METHOD FOR DEWATERING FINE COAL

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U.S. PATENT DOCUMENTS
3,992,784 11/1976 Verschuur et al. .................. 34/12
4,290,896 9/1981 Gordon et al. .................. 210/710
4,290,897 9/1981 Swihart .................. 44/626
4,484,928 11/1984 Keller, Jr. .................. 44/15 R
4,981,582 1/1991 Yoon et al. .................. 209/164
5,087,269 2/1992 Cha et al. .................. 44/626

OTHER PUBLICATIONS
"Oil Agglomeration For Fine Coal Refuse Treatment," Stuart K. Nicol, World Coal, pp. 14–16.

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ABSTRACT
Fine coals are dewatered in an energy efficient process in which a non-polar liquid or a mixture of different hydrophobic liquids are used to displace the water from the coal surface. This process works with higher rank coals that are naturally hydrophobic so that the coal surface from which the water is displaced has a stronger affinity for the hydrophobic liquid than the water. Thermodynamically, this process is spontaneous and, hence, requires no energy. The only energy required for this process is to recover the spent hydrophobic liquid(s) for recycling purposes. The hydrophobic liquids are recovered in gaseous form either by lowering the pressure or by heating, and coverted back to liquid form for re-use. The most economical reagents that can be used for this purpose include propane, butane, pentane, and ethane. Carbon dioxide can also be used for the dewatering process described in the present invention. The process of dewatering by displacement is capable of achieving the same level of moisture reduction as thermal drying but at substantially lower energy costs.

4 Claims, 4 Drawing Sheets
100: Coal
200: Hydrophobic Liquid
300: Water

Figure 3
METHOD FOR DEWATERING FINE COAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

The invention generally relates to processes and equipment for dewatering fine coal.

2. Description of the Prior Art

Most coals are cleaned at relatively coarse sizes typically in the range of two inches and 48 mesh. Finer coals are often discarded because of the high cost of processing. Although the amount of the fines discarded is relatively small as compared to the coarse particles that are cleaned, it represents a significant loss of valuable resources and creates environmental problems. It is estimated that there are approximately 500—2,000 million tons of the fine coals in abandoned refuse ponds and 500—800 million tons of fines in active refuse ponds in the U.S. Despite the technological advancement made in recent years, the U.S. coal industry is still discarding 30—50 million tons of the fine coal to refuse ponds.

There are two reasons for the high costs of processing fine coals. 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 advance coal cleaning technologies such as microbubble column flotation and selective agglomeration. 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 the fine coal particles. The finer the particle, the larger the surface area and, hence, the more difficult it becomes to dewater the clean coal product. Typically, 100 mesh flotation products contain 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 (i.e., ash-forming minerals) by another (i.e., water), offering no financial incentives for coal companies to clean fine coals. Thermal drying can remove the moisture, but it is costly and usually requires cumbersome permitting processes. The costs of thermal drying is estimated in the range of $2—25 per ton of coal, which are substantially higher than those for mechanical dewatering processes.

Many investigators suggested methods of improving the efficiency of mechanically removing water from bituminous coal fines. These include polymer addition, surfactant addition and use of electrical or acoustic energy to aid in the dewatering process. Some of these methods showed improvements in dewatering rate, but not necessarily in reducing the final moisture content. The use of high pressure filters vastly improved the kinetics and reduced the final moisture contents beyond what can be achieved with conventional vacuum filters; however, the final moisture contents are still far above the levels that can be achieved by thermal drying. Furthermore, the high-pressure filters suffer from high capital and maintenance costs.

The most commonly used mechanical dewatering devices are vacuum filters. With this technique, the fines particles fill the voids between coarser particles in the filter cake, significantly increasing the pressure drop. Various flocculating agents, such as organopolysiloxanes as disclosed in U.S. Pat. Nos. 4,290,896 and 4,290,897, are designed to minimize the blockage by flocculating the particles and thereby increase the filtration rate. Various surfactants have also been used as dewatering aids, the role of which is to increase the filtration rate rather than reduce the final moisture content.

