CHEMICAL COMMINUTION: A PROCESS FOR LIBERATING THE MINERAL MATTER FROM COAL

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Introduction

Conventional coal preparation consists of mechanical size reduction, which results in liberation of the pyritic sulfur and other mineral matter, followed by a separation step, the cost of which is dependent upon the size consist of the crushed coal. In general, as the coal size consist decreases, the amount of liberation of mineral matter and the cost of separation increase. Physical coal cleaning processes are not able to liberate organic sulfur and, therefore, the organic sulfur concentration places an upper limit on the amount of sulfur that can be removed.

Chemical comminution provides a unique way of crushing coal for mineral matter liberation. Instead of mechanical size reduction, the coal is treated with a chemical (usually ammonia gas or a concentrated aqueous ammonia solution), resulting in selective breakage which appears to occur along the bedding planes and along the mineral matter (e.g. pyrite) and maceral boundaries. Washability comparisons of mechanically crushed and chemically comminuted coal samples have indicated that, at a given size consist, more liberation of pyritic sulfur and comparable liberation of ash is possible with chemical comminution. Figures 1, 2, and 3 provide a typical comparison of mechanical and chemical breakage and liberation. The recoveries noted in Figures 2 and 3 only apply to +100 mesh product and, therefore, the -100 mesh weight should be considered when calculating recoveries based upon feed. In terms of decreasing size consist (Figure 1), the following order is found: 1 1/2" top size ROM > chemically fractured > 3/8" top size mechanically crushed > 14 mesh top size mechanically crushed. The same order is found for the ash vs. recovery curves in Figure 2. In contrast, the total sulfur vs. recovery curves (Figure 3) demonstrate that chemical fracture (only 4.53% is <100 mesh) liberates considerably more pyritic sulfur than mechanical crushing even to -14 mesh (21.9% is <100 mesh). Similar results have been found with Redstone, Pittsburgh, and Upper Freeport seam coals (1,2) and with some Iowa coals (3).

The fact that chemical comminution can liberate more of the pyritic sulfur without grinding to small sizes has considerable economic benefits. Although, at this stage in the development, it is difficult to estimate the exact costs of a coal preparation flowsheet using chemical comminution as the size reduction method, some preliminary estimates have been developed. The total capital and operating costs for the chemical treatment alone using ammonia vapor, under conditions shown to be technically feasible in the laboratory, vary from $1.00
to $1.50 per ton of coal product. Using relatively inexpensive density separation techniques, feasible because of the small amount of fines produced in the chemical fragmentation step, would bring the total cost for producing clean coal to between $2.50 - $3.00 per ton product. This is very competitive with other processes currently being considered for producing clean coal. It is envisaged that the chemically comminuted product after cleaning will contain 80-90% less pyritic sulfur and 50-60% less ash, and, in approximately 30-40% of the Northern Appalachian seam coals, will meet EPA new source emission standards.

Because of the commercial significance of chemical comminution, the effect of different reaction conditions have been preliminarily studied to provide some insight into the mechanism of the phenomena. The available information is presented in the following sections and further information is being developed.

Mineral Liberation

Microscopic examination of chemically comminuted coal has been conducted by Greer (4) of Iowa State University using a scanning electron microscope. The results demonstrated that fragmentation due to chemical treatment was strongly controlled by maceral boundaries and other deposits within the material such as pyrite bands.

The above result demonstrates the selective breakage that occurs with chemical comminution and explains why pyrite is liberated during chemical treatment without excessive size reduction. However, the difference between sulfur and ash liberation (Figure 2 and 3) has not been determined. Further petrographic studies of this effect are anticipated.

Effective Chemicals

Although a number of chemicals have some comminution ability (5), the chemicals that appear to have the greatest effect are ammonia (gas and anhydrous and hydrous liquid) and methanol. These compounds fall in a class of chemicals containing a non-bonding pair of electrons (oxygen and nitrogen compounds) which has been shown to swell (6,7) and dissolve (7) coal at ambient temperatures. Although swelling studies have not been conducted by us, it was determined that very little coal (<0.1%) was dissolved by either methanol or liquid anhydrous ammonia. The swelling effect, which has been observed with methanol treated coal by Bangham and Maggs (6), may cause the fragmentation which occurs during chemical treatment. Other analogies between coal solvents and coal comminutants include: (1) a decrease in effect as the coal rank increases, and (2) a reduction in effect as the solvent is diluted with water. Other specific solvents mentioned as good coal solvents (7), such as p-propylamine and pyridine, have been briefly examined. These chemicals do cause fragmentation but are not as effectively as ammonia. Since these chemicals are larger in molecular size, it is possible that molecular size is an important parameter for chemical comminution, especially if penetration of the coal is a rate determining factor.
Effect of Reaction Conditions

The fragmentation caused by chemical treatment is affected by such parameters as moisture, pressure, water concentration in the chemical, starting size of the coal, and preconditioning of the coal before treatment. These effects, using Illinois #6 seam coal as an example, are illustrated in Figures 4-7. Illinois #6 seam coal is very susceptible to chemical comminution and, therefore, the results with this coal are not necessarily representative of other coals. Figure 4 demonstrates the importance of evacuating the reactor before chemical treatment. The contrast in the effect of evacuation between liquid and gaseous conditions is quite apparent. This effect has also been noticed with other coals, although they have not been as demonstrative. For example, all the conditions used in Figure 4 would have no effect on a Pittsburgh seam coal that was examined.

