CHEMICAL COMMUTINATION OF COAL AND REMOVAL OF ASH INCLUDING SULFUR IN INORGANIC FORM THEREFROM

Inventor: Robert G. Aldrich, Manlius, N.Y.
Assignee: Syracuse University Research Corp., Syracuse, N.Y.

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References Cited
UNITED STATES PATENTS
3,815,826 6/1974 Aldrich et al. 241/1

OTHER PUBLICATIONS


Primary Examiner—Granville Y. Custer, Jr.
Attorney, Agent, or Firm—Blum Moscovitz Friedman & Kaplan

ABSTRACT
Treatment of coal with ammonia which contains water, whether the coal is in a sub-surface stratum or in large lumps as mined by standard means weakens interlayer forces at natural interfaces present in the coal. The extent to which the interlayer forces may be reduced by this treatment is such that the coal may be reduced to fragments without application of mechanical force. Further, inorganic compounds present in the coal are unaffected by said treatment, as a result of which inorganic components, and, particularly, sulfur compounds may readily be separated from the coal fragments by known means.

2 Claims, 5 Drawing Figures
FIG. 2

PITTSBURGH SEAM, DISTRICT 3, MARION COUNTY, WEST VIRGINIA - COMPOSITE SAMPLE

LEGEND: --- RAW COAL
------- COMMINUTED COAL

WEIGHT PERCENT RETAINED

0 25 50 75 100

TYLER SIEVE DESIGNATION

FIG. 3

PITTSBURGH SEAM, DISTRICT 3, MARION COUNTY, WEST VIRGINIA - FLOATS AT 1.62 SPECIFIC GRAVITY

LEGEND: --- RAW COAL
------- COMMINUTED COAL

FLOAT- SINK SEPARATION AT 1.62 SPECIFIC GRAVITY

WEIGHT PERCENT OF FLOATED FRACTION RETAINED

0 25 50 75 100

TYLER SIEVE DESIGNATION
FIG. 4

NO. 6 SEAM, DISTRICT 10, MONTGOMERY COUNTY, ILLINOIS - COMPOSITE SAMPLE

LEGEND: --- RAW COAL
--- COMMINUTED COAL

WEIGHT PERCENT RETAINED

100
75
50
25
0

TYLER SIEVE DESIGNATION

60x100 32x60 12x32 9x12 5x9 +5

FIG. 5

NO. 6 SEAM, DISTRICT 10, MONTGOMERY COUNTY, ILLINOIS - FLOATS AT 1.62 SPECIFIC GRAVITY

LEGEND: --- RAW COAL
--- COMMINUTED COAL

FLOAT - SINK SEPARATION AT 1.62 SPECIFIC GRAVITY

WEIGHT PERCENT OF FLOAT FRACTION RETAINED

100
75
50
25
0

TYLER SIEVE DESIGNATION

60x100 32x60 12x32 9x12 5x9 +5
CHEMICAL COMMINUTION OF COAL AND REMOVAL OF ASH INCLUDING SULFUR IN INORGANIC FORM THEREFROM

BACKGROUND OF THE INVENTION

According to usual coal-mining procedures, sub-surface coal is broken into pieces of manageable size by the use of explosives, picks or other mechanical means, and finally brought to the surface mostly in the form of large lumps which are then broken down by mechanical procedures such as crushing, milling, grinding, pulverizing, etc. The degree of reduction in size is suited to the application for which the coal is to be used.

Methods have been disclosed wherein the addition of inorganic or organic salts and weak aqueous solutions have suppressed the formations of fragments in the airborne size range during conventional coal cutting, although no particular advantage was cited in the size reduction processes. (Poelnév. A.P., et al., "Control of Coal Dust in Mines," Akad. Nauk SSSR Sb. Statu 7 (1967), 72.)