There is an entirely different kind of dewatering problem than discussed above facing the coal industry. The low-rank coals mined in the western U.S. contain 30—35% moisture as they are formed underground. The water in these coals is referred to as inherent moisture as it constitutes an integral part of the coal structure, and is distinguished from the free moisture adhering to the surface of higher-rank coals. The only way to remove the inherent moisture is to subject the coal to high pressure and/or temperature, which is substantially more costly than removing the free moisture from the higher-rank coals such as bituminous coals. There are many different methods of upgrading low-rank coals by removing the inherent moisture.

Some of the low-rank coal beneficiation techniques describe methods of removing water after removing the inherent moisture. For example, U.S. Pat. No. 4,185,395 to Nakako et al. discloses a method in which brown coal mixed with hydrocarbon oil is heated to 100°–130° C. and then passed through a gas-liquid separation process to separate the slurry into a stream containing the hydrocarbon vapor and a dehydrated slurry. The hydrocarbon oil is recycled in the process. The Nakako et al. process suffers from the drawback that it is a thermal drying process which is energy intensive.

The U.S. Pat. No. 3,992,784 to Verschuur et al. also discloses a method of heating an aqueous slurry of brown coal to 150° C. in the presence of hydrocarbon oils. In the example experiments n-C₁₂ hydrocarbon oils have been used to obtain products containing moisture in the range of 31 to 54%.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an inexpensive, less energy intensive means of dewatering fine coal.

According to the invention, a coal slurry is pumped into a mixing chamber along with a gas that can be converted into a non-polar, hydrophobic liquid. The pressure within the chamber is maintained sufficiently high enough to condense the gas into its liquid form. The hydrophobic liquid formed as a result of the condensation displaces the water from the surface of a coal because it has a higher affinity for the hydrophobic coal surface than does the water for the coal surface. When sufficient amount of the hydrophobic liquid is used, each coal particle is completely encapsulated by a film of the hydrophobic liquid without leaving water in between. The mixture of coal, water, and non-polar liquid is then passed into another chamber in which the coal and hydrophobic liquid are phase-separated from the displaced water. The hydrophobic liquid can be recovered from the coal either by lowering the pressure or by increasing the temperature above its boiling point. The recovered hydrophobic liquid is converted back to its gaseous form and recycled.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects, aspects and advantages will be better understood from the following detailed description of the preferred embodiments of the invention with reference to the drawings, in which:

FIG. 1 is a schematic diagram showing the conceptual flow sheet used to dewater fine coals;

FIG. 2 is a schematic diagram showing equipment and...
mizing the loss of the non-polar liquid. Air vent 35 allows the air to escape the condenser 24 after condensation has occurred.

FIG. 3 illustrates another schematic representation of the dewatering process as described in the present invention. It shows that a drop of hydrophobic liquid 200 positioned on a coal surface 100 immersed in water 300. When the hydrophobic liquid displaces the water from the surface, the contact area between the coal and the hydrophobic liquid will increase at the expense of the contact area between the coal surface and water. In order for the displacement to occur spontaneously, the free energy associated with it \( \Delta G_{dew} \) should be negative as follows:

\[
\Delta G_{dew} = \gamma_{12} \gamma_{23} - \gamma_1 \gamma_2 < 0
\]

in which \( \gamma_{12} \) is the interfacial tension between the coal surface 100 and the hydrophobic liquid 200, \( \gamma_{23} \) the same between the hydrophobic liquid 200 and water 300, \( \gamma_1 \) the same between the coal surface 100 and water 300, and \( \gamma_2 \) is the change in the contact area between the coal surface and the hydrophobic liquid.

