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FINAL REPORT

on

ASSESSMENT OF THE POTENTIAL
OF COLLOIDAL FUELS IN
FUTURE ENERGY USAGE

to

ADVANCED TECHNOLOGY PROJECTS
OFFICE OF ENERGY RESEARCH
U. S. DEPARTMENT OF ENERGY

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SUMMARY

Pulverized coal has been an increasingly important source of energy over the past century. Most large utility boilers, all modern coking plants, and many industrial boilers and blast furnaces employ pulverized coal as a major feed stream. In periods of oil shortages, such as during World Wars I and II, the concept of adding powdered coal to oil for use in combustion equipment originally designed for oil has been actively pursued but rarely used. Over this same period of time, there have been attempts to use air suspensions of coal dust in diesel engines in Germany, and in turbines in various countries.

More recently as a result of (a) the oil embargo of 1973, (b) the continued increase in oil prices since then, and (c) the expected decrease in oil availability in the future, the use of standard utility grind coal (70 percent through 200 mesh or a mean particle size of about 40 microns) in mixtures with oil is being aggressively pursued for use in boilers in the United States, Japan and Canada. There are also relatively minor efforts at present to burn slurries of powdered coal in which a significant fraction of the oil has been replaced with water, and private industry is probably conducting additional research in this area. Although there was a brief attempt a few years ago to develop uses for finer grinds of coal in oil, ie, the so-called colloidal fuels to fuel diesel engines and for turbines, there is apparently little activity at present in this field.

The economic advantages to be enjoyed by substitution of powdered coal in oil are not generally realized. Oil costs at \$30/bbl represent a fuel value of about \$5.00/10⁶ Btu; coal at \$25/ton is equivalent to approximately \$1.00/10⁶ Btu. Although capital costs for the use of coal are higher than those associated with the use of oil, coal is clearly becoming the least costly fuel. Not only are considerable cost advantages possible, but an improvement in balance of payments and an increase in reliability of fuel supplies are other potential benefits.

It is therefore recommended that increased national attention be given to develop these finer grinds of carbonaceous fuels to be used in

various suspending fluids. Technical areas where significant additional support appear desirable include desulfurization and deashing of the coal and/or colloidal mixtures; post combustion control of all emissions; techniques to modify and control the erosive characteristics of coal ash; more efficient comminution procedures; instrumentation to better control production and use; chemical means to produce finely divided fuels; expanded efforts on the use of water and air as the suspending medium; substitution of other carbonaceous materials such as peat, wood, and agricultural wastes for coal; modification of turbines and the internal combustion engines to best utilize such fuels; and encouragement of new conversion concepts specifically designed for colloidal fuel mixtures.

The major disadvantages of this technology concern the increased environmental control problems with the use of coal in colloidal form. These problems arise because of the high levels of noncarbonaceous material in coal, because finely divided coal itself is at least generally considered unsightly, it may be a significant health problem when inhaled, and because coal dust is highly combustible and even explosive under the appropriate conditions.

The major competition that colloidal fuel will have will be the synthetic fuels, especially methanol. In the longer run fuels like SRC and other direct liquefaction products may also become commercially available in large quantities. At present, this possibility would seem to be several decades away, and intermediate solutions, and possibly lower cost solutions, like the use of colloidal fuels, should be pursued.

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FINAL REPORT

on

ASSESSMENT OF THE POTENTIAL OF COLLOIDAL FUELS IN FUTURE ENERGY USAGE

By

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INTRODUCTION

Recent interruptions of oil supplies and major price increases have caused the United States to again attempt the use of coal-oil mixtures to reduce oil consumption, and to consider the possible use of coal-water or coal-air mixtures to eliminate the use of oil in some applications. Battelle prepared an examination of this technology for the Department of Defense in 1974,⁽¹⁾ and concluded:

"Overall, colloidal fuels offer sufficient potential for cost reduction and resource conservation that they deserve further and more detailed investigation for DoD applications. An immediate application is, of course, the use of colloidal fuel in power boilers for marine propulsion and utility supply at land-based military facilities. The intermediate-range potential for using these colloidal fuels in gas turbines should be studied in sufficient depth to determine the practicality for firing colloidal fuels in gas turbines. A long-range objective would be to utilize such fuels in land-based powered vehicles. However, it should be borne in mind that the ability of any process ..... to produce a suitable powdered fuel of general applicability in view of current U.S. environmental regulations remains to be demonstrated."

In 1979, the Department of Energy requested Battelle to again examine this technology, and to project the applicability of these fuels for all uses in the United States.

Historically, the idea of using a coal/oil mix as a pumpable fuel in times of fuel oil shortage is nearly 100 years old. This technology is a means of directly burning coal in systems that were designed for the use of oil without necessitating major changes of equipment. No simple and economically attractive procedures were previously found at oil prices below about \$10/bbl so earlier efforts, until very recently, were abandoned. Now that the times of inexpensive and abundant oil supplies are presumably gone forever, serious long-term efforts can be justified to find acceptable procedures for burning coal in basically oil-firing combustion systems. Coal may be used in natural form either as coal dust--which is injected into a combustion chamber by means of mechanical or aerosol-type injection nozzles, or as a composite mixture with fuel oil and/or water. Conversion of oil-burning systems to solid fuels can be quite expensive and, so far, the technical solutions for the use of coal dust alone in internal combustion engines or gas turbines have been far from satisfactory. On the other hand, colloidal fuel has been successfully used in stationary industrial boiler systems and on ships, and for short periods of time in diesel engines; it may be used in many systems with minimum conversion problems and its use may be extended to other applications. This report discusses the technical and economical potential for the use of all types of such mixed fuels.

A note on the definition of colloidal fuel also seems desirable as used in this report. The previous Battelle report on this subject considered all particle sizes which could be suspended in a carrier fluid, especially oil. Since then, investigations on the use of relatively coarse suspensions of coal-in-oil (COM), say in a coal mean particle size range of 50 to 70 microns, is now moving along fairly rapidly under both Department of Energy and private funding efforts. The work by General Motors⁽²⁾, Florida Power Corporation-Dravo Corporation⁽³⁾, New England Power Service Company⁽⁴⁾, and the Electric Power Research Institute⁽⁵⁾ are examples of private organizations taking action as the uncertainty of

oil availability and price increases becomes a major business challenge. These organizations have carried out large demonstration efforts. The Pittsburgh Energy Technology Center at Bruceton, Pennsylvania is the major government laboratory now exploring these COM fuels, and a 100 HP fire-tube boiler and a 700 HP water-tube unit are currently in operation.⁽⁶⁾ The total DOE funding on COM fuels is now approaching \$36,000,000 per year.

The thrust of this updated analysis will therefore be on applications and research needs which are not yet receiving significant attention from a national standpoint, ie, on coal particle sizes below about 325 mesh (40 μ) and with fluids other than oil, ie, water and air. Special attention will also be given in treating all such fuels, including COM, to remove sulfur, alkali, ash, and possibly nitrogen compounds, and thereby increase the possible utilization of such fuels and minimize their environmental impact.

EARLY STUDIES OF COAL/OIL MIXTURES

W. C. Schroeder⁽⁷⁾ in 1942 presented an excellent summary covering almost 100 years of the various efforts on the preparation and stabilization of colloidal coal/oil mixtures and their utilization. With few exceptions, these efforts were concerned with colloidal fuel for stationary boilers and boilers on ships. The major problem during that period was production of stable suspensions of rather coarse coal powder in fuel oil. Patents for stabilizing such suspensions were obtained as early as 1879⁽⁸⁾, but it was not until World War I (WWI) that serious studies were undertaken by the U. S. Submarine Defense Association (SDA) to develop stable colloidal mixtures by the use of stabilizing agents. In 1918 the SDA succeeded in operating a ship for the first time with a colloidal fuel 31 parts coal, 68 parts oil, and 1 part stabilizer. The heating value of this fuel was 17,100 Btu/lb. A relatively fine coal was used with a fineness 85 percent less than 55 microns. The viscosity of the mixed fuel was nine times that of the oil alone.

During the years after WWI most efforts in the field of colloidal fuels were devoted to improving the stabilizers which were believed to hold particles in suspension due to an increase of viscosity. A number of patents in the U. S., U. K., Germany, and Japan resulted from these efforts, which dealt with metal soaps, saponified products, and tars. In the United States, R&D activities in this field slowed considerably during this period. However, in Great Britain a number of both basic and applied studies were conducted by Bates⁽⁹⁾ as a continuation of the studies of the SDA. These included investigations of fuel stabilization and the related problems of ash removal, grinding, and mixing. As a result, a commercial plant for the production of colloidal fuels was built by Mineral Separation Ltd. In 1933 the Cunard Line successfully tested colloidal fuel on its ocean liner Scynthia, which travelled across the ocean on 150 tons of colloidal fuel containing 40 percent coal of 64-micron fineness. Conventional oil-burning equipment was used without apparent loss of power

or operational difficulties. The fuel was said to have been stable for several months. However, follow-up experiments with another ship using cheap high-ash coal were less successful.

Fundamental studies were conducted in 1933 by the British Fuel Research Board on colloidal suspensions of 40 percent coal mixed with various oils. The results extended knowledge of the stabilization mechanism in colloidal fuels. It was found, among other results, that viscosity per se does not improve the stability of an oil/coal mixture. Other stabilizing influences include electric charges, surface effects, and mechanical motion.

In Japan⁽¹⁰⁾, a colloidal fuel was stable up to 450 days with 30 percent bituminous coal of less than 10-micron fineness in a naphthalenic oil. Germany reported good success with tars as stabilizers. In 1932 German science developed its highly successful "Fließkohle" (flowing coal) having 55 percent coal of 55-micron fineness in tar oil. Its heating value was 15,345 Btu/lb.⁽¹¹⁾

The grinding of coal received considerable attention, since the energy absorbed and the corresponding costs are inversely proportional to the grain size of the coal. Attempts were made to grind the coal and oil together to achieve a more intimate mixing, but these efforts met with only fair success.

From the various experiments it appeared that some grinding methods yield coal which is more stable in an oil suspension than others. It may be speculated that the method of grinding may affect the basic structure of the coal particle, its surface roughness, porosity, and other physical parameters. An experiment by Kern⁽¹²⁾ appears pertinent, which showed that the porosity, and thus the specific gravity of fine coal in water can be changed by rapid heating to 550 C. Specific gravities between 0.3 and 0.5 were obtained, which indicates a product well suited for preparing coal for colloidal fuel. The observed porosity was explained as a pressure effect of the water vapor within the coal, which explodes it into a highly porous mass that can be reground into small particles of low specific gravity.

Some investigators have shown that it is not always necessary to grind coal into fine particles before mixing with oil. At the Koppers Company⁽¹³⁾ coal partly dissolved in tar could be precipitated as particles of 2 to 3-micron fineness by a small addition of a light petroleum fraction. The precipitate was somewhat difficult to separate from the tar but had an ash content of only 1/2 percent. Miyazaki⁽¹⁴⁾ developed a method in 1938 of preparing a colloidal fuel without grinding by heating a mixture of 40 percent coarse coal with oil in a hydrogen atmosphere at a pressure of 20 atm. to about 40 C for 1 hour. This resulted in a very stable (6-months) suspension. It was explained as being attributable to action of the hydrogen which caused deoxidation and splitting of the coal into very fine grains.

One of the most extensive U. S. studies was carried out at the Engineering Experiment Station of Kansas State College starting about 1938, and supported a few years later by the Pittsburg and Midway Coal Mining Company⁽¹⁵⁾. Studies on grinding, mixing, pipeline transport, mixture stability, combustion in locomotive type oil burners, and economics were carried out. It was found:

- "(1) That efficiency in grinding is dependent upon, but not necessarily directly proportional to, the size and uniformity of the charge of coal, the type and size of grinding agent used, and the length and speed of grinding.
- (2) That a propeller type agitator is most successful for mixing operations.
- (3) That successful mixing of coal and oil, either continuously or in batches by means of a propeller type agitator, requires the formation of a vortex into which the pulverized coal is fed.
- (4) That colloidal fuel having a coal concentration up to 40 percent by weight obeys the fundamental law for viscous flow of fluids in the laminar range, and may be transported satisfactorily and economically through pipes without clogging.
- (5) That spent alkylation acid was the only one of 148 surface active agents tested which was found to have a stabilizing action with industrial possibilities.

- (6) That combustion of colloidal fuel containing 40 percent of coal by weight was equal to, or better than, that obtained with either powdered coal or fuel oil alone.
- (7) That the economic advantages of colloidal fuel will become increasingly attractive as fuel oil supplies become more limited."

During WWII, greater efforts to increase production and utilization of colloidal fuels were sponsored by the Bureau of Mines in cooperation with the industry. Butcher⁽¹⁶⁾ reported positive results obtained in a boiler plant of the Gulf Oil Corp. with 45 percent coal added to fuel oil without using a Gulf stabilizer. To keep the coal from settling, the mixture was continuously agitated by circulation within a closed loop from which the fuel flow to the burner was tapped; this proved to be quite satisfactory. Although rather fine coal (59 percent below 45 micron) was used in the experiments, it was concluded that, with a circulation system, coal fineness up to 150 microns might be sufficient. The burner was equipped with steam atomizers. A 45/65 coal/oil mixture was considered optimal, primarily from the standpoint of the pumping power of the circulation pumps. This power increases with increasing viscosity of the mixture, which is controlled by the mixture ratio. Measured factors of the viscosity increase of the colloid over that of the oil were: 1.38 at 20 percent; 1.85 at 30 percent; 3.21 at 40 percent; 19.75 at 50 percent coal. Otherwise, no adverse effects on combustion and slagging were noted.

Barkley, et al.⁽¹⁷⁾, reported on tests made at a boiler plant of the Atlantic Refining Co. The colloidal fuel was prepared without a stabilizer by adding coal dust of about 62-micron fineness into the oil suction line to the storage tank. The mixture was circulated within the tank for 12 hours before the tests. During the combustion tests of 7 days duration each, no circulation in the tank was applied. The fuel was pumped through a 110-ft-long line to the burner at a temperature of 170 F. No difficulties arose during operation with a steam-atomizer type of burner. The flame was easy to control, and about the same boiler efficiencies were obtained with either oil or the colloidal fuel. It was

concluded that: "Burning colloidal fuel, after it is in the furnace, does not present much of a problem."

This conclusion and the recommendation to search for further methods of stabilization with and without chemical stabilizers seem to represent the general level of expertise at the end of WWII, at which time most of the efforts in this field were discontinued.

An effort to use colloidal fuel in a diesel engine was reported by Martin⁽¹⁸⁾ in 1936. A colloidal coal/oil fuel was successfully used in an 80 hp diesel engine which had been converted to operation with coal dust. German Fliesskohle was used as a fuel; this fuel, despite its lower heat value, yielded higher power output than did operation with either coal dust or oil.

During the postwar years the abundant availability and the low price of fuel oil rendered the use of colloidal fuel unattractive, because of the relative difficulty of its preparation and use. Most efforts in R&D on colloidal fuels were discontinued.⁽¹⁹⁾ No further publications were found which advocated the advantages of colloidal fuel as a substitute for fuel oil until the recent energy crisis again brought this problem into the limelight.

EARLY STUDIES ON COAL DUST FUELS

Past attempts to replace fuel oil by coal dust are pertinent because the experience with coal-dust operation may guide the future use of colloidal fuel in internal combustion engines and gas turbines. Such studies date back to 1903 when Rudolph Diesel unsuccessfully tried to develop an internal combustion engine for use with coal dust. Diesel's ideas were revived during the period from 1920 to 1940, primarily in Germany by a number of investigators. Their work is described by Wahl⁽²⁰⁾ in his book On the Limits of the Coal Dust Engine. The limited success of all these efforts is ascribed to the seemingly insurmountable problem of engine wear caused by erosive action of the ash particles in the relatively coarse coal dust available at that time. In contrast, Rohrbach⁽²¹⁾ has recently suggested that the problem of wear may be eliminated by using extremely fine coal powder of 4-micron size. Soehngen has recently carried out an extensive review of this prior art which he summarized as follows.⁽²²⁾

About 9 patents which issued between 1880 and 1900 were located in Germany that dealt with the subject of coal burning IC engines. Probably the most important patent was that of Diesel, whose basic patent on a "self-ignition" IC engine included liquid as well as solid fuels.

During the first decade of the 20th century more patents issued and literature was published which indicated some experimental efforts in this field. McCallum in England, and Vogt, v. Recklinghausen and Worgitzky in Germany, are said to have demonstrated that IC engines could operate on pulverized coal. However, the best known efforts are probably those by Diesel who conducted a number of experiments injecting coal powder into his self-ignition motors; however, being unable to sustain motor operation beyond 7 minutes, he gave up.

The most important experimental effort was conducted by Diesel's co-worker Rudolph Pawlikowsky who between 1911 and 1940 advanced more than any one else the cause of the coal-dust Diesel engines, not only through his ingenious technical developments, but also through his worldwide promotion of the basic concept of the coal-burning motor. In 1916

Pawlikowsky founded the KOSMOS Motor Company in Goerlitz, Germany, which was solely devoted to the development of the "RU-PA" coaldust motor. Pawlikowsky had more than 40 patents in many countries, designed, built and tested 7 different motors having one to three cylinders. He solved many of the basic problems concerning combustion, valves, seals, lubrication, etc. He demonstrated operation on hard coal, lignite, peat, rice shells, flour, saw dust and other solid fuels. One of his important developments was the pre-combustion chamber or "by-chamber" within which the fuel, injected at low pressure, was preconditioned for the combustion within the cylinder. One engine accumulated 9000 hours of operation over a period of 12 years.

