the clean coal product.

## Example 4

A volume (600 ml) of the fine coal slurry (100 meshx0) from the Cardinal plant was placed in a 1-liter separatory

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funnel, and pentane was added in the amount of 20% by weight of coal. With the stopper in place, the funnel was vigorously agitated by hand for 2 minutes, and the mixture was allowed to stand for phase separation. The aqueous phase containing mineral matter was removed from the bottom, and the pentane and coal mixture removed from the top. During this procedure, the mineral matter was substantially removed from coal, and most of the pentane evaporated away from the clean coal product. However, the moisture content remained as high as 52.2%, as shown in Table 4, mostly due to the entrained water globules stabilized by hydrophobic coal particles. The clean coal product was dewatered by a horizontal basket centrifuge to reduce the moisture content to 18.2%. The centrifuge product was then fed to a squirrel-cage fan by means of a vibratory feeder. The exit stream from the fan was collected in a small home-made bag house. The collected coal sample assayed 1% moisture, as shown in the table. Thus, the method disclosed in this example produced a dry coal with 1% moisture with the ash content reduced from 36.7 to 8.6% with a 90% combustible recovery. The ash content could have been reduced further, if the clean coal product was re-pulped and cleaned again before the centrifugation and high-shear dewatering (HSD) steps commenced.

TABLE 4

Product	Ash (%)	Moisture (%)	Recovery (%)
H. S. Dewatering	—	1.0	—
Centrifugation	—	18.2	95.3
Agglomeration	8.6	52.2	90.0
Feed	36.7	—	100.0

During the centrifugal dewatering step, the water droplets were reduced in size but still filled the void spaces in between the coal particles. The tiny droplets of entrapped water were then separated from the coal particles by the high-shear agitation in air. The tiny water droplets exited the system and/or evaporated quickly without applying heat due to the high curvature and/or the large surface area-to-volume ratio of the water droplets.

## Example 5

The Cardinal coal sample was treated with 200 lb/ton of pentane in the same manner as described in Examples 2 and 3. The clean coal product was dewatered by means of a vacuum filter rather than a centrifuge as in Example 4. The filter cake was then fed to a squirrel-cage fan to further reduce the moisture to 1.7%, as shown in Table 5. The ash content of the product coal was relatively high due to the entrainment of mineral matter. In a continuous process, this problem can be readily addressed by installing an appropriate agitator or implementing a two-step process.

TABLE 5

Product	Ash (%)	Moisture (%)	Recovery (%)
Clean Coal	12.1	1.7	87.2
Reject	86.6	—	12.8
Feed	49.3	—	100.00

## Example 6

The fine coal sample from the Cardinal plant was subjected to two stages of agglomeration using a total of 360

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lb/ton of pentane. The clean coal product was dewatered using a vacuum filter, and the filter cake dried using a squirrel-cage fan in one test and an air jet in another to obtain 1.4 and 2.1% moistures, respectively. Both of these devices were designed to provide high-shear agitation in air to dislodge the small droplets of water from the fine coal particles that had been dried by the displacement mechanism depicted in FIG. 1. Both of these mechanical devices seemed to be equally efficient in drying fine coal without using an external heat source. The results presented in Table 6 show that the ash contents were substantially lower than obtained in Example 5, which can be attributed to the two stages of cleaning operations employed.

TABLE 6

Product	Squirrel Cage Fan			Air Jet		
	Recovery (%)	Ash (%)	Moisture (%)	Recovery (%)	Ash (%)	Moisture (%)
Clean Coal	87.4	4.7	1.4	87.7	4.3	2.1
Reject	12.6	88.4	—	12.3	88.7	—
Feed	100.0	50.1	—	100.0	50.1	—

## Example 7

A coal sample from the Trans Alta fine coal impoundment, West Virginia, was screened at 100 mesh, and the screen underflow assaying 24.9% ash was treated with pentane (20% by weight of coal) to obtain a clean coal product assaying 8.1% ash and 57.1% moisture with 92.4% recovery. The high product moisture was due to the presence of the water globules stabilized by hydrophobic coal particles. The clean coal product was dewatered using a laboratory-scale horizontal basket centrifuge to reduce the moisture to 21.4%. The centrifuge product was then subjected to a high-shear agitation provided by a squirrel-cage fan to obtain 0.9% moisture. The recoveries for the centrifugation and high-shear agitation were not determined.