The usual methods for the breakage of coal which is found in the natural state as massive solid beds include the use of drilling, cutting or explosive mining techniques as aforesaid. All of these are normally used in conjunction with each other and require an excessive energy expenditure including man power. Since numerous industrial processes which consume coal use the extracted product in particulate form, e.g. ¼ inch size or less, further size reduction operations are required. Each of these subsequent processes employed for further particle size reduction requires large additional expenditures of energy and produces excessive volumes of coal dust, hazardous due to its explosive nature and the effect on the health of workers carrying out the operations.

SUMMARY OF THE INVENTION

The treatment of coal with moist ammonia where the water content may be as high as about 70 percent of the total, results in weakening of the interlayer forces at natural interfaces present in the coal. The weakening of the interlayer forces may suffice to cause fracture of the coal without application of mechanical stress. The weakening of the forces is sufficiently great so that in some cases the coal breaks into particles small enough to be carried by inert fluid or gas without application of further force. Since inorganic materials, and, in particular, inorganic sulfur compounds are unaffected by treatment with moist ammonia, inorganic sulfur-containing compounds as well as other types of ash may be separated from fragmented coal on the basis of size or density. A liquid having a density near 1.60 gm/ml is convenient for carrying out such a separation.

The chemical comminution of coal by means of moist ammonia can be used for mining coal from sub-surface strata by injecting said moist ammonia into a subsurface stratum, following this with the injection of an inert fluid at a rate high enough to form a suspension, and carrying the suspension back to the surface where the comminuted coal is separated from the carrier. A particularly valuable feature of the present invention is the fact that about 90 percent of the comminuted product is plus 32 mesh. Moreover, although there is some increase in the minus 100 mesh quantity, most of this fraction is not so small as to be difficult to separate same from a carrier stream. Consequently, protection against discharge of fines into the atmosphere during processing does not constitute a serious problem. Also, since the inorganic components of the coal are unaffected, most of the impurities of this type can be removed by sieving as well as by flotation.

Since moist ammonia is effective for weakening the interfacial bonds in coal and for fragmentation of certain types of coal, the presence of free water in the coal has little effect on the process other than to decrease the rate of said process.

The process is suitable for deep-mining, strip-mining and auger-mining in that the coal after being comminuted by moist ammonia, with or without the use of mechanical aids, can then be carried to the surface or exterior with an inert gas or liquid. A suitable inert gas is nitrogen and a suitable inert liquid is water.

Accordingly, an object of the present invention is to provide a chemical method for the fragmentation of raw coal.

Another object of this invention is to provide a chemical method for the fragmentation of raw coal in natural beds, seams or sub-surface strata.

A further object of the present invention is to provide a chemical method for the fragmentation of coal either as a step in mining said coal or subsequent to mining of said coal, thereby greatly reducing the energy requirement for mining coal and for fragmenting same.

Another object of the present invention is to provide a chemical method for the fragmentation of coal which produces relatively little fines difficult to separate from air.

An important object of the present invention is to provide a means for particle size reduction of coal without affecting the particle size of rock or mineral impurities.

A significant object of the present invention is to provide a chemical means for fragmentation of coal without detriment to the calorific value of the coal.

A further object of the present invention is to facilitate the separation of inorganic impurities and, in particular, the separation of inorganic sulfur compounds from coal.

Still another object of the present invention is to provide an economical method of mining coal in which the expenditure of mechanical energy is greatly reduced.

Yet a further object of the present invention is the size-reduction of coal without concomitant reduction of size of inorganic components, thereby making it possible to remove said inorganic components from said coal by sieving.

Still other objects and advantages of the invention will in part be obvious and will in part be apparent from the specification.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, which will be exemplified in the method hereinafter disclosed, and the scope of the invention will be indicated in the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a fuller understanding of the invention, reference is had to the following description taken in connection with the accompanying drawings, in which:

FIG. 1 shows schematically the fragmentation and mining of coal in accordance with the method of the present invention;
FIGS. 2, 3, 4 and 5 show the change in size distribution of two different types of coal after treatment with moist ammonia and the size distribution for that portion of the coal having a density less than 1.62.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Ammonia containing moisture in a quantity up to about 7 parts of water to 3 parts of ammonia, when brought in contact with massive coal, quickly impregnates the coal structure, causing a reduction in internal boundary strength. For many types of coal reduction in internal boundary strength is so great that the massive coal system after impregnation has almost no resistance to a crushing force; some coals virtually collapse under their own weight to a finely divided product when so treated. The following is a description of tests carried out on two types of coal and the results achieved.