Parellel to Pawlikowsky's efforts, IG Farben (Oppau) executed from 1925 to 1929 a test program on a large coal burning Diesel engine (4-cyl) of 450 HP, the largest coal burning engine in its time, and added 12 innovations to the patent literature. One of the more important contributions was the development of a method by which solvent refined ash-free coal (SRC) after the Pott-Broche pressure extraction method could be improved by raising its initial softening temperature from 200°C to 1000°C; this rendered the SRC ideal for use in coal burning Diesel engines.

In 1931 the Schichau Werke (Elbing), a shipbuilding company, started a development project on coal burning in a large low RPM ship-board-type Diesel engine. It specifically emphasized the problem of wear due to erosion. About 6000 hours of operation were logged. However, the project was terminated in 1939 on the reasoning that detailed studies of the economic potential of coaldust engines in competition with other engines or power systems had revealed a rather dim commercial future for the coaldust engine.

A more optimistic view prevailed at the I.Brüenner Maschinenfabrik, Brno, CSSR who also, on the general interest aroused by Pawlikowsky's publicity, had started a coaldust engine development program in 1931. Six different types of coaldust Diesel engines were tested and for the first time it could be demonstrated that despite the slow burning characteristics of coal, engine speeds up to 1200 RPM could be obtained. The program continued through 1945 when it was terminated at the end of WW II.

Stimulated by the national interest in fuel independence from foreign sources in 1934, The Hanomag Company (Hannover), in cooperation with a large steel corporation, the Bochumer Verein acquired a license and a test engine from the Kosmos Company and started a program to improve the Pawlikowsky engine for commercial applications (see Figure 1). Fuels like hard and soft coals, SRC, as well as coffee (for a potential Brazilian market) were tried. On the basis of many years of experience, the Pawlikowsky low pressure "By-chamber" fuel injection system was replaced by a newly developed high pressure coal-air injection system which seemed to improve the overall performance.

It appears that the German developments demonstrated successfully the technical feasibility of burning coaldust efficiently in IC engines. Thermal efficiencies of up to 32% were reported; operation with a variety of solid fuels beside coal appeared possible; thermal loading high enough to run a practical engine could be obtained. Engine wear could be reduced to about 3 times that of conventional engines.

With the end of WW II all German development efforts ceased up to date. However, in 1948, 1951 and in 1973 a number of interesting patents or patent applications were published; they were based on the concept of coal combustion in a chamber separate from the engine cylinder or even coal gasification in a pre-chamber; this should keep coal and ash particles from entering the engine cylinder and so reduce the engine wear.

During the period from 1945 to 1970, coal dust as a fuel became of interest to the gas turbine industry. According to Gyarmathy⁽²³⁾, considerable efforts have been spent at Brown Boveri Company, Switzerland, and the Aeronautical Research Laboratories, Melbourne, Australia, and in South Africa to develop direct coal-fired gas turbines. In the United States, the Locomotive Development Committee of Bituminous Coal Research, Inc. worked for 10 years to develop a pulverized-coal-fired gas turbine locomotive, and Union Pacific Railroad operated such a locomotive in regular service for 600 hours. The General Electric Company also, carried out research aimed at a gas turbine combined with a coal gasifier, including study of erosion and corrosion of turbine hot parts by coal ash.⁽²⁴⁾

FIGURE 1. The Hanomag 106 HP Coal-Dust Engine which operated for about 700 hours with an effective efficiency of about 29% on coal dust up to 250μ in diameter. (22)

The most severe problems encountered were blade erosion due to particulate matter in the fuel. The most dangerous components of the slag were alkali metals and sulphur, which at the high operational temperatures of the blades tend to dissolve the protective oxide coatings of the blade metal.⁽²⁵⁾ As found by the Australian studies⁽²⁶⁾, the blade damage seems to decrease with decreasing particle diameter of the coal. Particle sizes below 5 microns were said to cause only insignificant damage. Studies at Westinghouse Research Laboratories have suggested that blade erosion falls off sharply for particle sizes below 2 microns. General Electric studies were terminated for financial reasons.

One of the more interesting aspects of this previous technology is the work related to the so-called ILOK process, which was being widely promoted in the early 1970's by Krajcovic⁽²⁷⁾, and who at one time claimed energy requirements of only 25 kWh/ton to produce micron sized coal dust. The ILOK powder technology was ascribed to the work of Rohrbach in Germany, who worked on coal dust diesel engines and presumably developed technology to produce 4-micron and submicron coal powders.⁽²¹⁾ Rohrbach was one of Germany's most prolific inventors in the field of aircraft with over 400 patents credited to him. In 1936 he left the aircraft industry in order to pursue his "hobby", the development of coal-dust-operated diesel engines, following Diesel's original ideas. Rohrbach maintained that his success in this field was based on the results of systematic coal-dust combustion studies which led to the discovery that only coal dust of a fineness below about 4 microns has a sufficiently high rate of combustion. Subsequently, he spent considerable efforts on the development of methods of economically producing 4-micron coal powder of high uniformity. He developed a high-speed impact-beater mill which he claimed later was improved by the addition of an integrated ash/sulphur separation system. For reducing the 4-micron powder into submicron size, he also claimed to develop a unique system⁽²⁸⁾ to split the 4-micron particles explosively by thermal shock into particles of 0.002 to .003 micron. At the onset of WWII his work was stopped as not sufficiently relevant, and Rohrbach continued working under a classified project on the development of the submicron coal powders into a high-yield explosive. Allegedly, this work was later continued in Switzerland, also under a classified project. In 1971, Rohrbach

published his early work on the coal-dust diesel and the submicron powder⁽²¹⁾, apparently his only publication of these efforts. In this publication, Rohrbach stated values of the energy consumption for grinding which were ten times higher than the values quoted earlier by Krajcovic.

As shown by Figure 2, taken from Reference (21), the grinder for producing the 4-micron powder is a 35 hp impact mill with four rotors operating at 10,000 rpm. Their diameters increase in the flow direction from 600 to 1100 mm, the corresponding tip speeds from 300 to 575 m/sec (1800 ft/sec). Each rotor disc is equipped with a number of beater plates and operates in a separate chamber. The coal particles and their carrier gas (low-pressure nitrogen) are transferred through annular openings around the shaft within the separating walls. Through an attached blower wheel and centrifugal ejector tubes the heavier particles of the ash and pyrites allegedly are removed centrifugally. The sketch represents only the principal components; it in no way allows analysis of its operation and estimation of its energy absorption. Figure 2 provides only a hint of how the heavier ash and pyritic sulphur particles can be separated from the coal powder in the centrifugal ejector tubes. However, the arrangement shown in the sketch appears unlikely to be capable of cleanly separating the components of the comminution process.

The basic idea of producing submicron coal powder by thermally splitting a 4-micron particle is described in a German patent of 1940.⁽²⁸⁾ It is claimed that rapid injection of 4-micron powder into a heated chamber at about 1000 C will disintegrate the particles into very fine powder due to the high pressure of the gases which are enclosed in the cavities of the coal particle; it is maintained that this mechanism will work only in very small particles, whose wall thickness is sufficiently small to be cracked by the internal gas pressures. Figure 3 shows the basic reactor arrangement patented by Rohrbach. The fine submicron powder settles at the bottom of the reactor, while the volatiles including volatile organic contaminants leave the reactor at the top. Although it is claimed that all contaminants are removed from the coal, it is difficult to understand how this is accomplished.

FIGURE 2. ROHRBACH BEATER (IMPACT) MILL⁽²¹⁾

FIGURE 3. MEANS FOR PRODUCTION OF FINE PULVERIZED SOLID FUEL⁽²⁸⁾

CURRENT STATUS OF TECHNOLOGY

The best general references for the current status of colloidal fuels are certainly the proceedings of the two last symposia on coal-oil mixture combustion. (29, 30) However, numerous other pertinent publications exist, in fact, the number is so great that it is difficult to select typical ones for reference purposes. In order to summarize this area of technology, the technology itself has been subdivided into the categories of coal comminution; physical cleaning techniques; chemical cleaning techniques; mixing, storage and transfer; and final product use.

Coal Comminution Technology

Very little has changed over the past several decades with regard to size reduction and classification in commercial operations. Some equipment modifications have improved the efficiency of both the crushing and classification steps, but basically few major modifications and little change in procedures have occurred in commercial practice. Presently, most commercial plants operate to produce a minimum amount of undersized material. At the same time, as pressures mount to remove a higher fraction of the inorganic content of coal, or new ways are developed for using finely divided coals, the grind specifications may gradually be changed to maximize the finer sizes.

Size reduction in current commercial coal operations typically is carried out by rotary crushers and breakers. Some operations also employ impact-type crushers for size reduction. Typically, the coal is crushed and sized by dry screens to produce either a suitable feed to a beneficiation operation or to satisfy a certain market demand. Because of the finer sizes required for use as beneficiation plant feed in more modern facilities, hydrocyclones are now often installed to separate the finer sizes. The production of particle sizes less than 325 mesh (or 44μ), has been of little commercial interest in the past.

Four types of pulverizers are in general use for the comminution of coal:

(1) Low-speed mills. These devices contain parts resembling a ball thrust bearing, or rollers running in a ring, crush the coal that passes between these grinding parts. After each pass through the grinding zone, the coal is lifted to the top of the mill in air, where the fine coal is carried out and the coarser coal is recirculated to the grinding zone.

(2) High-speed impact mills. The coal particles in these devices are batted about between pins of hard material mounted on disks revolving at about 1800 rpm.

(3) Ball or rod mills. These are essentially barrels filled with iron balls or steel rods, into which coal is dumped. As the barrel revolves, the cascading charge grinds the coal. The fine coal is carried out by air circulated through the mill, and passes through a classifier which returns the oversize fraction to the mill.

(4) Hammer mills. These usually drop coal into the top of a grinding chamber in which the coal is battled about by hammers passing in close proximity to a screen or grid of circular section. When the coal is fine enough to fall through the screen, it passes out of the grinding chamber. Such mills are used to make finely crushed coal, but are not suitable for making pulverized coal of high fineness.

One of the most comprehensive reviews of conventional fine and ultrafine grinding technology was the work by Sun and Hsieh in 1969.⁽³¹⁾ For the purpose of ultrafine grinding, defined as the production of particles in the low micron or submicron range, vibratory and fluid energy mills were reported to be the most promising among the existing methods of comminution. Vibratory mills are basically a shell containing a charge of grinding balls, the entire assembly being subject to vibration at suitable frequencies by the use of an oscillating drive.

Fluid energy mills accomplish comminution by impact or rubbing of the particles undergoing comminution against other such particles, or against a mill surface or a target, or in a stream of compressed fluid ejected through suitable nozzles. The idea of shattering particles by entraining them in a fluid stream and causing them to impinge on a solid plate was apparently first patented in 1880. However, it was the Micronizer,® introduced in the early 1930's which has been and still is one of the most successful mills in use today.

There are therefore three types of processes for particle reduction in fluid energy milling. These are termed 'impact', which refers to the impact of the particles upon a relatively large target surface; 'attrition', involving the rubbing of particles upon each other or involving collisions between particles; and 'explosion', embodying the disruption of the particles by a sudden change in pressure.

The following examples of these processes were discussed:

1. Mills with impact-plate -- Nozzle crusher, dispersal tube mill, jet impact pulverizer and the sugar mill
2. Mills without impact plate -- Micronizer, Eagle mill, Reductionizer, Jet-O-Mizer, Majac pulverizer and the Gem fluid energy mill
3. Mills with pressure shocks -- Explosive-shattering devices of various designs.

The characteristics of these processes are further outlined in Table 1. Various other unconventional techniques were also summarized by Sun and Hsieh.

An example of the increasing energy requirements as the size of the coal is decreased is shown in Figure 4, where three grinding laws (Kich, Bond, and Rittinger) are compared with actual results. As may be noted, the well publicized Ilok process claimed an energy requirement of 24 kwhr/ton, which is an almost exact extrapolation of Bond's law for 4 μ coal, but is an order of magnitude lower than current practice.

The recent meeting on COM at Danvers⁽³⁰⁾ provided a large amount of information on the current status of this technology. The first commercial colloidal fuel plant needing fine grinding is that of CoalLiquid, Inc. at Shelbyville, Kentucky, and a description of the facility was provided. The slurry produced consists of 50 percent coal, 30 percent oil and 20 percent water by weight. Three cage mills in series were necessary to achieve the desired coal fineness of 80-90 percent minus 200 mesh. Work underway at the Pennsylvania State University to measure energy parameters for ball mill grinding of coal in various oils and in water, as well as air in the size range for use in coal-oil mixture fuels was reported. It was found that the breakage action parameters for all the coals tested did not change with the environment, as previously thought. The smaller coal size measured was 400 mesh, representing up to about 50 percent of the product. The University of Toronto is studying comminution of coal in an Szego mill, which is sketched in Figure 5, and

TABLE 1. FLUID ENERGY MILLS⁽³¹⁾

GROUP 1			GROUP 2		GROUP 3
1.FEED. 2.AIR INLET. 3.NOZZLE. 4.DISPERSING TUBE. 5.IMPACT PLATE. 6.CLASSIFIER. 7.DISCHARGE. 8.COARSE RETURN.	1.FEED. 2.AIR INLET. 3.NOZZLE. 4.DISPERSING TUBE. 5.IMPACT PLATE. 6.CLASSIFIER. 7.DISCHARGE. 8.COARSE RETURN.	1.FEED. 2.AIR INLET. 3.NOZZLE. 4.DISPERSING TUBE. 5.IMPACT PLATE. 6.CLASSIFIER. 7.DISCHARGE. 8.COARSE RETURN.	1.FEED. 2.AIR SUPPLY. 3.PRODUCT DISCHARGE. 4.COARSE MAT ^l RETURN.	1.FEED. 2.AIR SUPPLY. 3.PRODUCT DISCHARGE. 4.COARSE MAT ^l RETURN.	1.FEED. 2.AIR SUPPLY. 3.PRODUCT DISCHARGE. 4.COARSE MAT ^l RETURN.
WITH IMPACT PLATE			WITHOUT IMPACT PLATE		EXPLOSIVE
TYPE D = 2 1/2 IN.	L = 60 FT. OR 30 IN.	D = 2 IN. H = 3 TO 4 FT.	H = 4 FT. APPROX.	VARYING	VARYING
CAPACITY VARYING TO 1 TON/HR.	UP TO 1 TON/HR.	—	VARIES WITH MATERIAL	—	—
EXPERIMENTAL	COAL, ETC.	COAL, LIGNITE, ETC.	COAL, ETC.	SUPERFINE GRINDING	COAL, ETC. STILL EXPERIMENTAL
FINING 30-60% < 75 MICRONS	30-60% < 75 MICRONS (μ)	AIM NORMAL P.F.	100% < 10 MICRONS	100% < 44 MICRONS	WITH COLOIDER 60% < 44 MICRONS
STEAM 250 LB./SQ. IN.	AIR 2 TO 5 LB./SQ. IN.	—	UP TO 200 LB./SQ. IN.	100 LB./SQ. IN.	FROM 90 LB./SQ. IN.
FEED 10-100 LB./LB. FEED	—	—	AIR 15-150 LB./LB. FEED	APPR 15-150 LB./LB. FEED	STEAM 0.7 LB./LB. FEED AIR 15-150 LB./LB. FEED
POWER CONSUMPTION VERY HIGH	30 KWH/TON	20-30 KWH/TON	NO FIGURES	NO FIGURES FOR PULVERISED FUEL	EXPERIMENTAL
DEVELOPMENT TRENDS & COMMENTS	IMPROVED CLASSIFICATION. INCORPORATION OF ATTRITION MEANS. COMBINATION WITH GAS TURBINE TO REDUCE COST OF SUPPLYING PRESSURE AIR USED COMMERCIALY FOR SEVERAL YEARS	AIM TO UTILISE ALL KINETIC ENERGY IN CAUSING ATTRITION LITTLE DEVELOPMENT WORK DONE	DISPOSAL OF JETS & CHOICE OF DIMENS- IONS TO GIVE LOWER RUNNING COSTS. USED COMMERCIALY	VERY WIDE VARIETY OF TYPES	USE OF HIGHER ABSOLUTE PRESSURE MAKES THIS MORE ECONOMIC

FIGURE 4. ENERGY REQUIREMENTS FOR COMMINATION⁽³²⁾

FIGURE 5. THE SZEGO GRINDING MILL⁽³⁰⁾

involves helical grooved rollers. There is concern about long-term life of the grooves. For 80 percent less than about 20μ , energy requirements were in the range of 35 to 130 kwh/ton with #2 and #6 oils as the grinding environment. Lower energy requirements were obtained at lower mill speeds.

There was a considerable amount of information presented by Japanese investigators on the performance of "fine" particle COM at Danvers, but apparently this nomenclature refers to 75 percent less than 200 mesh, which is not particularly fine. British investigators announced an effort to produce less than 10μ material, but the details were not disclosed.

Florida Power Corporation and Dravo Corporation discussed their partnership called COMCO whose primary goal is to develop an ultrafine (100 percent minus 325 mesh) COM fuel. The pilot facility is located in Pittsburgh, Pennsylvania. The three types of fluid mills shown in Figures 6, 7, and 8 have been tested. The annular or so-called "doughnut" mill is comprised of a lower grinding zone coupled to a classification zone. Coal is fed into the intense turbulence of the grinding zone which is created by gas passing through several specially oriented nozzles. Pulverized coal is swept by the gas into the classifier where oversized material is rejected and transported back to the grinding zone. The toroidal or "pancake" mill features several tangential gas nozzles which create a turbulent vortex action within the mill. Coal feed is evenly distributed within this vortex, pulverized by impact, and the finer coal swept to the inner radius where it leaves the mill through a central classifier. In the opposed jet mill, an impact zone is created by two nozzles aligned in opposite directions on a common axis. The shattered coal is then transported to an external classifier where the oversize is rejected and returned to the nozzles for regrinding. Steam requirements to drive the mills are being established, which will eventually determine costs. A generalized curve has been presented, as shown in Figure 9, which would indicate that average sizes below about 7μ have not been obtained under practical conditions by COMCO.

