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A COMPARISON OF COAL BENEFICIATION METHODS

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A COMPARISON OF COAL BENEFICIATION METHODS

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Although iron pyrites and other minerals are removed from coal on an industrial scale almost exclusively by gravity separation methods at the present time, other beneficiation methods are coming into use. Among the developing methods, froth flotation (1,2,3) is the foremost, although the oil agglomeration method (4,5,6) is also promising. Both of these methods take advantage of the difference in surface properties of coal and inorganic mineral particles suspended in water to effect a separation. In the first method the hydrophobic coal particles are removed from the hydrophilic mineral particles by selective attachment to a mass of air bubbles, while in the second method the coal particles are selectively coated and agglomerated by fuel oil and then recovered by screening.

While gravity separation methods are well suited for removing coarse mineral particles from coal, they are generally ineffective for removing microscopic particles. On the other hand, both the froth flotation and oil agglomeration methods offer the potential for recovering and separating coal fines from microscopic impurities, thus complementing the gravity separation methods. However, none of these physical separation methods are effective unless the mineral impurities are first liberated or freed from the coal. Although mechanical crushing and/or grinding have always been used industrially to unlock impurities, the results have not always been satisfactory. Chemical comminution has been proposed as a means to unlock the impurities (7,8,9) and to solve this problem. This method of comminution uses specific chemical agents such as anhydrous ammonia to fragment coal. Since fragmentation occurs along bedding planes and boundaries between coal and mineral matter, the mineral impurities tend to be freed more completely for a given size reduction than would result from mechanical comminution (7).

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In the work described here, high-sulfur bituminous coals from two Iowa strip mines were subjected to a series of 16 different treatments to compare the effectiveness of various beneficiation methods. These treatments involved different combinations of size reduction methods (crushing, pulverizing, grinding, and chemical comminution) and of physical separation methods (gravity separation, froth flotation, and oil agglomeration). The results are compared below on the basis of product yield and on the percentage reduction in sulfur and ash brought about by the treatments.

Experimental

The following methods, equipment, and materials were used for the experimental investigation:

Roll Crushing. Lump coal (4 cm x 0) was crushed to 6 mm top size by passing it through a bench-scale double roll crusher manufactured by Smith Engineering Works, Milwaukee, WI.

Pulverizing. Previously crushed coal was pulverized to -35 mesh by a Mikro-Samplmill manufactured by Pulverizing Machinery Division, American-Marietta Co., Summit, NJ.

Ball Milling. Previously pulverized coal was ground to -400 mesh size in a ceramic jar mill. For this operation 200 g coal, 1000 g water, and 1900 g flint pebbles were placed in a 5.7-L jar mill, and the mill was then run for 20 hr.

Chemical Comminution. For this operation 500 g lump coal (4 cm x 0) were placed in a 2000-ml Erlenmeyer flask which was then placed in a cold bath of dry ice and methanol and cooled to -70°C. Liquid anhydrous ammonia was then added to the flask until the coal was immersed in the liquid. After the coal had soaked for 1.0 hr, the flask was removed from the cold bath and was placed in a well ventilated hood where the ammonia evaporated. When the odor of ammonia could no longer be detected, the comminution step was completed.

Gravity Separation. To effect the gravity separation of coal and mineral matter, 500 g crushed coal (6 mm x 0) were added to 2000 ml tetrachloroethylene (specific gravity = 1.613) in a large beaker placed in a well ventilated hood. The mixture was stirred by hand to insure wetting of all particles, and then it was allowed to stand for 30 min. The float product was subsequently skimmed off and placed on a 100-mesh sieve to allow any adhering liquid to drain away. The float product was then placed in a drying oven at 100°C for 4 hr.

Froth Flotation. To conduct a froth flotation test, 200 g pulverized coal (-35 mesh) were added to 2000 ml tap water in a bowl of a laboratory model Wemco Fagergren flotation cell. With the agitator running, the pH of the slurry was lowered below 5 by adding 10 ml acid solution containing 10 vol % concentrated hydrochloric acid. Both kerosene (1.0 ml) and methyl isobutyl carbinol (0.5 ml) were added to the agitated slurry, and the air flow to the cell was set at 9.3 L/min. The resulting froth was collected until it appeared that no more coal was being recovered. The material remaining in the bowl was poured out, the froth product was put back in the bowl, and fresh tap water was added to bring the slurry volume to 2000 ml. With the agitator running, the pH of the slurry was raised above 9 by adding 40 ml base containing 5 wt % potassium hydroxide. The coal was then refloated without adding further reagents and using the same air flow rate as before. A two-stage separation was made because a low pH seemed to favor the removal of ash whereas a high pH seemd to favor the removal of pyrite.

