Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Effect of Oil Types and Additives on the Separation by Flotation of Unconverted Coal and Mineral Matter from Liquefaction Products

E. T. Saad[a]; D. Bhattacharyya[b]; R. I. Kermode[b]
[a] Ashland Oil, Inc., Ashland, Kentucky [b] Department of Chemical Engineering, University of Kentucky, Lexington, Kentucky

To cite this Article Saad, E. T. , Bhattacharyya, D. and Kermode, R. I.(1980) 'The Effect of Oil Types and Additives on the Separation by Flotation of Unconverted Coal and Mineral Matter from Liquefaction Products', Separation Science and Technology, 15: 3, 185 — 200

To link to this Article: DOI: 10.1080/01496398008068479

URL: http://dx.doi.org/10.1080/01496398008068479

SEPARATION SCIENCE AND TECHNOLOGY, 15(3), pp. 185-200, 1980

THE EFFECT OF OIL TYPES AND ADDITIVES ON THE SEPARATION BY FLOTATION OF UNCONVERTED COAL AND MINERAL MATTER FROM LIQUEFACTION PRODUCTS

E.T. Saad
Ashland Oil, Inc.
Ashland, Kentucky

D. Bhattacharyya and R.I. Kermode
Department of Chemical Engineering
University of Kentucky
Lexington, Kentucky 40506

ABSTRACT

The flotation behavior of various solids (H-coal vacuum bottoms, SRC solids, and pure clays) of different sizes dispersed in light cycle oil (LCO) or H-coal or clarified solvent refined coal oil (SRC) is studied with CO_2 bubbles under semi-batch operation after precooking (at 100°C-120°C) the solids in oils for 30 minutes. In all cases maximum flotation efficiency is achieved with a bulk liquid temperature of 110°C, and a 30 to 40°C temperature gradient between the liquid and the upper foam layer. The flotation of particles is best with LCO containing 6% cresol as additive. The separation is negligible with SRC oil because of high viscosity.

With H-coal solids dispersed in LCO (+ 6% cresol) the separation is 85% with 100 μm particles and only 10% with 10 - 15 μm particles. By the addition of an agglomerating solvent (5% to 10% decane) the separation of 10 μm particles is increased to 45%. With respect to the separation of pure clays and minerals (dispersed in LCO) the separation of wollastonite (70% with 100 μm particles) is better than that of illite (35% with 100 μm particles). The flotation of kaolinite is always found to be insignificant.

INTRODUCTION

The large-scale removal of ash and unconverted coal solids from liquefaction products is still one of the areas where technological improvement is needed. Almost complete removal is essential for syncrude, as refining operations are not designed to process crude oils containing solids. A high degree of removal is desirable even in boiler fuel applications as this will lower both the ash and sulfur content of the fuel.

Methods investigated for removing solids include - filtration, hydroclones, centrifugation, magnetic separation, solvent deashing, agglomeration followed by settling or filtration, and flotation. The success of more traditional methods such as centrifugation and filtration has been limited, and in the case of precoated filtration, not only have rates been low, but the fouled filter cake disposal or regeneration is difficult. Problems associated with traditional methods are well-documented in the literature. (1)

The difficulty of solids separation is to a large extent attributable to small particle size, moderate to high liquid viscosity, and processing conditions which may include both elevated temperature and pressure. Figure 1 shows a typical particle size distribution curve for H-coal solids. Almost 20% of the particles are less than 5 microns and 60% less than 10 microns. Microscopic examination (2) of other product solids indicated even a smaller size distribution, with a significant fraction of particles near one micron in diameter. The present study focuses on an experimental evaluation of the potential for removing these small solids by flotation; and (or) solvent precipitation followed by flotation. In addition the relationship between flotation efficiency and particle size is established.