FIGURE 6. ANNULAR (DOUGHNUT) MILL⁽³⁰⁾

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FIGURE 7. TOROIDAL (PANCAKE) MILL⁽³⁰⁾

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FIGURE 9. TYPICAL FLUID MILL PARTICLE SIZE VERSUS ENERGY INPUT⁽³⁰⁾

J.W. COCHIRAN & F. R. SELL

Some of the most interesting recent research on coal comminution has been supported by Peters at Pittsburgh Energy Technology Center.⁽³³⁾ Contracts were awarded to Union Process, Inc. to use their Attritor® mills, originally developed for the production of paint pigments and paper coatings, for the production of low micron sized coal. Sketches of batch, circulation and continuous Attritor® mills are shown in Figure 10. Plant ground coal (70 percent less than 200 mesh), premixed with oil, was used as the feed, and a product consisting of 1-5 micron coal mean particle size was obtained, which had the consistency of India ink or black mayonnaise. Deflocculants were sometimes added to the fuel to improve dispersion and to reduce viscosity. The U. S. Bureau of Mines developed a similar attrition mill in the early 60's for the wet comminution of industrial minerals for extreme fineness.⁽³⁴⁾ Other attrition mill systems now include the Dyno-Mill, produced by Willy A. Bachofer, Maschinenfabrik, Basel Switzerland, and the Microprocesses Wet Grinding System by Microprocesses, Ltd, Buch, Switzerland. Herbst and Sejulveda at the University of Utah have investigated the energy requirements of the Union Process mill and estimated an energy requirement of 45 kwh/ton for 7 μ particles and 208 kwh/ton for 3 μ particles of Lower Freeport coal; and 178 kwh/ton and 917 kwh/ton for similar sized products from Montana Rosebud coal.⁽³³⁾ They also reported that a deflocculant, even though it modified the viscosity and flow characteristics of the ground coal, had no effect on the comminution energy requirements.

One of the most unusual approaches to coal comminution involves chemical procedures. This involves the permeation of certain low-molecular-weight compounds throughout the existing faults, pores, and other discontinuities in coal resulting in the weakening and disruption of the inter-layer forces. The chemical selectively affects the coal but not the mineral matter associated with it. The net result is the fracture of the coal, the breakage being induced selectively along the cleats, bedding planes, maceral boundaries, mineral constituents, and the mineral boundaries. The fragmented coal and unaffected mineral matter can then be separated by some conventional cleaning process. The chemicals that have been reported to have the greatest comminution ability are ammonia and methanol. In general, the higher the rank of coal, the less responsive it is to chemical

BATCH

CIRCULATION TYPE

CONTINUOUS

FIGURE 10. THE ATTRITOR® (UNION PROCESS, INC.) MILL⁽³³⁾

comminution. It is claimed that by varying the comminution conditions such as chemical concentration, pressure, temperature, and exposure time, coals of all ranks can be comminuted to a similar degree.

The chemical comminution of coal with ammonia has been studied by the Syracuse University Research Corporation⁽³⁵⁾ since 1971. Various organizations have investigated the use of sulfur dioxide for such purposes and at least one recent patent has issued (U.S. Patent No. 4,120,664). A 40-ton/day capacity pilot plant using chemical comminution with ammonia has been designed by Catalytic, Inc., who had an exclusive license to commercialize the process. Catalytic is actively seeking funding to construct and operate such a facility, and has recently obtained a small contract for further preliminary work from EPRI. The application of chemical comminution technique for underground mining, underground gasification, degasification, and general permeability enhancement of underground coal seams, has been proposed.

Physical Cleaning Technologies

The washing or cleaning of relatively coarse particle size coal is currently practiced commercially for the prime purpose of ash and sulfur removal. The sulfur occurs in coal in an organic, as well as an inorganic, form. In the inorganic form, the sulfur is present as iron pyrites and sulfate. In the past, the higher grade coals were upgraded by various gravity separation techniques such as tables, jigs, and heavy media separation. These processes removed only part of the pyritic sulfur. None of the organic or sulfate sulfur was removed by these means. The gravity separation techniques were (and still are) commonly applied to the coarser size fractions, ie, plus 35 mesh. These techniques were incapable of removing the finely disseminated pyrite.

As the utilization of lower grade coals began to increase, it became necessary to devise means other than gravity to remove the finely disseminated pyrite. This need resulted in finer grinding of the coal to liberate the pyrite. The finer ground coal, minus 35 plus 150 mesh, is currently being treated in hydrocyclones and by froth flotation. Generally, the hydrocyclone is superior to froth flotation for pyrite removal, because the reagents used tend to interact with the pyrite and report with the clean coal fraction. The use of hydrocyclones with subsequent flotation is finding increased application. Presently, other unusual methods of removing sulfur are being studied, such as electrical, chemical, and thermal techniques, but these are not being used commercially.

All of the coal cleaning methods in general use rely upon specific gravity separation except froth flotation. The most common test of washability involves float-sink analysis of the heavy and light fractions at various specific gravities.

A mammoth study was initiated in 1965 by the U. S. Bureau of Mines to determine the sulfur release potential of coals from principal utility-coal producing coalbeds of the U. S., as a function of coal particle size.⁽³⁶⁾ The samples were collected from working mines producing steam coals; where possible, the largest mines from a specific bed were sampled. Float-sink analyses are performed on these samples to determine the effects of crushing on the liberation of pyritic sulfur and other impurities.

The average raw coal contained 14.0 percent ash, 1.91 percent pyritic sulfur, 3.02 percent total sulfur, and 12,574 Btu per pound. This is equivalent to 4.8 pounds $\text{SO}_2/10^6$ Btu fired at the power plant. For a coal of 12,500 Btu per pound, a sulfur content of 0.75 percent is equivalent to 1.2 pounds $\text{SO}_2/10^6$ Btu. However, 63 percent of the sulfur in these coals was pyritic, so significant sulfur reductions by physical coal cleaning are possible. The results of this study are shown graphically in Figure 11, and are summarized as follows.

Crushing these coals to 14 mesh top size and removing the sink 1.40 specific gravity material provided a product analyzing 5.0 percent ash, 0.50 percent pyritic sulfur, and 1.69 percent total sulfur, with a heating value of 13,913 Btu per pound at a Btu recovery of 79.6 percent. This upgrading would reduce the ash by 60 percent, pyritic sulfur by 69 percent, and total sulfur by 38 percent, resulting in a clean coal which would produce 2.5 pounds $\text{SO}_2/10^6$ Btu fired.

The ash, pyritic sulfur, total sulfur, and heating value contents varied considerably, as would be expected when washability data of coals from various regions of the United States were evaluated. The coals in the eastern U. S. ranged in rank from low- to high- volatile bituminous. The low-volatile coals found in the southern part of this area contained, on the average, 1.0 percent total sulfur and 13,314 Btu per pound. Generally they could be upgraded upon crushing to a size level significantly coarser than that of interest in colloidal applications, and then by use of gravimetric separation, to meet a 1.2 lb $\text{SO}_2/10^6$ Btu emission standard.

The high-volatile coals found in the northern part of this area contained, on the average, 2.01 percent pyritic sulfur, 3.01 percent total sulfur, and 12,693 Btu per pound. Crushing these coals from 1-1/2 inches to 14 mesh top size and removing the sink 1.60 specific gravity material would provide a product analyzing 0.66 percent pyritic sulfur, 1.66 percent total sulfur, and 13,821 Btu per pound at a Btu recovery of 92.1 percent. Thus, physical coal cleaning on volatile coarse coal could provide reductions in pyritic sulfur of 65 percent, total sulfur of 41 percent, and pounds-of- SO_2 -emission-per-million-Btu of 46 percent.

FIGURE 11. WASHABILITY RESULTS ON TYPICAL U.S. STEAM COALS (36)

The coals of the midwest U. S. were on the average high-sulfur coals analyzing 2.70 percent pyritic sulfur and 4.34 percent total sulfur. Because of the average high-organic sulfur content of 1.63 percent, these coals generally could not be upgraded to meet the new source sulfur emission standard. However, upon crushing these coals to 14 mesh top size and removing the sink 1.40 specific gravity material, an average pyritic sulfur reduction of 68 percent would be obtained.

The coals of the western U. S. are generally of low-sulfur content s mined, averaging 0.68 percent total sulfur; however, because these lower rank coals contain up to 25 percent inherent moisture, they are low-Btu-content coals and just barely meet, on the average, the 1.2 pounds of SO_2 /M Btu new source emission standard.

By further comminution, at least in theory, all pyritic sulfur has the potential to be removed by physical coal cleaning. The desire to reduce the sulfur content of coal even further because of the environmental aspects has led to increased emphasis on further comminution and treatment of such finer coals by heavy liquid, selective agglomeration, flotation, magnetic, electrostatic, air classification, immiscible liquid, selective flocculation, and thermal methods. All of these methods have been studied over the years with variable degrees of emphasis as a means of desulfurizing and removing ash and thus pyritic sulfur, from coal.

Froth Flotation

Coal flotation is now considered one of the conventional methods for upgrading coal. Although flotation is normally classed as a physical separation method, strictly speaking, it involves both physical and surface chemical aspects, and the latter are normally considered more important than the former. In flotation the surface characteristics of minerals assume critical importance. The flotation feed consists of finely dispersed particles in an aqueous medium into which a continuous stream of air bubbles is introduced so as to effect contact between the air and selective mineral grains. Those particles which exhibit a nonpolar surface structure prefer air, are hydrophobic, and therefore tend to attach themselves to raising air bubbles. The net result is that these particles raise to the surface of the system where they collect in a froth.

Froth flotation is used to effect separation of the fines usually denoted 35 mesh x 0 (1/2 mm x 0). In this process the surface chemistry of the fine coal particles is frequently altered by addition of a collector [such as kerosene, potassium amyl xanthate, or MIBC (methyl isobutyl carbinol)] such that it becomes air avid. Fine air particles adhere to this surface and cause the particle to float. In many cases depressants (such as sodium or calcium cyanide) are added to enhance the selectivity of the separation by "depressing" the flotation of refuse particles. The typical effect of a depressant is usually very concentration dependent. In a flotation cell, the pulp (15 to 35 percent solids) is aerated and released, with a centrifugal force at the bottom of the device. The product forms a frothy layer at the surface and is skimmed off continuously.

The Bureau of Mines is one of the leading organizations investigating beneficiation by froth flotation.⁽³⁷⁾ Early experimental work showed that the quantity of pyrite reporting with the clean coal product increased with increasing additions of the frothing agent and with increasing pH values of the pulp. In addition, several polyvalent metal salts such as ferric chloride, aluminum chloride, chromium chloride, and cupric sulfate were found to be pyrite depressants. Other work demonstrated the effect of the concentration of frother and the rate of airflow through the pulp on the flotation of finesize coal and showed how these factors can be manipulated to clean finesize coal to lower sulfur levels. The work also ascertained the existence of critical ranges for floating the highest percentage of clean coal with the lowest sulfur content. Laboratory and pilot plant flotation tests with coals from various coal beds throughout the eastern U. S. showed that pyritic sulfur reductions of up to 80 percent could be achieved using this technique. The pilot plant work was done in a specially designed two-stage flotation facility.

Magnetic Separation

The literature confirms that the two most important factors in magnetic separation of coals are (a) the liberation size of coal impurities and (b) the development of adequate magnetic susceptibility in coal

impurities prior to separation. Magnetic concentration of coals appear most effective for removal of ferromagnetic and some paramagnetic minerals, and surface oxidation generally increases the response of paramagnetic impurities (such as pyrite) to magnetic fields.

Various methods are described in the literature to achieve partial conversion of paramagnetic minerals to a ferromagnetic form; in all cases, this allows the use of low intensity fields for practical and efficient separations. These methods include low temperature oxidation, thermomagnetic treatment of coals at low temperatures and high fields, high-temperature treatment based on phase transformations, thermal treatment with superheated steam, and high-frequency dielectric heating, or microwave irradiation. Although certain coals have shown little response to surface oxidation or phase transformation treatments, the bulk of the literature suggests that pretreatment of coals is a significant factor in achieving high separation efficiencies, with low intensity magnetic fields. Similar coal deashing and desulfurization results have been reported in the literature for untreated coals, but using high-intensity magnetic fields.

Recent studies at Indiana University indicate that the use of high gradient magnetic fields may be particularly suitable for fine coal beneficiation.⁽³⁸⁾ Preliminary experiments have shown that fine pyrite and similar paramagnetic impurities can be effectively removed from untreated coals by using high gradient field geometries and low field intensities. Work is continuing in this area at MIT and Oak Ridge National Laboratory.

Electrical Separation

Since substantial removal of pyrites in an electric field can be accomplished with dry powders systems and in suspensions in liquids in the laboratory, electrical separation processes potentially provide a method of removing the pyrite from coal. The principle of electric separation is based on the interaction of charged particles and electrical fields. In the dry systems, the electrical separation process depends on differences in the electrical properties such as the contact potentials of

the pyrite and coal which produce differences in the quantity and polarity of charge acquired and for the resistivities which determine the rate at which an applied charge drains off the particles. In liquid suspensions, differences in the amount and polarity of charge are produced by electrical double layers which are controlled with various additives. In either case, the electrical force is the product of the field intensity and the charge on the particles. Best separations are attained when the materials to be separated are charged to opposite polarities so that they move in opposite directions, but separations can be attained also when the materials have different charge levels and thereby move at different rates or when one material is uncharged and does not move at all.

In the early 1960's Glenn and Grace at Bituminous Coal Research, Incorporated, initiated a major study on coal pulverization and reported that the major portion of pyritic material exists as particles that can be liberated by controlled pulverization to sizes coarser than those used in modern pulverized coal-fired power plants.⁽³⁹⁾ Grinding to 80 percent minus 200 mesh released the major portion of the pyrite in the coal. Two comminution devices were employed, a ball mill run both under dry and wet conditions, and a Model 040S Jet-O-Mizer Fluid Energy Mill. Electrostatic and air classification techniques were studied. Battelle's Columbus Laboratories performed part of this work and demonstrated that several types of electrostatic separators including triboelectric and nonuniform field devices could remove pyrite from pulverized coal. In general, concentrating the pyrite was a relatively slow process and many cycles were necessary to concentrate the pyrite in a fraction that could be discarded economically.

Later, work at the Bureau of Mines⁽⁴⁰⁾ showed that separation efficiency was improved by confining the particle size of the feed to a relatively narrow range and by avoiding more than 10 percent dust in the coal. The best removal efficiency was attained when pyrite particles were as large as possible. In another study, Carpc Research and Engineering, Incorporated (Jacksonville, Florida), ran tests on a 10-foot-wide roll-type electrostatic separator which removed nearly all of the pyrite in certain coals at an estimated cost of 5 to 6 cents per ton of coal including drying the coal. Fine coal dust was a problem, however.⁽⁴¹⁾

Air Classification

The major air classification systems involve some sort of a change in flow direction of a particle suspension, and centrifugal separators are the most common device. However, since centrifugal separation depends on the particle mass as one criterion of separation, it is frequently not possible to distinguish between a relatively large pyrite-free low density coal particle and a relatively small high-pyrite particle of higher density. Therefore for efficient separation, steps must be taken to avoid too wide a range of particle sizes reaching the centrifuge section at any one time. Abel and his coworkers at Morgantown⁽⁴⁰⁾, developed the device shown in Figure 12, involving stepwise separation.

In the first step, the coal is pulverized and fed to the centrifugal separator with the entraining air set at a relatively low velocity. As the coal falls through the hollow drive shaft onto the spinning spreader disk, only those particles light enough to become entrained in the upward current of air will be carried to the centrifugal fan. Here the heavier, pyrite-rich particles are thrown to the chamber wall where they fall from suspension in the static air layer next to the wall and leave the separator via the heavy-product exit. The remaining entrained particles are carried into the annular space between the inner and outer cones where they fall from suspension and leave the separator via the lightweight product exit. The portion of the coal that was too heavy to become entrained as it was thrown from the spinning spreader disk falls from the separator as a heavy product. In the second step, the velocity of entraining air is increased, and the heavy product is resubmitted to the centrifugal separator in which a second light portion is removed. This procedure is repeated (usually three or four times) until the accumulated lightweight portions equal about 75 percent of the minus 200 mesh content of the coal. In practice, rather than refeed the heavy product several times to remove a series of light portions, the coal would probably be run through a series of separators with entraining air velocity increasing from separator to separator. For some coals, separation may be considerably improved by stage grinding as well; that is, by removing pyrite at intervals as the coal is pulverized to its final size.

FIGURE 12. CROSS SECTION OF CENTRIFUGAL SEPARATOR USED
AT MORGANTOWN⁽⁴⁰⁾

The air separation process was then combined with an electrostatic system and three coals from the Pittsburgh Seam were tested. Over 55 percent of the pyrite which amounted to 70 percent of the "available" pyrite, was removed in a reject of 10 to 20 percent from one of the coals. Similar treatment of the other four coals removed about 35 to 50 percent of the pyritic sulfur, which again represented about 70 percent of the "available" pyritic sulfur in these two coals. The centrifugal separators was also more efficient on the largest sized pyrite particles. It is also of interest that the mean pyrite particle size ranges from 20 to 400 microns in 61 coals used in electric power production and tested by the Bureau of Mines.