Oil Agglomeration. Oil agglomeration tests were carried out with a 14-speed kitchen blender (Sears Insta-Blend Model 400) which held up to 1200 ml fluid. For an agglomeration test, 200 ml of an aqueous slurry containing 10 wt % coal was placed in the blender together with 10 ml of solution containing 0.2 wt % sodium carbonate. The sodium carbonate not only increased the pH of the slurry but also served as a dispersing agent for the clay particles. The slurry was agitated for 5 min at the lowest speed. An emulsion of fuel oil and water was then added to the coal slurry, and the agitation continued for another 5 min at the same speed to form agglomerates. The emulsion was prepared by combining 2.0 ml of a mixture of No. 1 fuel oil (86 vol %) and No. 5 fuel oil (14 vol %), the mixture having a specific gravity of 0.83, with 200 ml tap water and emulsifying the mixture with an ultrasonic vibrator. The agglomerated coal slurry was poured into a 1000-ml separatory funnel whereupon the coal floated to the surface, and the refuse particles settled to the bottom. The water and refuse were drained out through the bottom opening, and the agglomerated coal was put back in the blender and mixed with 200 ml fresh tap water. After agitating the mixture for 2 min at the lowest speed, the coal slurry was poured back into the separatory funnel where the agglomerated coal was recovered again. This washing operating was repeated once more to reduce entrapped impurities.

Chemical Analysis Methods. Coal samples were analyzed for sulfur and ash by the standard ASTM procedures (10).

Materials. Coal from two Iowa strip mines was used for this investigation. A channel sample from the ICO mine and a run-of-mine sample from the Jude mine were the source of the materials used. The proximate analysis and sulfur distribution of each of these samples are shown in Table I. Although the sulfur and ash contents of these samples were widely different, the samples represented coal of the same rank (high volatile C). Investigation of the coal microstructure with a scanning electron microscope revealed substantial amounts of finely disseminated microcrystals of iron pyrites (11,12).

Each coal sample was crushed to 4 cm top size and then was divided into three size fractions (4 cm x 1 cm, 1 cm x 48 mesh, and 48 mesh x 0). Each size fraction was then float-sink tested

Table I. Composition of Coal from ICO and Jude Strip Mines

	Percent by Weight	
Type of Analysis	ICO	Jude
Proximate analysis		
volatile matter	44.0	39.4
fixed carbon	43.2	37.6
moisture	4.5	8.8
ash	8.3	14.2
total	100.0	100.0
Sulfur distribution		
pyritic	2.41	2.97
sulfate	0.05	0.44
organic	0.99	3.53
total	3.45	6.94

at various specific gravities using organic liquids of known specific gravity. The standard Bureau of Mines procedure was used for this test (13). The data for the different size fractions were combined to provide the composite washability analysis for 4 cm x 0 coal shown in Table II.

Treatment Results

The sequence of steps involved in each of the 16 treatments which were applied to each of the two coal samples is shown in Figure 1. The first treatment was the simplest and involved crushing with the roll crusher, pulverizing with the Mikro-Samplmill, and oil agglomeration. The second treatment included a ball milling step in addition to the other steps. The third and fourth treatments included a froth flotation step. In the fifth through eighth treatments the crushed coal was subjected to gravity separation before being pulverized and otherwise treated as in the first four treatments. In the last eight treatments the coal was chemically comminuted before being conducted through the roll crusher. Following the chemical comminution step, the pattern of treatments was the same as for the first eight treatments. The final step of each treatment was an oil agglomeration step.

After each separation step within any given treatment, the weight of coal recovered was measured after drying the material

Table II. Composite Washability Analysis of Coal (4 cm x 0) from ICO and Jude Strip Mines

Product Fraction	Direct Data (%) Weight	Direct Data (%) Ash	Direct Data (%) Sulfur Total	Cumulative Data (%) Weight	Cumulative Data (%) Ash	Cumulative Data (%) Sulfur Total
ICO Coal						
Float 1.30	78.7	5.36	1.80	78.7	5.36	1.80
1.30 - 1.35	6.3	11.98	2.74	85.0	5.85	1.87
1.35 - 1.40	2.8	15.63	3.66	87.8	6.16	1.93
1.40 - 1.45	2.9	16.84	4.18	90.7	6.50	2.00
1.45 - 1.50	2.0	20.47	4.83	92.7	6.80	2.06
1.50 - 1.55	1.5	22.50	4.01	94.2	7.05	2.09
1.55 - 1.60	0.5	25.39	6.46	94.7	7.15	2.11
Sink 1.60	5.3	42.05	17.57	100.0	9.00	2.93
Jude Coal						
Float 1.30	46.5	5.67	5.07	46.5	5.67	5.07
1.30 - 1.35	19.0	12.03	4.83	65.5	7.51	5.00
1.35 - 1.40	7.6	15.84	5.24	73.1	8.38	5.03
1.40 - 1.45	7.1	19.94	6.41	80.2	9.40	5.15
1.45 - 1.50	3.9	23.80	7.91	84.1	10.07	5.28
1.50 - 1.55	3.0	28.30	7.53	87.1	10.70	5.36
1.55 - 1.60	1.7	31.51	6.79	88.8	11.10	5.38
Sink 1.60	11.2	48.92	12.84	100.0	15.33	6.22

overnight in an oven at 80°-100°C. A small sample of the dried coal was subsequently analyzed for ash and pyritic sulfur. The percentage reduction in either ash or sulfur content was found for each separation step and for the overall treatment by using the relation:

$$\text{Reduction (\%)} = \frac{\text{content of feed - content of product}}{\text{content of feed}} \times 100$$

The yield of coal for each separation step and the total yield for the overall treatment were determined as follows:

$$\text{Yield (\%)} = \frac{\text{dry weight of product}}{\text{dry weight of feed}} \times 100$$

In the case of oil-agglomerated coal, the yield determined in this manner included the small amount of oil which was not vaporized during oven drying. Therefore, to express the yield on an oil-free as well as on a moisture-free basis, the calculated yield was reduced by 2%. It was assumed that losses of materials in the crushing and pulverizing steps was negligible.