PREVIOUS EXPERIMENTS

The use of flotation process to concentrate particles in the foam phase from aqueous systems is quite well-known, and the efficiency of flotation is directly related to the bubble attachment process and the interfacial properties of the solid-gas system. Important variables that affect flotation are bubble and particle size, pulp concentration, and temperature as it effects properties

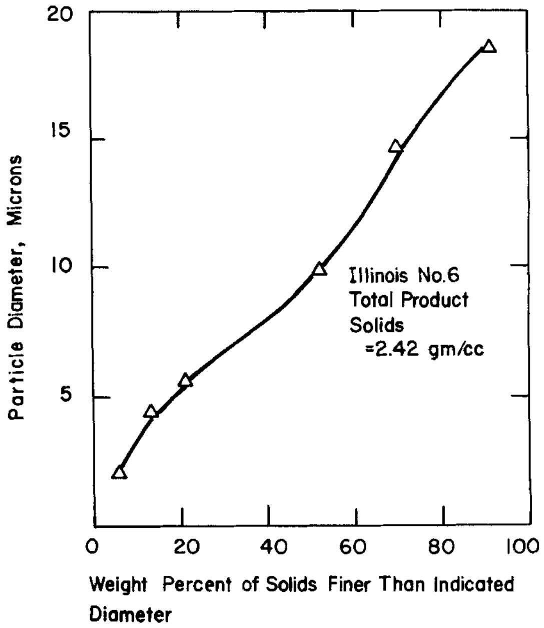

Figure 1 Particle Size Distribution of H-Coal Product Solids

such as surface tension, viscosity, and density. For coal derived liquid systems, where the viscosity and surface tension are strongly influenced by changes in temperature, solution and foam temperature would be expected to play an important role in the flotation process. While the relationship of these variables and the extent of separation with non-aqueous systems has not been established, it is reasonable to expect that the dependence of flotation efficiency on particle size, bubble size and foam stability would be similar to that observed in aqueous systems. (3)

The initial phases of this research project (4) focused on establishing the operating conditions (temperature, solids concentration, type of flotation gas, etc.) that yielded the best separation in a coal solids - organic liquid system. To avoid the difficulties of reproducing an H-coal liquid, a synthetic coal solids pulp was used for all of these studies. This liquid consisted of a petroleum refinery-derived light cycle oil plus about 6% cresol. This liquid was mixed with ground-up vacuum bottoms H-coal solids to simulate a coal liquid. This system had the advantage that the properties were not a function of the coal liquifaction process. Fresh feed was made up before every run, thus changes or deterioration with time did not occur. All of the studies were carried out in a semi-batch flotation column as reported previously by Murali, et al (5). The operation of the column involved periodically removing a foam sample from one of the foam sample spouts, and liquid from the liquid sample outlet. At the same time preheated feed material was added to compensate for the foam and liquid removed. The liquid and foam phases were heated independently. A magnetic stirrer prevented heavy particles from accumulating on the bottom of the apparatus.

Preliminary studies indicated (4,5) that solids flotation with diffusers of 50 μm porosity and a gas (CO_2) flow rate of about 400 cm^3/min was optimum. The extent of separation was based on the % ash in the liquid at any time. The material balance closure was obtained by analyzing foam phase ash content. Figure 2 shows a typical percentage separation versus time curve. Plus and minus two standard deviations for the exponential curve shows the large variation in results achieved even under standard conditions. On this figure the two different symbols O and Δ show the data points for two runs made under the same conditions using the same diffuser. The designations G_1 and G_4 mean the data shown are the first and fourth run on the diffuser used with the G series of runs. A temperature gradient (liquid temperature of 110°C and a foam temperature of 65°C) between the foam and liquid was essential if separation was to be achieved. A foam temperature of 65°C corresponded to no heating of this phase. When the foam was heated it tended to become unstable and drainage of foam into the liquid carried most of the floated particles with it.

The exponential shown on Figure 2 is typical of the separation versus time curves obtained from these experiments. The two con-