The two coals were Pittsburgh Seam, District 3, Marion County, W. Va. and Illinois Number 6 Seam, District 10, Montgomery County, Ill. Both coals had previously been crushed to 1/4 inches top size. These coals are of particular interest because they present notoriously difficult problems in the coal cleaning field and are representative of the major coals in the Interior Basin and Appalachian Region. The Pittsburgh Seam coal has the following delivered nominal quality:

- 3.21% moisture
- 6.94% ash
- 2.51% sulfur
- 13,612 BTU.

The Illinois No. 6 seam coal has the following delivered nominal quality:

- 14.8% moisture
- 22.0% ash
- 3.7% sulfur
- 9,500 BTU.

One pound representative samples of the coals were placed in each of two resin kettles and liquid ammonia was introduced into the kettles. The quantity of liquid introduced was sufficient to cover the coal in each case. The kettles were maintained in the open condition and were uninsulated. Following the period designated for comminution, the excess liquid was poured off, and the coal was allowed to stand in air to dry. There was no mechanical agitation at any time.

The results of chemical comminution by means of moist ammonia for varied exposure times are shown for each coal in Table 4. The extent of comminution is indicated by comparison of the material retained on each sieve before and after comminution. It is clear that static fragmentation is achieved with both of these coals although the extent of comminution is variable.

Under the conditions of these experiments, an apparent steady state with respect to the extent of chemical comminution is reached with the Illinois No. 6 coal after 15 minutes. The Pittsburgh Seam coal requires longer exposure under static conditions with effective breakage after 60 minutes in moist ammonia. The moisture content of the ammonia prior to addition to the coal was about 1 percent. It is thought that the lower rate of reaction of the ammonia with the Illinois coal is due to the greater moisture content of this coal. The following Tables show the results achieved:

### TABLE I

**SOURCE: PITTSBURGH SEAM, DISTRICT 3, MARION COUNTY, WEST VIRGINIA**

<table>
<thead>
<tr>
<th>Weight Percent (W/O) Retained</th>
<th>TYLER SIEVE</th>
<th>5×9</th>
<th>9×12</th>
<th>12×32</th>
<th>32×60</th>
<th>60×100</th>
<th>100×00</th>
</tr>
</thead>
<tbody>
<tr>
<td>TREATMENT: RAW—NO COMMINUTION:</td>
<td>61.15</td>
<td>13.74</td>
<td>5.38</td>
<td>9.59</td>
<td>3.99</td>
<td>2.06</td>
<td>4.09</td>
</tr>
<tr>
<td>TREATMENT: LIQUID AMMONIA:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 MINUTES</td>
<td>53.30</td>
<td>16.70</td>
<td>6.40</td>
<td>11.60</td>
<td>4.90</td>
<td>2.40</td>
<td>4.70</td>
</tr>
<tr>
<td>10 MINUTES</td>
<td>49.20</td>
<td>17.00</td>
<td>7.10</td>
<td>13.50</td>
<td>5.60</td>
<td>2.70</td>
<td>4.90</td>
</tr>
<tr>
<td>15 MINUTES</td>
<td>39.50</td>
<td>21.30</td>
<td>8.40</td>
<td>16.50</td>
<td>6.50</td>
<td>2.70</td>
<td>5.10</td>
</tr>
<tr>
<td>60 MINUTES</td>
<td>26.28</td>
<td>20.31</td>
<td>11.91</td>
<td>24.35</td>
<td>8.66</td>
<td>3.21</td>
<td>5.28</td>
</tr>
</tbody>
</table>

