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BENEFICIATION OF CANMET COPROCESSING RESIDUE BY OIL PHASE AGGLOMERATION TECHNIQUES

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ABSTRACT

CANMET's coal/heavy oil coprocessing unit yields a solid residue that contains all the ash originally associated with the feed coal as well as the added catalyst solids. Removal of these ash solids would make it possible to recycle the material to extinction, thereby increasing production of lighter oils. Also, it is desirable to separate selectively the siliceous matter so that the retained catalyst residues can be recycled with the pitch. In this investigation, we have attempted beneficiation of the organic matter in the residue pitch, using liquid phase agglomeration techniques. Prior to liquid phase agglomeration, the ash forming solids were liberated by grinding and then rendered hydrophillic by selective conditioning. The reagents used and their concentrations were optimized. The criteria used to judge the suitability of the selected conditions for agglomeration were: high recovery of organic material and high siliceous ash rejection. Levels of ash rejection in these tests ranged from 20% to 50%. Energy dispersive X-ray analysis of the agglomerated product and the reject material suggests that most of the iron is retained in the agglomerates.

INTRODUCTION

CANMET's coal/heavy oil coprocessing reactor yields a solid residue that contains all of the ash originally associated with the feed coal as well as the catalyst solids. The residue amounts to about 20% of the product stream. For both economical and environmental reasons it is desirable to beneficiate this material in order to minimize wastage and produce a value added product suitable as an asphalt binder or electrode coke. Alternatively, removal of the ash would make it possible to recycle the material to extinction and increase the production of lighter oils. In the latter case it is desirable to separate selectively the siliceous matter so that the iron content of the catalyst is retained for recycle with the pitch.

The liquid phase agglomeration technique, developed at the National Research Council of Canada, has the potential to play a major role in the beneficiation of finely divided carbonaceous solids [1-4]. This technique has the advantage of being able to separate fine solids while maintaining high recovery of the combustible, carbonaceous material. The principle of selective liquid phase agglomeration is based on the preferential wetting of a specific solid component, in liquid suspension, by a second, immiscible liquid (bridging oil). The formation and growth of oil agglomerates is governed by the amount of oil present in the capillary interstices between the fine particles of the solids.

In the coprocessing reactor an iron sulphate catalyst precursor is eventually converted to pyrite and/or pyrrhotite. Iron sulphides cannot be readily separated from a hydrophobic matrix due to their own hydrophobic character [5]. This factor may be utilized to advantage in the case of vacuum pitch deashing where it is beneficial to leave the iron compounds with the cleaned oil, thereby reducing catalyst make-up requirements.

In this investigation a series of tests were carried out using oil phase agglomeration for the selective deashing of the pitch residue from a coprocessing reactor. A number of conditioning treatments designed to improve selectivity in ash removal are also described.

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EXPERIMENTAL PROCEDURES

Materials. The vacuum residue used in this investigation was obtained from a bench scale CANMET coal-oil coprocessor. Table 1 lists the composition of this test sample.

Table 1. Composition of CANMET coprocessing residue

C	77.5 w/w%
H	6.2 w/w%
N	1.2 w/w%
S	4.4 w/w%
Toluene insoluble solids	19.7±1.3 w/w%
Ash at 600°C	11.8 w/w%
Major ash constituents	Al, Si, S, Ca and Fe
Al	4.3 w/w% of ash
Fe	20.5 w/w% of ash
Si	3.0 w/w% of ash
Average particle size of the ash	10 μm

Procedure. Pitch samples (100g) were dispersed in distilled water (500 mL) and ground using a 2 kg charge of 0.25" zirconia balls in a 10 cm porcelain ball mill. The average particle size of the ground material was determined to be 9.8±1.4 μm using a Malvern Master Particle Sizer M 3.1. A slurry, containing about 20 g of pitch, was first conditioned with an appropriate reagent by agitating in a Waring Blendor at 250 rps for one minute. After this time the agitation speed was lowered to 150 rps. An agglomerating liquid was then added drop-wise with mixing until discrete agglomerates formed. At this stage the blending speed was raised to 200 rps for 2-3 minutes to facilitate ash liberation. The agglomerated pitch was separated from the aqueous phase on a 100 mesh screen, washed several times with distilled water, dried at 100°C and then ashed to determine the degree of beneficiation.

RESULTS AND DISCUSSION

Spherical agglomeration techniques are best suited to handle solids in a finely divided state [6-7]. Several tests were carried out to agglomerate the carbon from this finely divided pitch, slurried in water, using either Stoddard solvent, No. 4 fuel oil or octane as bridging liquids. The various conditioning agents used to render the surface of the ash particle hydrophillic included: tannic acid, sodium silicate, sodium hydroxide, sodium oxalate, hydrogen peroxide, copper nitrate, iron sulphate, aluminium nitrate and triethylamine. Other variables investigated included pH of the slurry and the amount of collector oil used.

The Effect of pH

One of the objectives of this investigation was to explore the possibility of selective separation of the carbon components and iron compounds from the siliceous solids. This would allow in a significant reduction in catalyst requirements during pitch recycle. In our previous work [1] we have demonstrated that pH had a significant effect on the selective agglomeration of iron in the presence of siliceous matter, provided that the siliceous matter was liberated. Several tests were carried out to investigate the effect of pH on the beneficiation of coprocessing residue by oil phase agglomeration. The pH of the slurry was adjusted either with HCl or with NH_4OH. The results are summarized in Figure 1, which is a plot of the wt.% ash rejection as a function of the pH of the slurry.