TABLE 7

Product	Ash (%)	Moisture (%)	Recovery (%)
H. S. Dewatering	—	0.9	—
Centrifugation	—	21.4	—
Agglomeration	8.1	57.1	92.4
Feed	24.9	—	100.0

## Example 8

A nominally 100 mesh $\times$ 0 coal sample assaying 36.8% ash was obtained from the Litwar coal preparation plant, West Virginia. A size analysis of the sample showed that 7.8% of the material was coarser than 150  $\mu$ m and 80.1% was finer than 44  $\mu$ m. It was cleaned of its ash-forming mineral matter by froth flotation rather than using the DBD or the selective agglomeration processes described in the foregoing examples. A Denver laboratory flotation machine with a 4-liter stainless steel cell was used. The flotation test was conducted with 3 lb/ton diesel oil as collector and 1.2 lb/ton MIBC as frother at 2.6% solids. The froth product was subjected to another stage of flotation test without using additional reagent to obtain a clean coal product with 4.2% ash and 8.3% solids. The product was vacuum-filtered using

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5 lb/ton of sorbitan monooleate as a dewatering aid. The filter cake containing 19.6% moisture was then subjected to a high-shear agitation provided by a squirrel-cage fan to further reduce the moisture to 0.9% by weight.

TABLE 8

Product	Ash (%)	Moisture (%)	Recovery (%)
H. S. Dewatering	—	0.9	—
Filtration	—	19.6	—
Flotation	4.2	91.7	95.8
Feed	36.8	—	100.0

## Example 9

A copper ore sample was ground in a ball mill for 8 to 20 minutes and the mill products were subjected to a series of flotation tests. A composite of the reject materials at 10% solids was dewatered to 15.6% by means of an air pressure filter at 20 psi. The filter cake was then subjected to a high-shear agitation in a squirrel-cage fan to further reduce the moisture to 0.7% as shown in Table 9. In another test, the composite reject material was conditioned with 5 lb/ton

TABLE 9

Product	Pressure Filter at 20 psi		Vacuum Filter at 20 inch Hg	
	Recovery* (%)	Moisture (%)	Recovery* (%)	Moisture (%)
H.S. Dewatering	—	0.7	—	0.6
Filtration	96.0	15.6	95.8	17.5
Feed	100.0	—	100.0	—

\*weight recovery

of a cationic surfactant (Armeen C) at 30% solids and subsequently with 3 lb/ton of sorbitan monooleate before vacuum filtration. The filter cake containing 17.5% moisture was then subjected to the high-shear dewatering process to further reduce the moisture content to 0.6% as shown in Table 9.

## Example 10

In this example, a coal sample from the Pinnacle fine coal impoundment, Wyoming County, West Virginia, was tested for the DBD process. The coal sample was a cyclone overflow from a pond recovery plant containing mostly -44  $\mu$ m materials, which assayed 38% ash by weight. In the plant, the ultrafine coal was not being processed due the difficulties in both recovery, and dewatering. In this example, a volume of the coal slurry was added to a kitchen blender and diluted to approximately 3% solids with tap water. The amount of coal in the mixer was approximately 20 g. After adding 20 ml of pentane to the mixer, the slurry was agitated at a

TABLE 10

Product	Ash (%)	Moisture (% wt)	Recovery (%)
Clean Coal	3.57	4.28	87.27
Reject	81.97	—	12.73
Feed	37.93	—	100.00

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high speed for 45 seconds and then agitated for another 5 minutes at a low speed. During this time, coal particles agglomerated by the hydrophobic liquid, while mineral matter remained dispersed in the aqueous phase. The slurry was then poured over a 30-mesh screen to remove the dispersed mineral matter as underflow. Most of the +30 mesh material, except the largest of the water droplets stabilized by coal particles, was transferred to a stack of screens consisting of 50 and 70 mesh screens. The +50 and -70 mesh fractions assayed 9.8 and 3.2% moistures, respectively. Table 10 shows the composite results of the test, showing that the product moisture and coal recovery can be controlled using size-size separation devices such as screens.