Figures 2, 3, and 4 show the cumulative effects of the different separation steps within each treatment as well as the overall results of each treatment. In general the results were quite varied between treatments and between coals. Thus in the case of ICO coal, the overall yield varied among the different treatments between 74 and 96%, the overall reduction in pyritic sulfur content between 12 and 87%, and the overall reduction in ash content between 22 and 72%. Similarly in the case of Jude coal, the overall yield varied among the different treatments between 75 and 92%, the overall reduction in pyritic sulfur content between 31 and 88%, and overall reduction in ash content between 34 and 84%.

Although the first separation step of a multistep treatment produced the greatest reduction in level of impurities, subsequent separation steps also removed significant amounts of sulfur and ash (Figures 3 and 4). Hence, the separation methods appeared to be complementary, particularly when used in conjunction with particle size reduction.

Among the various treatments, treatment 16, which included all of the comminution and separation steps, produced the cleanest product from ICO coal. This product, recovered with an overall yield of 78%, contained only 2.3% ash and 0.3% pyritic sulfur which represented an overall reduction of 72% in ash content and 87% in pyritic sulfur content. Treatments 8, 12, and 14 were nearly as effective in removing sulfur and ash from ICO coal and provided higher yields than treatment 16.

Treatments 8, 14, and 16 were about equally effective in removing sulfur and ash from Jude coal. The product of these treatments contained about 0.4% pyritic sulfur and 2.2-2.7% ash which represented an overall reduction of 86-88% in pyritic sulfur content and 81-84% in ash content. However, treatments 14 and 16 provided a larger overall yield (84%) than treatment 8 (75%).

The relative efficiency of the various treatments is illustrated by Figures 5 and 6 in which the overall yield of product is plotted against the corresponding pyritic sulfur or ash content. The upper curve in each diagram is drawn through the points representing the treatments which provided the highest yields for the corresponding levels of impurities. Thus for ICO coal treatments 2, 10, 12, 14, and 16 were the most efficient from the standpoint of sulfur removal and treatments 2, 6, 8, 14, and 16 from the standpoint of ash removal. Similarly for Jude coal treatments 10, 11, 12, and 14 were the most efficient from the standpoint of sulfulr removal and treatments 10, 12, 14, and 16 from the standpoint of ash removal. For the most part, these treatments had two things in common. Thus, except for treatment 11 applied to Jude coal, all of the treatments involved fine grinding before the oil agglomeration step. In addition, except for treatments 2 and 6 applied to ICO coal, all of the treatments involved chemical comminution.

The upper curve in each diagram of Figures 5 and 6 illustrates the trade off between overall yield and level of impurities in the product. The yield fell off as the level of impurities was reduced through application of treatments of greater and greater complexity. With ICO coal the drop in yield was quite precipitous when the pyritic sulfur content was reduced below 0.5% or the ash content below 2.5% (Figures 5 and 6). Therefore for this coal, treatments 14 and 16, which provided the cleanest coal but at considerable sacrifice in yield, would be especially hard to justify.

Nearly all of the treatments described by Figure 1 were more efficient than single-stage gravity separation of 4 cm x 0 coal. The yield and corresponding ash content provided by gravity separation of the coarse materials in liquids of different specific gravity are represented by the washability curves in Figure 6. For either kind of coal the yield fell off sharply as the ash content was reduced to lower levels by separation in lighter liquids.

A comparison of the results of the first separation step of each of the various treatments indicates the relative efficiency of the different separation methods which were used. Thus in the case of ICO coal, the froth flotation step of treatments 11 or 12 reduced the pyritic sulfur content more than the first separation step of any other treatment, and the froth flotation step of treatments 3 or 4 reduced the ash content more than the first separation step of any other treatment. Also the respective froth flotation steps provided the highest yields for the level of impurities attained. The gravity separation step of treatments 5-8 was nearly as efficient in reducing the ash content of ICO coal as the froth flotation step of treatments 3 or 4, but it was not as efficient in reducing the sulfur content. However, gravity separation was applied to coarser material than froth flotation. In the case of Jude coal, the gravity separation step of treatments 13-16 provided the greatest reduction in pyritic sulfur and ash contents of any of the first-step separations as well as the highest yield for the level of impurities attained. The next most effective first-step separation was that provided by oil agglomeration of ball-milled Jude coal in treatment 10. This step reduced the ash content of Jude coal almost as much as the gravity separation step and also produced a higher yield. On the other hand, it was not nearly as effective in reducing the pyritic sulfur content as the gravity separation step of treatments 13-16.