Immiscible Liquid Separation

The use of immiscible liquid systems involves the selective migration of one or more species from a water suspension to the oil phase or to the oil-water interface. The concept is not new and patents for oil flotation date back to 1860. Interest in this method was renewed in recent years and significant work was conducted on a similar concept, the so-called Convertol Process.⁽⁴²⁾

Processes in which one of the constituents is concentrated by using an immiscible collecting oil phase is typified by the shell pelletization process. This is a nonselective process for removing fine carbon black particles from dilute aqueous suspensions. Puddington and co-workers using the same principle were able to reduce the ash and sulfur content of a fine coal.⁽⁴³⁾ A flow sheet for their process is shown in Figure 13. The coal formed spherical agglomerates while the hydrophilic ash and sulfur-containing components remained in aqueous suspension. In the above cases, the naturally hydrophobic material was agglomerated with the oil phase as a bridging agent. Puddington and co-workers used tall oil to agglomerate a naturally hydrophilic mineral by the use of surfactants.

The oil agglomeration process is the only cleaning process so far announced which is being used for the production of deashed coal for subsequent incorporation in COM fuel.⁽³⁰⁾ For the past four years, New Brunswick Power has had as its main goal the removal of 50 percent ash

FIGURE 13. FLOW SHEET FOR PUDDINGTON PROCESS⁽⁴³⁾

and 50 percent sulfur in a coal being fed as a slurry in oil to a 10 MW boiler. The raw coal contains 7-8 percent sulfur and 20 percent ash, and the main constraints on its use are excessive wear of burner tips, pumps and environmental repletions. Slurry concentrations of 30-40 percent have been reached, but a 20 percent mixture is considered near optimum when considering environmental repletions and wear on equipment. It is planned to test for fuel in a 100 MW unit in the future. A CE Raymond mill is used to pulverize the coal to 80 percent <200 mesh, and a light oil is used to effect selective agglomeration. However, losses of light oil are excessive, and sulfur and ash results have not been as high as desired. Support activities at Canada's National Research Council showed that with a mean particle size of 3.3 microns, 65 percent ash removal and 50 percent sulfur reduction was possible.

Selective Flocculation

In selective flocculation the principle is to selectively aggregate particles of one species into flocs while maintaining the other species fully dispersed. The flocs can then be separated by some conventional means, such as ordinary gravity settling.

Recent experimental studies have shown that reversible flocculation can be obtained in ultrafine particulate systems (630 A) by means of thermodynamic stearic effects. Flocculation-dispersion stability is controlled by the free energy of interpenetration of specifically absorbed organic groups which, in many systems, is a function of the temperature of the system.

Particular attention is being given to long-chained surfactants that exhibit a sharp reversal in the values of the free energy of interpenetration with temperature. The separation mechanism would be based on close control of the temperature of the system and would be reversible within a narrow range of temperatures. This feature of the proposed method allows spontaneous reversibility of suspension stability with temperature, and is a major advantage over current flocculation technology.

The fact that ash and inorganic sulfur in coals normally exhibit surface properties markedly different from those of coal makes this proposed technology particularly attractive for cleaning of ultrafine coal fractions.

Heavy Liquid Separation

Heavy liquid separation is frequently used in the laboratory to effect float-sink tests, but suspensions of iron oxide, usually referred to as heavy medium separation, are usually used in commercial plants to achieve a given separating density. However, heavy liquid separation is a practical extension of the laboratory float-sink test. The crushed raw coal is immersed in a static bath of a heavy liquid having a density intermediate between clean coal and reject. The float material is recovered as clean coal product and the sink material is rejected as refuse. The heavy liquid for coal separation does not react with the coal product or reject material. The specific gravity of the liquid can be regulated by the use of certain additives. The heavy liquid parting medium is recovered essentially completely by drainage and evaporation of it from the product coal and the reject material. It has recently been claimed that one version of the process may remove a fraction of the organic sulfur. This variation should therefore be more properly classified as a chemical-cleaning process when full details are released. It is understood that the process does not work too well with fines, but this may be a problem of optimizing conditions.

The use of a heavy liquid for coal cleaning is not new. In 1936, a 100-ton/hr semi-commercial plant was built by the DuPont Company using chlorinated hydrocarbons. However, the high losses of these heavy liquids and the toxic effects of the vapors prohibited DuPont's commercialization of their process and their interest in the process was terminated.

Recently, the Otisca Industries⁽⁴⁴⁾ reported the development of an anhydrous heavy liquid for gravity separation of coal. The chemical composition of their liquid is presumably a fluorocarbon, with a boiling point of 24 C, a heat of evaporation of 43.1 cal/g, a specific gravity of

1.50 at 16 C. A pilot plant with a nominal capacity of 20 tons per hour was built at the North Branch Mine of the Island Creek Coal Company in West Virginia. It operated on an intermittent basis from June through December of 1976 and the loss of heavy liquid was about 1 pound per ton of coal. However, losses are expected to be less than 0.2 percent raw coal in a plant of improved design. American Electric Power has a non-exclusive license to use the process and is now supporting work to enhance organic sulfur removal. The process is now being demonstrated at Ohio Power's Muskingum Mine near Cumberland, Ohio. Several patents have now issued (U.S. Patents No. 4,178,231 and 4,178,233).

Other Separation Techniques

Other nonconventional methods of coal preparation include magnetohydrodynamic separation, methods based on ultrasonic phenomena and fluid-bed techniques, among others. (45)

Interesting applications of magnetohydrodynamics (MHD) have been reported for coal beneficiation by Russian investigators. They have shown that fine coals (.5-2.5 mm) can be effectively concentrated in MHD separators using CuSO_4 and ZnCl_2 solutions as the electrolyte media.

Other publications describe the use of ultrasonics to effect selective coagulation of coal slimes in ultrafine coal/clay moistures, the use of heavy liquids [CaCl_2 , $\text{Ca}(\text{NO}_3)_2$] in high-speed centrifuges, and the use of liquid fluidization of coarse coal slurries for gravity separations of similar specific gravity fractions.

Chemical Coal Cleaning

In theory, the chemical cleaning of coal appears to offer many advantages. For example, the pyritic sulfur may be removed from coal as water-soluble ferrous sulfate (FeSO_4) and elemental sulfur or water soluble sodium sulfide (Na_2S) according to the following possible reactions:

Since pyritic sulfur in coal is present as a phase distinct from the coal matrix, its extraction would be achieved without disturbing the coal structure.

Organic sulfur, believed to be part of the coal molecule, is not readily susceptible to attack by chemical leaching. Organic sulfur compounds such as the thiophenes found in coal are very stable and resistant to attack, while those such as the mercaptans are less stable and subject to attack. Thus, removal of organic sulfur from coal could involve the extraction of that portion of the coal which is combined with the sulfur, rupturing the carbon-sulfur bond to convert the sulfur to a more readily extractable form.

Ash (mineral matter) like pyritic sulfur exists in coal as a phase distinct from the coal matrix and is therefore subject to removal by a variety of leachants without disruption of the coal structure. However, since the ash is distributed throughout coal as fine particles, it may be necessary to add swelling agents to open the coal structure and make the ash more accessible to the leachant. Also, swelling agents may aid in the extraction of pyritic sulfur and the organic sulfur by making these forms more accessible to the leachant. Furthermore, physical cleaning cannot be applied to those coals having the pyritic sulfur distributed as microscopic particles throughout the coal particles.

Chemical cleaning is an approach whereby pollutant-forming constituents are reduced by treating the raw coal with a reagent or reagents that react with and liberate these constituents. This approach could

increase significantly the quantity of our coal reserves which could be used directly as a solid fuel with minimal or no pollution control.

Many chemical coal-cleaning processes are under development within the United States. Some have been developed through miniplant stage. In order to gain an overview of the chemical coal-cleaning area, a number of these are discussed in the following paragraphs. The list is not complete; some twenty-three processes have been identified by the U.S. EPA. However, those technologies showing the greatest potential have been included in the sections that follow. As far as known, the only chemical process used so far to desulfurize colloidal fuels in the United States is the Battelle process. The chemical processes generally remove all the pyritic sulfur in coal and up to about 50 percent of the organic sulfur under the best conditions demonstrated to date.

Air Oxidative Leaching

This process is a wet oxidative process employing air in place of oxygen as used in other oxidative processes. Desulfurization of the coal is achieved by heating an aqueous slurry composed of coal ground to minus 200 mesh and water at elevated temperatures under an overpressure of air. The desulfurized coal is then separated from the slurry and washed with water to remove the soluble sulfates. The aqueous effluent from both the washing and leaching operations is treated with limestone. The solids are separated from the water and sent to a disposal area. The water is returned to the process. (46)

The process was originally patented (U.S. Patent No. 3,824,084) by the Chemical Construction Company in 1974. The process has been studied extensively on a laboratory (batch) scale by the Pittsburgh Energy Technology Center at Pittsburgh, Pennsylvania, under the support of the U.S. Department of Energy. A small, continuous unit capable of processing approximately 55 lb/hr is in operation.

It is claimed that the process is capable of extracting greater than 95 percent of the pyritic sulfur and up to 40 percent of the organic

sulfur from certain coals to produce clean, solid fuels containing from 0.50 to 1.8 lb $\text{SO}_2/10^6$ Btu. Typical conditions are:

Temperature	- 150 to 220 C
Pressure (air plus steam)	- 220 to 1500 psi at temperature
Residence time	- 60 minutes
Slurry concentration	- 26 percent coal.

However, the total sulfur in the product is frequently equivalent to the original level of organic sulfur in the feed coal. The thermal efficiency of the process has not been calculated but probably is about 85 percent.

Nitrogen Dioxide Oxidative Cleaning

The process consists of treatment of dry, pulverized coal with top size of about one-fourth inch with gaseous NO_2 . The oxidation removes some of the pyritic sulfur as gaseous sulfur dioxide which is removed from the closed oxidizing gas loop. The oxidation is followed by a water washing to remove oxidized pyritic sulfur compounds (FeSO_4). An additional step is caustic washing to solubilize and remove the oxidized organic sulfur converted during the NO_2 treatment. The active oxidant, NO_2 , is regenerated in the reactor by the addition of oxygen to the feed gas. Other gases in the feed gas are NO , N_2 , and O_2 .⁽⁴⁷⁾ The process was patented (U. S. Patent No. 3,909,211) by KVB Engineering Inc., Tustin, California, in 1975. KVB has studied the applicability of the process to 8 to 10 coals in a laboratory (batch) scale. No laboratory work is currently being done. KVB is seeking funds for further development, and DOE support is pending.

Limitations on coals are not known. Degree of desulfurization on 8 to 10 coals in the laboratory was not equal for each coal, possibly due to pyritic sulfur distribution in the various coals. The preferred particle size is minus 14 plus 28 mesh. Sulfur removal efficiency is lower on larger particles. Based on the examples in U.S. Patent 3,909,211, the process is capable of removing essentially all of the pyritic sulfur and up to about 40 percent of the organic sulfur from a Lower Kittanning coal to give a treated coal containing 0.47 percent sulfur. Thermal efficiency has been estimated to be approximately 97 percent by KVB. Nitrogen oxide emissions resulting from uptake of nitrogen by the coal could present a problem during combustion.

Ferric Salt Leaching

This process has been developed to extract 80 to 95 percent of the pyritic sulfur from coal ground from 10 to 100 mesh by leaching with an aqueous ferric sulfate solution at temperatures of 90 to 130 C. The leach solution is regenerated at similar temperatures using air or oxygen. Elemental sulfur, one of the reaction products, is removed from the coal product by solvent extraction, or possibly by vaporization.⁽⁴⁸⁾ The process is patented (U.S. Patent No. 3,768,988) and is being developed by Systems Group of TRW, Inc., Redondo Beach, California. Since the early 1970's, the process has received extensive study in the laboratory under the support of the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. A reactor test unit capable of processing 8 tons per day of coal has been constructed at TRW's Capistrano Test Site under the sponsorship of EPA. The facility is capable of evaluating the critical parameters--particle size effects, regeneration of the spent leachant, and liquid/solid separation. The process is claimed by TRW to be capable of removing 80 to 95 percent of the pyritic sulfur from coal, but none of the organic sulfur. Therefore, for coals having an organic sulfur content equivalent to or less than 1.2 lb of $\text{SO}_2/10^6$ Btu, such as Martinka coal, the process should be effective in reducing the sulfur content to meet present NSPS for new sources. Laboratory studies have shown it to be effective for removal of pyritic sulfur from Appalachian and Eastern Basin coals. It should be effective on other coals providing the pyritic sulfur is accessible by the leachant. However, only about 65 percent of the pyritic sulfur was removed in the pilot plant and with subsequent laboratory extractions. Overall, thermal efficiency based on an Exxon-developed flow sheet was calculated to be about 92 percent.

Carbonyl-Activated Magnetic Cleaning

Magnetic removal of pyritic sulfur and other mineral matter from coal can be achieved by first exposing coal which normally has been crushed to minus 14-mesh, to vapors of iron pentacarbonyl at approximately 170 C. It has been reported that during the reaction with iron carbonyl

the pyrite and other mineral matter becomes strongly magnetic without affecting the coal. The magnetic mineral components including pyritic sulfur, are subsequently removed from the carbonyl treated coal with dry induced-magnetic-roll magnetic separators.⁽⁴⁹⁾

The process is patented (U.S. Patents No. 3,938,966 and 4,120,655) and has been studied in a 200 pound per hour pilot plant at Hazen Research Incorporated with the support from Inex Resources, Incorporated. This process is frequently referred to as the Magnex process. It was reported that approximately 90 percent of the pyritic sulfur was removed from a number of coals in laboratory tests. Approximately 85 percent of the pyritic sulfur was removed from a coal from the Allegheny Group of Pennsylvania during pilot plant tests. On July 29, 1977, Inex Resources assigned all of its rights, title and interest in the Magnex Process to Roldiva, Incorporated, a Pennsylvania Corporation. Although plans were made for a 60-ton per hour process demonstration unit to be operational by 1980, interest has apparently waned.

Hydrothermal Leaching

Extraction of pyritic sulfur from a wide variety of coals, along with a portion of the organic sulfur from some coals, is achieved by heating an aqueous alkaline slurry consisting of coal ground to minus 14 mesh, water, and the selected leachant at elevated temperatures and the corresponding steam pressure. The resulting slurry is afterwards separated and the coal fraction washed with water and/or acid. The aqueous solutions from both the washing and leaching operations could be regenerated by, for example, the CO_2 -CaO process. The evolved hydrogen sulfide is converted to elemental sulfur by a Claus or Stretford process for marketing or stockpiling. The regenerated leachant would be recycled to the process. The process is applicable for pyritic sulfur removal from lignite, subbituminous and bituminous coals, and the removal of a significant portion of the organic sulfur from some coals, depending on the processing conditions.

The process has been studied at Battelle⁽⁵⁰⁾ and the U.S. Bureau of Mines^(51,52) since the late 1960's. Battelle has various

patents pending and issued on their process (U.S. Patents No. 4,121,910; 4,055,400; 4,092,125; and 4,095,955). The Bureau has one patent issued (U.S. Patent No. 3,993,455). It has been scaled-up to a miniplant scale at Battelle, and a conceptual process layout for a 400-ton/hr commercial plant has been conducted under the support of the Battelle Energy Program. Study of the combustion characteristics of the treated coals in laboratory (1 lb/hr) and multi-fuel (30 lb/hr) combustion units and assessment of the environmental impact of converting to coals cleaned by the hydrothermal coal process has been conducted under the support of the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. Significant sulfur is also captured by the alkali in the coal during combustion.

Promoted Oxidative Leaching

This process, which is in the exploratory developmental stage, is a wet oxidative process employing air or oxygen along with an oxidation promoter to desulfurize coal. Basically, an aqueous slurry containing ground coal, water, and a proprietary promoter is heated under an overpressure of air or oxygen. The desulfurized coal is separated from the slurry and washed with water to remove the soluble sulfates. Process conditions for regeneration of the spent leachant for removal of soluble sulfates and subsequent recycle to the process have not been reported.⁽⁵³⁾

The process was invented by ARCO. Several patents are pending. Numerous related patents have issued over the past decade. Some aspects of the process have been developed through the laboratory (batch) scale; others are in the exploratory stage. The desulfurization segment of the process was being developed by ARCO at one time under the sponsorship of EPRI. A small continuous unit capable of processing approximately 1 lb/hr of coal was developed and operated. Regeneration and recycle of the spent leachant was being studied by ARCO in the laboratory. It was claimed that the process is capable of extracting greater than 95 percent of the pyritic sulfur from all coals and up to 50 percent of the organic sulfur from certain coals. Processing conditions under which this has been achieved have not been reported.

Microwave Desulfurization

Microwave desulfurization of coal entails exposure of a mixture of coal, water, and a leachant, for example, sodium hydroxide to short duration microwave energy. The added water enhances coupling of the microwave energy to this coal slurry; the leachant promotes reaction of the sulfur with the alkali. Desulfurized coal and the residual leachant is separated from the resultant mixture by washing with water. Several schemes are under evaluation for recovery of the excess leachant.⁽⁵⁴⁾

Since 1975 General Electric has been developing this concept at its Valley Forge, Pennsylvania, Laboratory. A patent is pending. Thus far, this work has led to the removal of sulfur from several high-sulfur coals. General Electric's Re-entry and Environmental Division was developing this technology on the laboratory scale under the support of U.S. Environmental Protection Agency, ERDA, and The National Science Foundation. Prior to this work, the study was supported by GE.

It is claimed by GE that this proprietary one-atmosphere pressure and temperature process, combining microwave energy deposition with a sulfur leachant (currently sodium hydroxide--NaOH), removes in excess of 95 percent of both inorganic (FeS_2 --iron pyrites) and organic sulfur. Six types of coal have been exposed to date to the above process and all have exhibited the degree of sulfur removal noted above. These coals ranged up to 4.5 percent inorganic sulfur with minimal organic content (0.5-0.7 percent) to predominately organic sulfur (approximately 4.8 percent) with low-pyritic-sulfur content. Sources of specific coals include Lower Kittanning Seam, Pittsburgh Seam, Kentucky No. 9 Seam, and Clarion County (PA). The process appears relatively complicated.