## Example 11

The coal sample used in this example was the same as in Example 10. A volume (1 liter) of coal slurry containing approximately 40 g of coal was added to a kitchen blender (mixer). After adding 0.5 liter of pentane to the mixer, the mixture was agitated at a low r.p.m. The agitated slurry was slowly transferred to a 1-inch diameter phase separator, which was made of a 3/4-inch diameter glass column with a 9-inch height. At the base of the column, an ultrasonic probe was installed to provide a mechanical energy to dislodge the coal particles from the surfaces of the water drops, which tended to congregate at the phase boundary between water and oil due to gravity. The column was also equipped with an overflow launder at the top to collect the clean coal product semi-continuously. With the application of the ultrasonic energy, it was possible to dislodge the coal particles from the water droplets and allow them to be more fully dispersed in the oil phase. Water was then introduced to the base of the settling column to flood the organic phase into the launder, while the aqueous phase was removed from the bottom. The collected coal and ash products were weighed and analyzed for ash and moisture to obtain

TABLE 11

Product	Ash (%)	Moisture (%)	Recovery (%)
Clean Coal	3.9	0.54	94.3
Reject	87.9	—	5.7
Feed	31.2	—	100.0

the results shown in Table 11. As shown, the instant invention produced 94.3% recovery of combustible materials, with the product coal assaying 3.9% ash and 0.54% moisture.

What is claimed is:

1. A method for separating a first hydrophilic particulate material from a second hydrophilic particulate material dispersed in aqueous phase, the first hydrophilic particulate material being different than the second hydrophilic particulate material, the method comprising the steps of:

adding a hydrophobizing agent to said aqueous phase to render the first hydrophilic particulate material selectively hydrophobic;

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agitating a mixture of the selectively-hydrophobized first particulate material and the second hydrophilic particulate material in the presence of a hydrophobic liquid to allow the selectively-hydrophobized first particulate material to be dispersed in said hydrophobic liquid, while the second hydrophilic particulate material remains dispersed in aqueous phase;

phase separating a first phase containing said aqueous phase which includes the second hydrophilic particulate material dispersed therein from a second phase containing said hydrophobic liquid and said selectively-hydrophobized first particulate material, said second phase also containing water entrained by said selectively-hydrophobized first particulate material; providing mechanical energy to said second phase to detach said selectively-hydrophobized first particulate material from said entrained water; and separating said hydrophobic liquid from said selectively-hydrophobized first particulate material.

2. The method of claim 1 further comprising the step(s) of recycling said hydrophobic liquid from said separating step to said mixture in said agitating step.

3. The method of claim 1 wherein said steps are performed without the application of heat.

4. The method of claim 1, wherein said hydrophobizing agent is alkyl xanthate or thionocarbamate and said first hydrophilic particulate material is copper-sulfide minerals.

5. The method of claim 1 wherein said hydrophobic liquid is selected from ligroin, naphtha, petroleum naphtha, petroleum ether, kerosene, diesel fuel, heating oil, and mixtures thereof.

6. The method of claim 1, wherein said hydrophobic liquid is selected from shorter-chain n-alkanes and n-alk-

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enes, both unbranched and branched, cycloalkanes and cycloalkenes, with carbon numbers of less than eight, and liquid carbon dioxide.

7. The method of claim 1, wherein said hydrophobic liquid engulfs said selectively-hydrophobized first particulate material into the hydrophobic liquid phase.

8. The method of claim 1, wherein said separating step is performed with a size-size separator.

9. The method of claim 8, wherein said size-size separator includes a screen.

10. The method of claim 1, wherein said separating step is performed with a solid-liquid separator.

11. The method of claim 10, wherein said solid-liquid separator is a filter.

12. The method of claim 10, wherein said solid-liquid separator is a centrifuge.

13. The method of claim 1, wherein said separating step includes the application of mechanical means to dislodge said selectively-hydrophobized first particulate material from said entrained water so that they are dispersed in the hydrophobic liquid, while the water drains into said second phase.

14. The method of claim 13, wherein said mechanical means includes one or more of the sonic vibrator, ultrasonic vibrator, magnetic vibrator, grid vibrator, jig, and extraction column.

15. The process of claim 1, wherein said separating step includes evaporation and condensation.

16. The method of claim 1, wherein hydrophobizing agent is alkyl xanthate or thionocarbamate and said first hydrophilic particulate material is base-metal sulfide minerals and precious metals.

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