It has already been noted that generally the most efficient treatments involved fine grinding and chemical comminution. To examine the effect of fine grinding further, the overall results

Table III. Effect of Grinding on Overall Results

	Excluded (Odd Trt.)	Included (Even Trt.)
ICO coal		
ash reduction	47	55
pyritic sulfur reduction	58	67
yield	83	87
Jude coal		
ash reduction	65	71
pyritic sulfur reduction	61	71
yield	82	84

of the even-numbered treatments which included fine grinding and the overall results of the odd-numbered treatments which excluded this step were averaged separately. The two sets of values which are presented in Table III indicate that on the average the treatments which included fine grinding produced a cleaner product in greater yield than the treatments which did not include it. Therefore it appears that fine grinding is a very effective means for improving the separation of pyrite and other ash-forming minerals from both ICO and Jude coals.

Similarly to study the effect of chemical comminution further, the overall results of the last eight treatments which included this step and the results of the first eight treatments which excluded this step were averaged separately. The two sets of values (Table IV) indicate that on the average the treatments wich included chemical comminution provided a cleaner product than the treatments which did not. Also with Jude coal, but not with ICO coal, a larger yield was provided on the average by the treatments which included this step. Therefore, at least for Jude coal, chemical comminution is an effective method of improving the separation of mineral impurities.

The effectiveness of the gravity separation step was also evaluated further by averaging the overall results of the treatments which included it and the results of the treatments which excluded it separately. The average reduction in both pyritic sulfur and ash was much greater for those treatments which included this step than for those which excluded it (Table V). Although the average product yield was lower for the treatments which included gravity separation, the penalty in yield was rather modest for the large reduction in level of impurities which was achieved.

Table IV. Effect of Chemical Comminution on Overall Results

	Excluded (Trt. 1-8)	Included (Trt. 9-16)
ICO coal		
ash reduction	50	52
pyritic sulfur reduction	55	70
yield	88	82
Jude coal		
ash reduction	63	73
pyritic sulfur reduction	63	68
yield	80	86

Table V. Effect of Gravity Separation on Overall Results

	Excluded (Trt. 1-4,9-12)	Included (Trt. 5-8,13-16)
ICO coal		
ash reduction	41%	62%
pyritic sulfur reduction	51%	74%
yield	88%	82%
Jude coal		
ash reduction	60%	76%
pyritic sulfur reduction	54%	77%
yield	86%	80%

Table VI. Effect of Froth Flotation on Overall Results

	Excluded (Trt. 1,2,5,6, 9,10,13,14)	Included (Trt. 3,4,7, 8,11,12,15,16)
ICO coal		
ash reduction	40%	62%
pyritic sulfur reduction	50%	75%
yield	87%	83%
Jude coal		
ash reduction	61%	74%
pyritic sulfur reduction	56%	75%
yield	84%	82%

The effectiveness of the froth flotation step was also evaluated by comparing the average overall results of the treatments which included this step with the average results of the other treatments Table VI). Here again the treatments which included this method of separation provided a much cleaner product than those which did not include it while experiencing only a modest reduction in yield. The effectiveness of froth flotation was very similar to that of gravity separation, although the two methods were applied to different sizes of coal.

The results of the individual steps of oil agglomeration and froth flotation were averaged to compare the effectiveness of one method against the other. Also in the case of oil agglomeration, the results of agglomerating -35 mesh coal were averaged separately from the results of agglomerating -400 mesh coal to determine the effect of particle size on this method of separation. From the data presented in Table VII it can be seen that the oil agglomeration step was much more effective when it was applied to -400 mesh coal than when it was applied to -35 mesh coal; not only did a cleaner product result, it was recovered in a larger yield. In addition the oil agglomeration step applied to -400 mesh Jude coal was more effective on the average than the froth flotation step applied to -35 mesh material. However, in the case of ICO coal the results were mixed with froth flotation appearing to have the edge with regard to sulfur removal but not with regard to ash removal.

Conclusions

The laboratory application of 16 different treatments in-

Table VII. Oil Agglomeration Step vs. Froth Flotation Step

	Oil Aggl. -35 mesh (Trt. 1,5, 9,13)	Oil Aggl. -400 mesh (Trt. 2,6, 10,14)	Froth Flot. -35 mesh (Trt. 3,7, 11,15)
ICO coal			
ash reduction	20	34	30
pyritic sulfur reduction	16	40	51
yield	89	95	93
Jude coal			
ash reduction	36	47	31
pyritic sulfur reduction	23	44	35
yield	88	93	94

volving size reduction and physical separation to high-sulfur coal containing substantial amounts of finely disseminated microcrystals of iron pyrites provided several interesting and important results. Comparison of these results with a standard washability analysis showed that most of the treatments produced a cleaner coal for a given yield than could be obtained by gravity separation alone of 4 cm x 0 size coal. In this regard the treatments which failed to produce coal with a lower sulfur content were generally those which involved only size reduction and oil agglomeration.

Treatments involving two and sometimes three methods of separation in sequence proved particularly effective. Thus the pyritic sulfur content of two Iowa coals was reduced 85-86% with an overall yield of 82-84% by treatment 14 which included chemical comminution, roll crushing, gravity separation, fine grinding, and oil agglomeration. This sulfur reduction was considerably higher than that provided by single-stage separation. Thus a maximum reduction of 66% in the pyritic sulfur content of ICO coal was realized during the froth flotation step of treatments 11-12 and of 64% in the pyritic sulfur content of Jude coal during the gravity separation step of treatments 13-16.