Desulfurization by Chlorinolysis

Desulfurization of coal by chlorinolysis is achieved by bubbling chlorine gas through a slurry consisting of powdered, moist coal and methyl chloroform at 74 C and atmospheric pressure for less than about 2 hours. The slurry is then distilled to recover the solvent. Chlorinated coal is washed with water at 60 C and finally dechlorinated by heating to

300 to 450 C and atmospheric pressure.⁽⁵⁵⁾ Desulfurization of coal by chlorinolysis is in its early stage of development. However, from results of the research reported by the Jet Propulsion Laboratory, California Institute of Technology (CIT), Pasadena, California, this method would appear to be a potential approach for removing the pyritic sulfur and at least a portion of the organic sulfur from an Illinois coal. A patent on the process is pending.

Laboratory-scale (bench) work is continuing at the Jet Propulsion Laboratory at CIT. Level of effort is about \$100,000/year. Work has concentrated on minimizing chlorine retention by the coal, chlorine regeneration and recycle. It is now claimed that the chlorine levels in the product can be reduced to below those in raw coal. Reportedly the process is capable of extracting approximately 90 percent of the pyritic sulfur and over 70 percent of the organic sulfur from some coals. However, much R&D remains to be done to develop the process.

Oxygen Leaching

Oxygen leaching is a process for extracting up to 90 percent of the pyritic sulfur, and up to 30 percent of the organic sulfur, from coal. This desulfurization is achieved by heating a slurry of ground coal in water, or in aqueous ammonia, under an oxygen overpressure, converting the pyritic sulfur to soluble sulfate ion. The water leach only destroys pyritic sulfur; if the ammoniacal leach mode is used, part of the organic sulfur is also destroyed, entering solution as soluble sulfonates. After leaching, the clean coal is settled, filtered, washed with water, and pelletized. The spent leach and wash solutions are treated with lime or limestone to remove sulfur as a solid waste, mainly gypsum. In the water leach mode, the leach solution also contains some iron, which separates as ferric hydroxide with the gypsum. After solids removal, the solution is recycled to the leach reactors.⁽⁵⁶⁾ Developer of this process is Kennecott Copper Corporation, Lexington, Massachusetts. Since the early 1970's, the process has been studied extensively in the laboratory and a conceptual process layout and cost study has been conducted. A patent on the process

has now issued (U.S. Pat. No. 3,960,513). The use of ammonia additions to the water have also been studied and patented. It has now been licensed to Hydrocarbon Research, Inc.

The process is applicable to coals of widely differing ranks, ranging from semi-anthracite to lignite. Greater than 90 percent of the pyritic sulfur was removed from these coals by autoclave treatment under the following typical conditions:

(1) Coal grind	- minus 100 mesh
(2) Slurry concentration	- 20 percent coal in water
(3) Temperature	- 130 C
(4) Oxygen pressure	- 300 psi
(5) Time	- 2 hours.

When aqueous ammonia, 0.5 molar to 5 molar, was used in place of water under otherwise identical conditions, up to 30 percent of the organic sulfur was also removed. Coal losses during oxidation were of the same order of magnitude, regardless of whether water or ammonia leaching was used. Accordingly, the water leach can desulfurize coal to meet present NSPS if the coal contains less than the organic sulfur equivalent of 1.2 lb of $\text{SO}_2/10^6$ Btu. The ammoniacal leach achieves the same goal if the coal contains less than the organic sulfur equivalent of about 1.6 lbs of $\text{SO}_2/10^6$ Btu.

Selective Hydrodesulfurization

The process is directed at the production of solid fossil fuel (most likely a char because of the desulfurization temperatures) that can be consumed directly in existing equipment in an environmentally acceptable manner. Desulfurization is achieved by heating ground, pretreated coal at temperatures in the range of 1400 to 1500 F for periods of time up to 2 hours. Pretreatment of the coal in an oxidizing atmosphere is carried out to destroy the caking properties of some coals and to improve sulfur removal.⁽⁵⁷⁾ The process has been patented and developed by the Institute of Gas Technology (IGT). Development has involved demonstrating technology feasibility of the process in a batch reactor to remove 97 to 100 percent of the pyritic sulfur and 80 to 88 percent of the

organic sulfur from a number of coals at temperatures ranging from 1300 to 1500 F. Product recovery is about 60 percent; part of the coal is converted to low-Btu gas during the oxidative pretreatment step, and could supply the energy needs of the process. The remainder of the coal is converted to intermediate-Btu (about 500 Btu/SCF) gas for export. Volatile matter content of the product is reduced to about 3 percent.

The work has progressed to about the PDU stage--a 10-inch fluidized-bed unit which can be fed continuously at feed rates of 25 to 200 lb/hr. This work was being carried out by IGT in Chicago, Illinois, under the sponsorship of U.S. Environmental Protection Agency, Research Triangle Park, North Carolina. This process is capable of removing 97 to 100 percent of the pyritic sulfur and up to 88 percent of the organic for coal to produce a char containing about 0.6 percent sulfur (dry basis) at 1500 F. Organic sulfur makes up the majority (about 80 percent) of the total sulfur contained in the product. While very good sulfur removal is achieved, the product does not have a correspondingly low-sulfur content because of the low ash-free coal recovery of about 60 percent. The process is so designed, however, that the solid product would meet the old NSPS when burned.

Hydrogen Peroxide/Sulfuric Acid Leaching

Treatment of coal with hydrogen peroxide in sulfuric acid results in the extraction of the pyritic sulfur and a portion of the ash. This is achieved by slurring coal ground to minus 32 mesh in an aqueous solution consisting of 7 to 17 percent hydrogen peroxide and 0.1 to 0.5 N dilute sulfuric acid for a period of time of about 1 hour and at temperatures less than about 100 C.⁽⁵⁸⁾ The process was studied by ERDA, Laramie Energy Research Center, Laramie, Wyoming, in cooperation with the University of Wyoming. It was demonstrated that the process is effective in extracting up to about 90 percent of the pyritic sulfur, but none of the organic sulfur from a number of coals.

Currently, no work is being done. Additional work may be done jointly by the Laramie Energy Research Center and the University of Wyoming as represented by the Rocky Mountain Institute of Energy and Environment.

The process is capable of extracting the majority of the pyritic sulfur, but none of the organic sulfur.

Fluidized-Bed Air Oxidation

The treatment of coal with air at elevated temperatures has been found to be effective in removing a significant portion of the sulfur. This is achieved by passing air through a fluidized-bed of coal heated to temperatures ranging from about 350 to 550 C. Air may also be used in combination with steam. The concept dates back quite a number of years. Work at Carnegie Tech⁽⁵⁹⁾ on a fluid-bed process to study pyritic sulfur oxidation rates in the presence of excess air showed preferential sulfur oxidation at temperatures of about 550 C. Similar results were found by United Engineers and Constructors.⁽⁶⁰⁾ Studies in Romania⁽⁶¹⁾ have shown good success when carrying out desulfurization at 380 C using an air-stream mixture in a 15/85 ratio, and researchers at Penn State⁽⁶²⁾ have studied sulfur removal from seven U.S. coals at temperatures between 350 and 450 C and consider it a promising approach.

Currently there appears to be no direct work studying this approach. However, the oxidation concept employing aqueous solutions under elevated pressure is being explored by several organizations as discussed previously. Battelle is actively seeking support on this process. The process is capable of removing essentially all of the pyritic sulfur using a mixture of steam and air. During the treatment, the organic sulfur might be oxidized to a more extractive form and, thus, be subject to removal by volatilization or by posttreatment with, for example, an alkali; however, this has not been investigated. Depending on the treatment conditions, the final product may be a char.

Hydrofluoric Acid Leaching

Although various organizations have used acid treatment of coal over the years to remove ash, it is believed that the Kintyre process, which is based on developments at Energy Recycling Corporation of Sydney, Australia, is based on hydrofluoric acid treatment of finely divided coal.

Small samples of the product have very high acidity ($\text{pH} = 2.0$). A patent on this subject recently issued to Chevron Research Corporation (U.S. Patent No. 4,169,710) and there is considerable prior art. Kintyre has claimed particle sizes in the $4\text{--}15\mu$ range and presumably a comminution step precedes physical and chemical treatments. Very low ash contents (ca. 1 percent) and sulfur levels (originally 0.008 percent, but now about 0.2 percent) have been claimed. The lower Colorado River Authority has an option on the process for use in Texas if the claims can be demonstrated in a practical operation.⁽⁶³⁾ Patents are on file but none have issued.

Other Techniques

Various patents on this subject have issued with increasing frequency over the past few years. These include froth flotation in the presence of acids (U.S. Patent No. 3,998,064), oxidation in the presence of an iron complexing agent followed by hydrogen donor treatment (U.S. Patent No. 4,105,416), chlorination in a fused salt bath (U.S. Patent No. 4,118,200), microwave treatment with hydrogen (U.S. Patent No. 4,123,230), treatment with caustic, then mineral acid and finally nitric acid (U.S. Patent No. 4,134,737), treatment with sodium sulfite (U.S. Patent No. 4,168,148), sodium chloride (U.S. Patent No. 4,127,390), and sodium chloride and hydrogen peroxide (U.S. Patent No. 4,183,730). The addition of finely divided limestone to a coal-oil-water slurry to control emissions upon combustion (U.S. Patent No. 3,941,532) was also recently claimed.

Mixing, Storage, and Transfer

At least for the larger particle sizes used in current generation coal-oil mixture systems, mixing does not seem to be much of a problem. The coal is frequently charged from a suitable lock-hopper, usually in a batch mode, to the mill, where it is mixed with oil as it is comminuted, and discharged as a mixed slurry. For coal-oil-water systems more elaborate systems are apparently needed, particularly to homogenize the oil-water system. For extended storage of such fuel, particularly for the coarse materials, the use of various stabilizers is under study.

Equipment Descriptions

CoaLiquid, Inc.⁽³⁰⁾ has selected a "continuous batch" multiple tank concept, in which one tank is filled with preground coal, oil and water, and a twin impeller mixer is used to begin the blending process. While ingredient addition and blending are occurring in one tank, blended material in a second tank is discharged as needed through an in-line agitator into an ultrasonic mixer. Material flows through the ultrasonic device on a continuous basis directly to storage tanks adjacent to the processing area. Germantown Laboratories are investigating four different mechanical mixing devices to produce stable coal-oil-water mixtures.⁽³⁰⁾ These are a Gaulin Corporation Model 15 Homogenizer, a Sonic Corporation Triplex 1000A, a Branson Sondi Power Model 190 Ultrasonic Processing System, and a Total (French) System.

The system with the most advanced design for handling coal-oil mixtures is probably that of the New England Power Service Company (NEPSCO), and will therefore be described for reference state-of-the-art purposes⁽⁴⁾. Their Salem Harbor Unit No. 1 is rated at 80 MW and is being retrofitted to use a mixture of 30 percent coal and 70 percent oil. A schematic flow sheet for the facility is shown in Figure 14. Because on-site COM production was part of the original objective, it was decided to locate the COM preparation facility in a separate metal building constructed as a temporary addition to the existing boiler enclosure. Conventional grinding with a Babcock & Wilcox Type E pulverizer is used to produce a

FIGURE 14. SCHEMATIC DRAWING OF NEPSCO COAL-OIL MIXTURE FACILITY (4)

standard utility grind and therefore avoid difficulties with the introduction of untested new comminution technology. Primary air from the boiler is used for coal drying. Nitrogen is used to blanket the coal storage bin and COM blending tank.

A 100 ton pulverized coal storage bin was constructed above the COM blending facility. The bottom of the bin is an inverted pyramid with a slope of 60°. The bin is thermally insulated and heated with electric heat tracing cable to insure that coal remains dry. There have been a number of operating problems with proper feeding from this coal storage bin through a gravimetric feeder to the COM blending tank at the desired rates. Transport air used to convey the ground coal from the pulverizer to the coal storage bin is exhausted into the boiler itself to avoid a separate cleanup system for used transport air. The coal is separated from the transport air in a cyclone, which itself is isolated from the coal storage bin with a rotary airlock so that the bin can be maintained at a positive nitrogen pressure.

Continuous COM blending was preferred over batch operation, and a conventional bladed turbine agitator was selected over various peripheral and injection type mixers available. A type HID agitator, which is a medium shear device with two sets of pitched blade turbine impellers, was installed on top of the 8000 gallon COM blending tank. Prior to initial startup, a rotary airlock was added between the COM blending tank and the gravimetric coal feeder to isolate the feeder from pressure fluctuations in the tank.

An Acrison gravimetric feeder Model 203B was provided by Combustion Engineering, supplier of the storage bin, cyclone separator, rotary air locks and related coal piping. The #6 oil flow to the COM blend tank is controlled by the blend tank level controller. Because equipment for measuring or controlling COM concentration was not found for continuous in-line blending, COM concentration is controlled by a pulverized coal flow ratio controller. Coal flow and oil flow ratio is preset to produce the desired COM concentration. COM concentration is verified in a support laboratory using a solvent extraction technique.

An existing 700,000 gallon oil tank was modified to store the COM. A 75 HP Chemineer bladed turbine agitator with 120 inch blades is supported above the tank roof. Four vertical mixing baffles are installed on the tank walls. Thermal insulation was applied to the tank and an internal steam heating header was installed. The COM storage tank is located several hundred feet from the boiler and the COM preparation facility requiring several oil and COM pipelines of up to 500 feet. Three in-line Kenics Turbu-mixers, which are vaned static devices, were installed in an attempt to resuspend coal particles that might tend to settle out in the piping. All fuel piping is insulated and heat traced with electric heat tracing. Electric tracing is recommended over steam tracing because it tends to permit more accurate temperature control and condensate return lines are avoided.

The COM is transferred from the blending tank to the storage tank, and from the storage tank to the burner supply pumps, by utilizing two Tuthill Model 600 lobe type pumps. Each pump is equipped with #6 oil flushing connections on the shaft seals to minimize damage from coal particles. On two occasions a pump has tripped from overload, apparently due to accumulation of coal in the suction line. Solutions to this problem are being developed.

The four 25 GPM burner supply pumps are Viking abrasive liquid rated which were supplied by Forney Engineering. Pumps equipped for abrasive service are equipped with ceramic shaft seals, a carbide idler pin and case hardened gears. Each pump is driven by a variable speed SCR drive. The variable speed pump operates as a fuel orifice delivering COM to the burners at approximately 50 psi. Two MAPCO sonic flow meters are used for COM fuel supply and blending plant output flow measurement. Their performance has not been entirely satisfactory. A BASF Wyandotte Corporation stabilizer, ES-7071, was selected for use during the first six months of the one year demonstration based on laboratory evaluations with a sedimentation column and on costs for the 0.25 percent surfactant continuous feed.

Stabilizing Agents

There has also been much recent interest in enhancing the stability of coal-oil mixtures with other stabilizers at various other locations.⁽³⁰⁾ Batra and his coworkers at NPESCO have been involved in much of the U. S. efforts. Other researchers are at the University of Massachusetts, Tufts, Adelphi University, University of Kentucky, Pittsburgh Energy Technology Center, Atlantic Research Center, British Petroleum, etc. W. C. Meyer at Dow Chemical has indicated that water may be an effective means to stabilize COM against settling by acting as a flocculating third phase. The Japanese have been especially active in this area. For instance, Naka has reported the testing of over 1300 types of additives with 10 different coal-oil-mixtures. However, specific compositions are frequently not disclosed. Matsuno of Mitsubishi Heavy Industries investigated the relative stability of COM under the special conditions characteristic of ship transport.