Figure 5 illustrates the effect of pressure and water content and demonstrates that methanol is not as effective a comminuting agent as even a dilute ammonia-water solution. With gas treatment, it appears that a little moisture in the coal aids fracture. Also, when using gas, a change of pressure from 90 psig to 120 psig has considerable impact on the amount of breakage. Determination of any trends with the liquid systems is difficult because the pressure was not held constant.

As might be expected, the initial size of the coal before treatment can effect the size of the treated product. This effect is illustrated in Figure 6.

As noted previously (Figure 4), evacuation before treatment appears to have a considerable effect, especially with gaseous treatment. Evacuation after treatment also appears to have an effect (Figure 7) which may be due to just a difference in reaction time, since reaction in the evacuated sample should stop rapidly while the unevacuated sample may continue to react even after the pressure is removed.

Effect of Coal Type

In general, the chemical fragmentation of coals decreases as the coal rank increases. Figure 8 depicts the size consist of sized samples of Upper Freeport (carbon 70.32%; ash 18.16%) and Illinois #6 (carbon 70.01%; ash 12.52%) seam coals which have been treated under comparable conditions. Illinois #6 coal is slightly lower in rank than Upper Freeport and considerably more breakage occurs. However, a Pittsburgh seam coal, which is lower in rank than the Upper Freeport, would not react at all in liquid anhydrous ammonia at atmospheric pressure and, therefore, the correlation does not always hold. Lignite and anthracite samples have shown some susceptibility to chemical fracture, but not as much as bituminous coals. This slight correlation between rank and comminution may be fortuitous and due instead to differences in micro or macro porosity, maceral content, cleat system, swelling ability (8), mineral matter distribution, or perhaps other factors.
Chemical Reactions

Chemical reactions between the ammonia and coal could have an adverse effect on the recovery of the ammonia and on the amount of NO$_x$ emitted when the coal is combusted. Therefore, the nitrogen content of coal before and after ammonia treatment was determined for a variety of coal seams. The results presented in Table 1 vary slightly for different coals and the increase in nitrogen appears to be in correlation with a decrease in rank. No increase appears to take place with Upper Freeport seam coal, a slight increase (6%) with Pittsburgh seam coal, and approximately a 20% increase with Illinois #6 seam coal when the sample is air dried. However, some of the nitrogen can be removed by hot water washing. In general, the +8 mesh particles show a lower increase in nitrogen than the other sizes. The nature of the chemical reaction that may be taking place is unknown, but there are functional groups (e.g. esters) in coal that could form nitrogen compounds. With Illinois #6 seam coal, the loss of ammonia would still be small (4.4 lbs ammonia per ton of treated coal when a hot water wash is used) and it is unknown whether NO$_x$ emissions would change.

From the above results, it can be seen that considerably more information is necessary before the mechanism of chemical comminution is understood. Studies directed at a better understanding of the phenomena and the effect it has on the chemically treated coal are presently underway.

REFERENCES


<table>
<thead>
<tr>
<th>Coal</th>
<th>Ammonia Treatment</th>
<th>Treatment to Remove Ammonia</th>
<th>Original ROM % in 60°C</th>
<th>Air Dried at 60°C</th>
<th>Air Dried at 60°C and Stared at 100°C for 4 hrs</th>
<th>Air Dried at 100°C for 2 hrs</th>
<th>Air Dried at 100°C for 3 hrs</th>
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<td>Pittsburgh, Green County, PA</td>
<td>180 min., NH₃ gas, 120 psi, 75°F</td>
<td>Air dried, 2 hrs, 60°C</td>
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<td>Upper Freeport, Westmoreland County, PA</td>
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<td>Air dried at 60°C</td>
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Figure 1. Size Consist of Illinois Number 6 Coal Samples (Franklin County, IL)
Figure 2. Ash vs. Recovery Curves Comparing the 3 Hour Chemical Communion to the Mechanical Crushing of the Illinois Number 6 Seam Coal Sample (Franklin County, IL)
Figure 3. Sulfur vs. Recovery Curves Comparing the 3 Hour Chemical Comminution to the Mechanical Crushing of the Illinois Number 6 Coal Sample (Franklin County, IL)
Figure 4. Effect of Preevacuation on Chemical Comminution of Illinois No. 6 Coal

Figure 5. Effect of Reaction Pressure and Water Content in the Coal or Comminuting Agent on Fragmentation of 3/4" x 1/4" Samples of Illinois No. 6 Coal
Figure 6. Effect of Starting Size on Chemical Communion of Illinois No. 6 Seam Coal

Figure 7. Effect of Evacuation After Chemical Treatment of Illinois No. 6 Seam Coal
Figure 8. Size Consist of Illinois No. 6 and Upper Freeport Seam Coals (3/4" x 1/4" starting material) After Chemical Treatment