By dividing Eq. 1 with \( dA \), one can obtain the following relationship:

\[
\frac{dG}{dA} = \gamma_{12} + \gamma_{23} - \gamma_1 - \gamma_2 < 0
\]

in which \( \frac{dG}{dA} \) is the free energy of displacement per unit area. One can substitute the following relationships:

\[
\gamma_1 = \gamma_1 - 2 \sqrt{\gamma_1 \gamma_2} - 2 \sqrt{\gamma_2 \gamma_3}
\]

Eq. 3

\[
\gamma_2 = \gamma_2 - 2 \sqrt{\gamma_1 \gamma_2} - 2 \sqrt{\gamma_2 \gamma_3}
\]

Eq. 4

\[
\gamma_3 = \gamma_3 - 2 \sqrt{\gamma_1 \gamma_3} - 2 \sqrt{\gamma_2 \gamma_3}
\]

Eq. 5

which are generally known as Fowkes equation, and where \( \gamma_1 \) is the surface tension of coal, \( \gamma_2 \) is the surface tension of the hydrophobic liquid, \( \gamma_3 \) is the surface tension of water, the superscript d refers to the dispersion component of the respective surface tension, and the superscript p refers to its polar component. Eq. 2 then becomes:

\[
\frac{dG_{dew}}{dA} = 2(\gamma_1 - \gamma_2 - \gamma_3) + \frac{\sqrt{\gamma_1 \gamma_3}}{\gamma_2} + \frac{\sqrt{\gamma_2 \gamma_3}}{\gamma_1} + \frac{\sqrt{\gamma_1 \gamma_2}}{\gamma_3} < 0
\]

from which one can obtain the following relationship:

\[
2\gamma_2 < (2 \sqrt{\gamma_1 \gamma_3} + 2 \sqrt{\gamma_1 \gamma_2} + (2 \sqrt{\gamma_2 \gamma_3} + 2 \sqrt{\gamma_2 \gamma_3} - 2 \sqrt{\gamma_1 \gamma_3})
\]

which represents a thermodynamic criterion for the dewatering process as described in the present invention.

The term \( 2\gamma_2 \) is the work of cohesion of the hydrophobic liquid, while the first, second and the third terms on the right-hand side of Eq. 7 represent the work of adhesion between coal and hydrophobic liquid, hydrophobic liquid and water, and coal and water, respectively. Therefore, Eq. 7 can be explained qualitatively as follows:
be used for dewatering may be butane which can be liquified
that they are in gaseous form at ambient or room tempera-
time, the non-polar liquid employed within the practice of
the liquid on water minus the work of adhesion on water on
Usually, the work of adhesion of a hydrophobic liquid on
is significantly smaller than that between coal and
hydrophobic liquid. Therefore, the thermodynamic criterion
for dewatering by displacement dictates that the interaction
energy between the hydrophobic liquid and coal should
exceed that between the coal and water, and that the differ-
ence between the two be larger than the work of cohesion of
the hydrophobic liquid.

Based on the thermodynamic reasoning discussed above,
the non-polar liquids that can be used for the dewatering
process as described in the present invention should have as
high affinity as possible for the coal to be dewatered, which
in turn suggests that the coal should be as hydrophobic as
possible. Therefore, the dewatering process based on dis-
placement works only with hydrophobic coals such as the
bituminous and anthracite coals mined in eastern U.S. The
interaction between the coal and hydrophobic liquid is
驱动 by the hydrophobic force, which was first measured
and reported in scientific literature in 1984 by Israelachivili
and Pashley.

Another important criterion for the hydrophobic liquid is
that its work of cohesion be as low as possible. At the same
time, the non-polar liquids employed within the practice of
this invention should have high enough vapor pressure so
they are in gaseous form at ambient or room tempera-
ture, but can readily be converted to liquid form through
application of pressure.

Suitable non-polar, hydrophobic liquids that meet these
criteria include the normal paraffinic hydrocarbons (such as
ethane, propane, butane and pentane), aromatic compounds,
and carbon dioxide. The most ideal non-polar liquid that can
be used for dewatering may be butane which can be liquified
at a pressure between 25—35 psi above atmosphere at
ambient or room temperature. Mixtures of non-polar liquids
(e.g., 5—95% butane and 5—95% propane) can also be used
and may provide benefits in terms of cost and safety of
operation.