The patent literature is an especially useful reference source for new developments in stabilization technology. For instance, one claimed method of stabilizing a suspension of coal in fuel oil consists of mixing an amount of a polyfunctional amine such as N-alkyl 1,3 diaminopropane into a fuel oil, mixing in coal ground to 70 percent -200 mesh (Tyler) and then adding a stoichiometric amount of polyfunctional carboxylic acid sufficient to react with the amine.⁽⁶⁴⁾

Another method consists of subjecting a coal to low or medium temperature pyrolysis to form oil, char, and water fractions. The char is micronized to less than 200 mesh and mixed with water in a 5:15 ratio of oil to water, while the oil is mixed with water in a 3:0.5 ratio, followed by combination of the two mixtures.⁽⁶⁵⁾

Another method consists of adding coal or charcoal (5 to 75 vol percent) to a liquid feed containing 1 to 10 wt percent of a combustible gelling agent, such as Thixcin R (a modified castor oil polymer) and optionally, an ash modifier, such as MgO, CaO, dolomite, kaoline, etc. The mixture is stable to transportation and storage and less susceptible to temperature thinning than conventional compositions.⁽⁶⁶⁾

A suspension of coal-oil stable for 3 months or longer can be prepared at 100 C by mixing coal (35 weight percent), water (3 weight percent), petroleum oil (58 weight percent), and a polyester or derivative (MW 10,000 to 100,000) 0.2 weight percent. (67,68)

A thixotropic emulsion having aqueous rich external phases and oil-rich internal phases can be prepared by mixing in a Daymax disperser No. 6 fuel oil (30 parts), Illinois No. 6 coal (<5 cm particle size, 65 parts), H₂O (4.5 parts), and polyoxyalkylene surfactant (0.5 parts). (69a,b)

A fluid fuel containing reduced sulfur and water can be produced from coal by a process which consists of conventional liquefaction followed by suspension of the residual coal particulate in the liquid phase using the Foulke process. The process consists of allowing the heavier particles such as pyrite to settle and recovering the suspension of coal in oil. (70)

A stable, pumpable suspension of coal in hydrocarbon fuels ranging from naphtha to crude oil can be prepared by coating the surface of the coal particles (-8 mesh, mostly -100 mesh) with C₁-C₄ alcohol vapor and CO₂ and mixing the coated particles with the hydrocarbon liquid. (71)

A storage stable mixture of powdered coal and fuel oil can be prepared using an emulsifier made by treating unsaturated aliphatic and cycloaliphatic carboxylic acids (such as crude tall oil) with alkali metal hydroxides or amines at 70 to 100 C for 1 hour. An emulsion stable at 75 C for 4 months was prepared by mixing coal (35 parts), No. 6 fuel oil (59 parts), water (5 parts), and 1 part emulsifier. (72)

A colloidal fuel having increased storage stability can be prepared by mixing 100 parts fuel oil with <2 parts nonionic surfactant and dispersing in it a slurry of 40 to 200 parts pulverized coal and 3 to 40 parts H₂O. (73)

Metal salts of α -sulfo fatty acid esters can be used to disperse coal in fuel oils. Thus, fuel oil (222.5), water (25), coal (250), and Na Et α -sulfolaurate (2.5) were stirred in a homogenizer (5000 rpm) at 70 C for 20 minutes to obtain a dispersion which remained stable at 70 C for 30 days. (74)

A thixotropic fuel suspension can be prepared by mixing a particulate solid fuel (35 to 70 parts), with an organic liquid such as heating oil (28 to 56 parts), a gel-forming clay (0.5 to 3 parts), and an organic dispersing agent (0.1 to 1 part).⁽⁷⁵⁾

A combustible slurry of coal in fuel oil can be prepared by mixing 100 parts bituminous coal (80, <325 mesh) with 4 parts of a mixture of alkylstyrene polymers and 229 parts of No. 2 fuel oil.⁽⁷⁶⁾

A nongel, nonsettling mixture of coal and fuel oil can be prepared from 60 parts No. 6 fuel oil, 40 parts pulverized bituminous coal, containing 0.05 weight percent starch (suspension stabilizer) and 0.28 weight percent aqueous soap solution (viscosity reducer). The slurry did not settle or form a gel after storage at 175 C for 30 days.⁽⁷⁷⁾

A liquid fuel can be prepared by mixing an aqueous coal slurry with a hydrocarbon binder to produce agglomerates with reduced ash contents which are then dispersed in a hydrocarbon fuel.⁽⁷⁸⁾

A much older patent describes a process in which a stable suspension of coal in No. 6 fuel oil is obtained by mixing 15 to 25 weight percent of coal particles not larger than 0.5μ with a fuel oil capable of producing Brownian movement with the particles. When the movement is sufficiently intense to sustain them, particles up to 200 mesh are introduced with thorough mixing until coal forms 30 to 60 weight percent of the mixture.⁽⁷⁹⁾

Combustion Results

Major recent efforts related to colloidal fuels have been limited principally to the combustion of coal-oil mixtures in industrial and utility boilers, although there was one experiment carried out a few years ago with a coal-steam mixture fed to a boiler originally designed for natural gas. There are some conceptual design studies on burning coal-water slurries containing up to 70 percent coal (achieved by using blends of various sized coal particles) underway. There have also been numerous proposals to develop and use slurries of coal in alcohol, but little experimental work has been reported. Modern work on colloidal type fuels in diesel engines is very limited and very recent. The use of relatively coarse coal (ie, pulverized) suspended in air and fed to turbines was extensively investigated after the turbine engine had been developed for aircraft use in the 1940's, but most work was terminated in the 1950's. This current status review will start with a summary of this turbine work.

Combustion in Turbines

After World War II, seven programs aimed at coal firing of gas turbines were undertaken in the United States. The Locomotive Development Committee of Bituminous Coal Research, Inc., (LDC), developed a 4250-hp coal-fired gas turbine locomotive power plant.⁽⁸⁰⁾ The development included 5010 hours of operation of full-scale coal-fired gas turbines, of which 3760 hours were run on the laboratory locomotive unit. Various equipment problems limited the length of operating periods, but it appeared possible to operate the system under locomotive service conditions with sufficient periodic maintenance. The major unresolved problem at the end of the program, which was terminated in 1957, was erosion of turbine blades by ash passing through the dust collectors and turbine.

In support of this effort, tests at Battelle were carried out in which pulverized coal was fired to a J47 turbojet combustor and it was found that with residence time of 15 to 30 millisec, 60 to 80 percent of the coal was burned and the remaining fixed carbon passed through the combustor without burning. However, combustion stability and turndown range were as good as for kerosene fuel.⁽⁸¹⁾ Scaleup from the aircraft-combustor diameter of 9 inches to a diameter of 30 inches produced identical data. Good efficiency was obtained only after redesign for burning with near-stoichiometric conditions at the burner, followed by an extended combustion period at high temperature before dilution.⁽⁸¹⁾

The Union Pacific Railroad, in 1957, constructed and tested in railroad service, a locomotive based on the LDC development.⁽⁸²⁾ Union Pacific had, at that time, 50 gas turbine locomotives which were approaching retirement. One of these, with a 4800 hp General Electric gas turbine, was fitted with the LDC-developed coal firing system and evaluated in rail service. Turbine erosion was much more severe than had been experienced in the LDC laboratory, with the result that the turbine was rebladed after about 250 hours of operation, and was again in need of reblading after an additional 400 hours of operation.⁽⁸³⁾ The high erosion rates were probably the result of very high turbine blade-path velocities in the 2-stage General Electric impulse turbines, compared with much lower velocities in the 5-stage Allis Chalmers turbine used by LDC.

In the early 1960's, the LDC gas turbine was obtained by the U.S. Bureau of Mines and installed in their laboratory at Morgantown, W. Va. Here various means of reducing erosion by changes in the turbine blading were investigated. The research was, in general, unsuccessful.

The General Electric Company started a program based on an integrated coal gasifier in 1945, and carried it on through about 1957. A laboratory gasifier with a 14-inch grate diameter was constructed and operated at Battelle for General Electric over a five-year period during which gas cleaning and gas combustion was investigated experimentally, along with the use of stirring mechanisms to permit use of caking coals.⁽⁸⁴⁾ This gas producer was operated at 100 psi, the then-current cycle pressure for GE gas turbines. Later, in 1957, General Electric investigated dust-collector design and performance and carried out extensive research on turbine-blade erosion.⁽⁸⁴⁾ All of the GE research on coal firing was terminated in 1958 in an effort to make the gas turbine department financially self sufficient.

The British Ministry of Fuel and Power undertook an extensive program of developing coal-fired gas turbines in 1945, and continued it through 1955.⁽⁸⁵⁾ At some later date this program was terminated. Although the reason for this abrupt termination of all projects was not announced, to our knowledge, it is probably that coal firing, in general, lost its attractiveness as low-cost middle-east oil became available.

The program of the Ministry of Fuel and Power was described in detail by H. R. Cox^(85,86) in a 1951 lecture. The combustor development aspects of this program were discussed in detail in 1955 by Battcock, Hurley, and Voysey.⁽⁸⁷⁾ This program included eight major projects, including laboratory development of dry-ash tubular combustors and slagging cyclone combustors, and construction and operation of five gas turbines incorporating different firing methods and cycles. These included a 500-kw unit with a dry-ash tubular combustor and cyclone dust collectors; a 2000 kw unit with a slagging, cyclone-type combustor for high ash retention followed by a dust collector; a 2000 hp open-cycle unit fired with an integrated gas producer; a 1600 hp external-combustion, open-cycle gas turbine in which cycle air was heated by a coal-fired heat exchanger; and

a 500 and 1000 hp closed-cycle gas turbine fired by a combustor suitable for either slagging or dry ash removal. None of these projects passed the stage of laboratory operation before cancellation of the program.

The heat-exchanger open cycle was also investigated by Mordell,⁽⁸⁸⁾ who constructed and tested a 500-hp unit designed as a locomotive power plant at McGill University. This unit utilized a slagging cyclone-type combustor, and was operated for about 100 hours up to 1955.

A large effort on firing of pulverized coal to a gas turbine was carried out in Australia over a 10-year period, and was terminated on the death of the principal investigator.⁽⁸⁹⁾ This unit was operated for several thousands of hours with reasonable success. It was found that turbine-blade erosion was acceptable when firing brown coal which produced a soft, friable ash. However, when firing black coal, which produced a hard, abrasive ash, turbine blade life was unacceptable short. During this program a great deal of information was developed relative to combustion, dust collection, and turbine-blade erosion, all of which is summarized in a final report.⁽⁸⁹⁾

The most recent studies on coal firing in turbines are related to fluidized bed combustion efforts in the United States and the United Kingdom. Work has been or is being conducted at Leatherhead in England, and at Pratt and Whitney, Curtis Wright, General Electric, Solar, Westinghouse Electric, and the University of Cincinnati in the United States on elutriated solids from fluidized beds. Most of this work is very preliminary, and confirms the earlier turbine studies. It is thought that 7-micron fly ash is probably too coarse, and 80 ppm total suspended solids are too high, for equipment of present design. Obviously, these limitations represent a major challenge for the use of colloidal fuels, particularly if coal is the principal solid fuel in the mixture. The most recent activity in this area is the addition of graphite particles to jet fuel to increase fuel density for military aircraft. The Department of Defense is supporting work at Exxon on this subject.

A contract was awarded by PETC in 1978 to United Technologies to study the combustion of micronized coal-oil mixtures (MICO), but no actual turbine studies were carried out.⁽⁹⁰⁾ Single droplet studies

indicated a microexplosive combustion behavior; experiments with spray combustion in a swirl type chamber, patterned after the IFR Foundation combustor, showed rather inefficient combustion at feed rates of about one pound per minute, which seems surprising.

Industrial and Utility Boilers

The most important work on COM firing in recent times is the General Motors program.⁽²⁾ GM first tried to burn COM in a boiler in August 1974. The coal-oil mixture consisted of 30 percent pulverized coal and 70 percent No. 2 oil. Ten thousand gallons of the mix was made at Cadiz, Ohio and shipped by truck to Saginaw, Michigan for test firing in a 30,000 lb/hr packaged oil-fired boiler. Later a fuel preparation plant was also installed at the Chevrolet Saginaw site and larger quantities were burned. Although some burner modifications were necessary, it was generally concluded that COM could be burned in packaged oil-fired boilers with little or no modifications. Further work to improve the stability of the COM upon storage was the chief recommendation. The Acurex Corpor-

The Acurex Corporation is carrying out similar studies at the Danville, Virginia facility of the Lorillard Company, with technical support from Kennedy van Saun Company, Coen Company, Carbonoyl Company, and the Colorado School of Mines Research Institute.⁽³⁰⁾ Aldephi University is undertaking combustion studies with coal-oil-water mixtures, and Northwestern University is studying the disruptive combustion of COM droplets.⁽³⁰⁾ EPRI is presently contemplating burning a coal-water slurry with up to 75 percent coal by direct injection of the slurry into a utility boiler⁽⁹¹⁾, and Alfred University is attempting to prepare such aqueous based fuels.

The Pittsburgh Energy Research Center has been involved in COM research for a number of years.^(6,30) In 1976, PERC successfully concluded a 1000 hour test on a 100 HP firetube package boiler, fired with a 20 percent coal-oil mixture. The major objectives of this study were to pinpoint major problem areas associated with burning COM in a boiler originally designed to burn oil and gas, and to ascertain the degree of corrosion and deposits on heat-transfer surfaces after long operation.

Despite the preliminary nature of this test, the results were encouraging. The combustion characteristics of COM in this boiler were highly satisfactory. No difference in flame stability was observed between a No. 6 fuel oil flame and a COM flame. Carbon burnout was essentially complete and exceeded 99 percent. Boiler efficiency with COM combustion was essentially the same as that for No. 6 fuel oil. At the end of the 1000 hour test, a light ash deposit was observed on the internal tube surfaces, but there were no slag deposits despite the high heat release. Following a metallographic examination, the corrosion rate on the boiler tubes was deemed acceptable. Some operational problems were encountered with char deposits in the combustion chamber, but were resolved by changes in diffuser and nozzle design. A 700 HP watertube unit has been more recently fired at PETC with COM with similar results. As long as the flame does not impinge on boiler surfaces, the ash accumulation does not seem to be particularly troublesome. The control strategy recommended by Bruceton is to use baghouses for particulate control and bicarbonate injections for SO_2 removal efficiencies of about 80 percent at a cost of \$10-\$20/ton of coal. DOE is presently contemplating supporting work on firing of COM in marine boilers as well.

In 1977, Coaltech-Farrier and Celanese Fibers Company carried out experiments to burn the mixed coal-steam output of a fluid energy mill directly in a boiler originally designed for gas.⁽⁹²⁾ The boiler was a CE VP-14 two burner unit. Coal particle size was about 10μ and steam requirements were about 6 percent. Although the test was terminated after 300 hours of on-off operation because of problems with the mill, it was felt the combustion itself proceeded without presenting any new problems other than stack emissions. Since then, Coaltech-Farrier now recommends the use of a Majac mill for coal preparation.

About this same time, Florida Power Corporation carried out COM firings in a 2.5×10^6 lb/hr tangentially fired utility boiler, set-up for oil firing. Fluid energy grinders were again used. Low concentrations of coal in oil were used initially, but concentrations of 45 percent coal and 55 percent No. 6 fuel oil were eventually studied. The boiler fires seem stable and to have a high combustion efficiency. The flame was more radiant than a 100 percent oil flame. It was concluded

that conversion of the oil-fired plant to one that would burn coal-oil mixtures could be accomplished in considerably less time and at a much lower cost than a total conversion to coal burning.

The most recent work is that, of course, at Salem Harbor.⁽⁴⁾ Most preliminary combustion problems involve coking of the diffusers and burner tips, but equipment modifications have seemed to solve these difficulties. Up to 20 percent coal concentration has been burned for tests with no evidence of combustion problems per se. When switching from residual oil to COM, certain rows of burners are often firing COM while others remain on oil. The COM flames appear to be indistinguishable from oil when viewed through an ordinary opaque glass plate. The most important point to be learned from the burner retrofit experience is that injector design and use are critical procedures which require rather sophisticated boiler and burner engineering skills.

Diesel Engines

Only a limited amount of post World War II work has been carried out on the use of colloidal fuels in diesel type engines. Southwest Research Institute (SwRI) investigated this type of fuel in a preliminary way in 1957.⁽⁹³⁾ In 1969, Howard University, and more recently Virginia Polytechnic Institute, studied the feasibility of using coal-in-oil (slurry) fuels in conventional diesel engines.^(94,95) These studies were not entirely successful, because they encountered several problems. Many engine components wore out rapidly. Particulate emissions and smoke were high. This was partly because the particle size of the pulverized coal was not small enough to burn rapidly (at high speeds) and generate comparable mechanical work in these engines.

The most recent work has been carried out under the auspices of the MICO program at SwRI and at Sulzer Brothers in Winterthur, Switzerland. The particle size of this MICO fuel was about an order of magnitude smaller than all previously used fuels. The test fuels at SwRI were mixtures of micronized coal and No. 2 diesel fuel.⁽⁹⁶⁾ The supplied test fuels contained 20 percent, 35 percent, and 40 percent coal by weight. A locally-obtained clear No. 2 diesel fuel was used for comparison purposes. Since

the fuels containing 35 percent and 40 percent coal were very close to each other in coal concentration, a new slurry fuel was prepared by mixing locally-obtained clear fuel and 20 percent weight slurry fuel in equal weights. With this addition, the test fuels were clear diesel, 10 percent weight, 20 percent weight and 40 percent weight slurry fuels. All the coal particles were in the range of 0.5 to 10 microns. The mean, mode, and standard deviation of this distribution are, respectively, 2.048, 2.074, and 1.644 microns. Three slurry fuels were tested in a Mercedes 4-cylinder diesel engine equipped with modified injectors under various loads and speeds. Exhaust temperatures, smoke, blowby, and brake thermal efficiencies were determined under these conditions. The individual contributions of coal and diesel fuel to power output were estimated. In general, at higher speeds, exhaust temperatures and smoke increased with the concentration of coal while brake thermal efficiency decreased. However, at high loads (above 60 psi BMEP) and a lower speed of 800 rpm, the contribution of coal to power output was approximately that of diesel fuel. The blowby increased significantly in a period of 14 hours at the end of which the fuel pump failed. A single cylinder engine was used in a subsequent study. Total engine hours are about 100 or so and wear (cast iron rings) appeared to be severe. Coal combustion efficiency was also relatively low in these small engines. From these two studies, it appeared that slurry fuels could be used in diesel engines at low speeds and high loads, although major engine modifications might be necessary.

Sixty-five drums of similar material containing 32 wt percent Lower Freeport seam coal was shipped to Sulzer Brothers for combustion tests in a large single cylinder research engine (29 in bore, 2 cycle, 120 rpm, 1470 kw). Detailed results are not yet available, but it was reported that the fuel burned without difficulty.⁽⁹⁷⁾

The most interesting recent information on the work at Sulzer, orally disclosed by at least four different organizations, is the reported success that Sulzer has had burning a mixture of coal and water in a diesel engine. No information other than these oral reports is available to Battelle at present. This obviously represents another technical opportunity for saving oil.

SELECTED NEEDS AND OPPORTUNITIES

This section of the report discusses some general thoughts about the needs and opportunities for further research in critical areas in order that extensive use of colloidal type fuels occurs in the future.

This is not meant to be an extensive discourse on the subject, but is designed to indicate some major areas which might benefit by future funding by either public or private organizations. It should also be borne in mind that some of these activities may already be underway. Many of the suggestions have been discussed for decades by those knowledgeable in this art, and at least some of these concepts are the basis of issued patents, or filed patent applications, by various organizations, including Battelle. On the other hand, there is hopefully a significant amount of new material, or at least material not well known, contained herein to stimulate additional creative activity by the scientific community.

Not all areas needing solutions, and obviously not all possible solutions available, are covered in this discussion. However, the section titled Recommendations, which follows at the end of this report, has been drawn up to cover most, if not all, of the important actions which should be taken to accelerate the development of colloidal fuels.