### TABLE II

**SOURCE: ILLINOIS NUMBER 6 SEAM, DISTRICT 10, MONTGOMERY COUNTY ILLINOIS**

<table>
<thead>
<tr>
<th>Weight Percent (W/O) Retained</th>
<th>TYLER SIEVE</th>
<th>5×9</th>
<th>9×12</th>
<th>12×32</th>
<th>32×60</th>
<th>60×100</th>
<th>100×00</th>
</tr>
</thead>
<tbody>
<tr>
<td>TREATMENT: RAW—NO COMMINUTION:</td>
<td>59.40</td>
<td>13.30</td>
<td>5.10</td>
<td>10.50</td>
<td>5.00</td>
<td>2.50</td>
<td>4.20</td>
</tr>
<tr>
<td>TREATMENT: MOIST LIQUID AMMONIA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 MINUTES</td>
<td>23.10</td>
<td>15.60</td>
<td>14.80</td>
<td>25.40</td>
<td>8.50</td>
<td>3.50</td>
<td>8.10</td>
</tr>
<tr>
<td>5 MINUTES</td>
<td>24.60</td>
<td>15.40</td>
<td>14.60</td>
<td>26.40</td>
<td>8.20</td>
<td>3.60</td>
<td>8.20</td>
</tr>
<tr>
<td>15 MINUTES</td>
<td>15.40</td>
<td>19.90</td>
<td>16.40</td>
<td>27.40</td>
<td>8.30</td>
<td>3.90</td>
<td>9.30</td>
</tr>
<tr>
<td>30 MINUTES</td>
<td>15.70</td>
<td>19.50</td>
<td>15.40</td>
<td>26.90</td>
<td>9.10</td>
<td>4.10</td>
<td>9.20</td>
</tr>
</tbody>
</table>
Tests with other bituminous coal samples have given similar results. Coals from the Western Interior Basin respond most rapidly to the comminuting environment with, in general, increasing times for coals selected from seams located progressively to the East. For example Iowa Lower Cherokee presents one extreme with substantial size reductions, similar to those shown for Illinois Number 6 blocks several inches in each dimension after less than two minutes exposure to moist liquid ammonia. Pittsburgh Seam Coals are the most difficult bituminous coals to comminute with maximum exposure times of one hour needed to effect the necessary size reduction.

Tests were carried out to establish that the comminution effect could not be attributed to the low temperature of the moist liquid ammonia. In these tests, samples of Illinois Number 6 and Pittsburgh coals were immersed in tap water at room temperature for one hour, cooled in air at an approximate rate of 50°F/hour to 0°F and thawed at room temperature in tap water. No effects were observed to occur during or as a consequence of these processes. Similarly, a sample of Lower Cherokee Coal, the most sensitive coal to the comminuting effects of moist liquid ammonia, was chilled by immersion in a liquid-gas stream of nitrogen for approximately 5 minutes and thawed in air. Microscopic examination indicated that coal breakage had not been effected by the freezing process. It can therefore be concluded that it is the chemical effect of the moist ammonia which has caused weakening or fracture of the interfacial bonds and not the freezing and thawing. However, expansion of the ammonia from the liquid phase to the vapor phase have a role in the process.

Float-sink tests in 1.62 specific gravity tetrachloroethylene were conducted to determine the relative amounts of coal and rock and mineral matter for raw and chemically comminuted samples in each sieve range through 100 mesh. The 100 × 0 fraction was deleted for the attendant difficulties in handling.

FIG. 2 shows graphically the size distribution of raw and comminuted Pittsburgh coal. The large decrease in the +5 fraction and the small increase in the 60 × 100 fraction are particularly significant. FIG. 3 shows the size distribution of that portion of the raw and comminuted coal having a specific gravity less than 1.62, in other words, the organic portion of the coal. Comparison of the values of the various fraction of the untreated coal with and without separation by flotation shows little difference between them. This result implies that the inorganic material is suspended in enough organic material so that the particles float. However, comparison of the +5 fractions of the untreated and treated coal shows that the treated coal fraction is substantially smaller. Consequently, it can be inferred that treatment has separated a large portion of the inorganic matter from the organic matrix, allowing the inorganic matter to sink.