Each of the separation methods used in these treatments proved effective in itself. Moreover the methods seemed to complement each other, particularly when used in conjunction with particle size reduction.

Chemical comminution generally improved the separation efficiency of the various treatments and fine grinding the separation efficiency of the oil agglomeration method of separation in particular.

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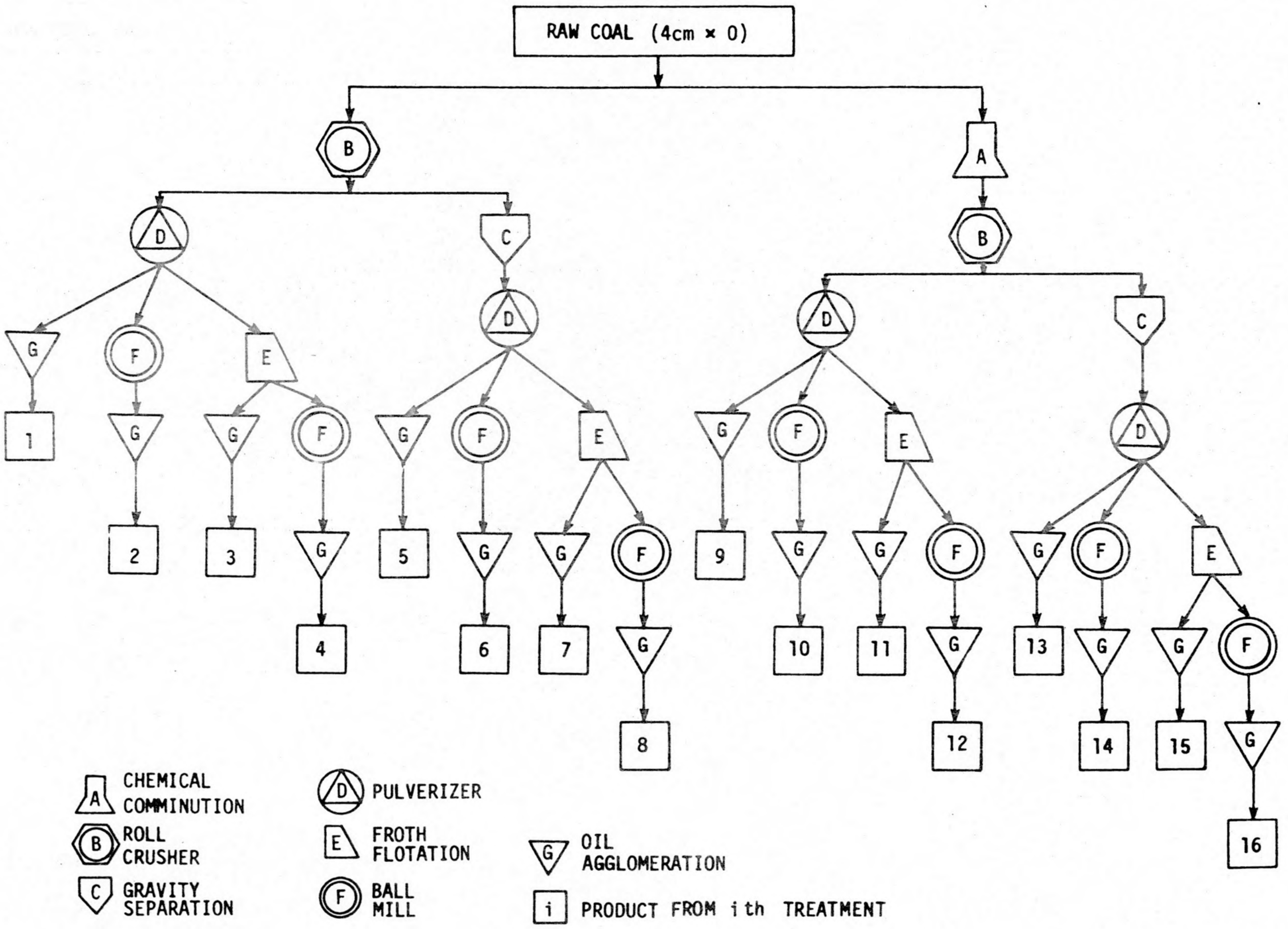
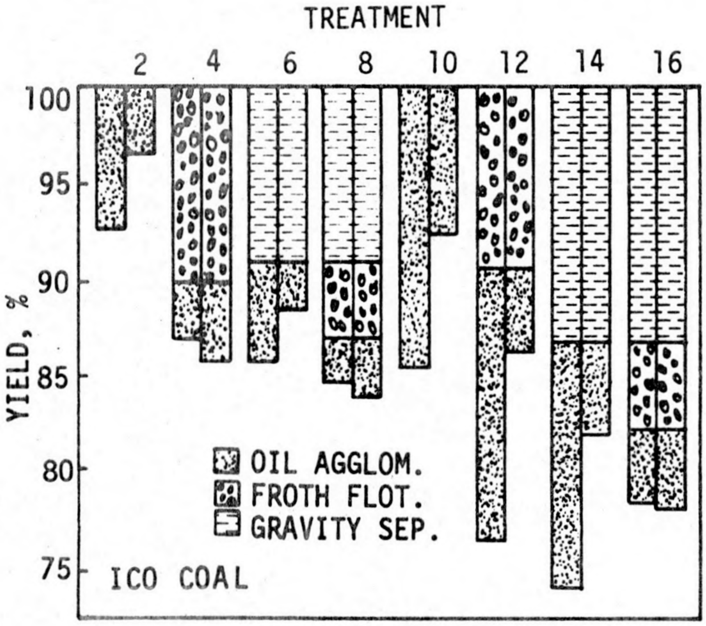