Comminution to Fine Particles

Development of methods of more selective comminution, to fracture minerals along crystal grain boundaries, would be a significant achievement as it would result in improved liberation of the individual mineral constituents present in coal. It should be borne in mind that the purpose of comminution in the mineral industry is generally not grinding per se, but liberation of some component in the mixture. Studies related to fracture behavior of coals and methods to accomplish selective size reduction are needed. Studies conducted at the Illinois State Geological Survey have shown that coal lithotypes have a definite influence on breakage characteristics, and that band orientation in coal greatly affects the energy requirements for size reduction. Similar studies by Neavel indicate that dessication of coal laminae may be responsible for significant size degradation in coal samples. Further work is warranted in this area to examine the possible applications of moisture-control techniques as well as petrographic coal characteristics to comminution operations.

In terms of possible industrial impact, research in novel grinding systems is assigned a high priority for further development. An essential aspect of novel beneficiation technology is the need for proper physical liberation of the gangue constituents. In the case of coal, current grinding technology is capable of providing an effective size reduction for use in conventional concentration steps, although additional research and development is needed to increase the yield in the desired size range. As discussed previously, grinding technology becomes increasingly costly in the size ranges below 325 mesh (40 microns). Most coals are insufficiently liberated in this range and in the case of most applications for colloidal fuels, particles above about 10 microns in size will lead to many operating problems. Research and development on grinding methods that are capable of select size reduction, and especially in the micron and submicron range, are needed to assist in implementation of colloidal fuel technology.

Chemical Means to Produce Colloidal Fuels

Another interesting possibility for the production of colloidal fuels is to use a chemical treatment or solvation process to produce the finely divided carbonaceous fuels. Research Service Corporation pyrolyses submicron polymer particles to produce submicron carbons, although of course, as now conceived, this represents too costly an approach. Solvent refining of coal comes closer to embodying some elements of this approach, but at least at present a method to precipitate SRC colloids has not yet been developed. For the purpose of this discussion on chemical techniques, two general approaches will be proposed.

Organic Based Systems

Two investigators have reported that certain types of coal consist of a solid-solid colloid. H. Brusset, in 1948, reported that small angle X-ray scattering and Debye diffraction patterns showed that lignite consists of "an ensemble of micelles of varying sizes between 40 and 200 Å diameter in an amorphous medium (bitumen)". Each micelle was believed to consist of crystallites of humic acid. More recently, Camier and Siemon have reported that brown coal consists of up to 42 percent of rod-shaped colloidal sized particles, $\sim 1\mu$ in diameter and 2 to 8μ long. They are believed to be derived from the cell walls of wood. The difference in colloidal structure between brown and black coals has been cited as the reason for the apparent absence in lignites of capillaries with diameters between 1.2 and 30 nm.

The colloidal nature of Bruceton coal has been shown indirectly by depolymerizing it in refluxing phenol and p-toluenesulfonic acid. The pyridine solubles "had a number average molecular weight of 400 but consisted primarily of colloidal material and polymers having molecular weights >3000 ." The colloidal material was removed by ultracentrifugation and subjected to depolymerization a second time. Additional pyridine solubles were formed but no low molecular weight material was reacted off of the coal structure. The fact that much of the coal is liquefied to colloids,

which do not respond to many instrumental analysis methods such as NMR and IR, has led to some incorrect inferences about coal structure resulting from such measurements. Coal chemists will need to learn colloid chemistry and analysis techniques to properly handle these materials.

It has also been reported recently that the colloidal size of the lower molecular weight bituminous coal asphaltenes was below the limit of resolution of small angle X-ray scattering ($\sim 10\text{\AA}$). There will, of course, be more studies of the agglomerating arrangement of molecules in coal and liquefied coal. This should lead to a better understanding of how coal "dissolves" during coal liquefaction.

An interesting research problem for process chemists is the possibility to directly produce an all-coal liquid containing a maximized amount of colloid by liquefying coal under very mild conditions. Such a liquid could be filtered to remove inorganic sulfur and ash and would not need to be stabilized because of its colloidal nature. Several patents have issued on methods to produce stabilized coal liquids by processes consisting of direct liquefaction followed by reslurrying the unreacted particles. Reslurrying may not be necessary since some coal will be required to produce heat for the process. The previous studies have also not been directed toward the production of a maximized amount of colloidal material.

Aqueous Based Systems

Another approach is to use aqueous systems to produce colloidal fuels. One such system that has been patented by Stambaugh at Battelle and is described as follows. A schematic flow sheet is shown in Figure 15.

Basically, the process entails heating the raw coal in an aqueous alkali solution to separate the organic fraction of the raw coal from the mineral matter, ie, by dissolving the organic fraction and converting most of the sulfur to a water soluble form. The resulting slurry is then filtered to separate the solubilized coal from the insoluble mineral matter. After which, the ultrafine clean coal--is separated from the coal solution by pH adjustment.

FIGURE 15. FLOWSHEET OF PROCESS FOR PRODUCING COLLOIDAL FUEL BY THE HYDROTHERMAL PROCESS

The product is an ultrafine, low sulfur, low mineral matter solid fuel. Some particle sizes are estimated to be less than about 0.02 micron. Molecular weight is in the range of 300 to 1200 with an average of about 700. Total mineral matter content ranges from 0.4 to 0.6 percent (MF basis) and total sulfur content is in the range of 0.3 to 0.5 percent (MAF basis). Heat content of clean fuels produced from a subbituminous coal was in the range of 13,600 to 14,300 Btu/lb (MAF basis). Heat content of the raw coal was 12,500 Btu/lb (MAF).

This clean coal should be an excellent solid (powdered) fuel for heat engines and conventional furnaces and as a feed for the production of coal-oil-water slurries. Preliminary work indicates that the material is readily dispersible in liquid fuels such as diesel oil, No. 2 and No. 6 fuel oils, gasoline, and alcohol.

Evidence from other work at Battelle on chemical cleaning of coal suggests that this ultrafine, clean coal should have improved combustion characteristics in terms of ignition, reactivity, and flammability. In fact, in a strictly exploratory test, a small amount of a slurry consisting of precipitated fuel and gasoline was used as a fuel in a two-cycle motorcycle. The slurry was found to burn, as expected, very well without the formation of visible smoke. The small particle size of the coal (less than about 0.02 micron) should result in instant combustion of the coal.

It would be premature to suggest that this process has, in fact, been demonstrated to be a leading candidate for the production of colloidal fuels of practical importance, but it does again represent an approach to a field which has been generally neglected in the past.

Fine Particle Separation

Further efforts are specifically recommended to develop fine particle separation methods applicable to colloidal systems. Several potentially promising technologies have been identified that can improve the ability to selectively separate ash and sulfur contaminants from ultrafine coal fractions. Those believed to offer the best opportunities for eventual commercialization are summarized below.

Electrostatic Separation

Most dry electrostatic processes work best on larger particles. Extremely fine dust generally causes problems in existing types of equipment; however, some types of electrostatic systems can handle fine powders also. Studies are needed in several areas.

Because pyrite occurs in different particle-size ranges in different coals, information is needed to define the range of particle sizes likely to occur and to determine what separation processes work best with the various sizes.

Narrow ranges of particles in various sizes should be studied to establish the best separation technique for each size range. This would provide a basis for determining which processes should be used to effect optimum removal of pyrite from coals which require grinding to different size ranges to release the pyrite.

Preconditioning of the coal and control of the handling can be very important factors in electrostatic separation of particulates. In 1967, Reif of Battelle noted two factors that could be of considerable importance in the electrostatic separation of pyrite from coal:

- (1) Electrostatic separation tests are especially sensitive to sample aging. Sulfur compounds, resins, and certain mineral sulfides in coal change rapidly. Oxidation causes most of the trouble. Specularite iron ore, which separates cleanly immediately after it has been ground, may become oxidized to such an extent in storage that a sharp separation becomes impossible.

- (2) Many materials show changes in electrical charge when their temperature varies. Sylvite requires a contact temperature of about 900 F to exchange charges with halite, but will not begin to separate until cooled to about 300 F and discontinues separation below 190 F. When studying the electrostatic separation of glass sand from feldspar, separation was possible in the range from 400 F to 139 F with some difficulties experienced around 200 F. The quartz at 200 F developed a distinct dipole condition causing a ropiness that was visible to the naked eye.

Further, it is known that the resistivity of materials is affected by temperature. As the temperature increases initially up to 200 F, surface moisture is driven off and the resistivity generally increases. However, as the temperature of nonmetals is increased above 300 or 400 F, the resistivity begins to decrease again. The increase and decrease of resistivity of different materials occur at different rates and at different temperatures. Thus, heating can be used to effect charge generation, enhance charge differences, or to enlarge differences in resistivity which can be expected to enhance separation of the materials in electrostatic systems.

Improved separator designs have been developed for other applications. For example, a roll-type electrostatic separator with a dielectric covered roll will separate materials which have very small differences in their properties and which cannot be separated by other electrostatic separators. Also combinations of known separator techniques are likely to produce improved systems. The Bureau of Mines used a centrifugal separator to concentrate pyrite in a fraction which was then processed through the electrostatic separator. Simultaneous application of electrostatic and centrifugal effects recently has been used to handle particulate material in other studies, and it is quite likely that such combinations can be used to effect improved particulate separations.

Overall, the electrostatic methods for separating pyrite from coal should be reexamined using advanced technology and separation techniques developed in recent years.

Electrophoretic Separation

Wet electrophoretic processes work best on small particles. Thus, electrophoretic processes might be desirable for use on coals which require extremely fine grinding to remove the pyrite or to clean up the fines produced in coarse grinding for electrostatic processes. No data are available for electrophoretic processes; however, some effects have been demonstrated. Todd and Wild separated mixtures of various minerals by an electrophoretic process. Because of the high viscous drag of the liquid media on the coal and pyrite particles, migration rates are extremely slow and relatively large-sized equipment would be needed to process coal on a tonnage basis. Additives may be necessary to control the zeta potential of the materials in order to effect differences in responses to the electrical field, and these additives are a significant cost factor. Also low voltage operation which is needed to keep power down further limits migration velocities. Nevertheless, augmentation of other wet processes or cleanup of fines that cannot be handled by dry methods might be possible with electrophoretic separation methods.

Electrophoretic methods should be considered to remove pyrite in at least three situations: (1) cleaning of extremely fine coal dust that cannot be handled by dry methods, (2) cleaning fine ground coal while it is being transported in slurry form, and (3) assisting other wet separation systems. Study is needed to measure the zeta potentials of pyrite and coal obtained from various veins and to develop effective means of controlling the zeta potentials if significant differences do not occur naturally between pyrite and coal particles. Factors affecting the process such as the pH of the slurry, surfactants, particle size, concentration, and preconditioning of the particulates need to be investigated on small scale before scale up is attempted.

Thermal-Magnetic Separation

The concept involves selective heating of pyritic impurities in coal by dielectric means. Reportedly, the method would convert pyrite to

magnetic pyrrhotite while leaving the coal constituents undisturbed. Conventional magnetic separation would be used to selectively remove the inorganic sulfur after dielectric treatment. The technique was under investigation by the Bureau of Mines and was estimated to be a low-cost operation.

Previous studies in the USSR, and more recently in the United States, have shown that significant reductions of inorganic sulfur in coals are possible following low-temperature treatment of coals in the range of 190 to 360 C. The concept is similar to dielectric heating and involves phase transformations of pyrite into magnetic species. Steam heating reportedly results in effective sulfur removal by conventional magnetic separation methods.

Methods involving such phase transformations are of interest because of the potential application to ultrafine coal systems, that is, those systems where effective liberation of coal impurities is normally achieved. Furthermore, magnetic separation is classified as a low-cost unit operation. Research and development in this area could have practical economic considerations.

Immiscible Liquid Separation

This technique of using an added immiscible component to a coal slurry may be used for fine coal separation. It involves the selective migration of one or more species from a water suspension to the oil phase or to the oil-water interface. The concept is not new and patents for oil flotation date back to 1860. Interest in this method was renewed in recent years and significant work has been conducted. A considerably greater effort is needed, particularly as it applies to colloidal sized coal particles.

Selective Flocculation

It is apparent from the literature that concentration of extremely fine particles can be affected by certain organic liquids. Studies to control interfacial spreading is considered one of the most promising areas for significant development and warrants basic and applied research.

The proposed concept differs from conventional flotation technology in two major respects. First, it makes possible control of the size distribution of the dispersed phase in the size range most effective for efficient separation. Second, it allows particles to migrate into the bulk immiscible phase, thus providing a nearly constant interfacial area for collection. This last feature would allow the collection efficiency to remain high during the entire period of contact of the two phases and, thereby, provide a nearly constant interfacial area for collection. In addition, migration of solids from the aqueous phase into the organic phase would minimize disruption of particle-droplet pairs. This disruption of the particle-bubble attachment occurs in conventional flotation systems and is a disadvantage in treatment of fine particle systems.

Particulate Bed Classification

It is recommended that consideration be given to dry separation techniques based on fluidized or moving-bed technology. One of the properties of a fluidized bed is that its buoyancy effect on suspended objects can be varied by choice of bed material and fluidizing conditions. For this reason, it is believed that coal preparation might be carried out in one or more fluidized-bed units whereby an enrichment in organic material and a rejection of ash components could be achieved without the use of water, which is a scarce commodity in many parts of the country, and without the dusting problem associated with classification schemes based on vibration, since the gas in a fluidized-bed unit could be readily reused on a closed-cycle basis. Another possibility, of course, is to use a moving bed of coarse material as a separating medium for finely divided ash and coal.

Combustion Equipment

Obviously a considerable amount of attention should be devoted to designing engines specifically for use with colloidal fuels if the nation decides to proceed with such a fuel program. The present generation of turbines and diesel engines was constructed on the basis that the various fuels would be relatively particulate free, and no attempt has been made to optimize design and materials for use in a coal fed system. What is remarkable about the current status of colloidal fuels is the fact that so much success has been attained in equipment unintended for such heavy duty use.

The Australians have demonstrated some of what can be accomplished in this regard. A three-stage compressor (high pressure) turbine to replace the two-stage unit of the standard (original) engine was designed in the mid-1960's to meet the problem of excessive turbine blade erosion. The new turbine featured lower gas velocities and blades of greater trailing edge thickness to withstand a larger metal loss before their aerodynamic performance was impaired.

Blade erosion rates were reduced by a factor of 10 to 20 times in comparison with those measured on the original engine using Greta-seam coal. Estimated blade life in this engine based on the preservation of an effective aerodynamic blade profile was in the range of 25,000-50,000 hours depending on the position of the blades. This order of blade life was believed adequate to meet commercial requirements and that an engine of higher output, with its larger blades, would have a even longer blade life than the experimental turbine. In addition, tests carried out with sample blades treated with hard surface coatings such as chromium indicated that such treatment could further reduce blade erosion rate.

Recent work on coatings has given evidence that materials with better erosion and corrosion resistance than chromium are now available. The most recent work on liquefaction valve trim at Battelle for instance, indicates that vapor deposited silicon carbide was most effective from an erosion standpoint, and such materials should be at least considered for valves and components of diesel systems.

Obviously, further investigation of the characteristics of coal-in-water mixtures that might permit handling of coal mixtures as liquid fuels is also warranted. The handling characteristics, the atomization characteristics should all be investigated. This approach may be particularly pertinent for use with pulverized solvent-refined coals. These coals may pulverize most easily by wet grinding to prevent agglomeration, and the wet mixture of up to 50 percent coal may prove to be a practical pulverized product.

One might think of water as a "lubricant" in colloidal fuel systems if a water based fuel is employed, or possibly high oil "bleeds" through rings or seals in oil-water systems, but with only the water injected with the coal. More attention should be paid to the nature of the ash in the various coals, ie, coals should be selected for the behavior of their ash in a combustor, as they now are, or at least should be, in steam boilers. A nomograph relating base-acid ratio, ash content, and ash softening temperature for boiler furnace cleanability is shown in Figure 16. This nomograph predicts the effectiveness of soot blowers in removing ash deposits before they fuse to a nonremovable condition as a function of ash properties. Similar considerations should be given to modifying ash behavior in diesels and turbines.

Further conceptual development of combustors for firing pulverized coal, with consideration of pollution emissions, which have not been investigated in past R&D, is needed. The effects of staged combustion, of air distribution, and turbulence levels need clarification. The effects of coal type, ash characteristics, and coal fineness are not well defined. Work of this nature could be carried out at atmospheric pressure and at moderate scale.

FIGURE 16. NOMOGRAPH RELATING BASE-ACID RATIO, ASH CONTENT, AND ASH SOFTENING TEMPERATURE TO FURNACE CLEANABILITY

Control Technology

It is not evident, at this time, that firing of gas turbines or diesel engines with colloidal fuel, especially with coal as the particulate phase, is practical. The ECAS program addressed the question of advanced power systems fired with coal for base-load power generation, and the results of this study encourage the use of low-Btu gas from an integrated gasifier, or the use of semiclean solvent refined coal, to solve the sulfur control problem. The direct firing of pulverized coal was not addressed because no system for sulfur removal was proposed for analysis.

If the question of sulfur removal is temporarily bypassed by the assumption that a low-sulfur fuel, or a coal treated to remove sulfur, is to be burned, the question of practical firing hinges upon the ability to provide adequately clean combustion products. The key question of reliability and durability cannot be answered without more research on erosion and corrosion by various coal ashes, and the development of suitable dust-collecting equipment that will provide gas of the needed cleanliness once the engine itself has been optimized for use with heavy particulate loadings.