EXAMPLE

The process of the present invention will be further
illustrated by the following example. A 400 mesh bitumi-
nous coal from Pittsburgh No. 8 seam was dispersed in tap
water to prepare a 5% by weight of coal slurry. The coal
sample had been stored in a freezer to keep it from loosing
its surface hydrophobicity due to superficial oxidation.
Approximately 75 ml of the slurry was placed in a copper
tubing with two valves on each end. With the tubing
standing vertically, a stream of butane gas was injected
through the valve at the bottom until the pressure was high
enough to convert the gaseous butane into its liquid form.
After closing the valve at the bottom, the mixture of coal,
water and liquid butane was agitated for a few minutes by
shaking the tubing vigorously by hand. The copper tubing
was then let to stand vertically to allow phase-separation.
The water was slowly removed from the tubing by opening
the valve at the bottom. The valve was closed when the
mixture of coal and butane began to come out of the tubing.
At this point, what was left in the tubing was a mixture of
mostly coal and butane in liquid form. The butane was
removed from the coal by opening the valve at the top so that
it can exit the copper tubing as gas. The coal was removed
from the copper tubing and analyzed for moisture. The
product coal assayed 3.6% moisture.

As such, the process is capable of dewatering coals
containing a wide range of moisture (10—98% by weight).
The moisture contents of the product is comparable to those
by thermal drying, but requires significantly less energy.
FIG. 4 illustrates the reason why the dewatering process
described in the present invention should be cheaper than
the thermal drying. In the latter, a large amount heat exceeding
the latent heat of evaporation is required to remove all the
water molecules which are deposited in multilayers. On the
other hand, the dewatering process based on displacement as
described in the present invention requires only the energy
necessary to displace the water molecules in the first mono-
layer. The only significant energy consumption in the
present invention would be to recycle the hydrophobic
liquid, which is minimal as compared to thermal drying.

The displacement of water by an easily recoverable,
non-polar liquid will provide substantial savings in energy
costs since water will not need to be evaporated. Since the
process can handle coal slurries and cakes having a wide
range of solids contents, no other dewatering step is required
to obtain suitable feed. Dust and explosion hazards are also
reduced since no heating is involved. The process is capable
of treating even the finest coal sizes with little difficulty.

While the invention has been described in terms of its
preferred embodiments, those skilled in the art will recog-
nize that the invention can be practiced with modification
within the spirit and scope of the appended claims.

We claim:
1. A method for dewatering bituminous and anthracite
coal fines, comprising the steps of:
adding to a mixture comprised of water and a hydropho-
bic coal selected from the group consisting of bitumi-
nous coal fines and anthracite coal fines, a quantity of
at least one hydrophobic compound which is in a
gaseous state under atmospheric pressure and in liquid
state at higher pressures, said hydrophobic compound
being under pressure and in said liquid state during said
adding step, said quantity of said hydrophobic compo-
und being sufficient to displace water from surfaces
of said hydrophobic coal;
spontaneously displacing water from said surfaces of said
hydrophobic coal while said hydrophobic compound is
in its liquid state;
separating said hydrophobic compound and said hydro-
phobic coal from said water by the steps of
floating said hydrophobic compound and said hydro-
phobic coal on top of said water, and
recovering a binary composition of said hydrophobic
compound and said hydrophobic coal from said
mixture;
reducing the pressure of said binary composition to cause
said hydrophobic compound to change to said gaseous
state and separate from said hydrophobic coal;
collecting dried hydrophobic coal after said step of reduc-
ing pressure; and
recycling said hydrophobic compound for use in said
adding step.
2. The method of claim 1 wherein said hydrophobic
compound is selected from the group consisting of ethane, propane, and butane.

3. The method of claim 2 wherein said hydrophobic compound is butane.

4. The method of claim 1 wherein said step of reducing pressure causes said hydrophobic compound to intermix with air, and wherein step of recycling includes the steps of: pressurizing said hydrophobic compound to cause said hydrophobic compound to change to said liquid state; condensing said hydrophobic compound; and separating said air intermixed with said hydrophobic compound during said releasing pressure step from said hydrophobic compound after condensing during said recycling step.