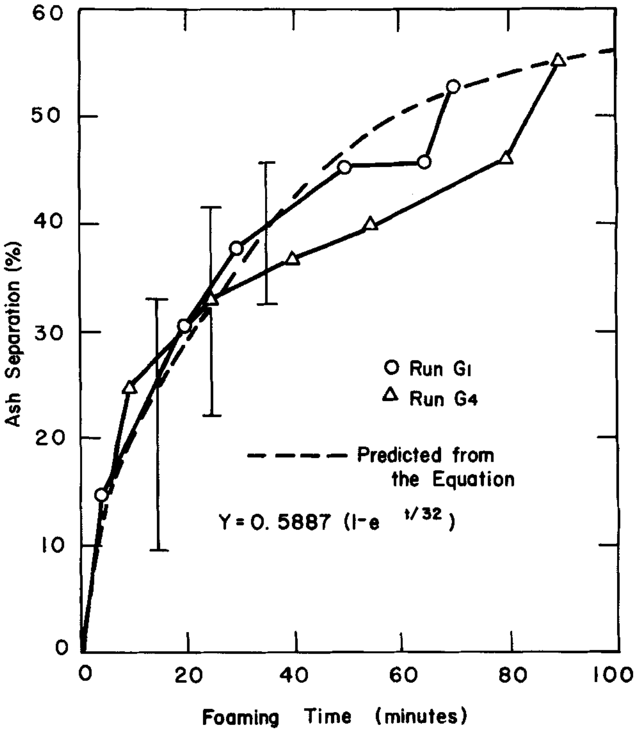

Figure 2 Typical Experimental Separation Curves (Reference 5)

stants in the equation were determined empirically from the G series of runs. The standard deviations were also estimated from the same runs. The two curves shown lie below the empirical line, however, the standard deviation lines indicate that curves both above and below were present in the data.

EXPERIMENTS WITH PURE CLAY AND MINERAL MATTERS

The residue from coal liquefaction processes contains a mixture of original ash-forming clays and mineral matter present in coal. The minerals present in bituminous coals are pyrite, quartz, calcite, illite, expandable clays, and kaolinite, and the composition could be estimated from major inorganic elements. The mineral matter is quite stable under liquefaction conditions (6) except the conversion of pyrite to FeS and partial conversion of quartz and calcite to wollastonite ($CaSiO_3$). Most of the clays will change little with the exception possibly of some dehydration. Russell (6) in a study with H-coal vacuum bottom showed the presence of 38% expandables, 50% illite, and 12% kaolinite in the sample.

A series of flotation runs were made to determine the separation which could be achieved using the pure minerals and clays with the light cycle oil (LCO)-cresol mixture, H-coal oil, and clarified SRC oil. (3,7) Table 1 summarizes these results. Kaolinite could not be separated to any measurable extent even for particles as large as 35 mesh. Almost immediate disintegration of even the largest particles was determined to be the cause of this lack of separation.

Illite and wollastonite did not tend to disintegrate into small particles in any of the oils. Thus the original particle size distribution was preserved during flotation. Table 1 shows that the separation of Wollastonite in LCO and SRC oils was extremely good and probably would exceed 90% for longer flotation times. Figure 3 shows the extent of separation of wollastonite from three coal liquids. The high degree of separation is most likely a result of interaction between the CO_2 and calcium sites. This idea was tested by using nitrogen gas for flotation. Under these conditions wollastonite and illite showed very similar separation patterns.

The flotation rates of pure clay and mineral matter are compared with H-coal solid in Figure 4. Hence it would be expected that the overall ash separation from a liquefied coal residue would be strongly dependent on the liquefaction conditions (which determines wollastonite formation, and kaolinite breakdown) and on the types of clay present in the original coal.

SEPARATION OF LIQUEFACTION SOLIDS

In addition to floating minerals and clays, numerous flotation experiments involving two H-coal and SRC solids were carried out.

Table 1 - Flotation Behavior and Particle Characteristics of Pure Clay and Mineral Matters

Mineral or Clay	Flotation Liquid	Maximum Separation	Comments
Kaolinite 120X200 Mesh	LCO-Cresol	0	Microscopic examination of particles in all three solvents showed rapid disintegration. 325 μ particles reduced to 50 μ in heating to 100°C, after one hour at 100°C average particle less than 15 μ diameter.
	H-Coal	0	
	Clarified SRC Oil	0	
Illite 120X200 Mesh	LCO-Cresol	34% @ 100 min	Microscopic examination of particles in all three solvents showed no change in particle diameter during heating to 100°C. After one hour only minor evidence of disintegration was observed.
	H-Coal	0	
	Clarified SRC Oil	34% @ 100 min	
Wollastonite 120X200 Mesh	LCO-Cresol	78% @ 110 min	Microscopic examination of particles showed no tendency to disintegrate. Both the LCO-Cresol and SRC separation curves had not reached a maximum and it appeared that greater than 90% separation could be achieved. The H-Coal curve appeared to be near its maximum.
	H-Coal	38% @ 110 min	
	Clarified SRC Oil	65% @ 110 min	