FIGS. 4 and 5 give the results of similar tests on Illinois No. 6 seam coal. Here the reduction in the float portion of the +5 fraction by treatment with moist ammonia is even more striking. Also, as can be seen from FIG. 4, the degree of fragmentation by treatment with moist ammonia is greater than with the Pittsburgh seam coal.

The quantity of coal in the size range 9 × 32 after comminution at the expense of the plus 9 mesh coal with the build-up of relatively few very fine particles is characteristic of fragmentation by moist ammonia. The absence of plus 5 floating material and minus 60 floating material in the case of Illinois Number 6 is especially indicative of the ability of the comminution effect to reduce the size of large pieces with little increase in the range minus 60 mesh. Further, for most of the coals tested, approximately 90 percent of the recoverable coal is plus 32 mesh. This reduction in the amount of fines to be handled is a significant economic factor and greatly simplifies handling, transportation and storage of the cleaned coal fuel.

Table III summarizes the data in analyzing the float and sink portions of each of the sieve fractions of the Illinois Number 6 samples. The samples were analyzed for ash, pyritic sulfur and thermal value.

The data show that the float fraction represents 98 percent of the thermal value of the composite samples with 66 percent less ash and 71 percent less pyritic sulfur than in the original.

Table IV shows results with a similar analysis made from a mechanically ground sample having a similar size distribution.

### TABLE III

<table>
<thead>
<tr>
<th>ANALYSIS OF CHEMICALLY COMMUNICATED SAMPLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLOAT &amp; SINK WEIGHT %</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Float at 1.62</td>
</tr>
<tr>
<td>Sink at 1.62</td>
</tr>
<tr>
<td>Composite</td>
</tr>
</tbody>
</table>

### TABLE IV

<table>
<thead>
<tr>
<th>ANALYSIS OF MECHANICALLY GROUND SAMPLE HAVING SIMILAR SIZE DISTRIBUTION TO THAT OF TABLE III</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLOAT &amp; SINK WEIGHT %</td>
</tr>
<tr>
<td>------------------------</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Float at 1.62</td>
</tr>
<tr>
<td>Sink at 1.62</td>
</tr>
<tr>
<td>Composite</td>
</tr>
</tbody>
</table>
The results achieved by mechanical grinding are equivalent to those for chemical comminution as far as ash reduction is concerned and somewhat inferior with respect to pyritic sulfur. However, it must be noted that separation was carried out by flotation, which is not a production procedure. Separation into organic matter and inorganic matter by sieving would have failed completely, by definition.

Despite fluctuations in total pyritic sulfur content among various samples tested, the results indicate that the comminution process of the present invention consistently yields the lowest overall pyritic sulfur and total sulfur contents. The principal reason, of course, is that the comminution with moist ammonia does not reduce the size of the inorganic impurities, so that either sieving or flotation processes can be used for separation of the ash and pyrite from the coal itself.

For many coals the organic sulfur content lies between 0.4 and 0.7 percent by weight. Other coals such as Pittsburgh Redstone have from 0.7 to 1.0 percent of organic sulfur. Since virtually all of the inorganic sulfur is removable by treatment with moist ammonia, it is evident that there is a huge quantity of coal which can be treated to bring the sulfur content to 1.0 percent or lower.

As aforesaid, the effect of increasing the moisture content in the ammonia is to decrease the rate at which weakening of interfacial bonds and comminution occur. In one test, successive batches of bituminous coal containing up to 11 percent moisture were treated with recycled ammonia. The ratios were 1 pound of ammonia to 10 pounds of coal. Starting with essentially anhydrous ammonia, the water content after treating each successive batch of coal was as follows:

<table>
<thead>
<tr>
<th>Water content of Ammonia</th>
<th>2.0</th>
<th>4.4</th>
<th>7.7</th>
<th>12.1</th>
<th>17.3</th>
<th>20.7</th>
</tr>
</thead>
</table>

The entries in the above Table are given in terms of weight percent of water in the composition.