Figure 1. Flow diagram of 16 different treatments.



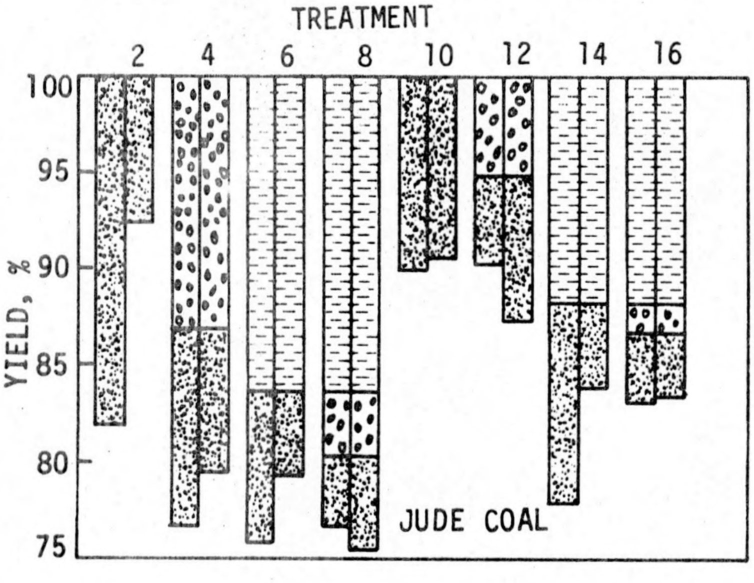


Figure 2. Weight yield of product from the different treatments.

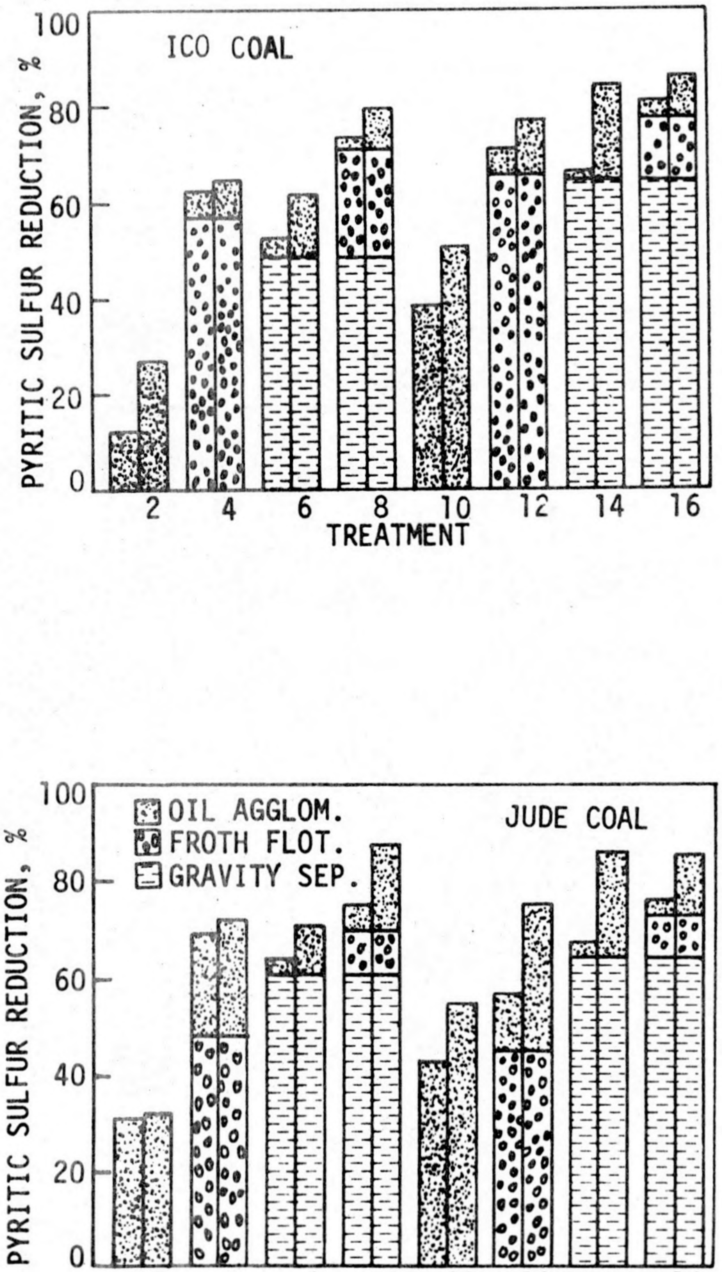


Figure 3. Reduction in pyritic sulfur content provided by the different treatments.