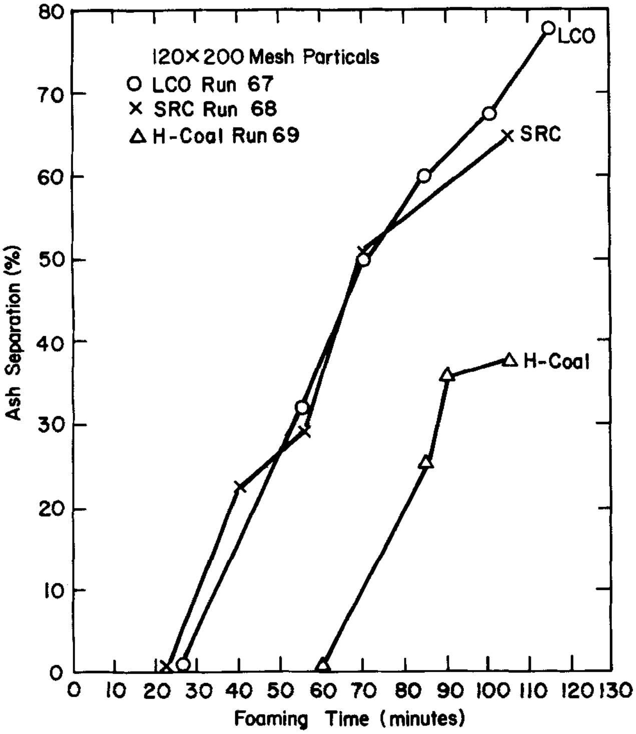

Figure 3 Separation of Wollastonite from the Three Oils

The details of the procedure are presented in the literature (3,4). The term H-coal solids refers to vacuum distillation bottoms material from the H-coal process. This material was a solid at room temperature which contained all of the ash forming components of the coal, unconverted coal, and the asphaltene residue not converted to a syncrude product by the liquefaction reactions. In addition to the dependence of flotation behavior on the type of clay and mineral matter present in the liquefied residue, the influence of particle charge characteristics by asphaltenes may significantly alter particle separation efficiency.

Prior to the start of a flotation experiment a predetermined amount of the solids (SRC or H-coal) of selected mesh size was mixed

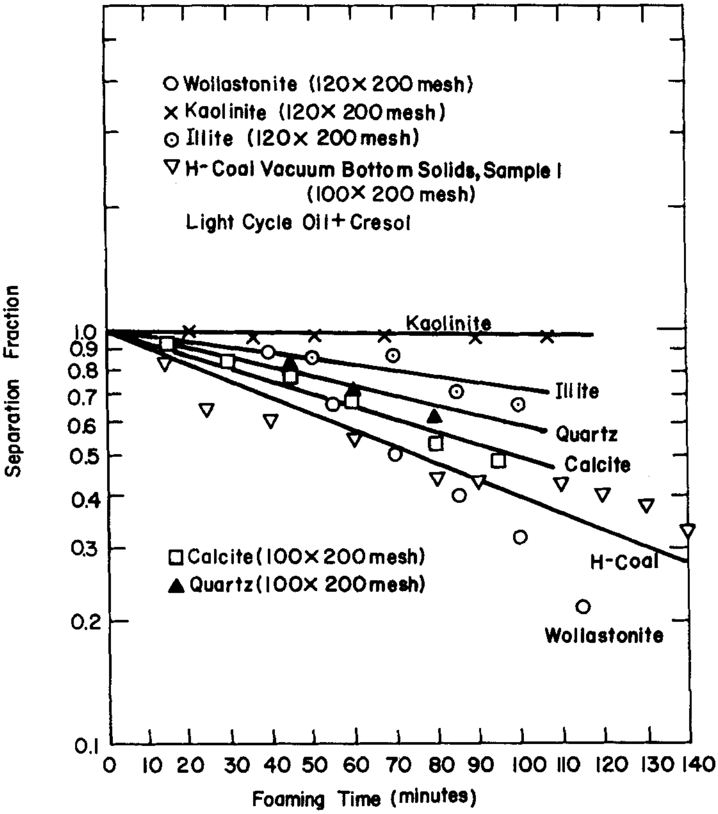

Figure 4 Comparison of Mineral and Clay Separation with Vacuum Bottoms (Reference 7)