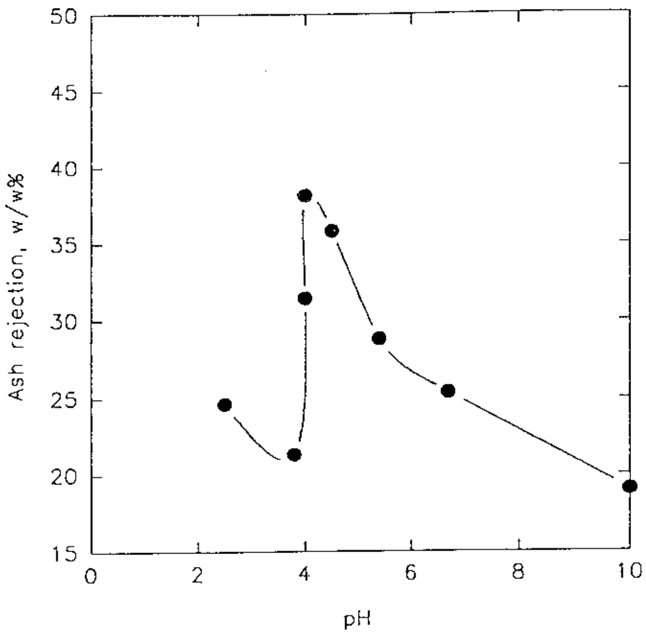

Figure 1. The effect of pH on the beneficiation of CANMET coprocessing residue

Best ash rejection results were achieved in the pH range 4-5. SEM and EDXA results for the ash and oil agglomerates showed that all of the iron was associated with the oil agglomerates. These results also showed that the agglomerates obtained under optimum ash rejection conditions did not contain any siliceous matter. This suggests that the remaining ash consists of iron based compounds desirable for their catalytic activity. These results are also consistent with the analysis of ash from the feed material (Table 1), which suggests that the quantity of iron compounds in the ash is about twice that of the alumino-silicates. The carbon recovery in most of these tests ranged between 80-90 w/w%.

The Effect of Conditioning Agents

The effect of various conditioning agents tested in this investigation is demonstrated from the results listed in Table 2.

Table 2. The effect of conditioning agents on the beneficiation of pitch

Test #	Conditioning agent*	pH	Ash Rejection (w/w%)
1	Blank	6.7	25.4
2	Tannic Acid (16)	6.7	21.2
3	Tannic Acid (30)	6.7	35.3
4	Tannic Acid (20)	4.0	33.9
5	Tannic Acid (30)	8.0	36.2
6	Sodium silicate	7.0	34.7
7	Triethylamine	7.0	27.1
8	Sodium oxalate (4)	-	22.9
9	Hydrogen peroxide	-	30.5
10	copper nitrate (3.8)	-	23.7
11	ferric sulphate (5.4)	-	23.7
12	Aluminium sulphate (4.3)	-	28.0

* Values in parenthesis represent amount of additive in mg/g of pitch; all tests were carried out using Stoddard solvent as a bridging liquid.

Only tannic acid, sodium silicate and hydrogen peroxide had any effect on the beneficiation process. The best results were obtained with tannic and sodium silicate.

Oil Characteristics

The type of oil used as the bridging agent is as important a concentration in the agglomeration of hydrophobic materials, [7]. Lig more refined oils, with high paraffin content, are more efficient selective agglomeration, especially when the rejection of siliceous mat is an important consideration. In addition to their more desirable wei properties, these lighter oils achieve efficient and economical coatin the organic particles during mixing. Denser, more viscous oils generally less selective for the rejection of siliceous compounds. In investigation most of the tests were carried out with Stoddard solve reference oil normally used for comparison purposes [7]. Howe preliminary tests were also carried out with dodecane and Fuel oil N The comparative ash rejection levels obtained with these oils under sir experimental conditions are listed below.

Table 3. Comparative ash rejection levels achieved with various oils

Test #	oil	ash rejection (w/w%)
1	Stoddard solvent	30
2	Dodecane	36
3	No.4 fuel oil	43

The best results were obtained with Fuel oil no.4.

CONCLUSIONS

Liquid phase agglomeration techniques were successf applied to the selective agglomeration of organic matter and compounds from CANMET coprocessing residues. Over 40 w/w% rejection levels were achieved. SEM and EDXA results for agglomerated product and the reject material suggested that most of iron compounds were retained in the agglomerates. This is benefi because it reduces catalyst make-up requirements if the pitch is recy These results also show that very little, if any siliceous matter rem with the cleaned pitch. This suggests that most of the undesir components of the solids present in CANMET coprocessing residues be removed by an oil agglomeration technique.

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REFERENCES

1. Sirianni, A. F., Capes, C. E. and Puddington, I. E.: Can. J. Chen Eng., 1969, 47, pp. 166-170.
2. Puddington, I. E. and Sparks, B. D.: Minerals Sci. Eng., 1975, 78, 282-288.
3. Capes, C. E., McIlhinney, A. E. and Sirianni, A. F.: Agglomerat 77, K. V. S. Sastry (ed.), A. I. M.E. 1977, pp. 910-930.
4. Sparks, B. D., Farnand, J. R. and Capes, C. E.: J. Separ. Proc. Technol., 1982, 3, pp. 1-15.
5. Winschel, R. A. and Burke, F. P.: Fuel, 1987, 66, pp. 851-858.
6. Capes, C. E.: Can. J. Chem. Eng., 1976, 54, pp. 3-12.
7. Capes, C. E. and Germain, R. J.: Physical cleaning of Coal, Y. A. I edit. Marcel Dekker, Inc. New York, 1982, pp. 293-351.

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