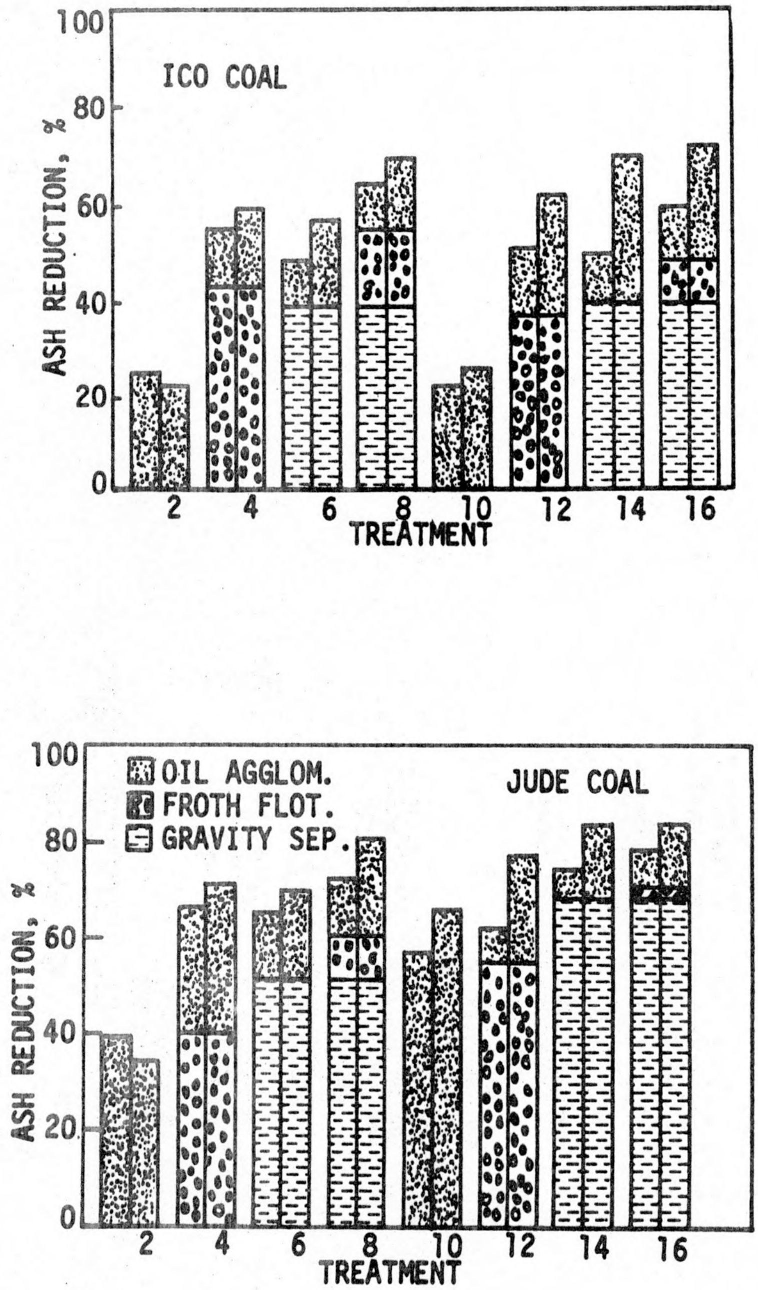


Figure 4. Reduction in ash content provided by the different treatments.