with one of the three liquids (H-coal oil, clarified SRC oil or the LCO-cresol mixture) and then precooked for 30 minutes. Figure 5 shows the effect of the three different liquids on the flotation of SRC solids. The extent of separation is greatest for the LCO-cresol mixture and least for the H-coal oil, however, statistically all three are the same up to 30 minutes. At times greater than 60 minutes only the LCO-cresol mixture appears to yield a statistical improvement in separation.

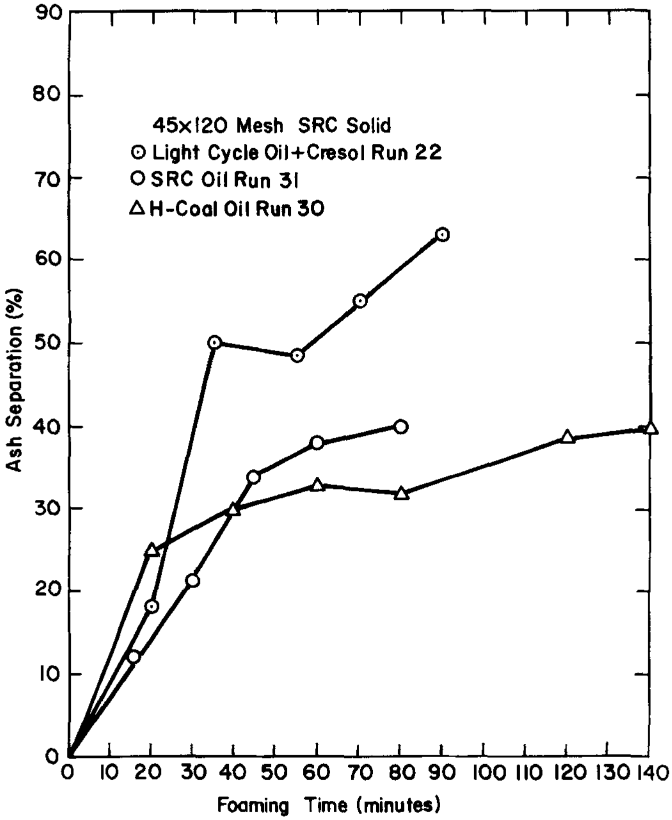

Figure 5 Effect of Type of Oil on the Separation of SRC Solids

Figure 6 shows a more dramatic difference between the two types of H-coal solids dissolved in the LCO-cresol mixture. Two pairs of symbols, ., O and Δ, X, show typical variation between runs that are made using the same operating conditions. If exact duplication were possible, the circles and filled in circles would coincide and the deltas and X's would coincide. While only two runs are shown, additional runs substantiated the 50% difference in separation shown after one hour. All of the preliminary experiments (3,4) were run with H-coal solids I, and it was not until the final phase of the project that a totally different sample of H-coal solids was used.