As aforesaid, the moisture content can range up to about 70 percent of the total of the water-ammonia solution. Even concentrated ammonium hydroxide having an ammonia content of 28–29 percent can be used, but the reaction rate is low. From the standpoint of the kinetics of the reaction, the preferred maximum concentration of water is 25 percent by weight. When the water content of the solution reaches a level such that the kinetics are judged uneconomical, the ammonia can be separated from the water by known means and reused. The quantity of ammonia lost in the process is small, so that the cost of ammonia does not represent a major factor in the economics of the process.

The process has been tested on coals ranging from lignite to anthracite. It has been found effective with all of these types of coal; however, the rate of comminution with anthracite is lower than with the other coals tested. It appears that the rate of comminution is proportional to the inorganic impurity content of the coal. For this reason the the process is particularly important and valuable where the pyrite content is high.

Comminution of coal with moist ammonia can be effectively utilized in the mining of coal where the coal is located either in sub-surface strata or surface strata. A boring tool is first used as a means of reaching a sub-surface coal seam and for providing a passage through which one or more pipes can be inserted into the seam. The pipes essentially seal the passage, and the pipes can be arranged, preferably essentially concentrically, so that moist liquid ammonia and an inert carrier fluid can be brought to the seam (not necessarily simultaneously) and a suspension of comminuted coal can be brought to the surface where the contaminants can be separated from the suspension. An inert gas flowing at high rate can be used and the comminuted coal can be fluidized. Alternatively, the moist ammonia can first be injected or circulated through the coal seam using appropriately placed conduits, and the comminuted coal can then be flushed out with inert gas such as technical grade nitrogen or with water. This latter procedure is particularly suitable for auger and strip mining. The ammonia can be recovered by a suitable process for recycling. The coal particles can then be classified for further size reduction in an ammonia atmosphere, for further contaminant isolation or for direct sale.

FIG. 1 shows schematically how such a process is carried out. Moist liquid ammonia, stored in tank 1 is supplied to pipe 2 and transported therethrough to coal seam 3 lying below the surface of the earth 4. An inert fluid stored in tank 6 is likewise transported through pipe 2 to coal seam 3. The rate of supply of inert fluid is such that coal fragments produced by contact of the moist ammonia with the coal seam are suspended or fluidized and carried upward through pipe 7. From pipe 7 the product is carried to separator 8 which screens the coal fragments from rock and other impurity objects which are of larger size. The fragmented coal is transferred to coal storage bin 9. The ammonia recovered in separator 8 is transferred back to tank 1. Similarly, when an inert gas is used for fluidizing the coal fragments, it is returned to storage tank 6. The various pumps, valves, etc. necessary for the operation are not shown since the provision of such accessories would be well within the skill of one familiar with the art. Furthermore, although pipes 2 and 7 are shown as being concentric, this is merely a matter of convenience since the drilling of only one hole is required with such an arrangement. Also three concentric tubes could as conveniently be used, one to carry the moist ammonia, a second to carry inert gas, and a third to lead the fluidized coal fragments to the surface.

Treatment of coal chunks with liquid ammonia in accordance with the present invention is also useful where the chunk coal is produced mechanically as by a borer or auger.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and, since certain changes may be made in carrying out the above method without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific fea-
3,870,237

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tures of the invention herein described, and all state-
ments of the scope of the invention, which, as a matter
of language, might be said to fall therebetween.

What is claimed is:

1. A method of reducing interlayer forces at natural
interfaces present in coal, comprising the step of treat-
ing said coal with an effective amount of moist ammno-
nia where the ratio of water to ammonia is up to 72:28
by weight.

2. The method as defined in claim 1, where the ratio
of water to ammonia is up to 25:75 by weight.

* * * * *