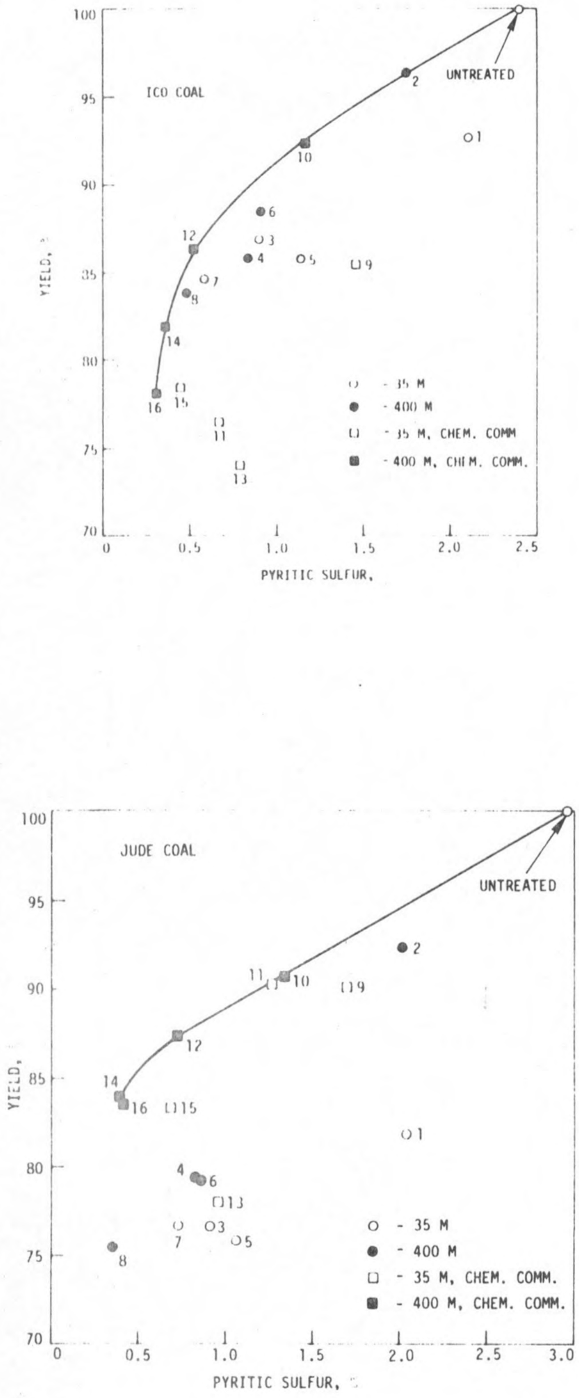


Figure 5. Overall yield versus final pyritic sulfur content of the product from the different treatments.

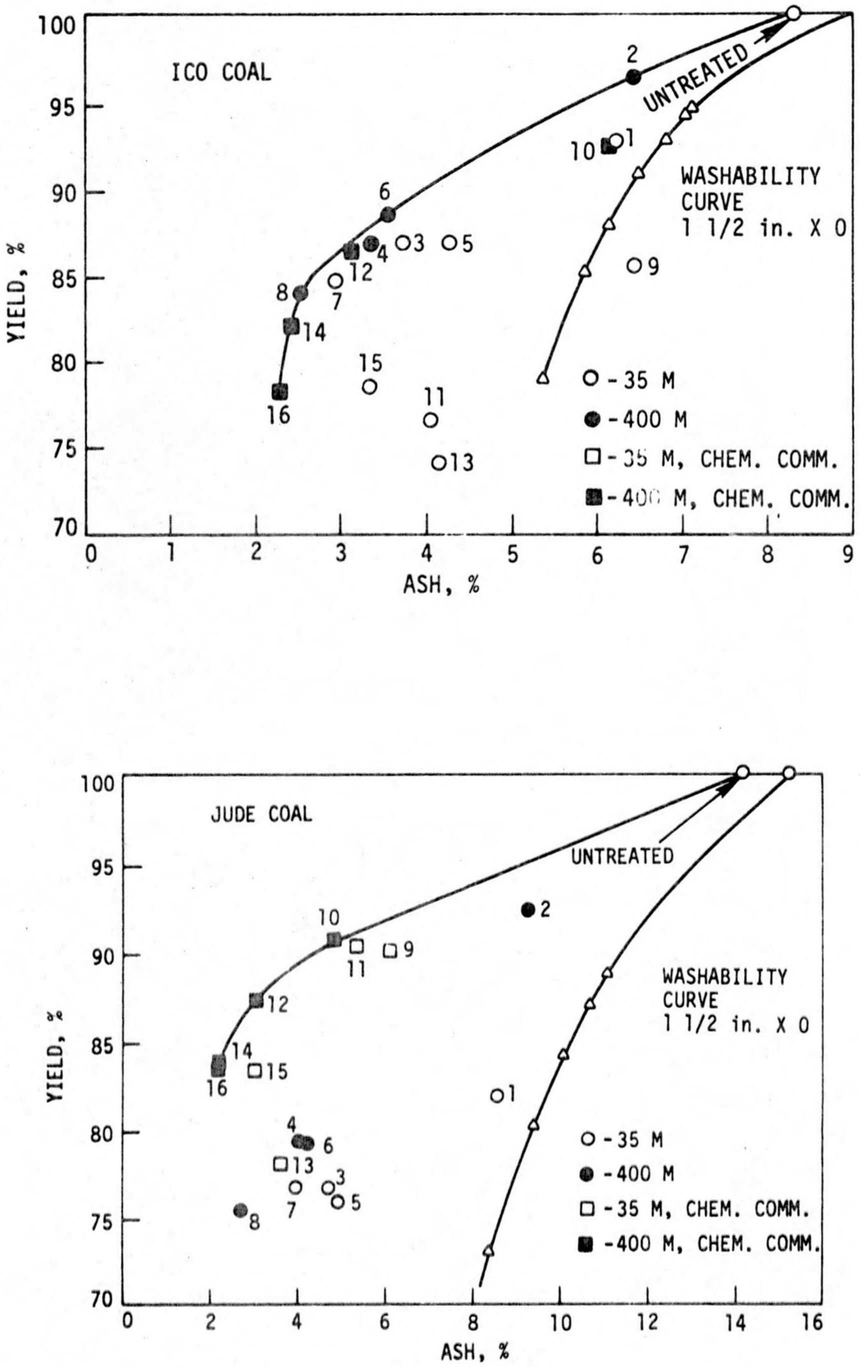


Figure 6. Overall yield versus the ash content of the final product from the different treatments.