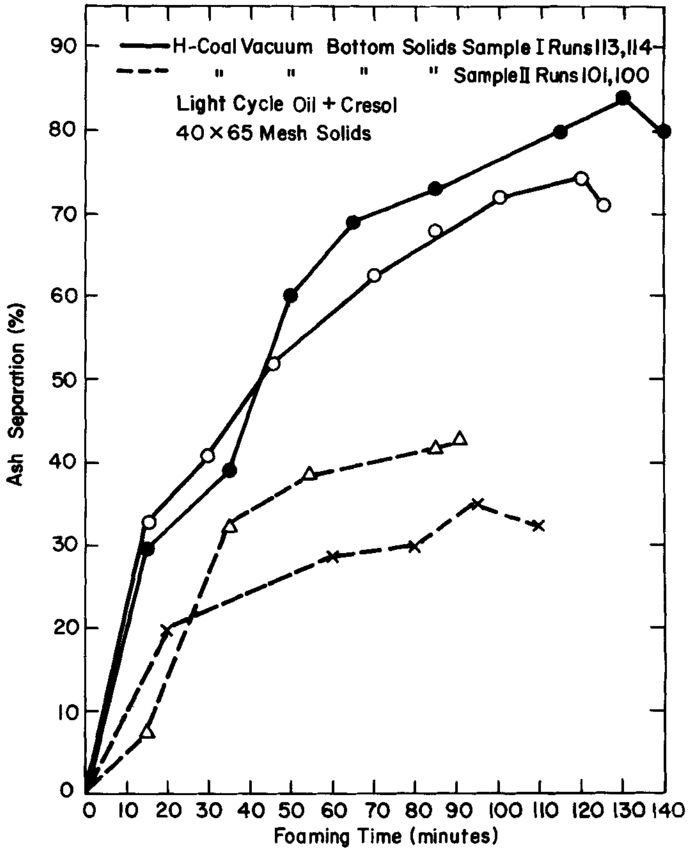

Figure 6 Comparison of Ash Separation for Two Different Batches of H-Coal Solids in LCO-Cresol Mixture

The difference in separation even in the LCO-cresol mixture was not expected. Attempts at reconciling this difference, including ultimate and proximate analysis as well as some analysis of the mineral matter and trace elements, were unsuccessful. It was also impossible to trace the processing conditions used in the H-coal reactor or the exact coal which was the precursor of the H-coal solids II. Microscopic examination of the behavior of the solids during the precooking step showed that H-coal solids II disintegrated more rapidly than solids I.

Since ash separation efficiency is a strong function of particle size that exists during flotation, a study was conducted to observe the particle dissolution (from an initial solid size of 40 X 65 mesh) behavior during precooking. Figure 7 shows the change in particle size with time during precooking. Two different H-coal vacuum bottoms samples solids I and II were used and two liquids. Figure 7 shows that the solubility of the two different H-coal solids vary considerably. Sample II of solids is much more soluble than sample I in both the liquids. In addition for a given

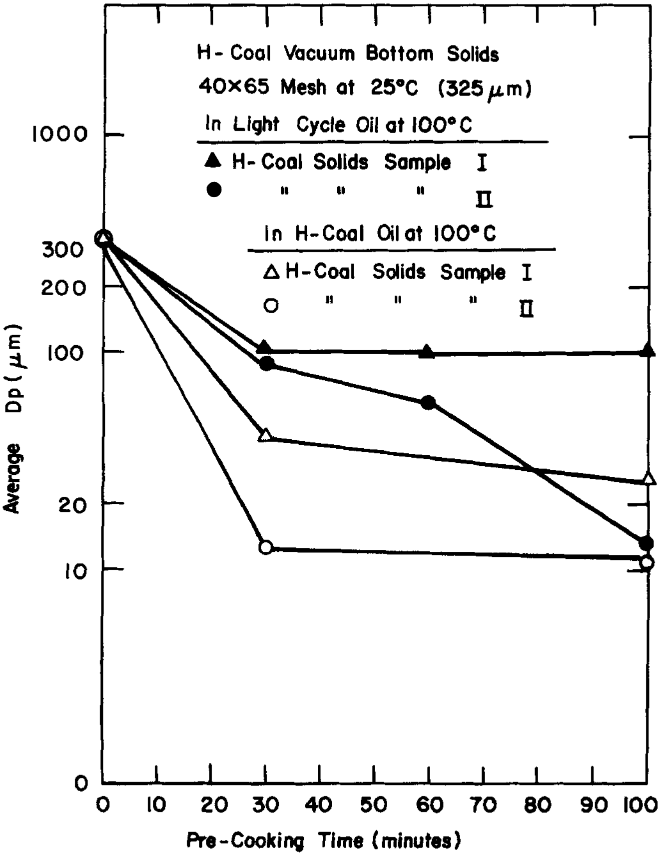

Figure 7 Effect of Pre-Cooking Time on H-Coal Solid Dissolution

precooking time both samples are more soluble in the H-coal oil than in the LCO-cresol mixture.

The effect of reduction in particle size on flotation is illustrated in Figure 8. Various initial (prior to precooking) mesh sizes (35 X 60 up to much smaller than 200 mesh) of sample I H-coal solids illustrate that for particles starting out much less than 200 mesh a maximum separation of 10% can be achieved. As in the case of mineral and clays very small particles are not readily separated. Photographic measurements of actual particle sizes existing during flotation showed that with an initial size of 200 mesh, the particles

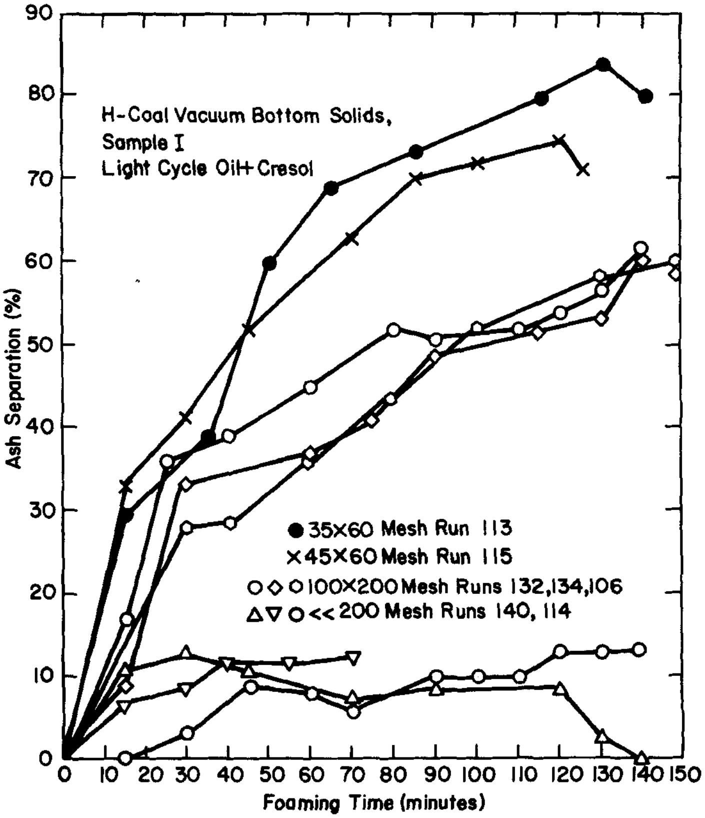

Figure 8 Effect of Particle Size on H-Coal Vacuum Bottoms Separation

were 10-15 μm size whereas with 35 X 60 mesh initial size the particles existed as 50 to 80 μm. Hence, it can be concluded that direct flotation of 10-15 μm particles would not be possible.

Various additives (decane or surfactants) were used to observe the improvement in flotation behavior of small particles. Figure 9 shows the flotation of 10-15 μm ash particles was improved from 10% to 35% with the addition of 10% decane during the precooking step. In addition the separation of particles in the presence of decane increased with time for at least 70 minutes whereas in the absence of decane the separation did not improve after 20 minutes. The improved separation of small particles may have been due to decane acting as a collector and/or as an agglomerating agent for growth of particles. Use of decane did not improve separation of particles

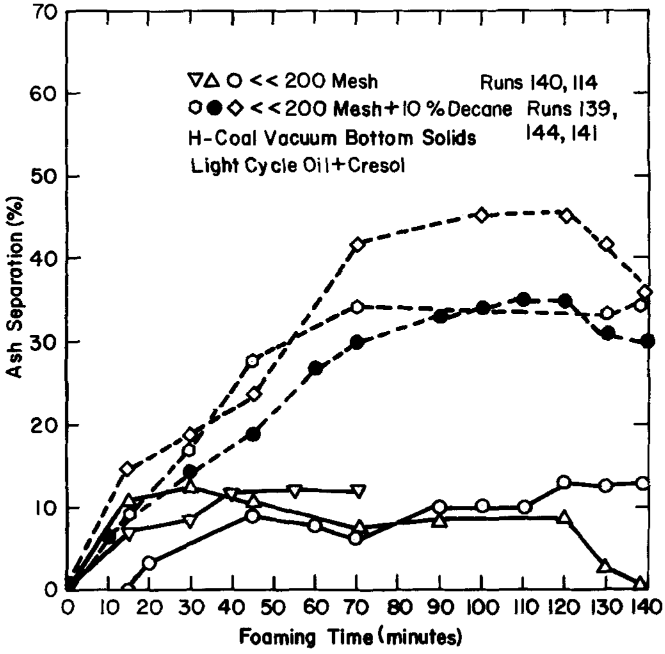

Figure 9 Effect of Addition of Decane on Particles Smaller than 200 Mesh

with larger initial mesh size of 100 X 200 mesh (before precooking). The use of anionic surfactants did not improve the flotation behavior of small, medium and/or large particles.

DISCUSSION AND CONCLUSION

Liquefaction conditions are sufficiently mild that much of the mineral matter and clays is modified only through the loss of water of hydration. This suggested that the flotation of pure minerals and clays would aid in the understanding of the separation process. The extent of separation was wollastonite > illite > kaolinite = 0. Microscopic examination of the particles during flotation indicated that this was related to the extent of particle disintegration; kaolinite disintegrated to particles less than 15 μm in size whereas other clay particles showed no size change during precooking. The influence of the liquid type was demonstrated using wollastonite where the flotation with LCO-cresole mixture and SRC oil >>H-coal liquid. This same trend appeared with actual coal solids dissolved in these three liquids.

Because of the strong influence of particle size on the extent of separation a series of experiments were run using the three liquids and three coal solids SRC, H-coal I and H-coal II. The decrease in particle size with time in the liquid was a function of the liquid coal solid system. As expected this difference was accentuated with smaller initial mesh sizes. Starting with 35 X 60 mesh H-coal I particles and the LCO-cresol mixture 85% separation could be reached. In contrast particles much less than 200 mesh showed a maximum separation of 10%.

The addition of several surfactants did not improve the separation. The addition of an agglomerating solvent (10% decane) significantly improved the flotation of small (10-15μm) H-coal solid particles to 35%. Decane had no effect on the flotation of larger particles.

Finally, a different source of H-coal solids was used with each of these liquids. The separation achieved was about 50% of those for H-coal I. This difference was largely related to a more rapid formation of small particles. Attempts at explaining this in terms of composition were unsuccessful. This dependence on coal and liquefaction processing conditions would obviously be important in the development of a flotation process.

ACKNOWLEDGMENT

Funds for this research were supplied by the National Science Foundation, RANN Division through grant number AER-02359-A08, and by the State of Kentucky through the Institute for Mining and Minerals Research.

REFERENCES

1. J.D. Batchelor and C. Shih, "Solid-Liquid Separation in Coal Liquefaction Processes", Preprint of Paper Presented at 68th National AIChE Meeting, Los Angeles, (November 1975).

2. C.W. Curtis, A.R. Tarrer, and J.A. Guin, "Particle Size Variation in the Solvent Refined Coal Process", Ind. Eng. Chem. Process Des. Dev., 18, 377 (1979).

3. E.D. Saad, Ph.D. Dissertation, University of Kentucky, Lexington, Kentucky, (1977).

4. D. Murali, M.S. Thesis, University of Kentucky, Lexington, Kentucky, (1976).

5. D. Murali, D. Bhattacharyya, and R.I. Kermode, "An Experimental Investigation of the Flotation of Residue Solids from Liquefied Coal", Separation Science and Technology, 13 (7), 547-563 (1978).

6. S.J. Russell, Proc. 10th Annual Scanning Electron Microscope Symposium and Workshop, Vol. I, IIT Research Institute, March 28-April 1, 95-100 (1977).

7. E.T. Saad, D.R. Rubin, D. Bhattacharyya, and R.I. Kermode, "The Separation of Clays and Major Minerals in Coal Residues from Coal and Petroleum Derived Solvents", The Canadian Journal of Chemical Engineering, 56, 6, 406-411 (1978).