Control technology therefore represents one of the major problems in the use of colloidal fuels, particularly if coal is to be used as the primary fuel. For this reason, other fuels should also be considered, including the use of wood and wood wastes and possibly peat and lignite. Chemical approaches to producing refined coal by precipitation should be explored. High temperature gas cleaning systems are needed, and although there is some related work going on in this area around the world, progress has been slow. Borrowing from current utility trends, perhaps the use of hot precipitators should be recommended for smaller applications. Improvements in injection control technology should continue to be pursued. However, the greatest opportunity for emission control probably lies in precombustion treatment, since such treatment should minimize corrosive and erosive attack within the engine itself as well as directly attack the environmental problems associated with the use of coal. Although chemical

treatment of coal to remove sulfur (and ash) has not yet been viewed as commercially viable, and there are numerous problems still to be solved, further research in this area should be intensified with particular emphasis on the fuel specifications needed for turbines and diesel engines.

ECONOMIC POTENTIAL OF COAL-OIL MIXTURES

The economic gains to be made by partial or total displacement of oil in a fuel for use in a combustion device designed to use oil obviously becomes more attractive as the price of oil rises. Because the costs of coal and oil are most commonly expressed on different bases (ie, \$/ton for coal and \$/bbl for oil), and because the costs of grinding are even more difficult to put into perspective (ie, various values for energy in kwh/ton for various sizes of pulverized coal, at costs expressed in terms of cents per kwh), it is not generally recognized what huge savings are possible even for "relatively" severe energy requirements for the comminution of coal.

Rather straightforward mathematical expressions can be set up to express these relationships as follows:

Let:

C_o	=	Cost of oil,	\$/barrel
C_c	=	Cost of coal,	\$/ton
C_e	=	Cost of electricity,	\$/kwh
C_g	=	Fixed grinding cost,	\$/ton
C_b	=	Fuel blending cost,	\$/barrel
E_g	=	Grinding energy required,	kwh/ton
R	=	Coal-to-oil weight ratio,	percent
W_o	=	Weight of oil,	lb/barrel
H_o	=	Heating value of oil,	Btu/barrel
H_c	=	Heating value of coal,	Btu/ton

Basis: 1 ton of colloidal fuel (ie, coal-oil mixture)

If:

X_c = weight of coal in mixture, ton

and X_o = weight of oil in mixture, ton

then:

$$X_c + X_o = 1 \quad (1)$$

$$\frac{X_c}{X_o} 100 = R \quad (2)$$

Solving (1) and (2) gives:

$$X_c = \frac{R}{100+R} \quad (3)$$

$$\text{and } X_o = \frac{100}{100+R} \quad (4)$$

Heating value of 1 ton of colloidal fuel is:

$$H = X_c H_c + X_o \left(\frac{2000 \text{ lbs}}{\text{ton}} \right) \frac{H_o}{W_o} \quad (5)$$

Estimated cost to produce 1 ton of colloidal fuel is:

$$C = X_c (C_c + C_e E_g + C_g) + \frac{X_o}{W_o} \left(\frac{2000 \text{ lbs}}{\text{ton}} \right) (C_o + C_b) \quad (6)$$

Fuel cost, in terms of $\$/10^6$ Btu, would then be:

$$C_F = \frac{C}{H} \times 10^6 \quad (7)$$

where: C = fuel cost, $\$/\text{ton}$

H = heating value, Btu/ton

To combine (3), (4), (5) and (6) into one equation, (7) can be written as:

$$C_F = \frac{\frac{R}{100+R} (C_c + C_e E_g + C_g) + \frac{100 \times 2000}{W_o(100+R)} (C_o + C_b)}{\frac{R}{100+R} H_c + \frac{100 \times 2000}{W_o(100+R)} H_o} \times 10^6 \quad (8)$$

or:

$$C_F = 10^6 \left[\frac{RW_o (C_c + C_e E_g + C_g) + 2 \times 10^5 (C_o + C_b)}{RW_o H_c + 2 \times 10^5 H_o} \right] \quad (9)$$

Example:

Say,   R   =   30. percent
                   W_o   =   325. lb/bbl
                   H_c   =   25.5 x 10⁶ Btu/ton
                   H_o   =   6.2 x 10⁶ Btu/bbl
                   C_c   =   40. \$/ton
                   C_e   =   0.05 \$/kwh
                   E_g   =   100. kwh/ton
                   C_g   =   5. \$/ton
                   C_o   =   30. \$/bbl
                   C_b   =   1. \$/bbl

then:

$$\begin{aligned} C_f &= 10^6 \left[\frac{30 \times 325 (40 + 0.05 \times 100 + 5) + 2 \times 10^5 (30. + 1)}{(30 \times 325 \times 25.5 + 2 \times 10^5 \times 6.2) 10^6} \right] \\ &= \frac{9750 (50) + 2 \times 10^5 (31)}{248625. + 1240000.} \\ &= 4.492 \text{ \$/10}^6 \text{ Btu} \end{aligned}$$

Despite the fact the costs for these mixtures can now be easily calculated, and values for various coal and oil parameters have been tabulated in the Appendix to this report, it is still difficult to establish perspective. For this reason, Figures 17, 18, and 19 have been drawn up to graphically represent these parameters.

FIGURE 17. Coal-Oil Colloidal Fuel Cost Estimate

At Oil Price Of 20. Dollars/Barrel

FIGURE 18. Coal-Oil Colloidal Fuel Cost Estimate

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At Oil Price Of 30. Dollars/Barrel

FIGURE 19. Coal-Oil Colloidal Fuel Cost Estimate

At Oil Price Of 40. Dollars/Barrel

Prices were calculated for the following perturbed 3 x 3 matrix:

Coal Cost	\$20/ton	\$40/ton	\$60/ton
Grinding	25 kWh/ton	100/kWh/ton	250 kWh/ton
Oil Costs	\$20/bbl	\$30/bbl	\$40/bbl

The lowest energy requirements for grinding coal correspond to the claims of Krajcovic in 1973, while the higher values are believed to be more realistic for most colloidal fuels, although Bill Peters at Bruceton has reported values of about 100 kWh/ton for some of his work.⁽³³⁾ Current costs (early 1980) for coal are about \$25/ton and oil costs are in the range of \$30/bbl. Transportation costs for coal can add significantly to these costs.

At oil costs of \$30 and \$40 per barrel, all calculated combinations of coal costs and grinding requirements are significantly below the price of oil even at coal-oil slurry combinations as low as 30 percent coal-to-oil weight ratio. At \$20/bbl for oil, which at present would seem to be a lost opportunity, only coal prices above about \$60/ton would rule out the attractiveness of colloidal type fuels.

RECOMMENDATIONS

On the basis of the information developed in this study, the following recommendations concerning the future of colloidal fuels have been formulated:

1. The potential for colloidal fuels to meet a significant fraction of our future energy requirements appears to be large and represents an attractive national goal. That is not to say that there are not numerous problems to be faced, and that there are not other energy alternatives which may prove to be at least as attractive. However, colloidal fuels are characterized by having been clearly established to be technically feasible; their economics indicate that large cost margins are available to absorb possible increases in technical complexities which may be encountered in the future, and our present scientific knowledge suggests that many problems still to be faced will in fact be solvable.

2. The present national effort on coal-oil mixtures should therefore be seriously examined for possible expansion to include finer particulate matter as a component of this fuel, and to other fluids as the suspending vehicle for use in energy conversion devices other than steam generators. There is a substantial resource base of personnel and organizations with previous experience and leadership in related areas of technology. In addition, new talent and knowledge should be developed to assist in the exploitation of this energy alternative.

3. Research should be supported on methods to remove inorganic components in coals that are suitable for use as colloidal fuels. Such action is needed to minimize environmental and materials problems which would be associated with the use of colloidal fuels in engines. Sulfur and sodium are especially harmful to most known materials of construction that are used in gas turbine and diesel engines. Acceptable levels for sulfur and sodium in the fuel for gas turbines of current design may be as low as one part per million. On the other hand, most No. 6 diesel oil used in turbines today is washed to remove harmful contaminants. The

erosive problem with particulates from coal is well known and the removal of the organic nitrogen from coal would also be a desirable accomplishment from an environmental standpoint.

4. Post combustion emission control technology should be developed for the special requirements of relatively small scale equipment which would employ fuels containing significant amounts of coal. The most common sulfur control technique now in use for the combustion of COM in industrial boilers is the use of sodium bicarbonate injection, which is a less than perfect technology so far rejected by the utilities as being too costly and environmentally unacceptable. Particulate emissions from the combustion of colloidal fuels in mobile power plants may be particularly troublesome problem from a control standpoint.

5. A major effort should be made to modify the character of the ash which is formed upon the combustion of coal. Smaller particle sizes and softer crystalline forms are needed in order to minimize the abrasive action of fly ash in engines. Pretreatment of the coal, modifications of the combustion conditions, and possibly even additives should be considered. This area of research has received essentially no attention previously by the scientific community.

6. Additional research on improved comminution technology appears desirable. Although it is difficult to judge how much work is actually underway in the private sector, it seems safe to say that more efficient techniques to make even finer fuels are needed. The development of staged comminution technology, with intermediate classification, appears technically and economically attractive.

7. Adequate instrumentation to better control grinding levels, deashing procedures, mixing, and feeding, and even for post combustion gas analysis is generally lacking. The steady feeding of finely divided particulate matter at known and reproducible conditions will become an increasing important factor if attempts to commercialize this technology are pursued.

8. Chemical means should be developed to produce finely divided carbonaceous fuel from all sources, especially coal. Both organic and aqueous based processing systems should be investigated. The pulp and

paper industry is an example of the development of relatively low cost chemical technique to produce processed finely-divided solids from relatively crude raw materials like trees.

9. Serious work on the use of air and/or water as the suspending fluid for fuel particles in the colloidal size range is almost non-existent at present. A significant effort in this direction would obviously provide a major opportunity to avoid the use of large amounts of oil.

10. The use of carbonaceous fuels other than coal should be investigated. Cellulosic materials would seem to be good candidates for use as colloidal fuels. Even peat might find a major role to play as an alternative fuel in engines originally designed to burn oil or gas.

11. Work should be undertaken on how to best modify present engines to accept colloidal type fuels. Further work on coatings on turbine blades, on rings and as cylinder liners should be carried out. Heavier duty construction might be pursued. Recent results obtained with new materials in other fields, for instance, coatings on liquefaction valves, might be at least partially transferable to coatings for engines operating with colloidal fuels.

12. Encouragement to devise new energy conversion schemes, especially conceived for use with colloid fuels, should be provided by awarding pioneering research grants for innovative approaches in this area of technology.

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APPENDIX

COST SAVINGS FOR VARIOUS
FUEL MIXES

COLLOIDAL FUEL COST ESTIMATE FOR 25. KWH/TON GRINDING ENERGY

COST OF OIL \$/BBL	COST OF OIL \$/MBTU	COST OF COAL, \$/TON	COAL/OIL RATIO, WT. PERCENT	ELEC. ENERGY COST, CENIS/KWH	FUEL COST, \$/MBTU	NET SAVINGS COMPARED TO OIL, \$/MBTU
(1)	(2)	(3)	(4)	(5)	(6)	(2)-(6)
20.0	3.226	20.0	30.	5.	2.990	.236
				5.	2.993	.232
				7.	2.997	.229
			50.	5.	2.792	.434
				5.	2.797	.429
				7.	2.801	.424
		40.0	30.	3.	2.629	.596
				5.	2.636	.590
				7.	2.642	.584
			50.	3.	3.121	.105
				5.	3.124	.101
				7.	3.128	.098
		60.0	30.	3.	2.988	.238
				5.	2.993	.233
				7.	2.998	.228
			50.	3.	2.879	.346
				5.	2.886	.340
				7.	2.892	.334
30.0	4.839	20.0	30.	3.	3.252	-.026
				5.	3.255	-.030
				7.	3.259	-.033
			50.	3.	3.185	.041
				5.	3.189	.036
				7.	3.194	.031
		40.0	30.	3.	3.129	.096
				5.	3.136	.090
				7.	3.142	.084
			50.	3.	4.334	.505
				5.	4.337	.502
				7.	4.340	.499
		60.0	30.	3.	4.001	.838
				5.	4.005	.833
				7.	4.010	.828
			50.	3.	3.728	1.110
				5.	3.734	1.104
				7.	3.741	1.098
40.0	6.451	20.0	30.	3.	4.465	.374
				5.	4.468	.371
				7.	4.471	.368
			50.	3.	4.197	.642
				5.	4.202	.637
				7.	4.207	.632
		40.0	30.	3.	3.978	.861
				5.	3.984	.854
				7.	3.991	.848

COLLOIDAL FUEL COST ESTIMATE FOR 25. KWH/TON GRINDING ENERGY

COST OF OIL \$/BBL	COST OF COAL, \$/MTU	COAL/OIL RATIO, WT. PERCENT	ELEC. ENERGY COST, CENTS/KWH	FUEL COST, \$/MTU	NET SAVINGS COMPARED TO OIL, \$/MTU
(1)	(2)	(3)	(4)	(5)	(6)
30.0	4.839	60.0	30.	3.	4.596
				5.	4.599
				7.	4.602
		50.	30.	3.	4.393
				5.	4.398
				7.	4.403
		70.	30.	3.	4.228
				5.	4.234
				7.	4.241
40.0	6.452	20.0	30.	3.	5.677
				5.	5.680
				7.	5.684
		50.	30.	3.	5.209
				5.	5.214
				7.	5.219
		70.	30.	3.	4.827
				5.	4.833
				7.	4.840
		40.0	30.	3.	5.808
				5.	5.811
				7.	5.815
		50.	30.	3.	5.406
				5.	5.411
				7.	5.416
		70.	30.	3.	5.077
				5.	5.083
				7.	5.090
		60.0	30.	3.	5.939
				5.	5.942
				7.	5.946
		50.	30.	3.	5.602
				5.	5.607
				7.	5.612
		70.	30.	3.	5.327
				5.	5.333
				7.	5.340

COLLOIDAL FUEL COST ESTIMATE FOR 100. KWH/TON GRINDING ENERGY

COST OF OIL \$/BBL	COST OF COAL, \$/MBTU	COAL/OIL RATIO, \$/TON	COAL/OIL RATIO, WT. PERCENT	ELEC. ENERGY COST, CENTS/KWH	FUEL COST, \$/MBTU	NET SAVINGS COMPARED TO OIL, \$/MBTU
(1)	(2)	(3)	(4)	(5)	(6)	(2)-(6)
20.0	3.226	20.0	30.	3.	3.005	.221
				5.	3.018	.208
				7.	3.031	.195
			50.	3.	2.814	.412
				5.	2.833	.392
				7.	2.853	.373
			70.	3.	2.658	.568
				5.	2.683	.543
				7.	2.708	.518
		40.0	30.	3.	3.136	.090
				5.	3.149	.077
				7.	3.162	.064
			50.	3.	3.010	.216
				5.	3.030	.196
				7.	3.049	.176
30.0	4.839	20.0	30.	3.	2.907	.318
				5.	2.932	.293
				7.	2.957	.268
			50.	3.	3.267	-.041
				5.	3.280	-.054
				7.	3.293	-.067
			70.	3.	3.207	.019
				5.	3.226	-.000
				7.	3.246	-.020
		40.0	30.	3.	3.157	.068
				5.	3.182	.043
				7.	3.207	.018
			50.	3.	4.348	.490
				5.	4.361	.477
				7.	4.375	.464
40.0	6.452	20.0	30.	3.	4.023	.816
				5.	4.042	.796
				7.	4.062	.777
			50.	3.	3.756	1.082
				5.	3.781	1.057
				7.	3.806	1.032
			70.	3.	4.479	.359
				5.	4.492	.346
				7.	4.506	.333
		40.0	30.	3.	4.219	.620
				5.	4.239	.600
				7.	4.258	.580
			50.	3.	4.006	.832
				5.	4.031	.807
				7.	4.056	.782

COLLOIDAL FUEL COST ESTIMATE FOR 100. KWH/TON GRINDING ENERGY

COST OF OIL \$/BBL	COST OF OIL \$/MBTU	COST OF COAL, \$/TON	COAL/OIL RATIO, WT. PERCENT	ELEC. ENERGY COST, CENIS/KWH	FUEL COST, \$/MBTU	NET SAVINGS COMPARED TO OIL, \$/MBTU
(1)	(2)	(3)	(4)	(5)	(6)	(2)-(6)
30.0	4.839	60.0	30.	3.	4.610	.228
				5.	4.623	.215
				7.	4.636	.202
			50.	3.	4.416	.423
				5.	4.435	.404
				7.	4.455	.384
			70.	3.	4.256	.582
				5.	4.281	.557
				7.	4.306	.532
40.0	6.452	20.0	30.	3.	5.692	.760
				5.	5.705	.747
				7.	5.718	.734
			50.	3.	5.232	1.220
				5.	5.251	1.200
				7.	5.271	1.181
			70.	3.	4.855	1.596
				5.	4.880	1.571
				7.	4.905	1.546
		40.0	30.	3.	5.823	.629
				5.	5.836	.616
				7.	5.849	.603
			50.	3.	5.428	1.024
				5.	5.448	1.004
				7.	5.467	.984
			70.	3.	5.105	1.346
				5.	5.130	1.321
				7.	5.155	1.296
		60.0	30.	3.	5.954	.498
				5.	5.967	.485
				7.	5.980	.472
			50.	3.	5.624	.827
				5.	5.644	.807
				7.	5.664	.788
			70.	3.	5.355	1.096
				5.	5.380	1.071
				7.	5.405	1.046

COLLOIDAL FUEL COST ESTIMATE FOR 250. KWH/TON GRINDING ENERGY

COST OF OIL \$/BBL	COST OF COAL, \$/MTU	COAL/OIL RATIO, WT. PERCENT	ELEC. ENERGY COST, CENTS/KWH	FUEL COST, \$/MTU	NET SAVINGS COMPARED TO OIL, \$/MTU
(1)	(2)	(3)	(4)	(5)	(2)-(6)
20.0	3.226	20.0	30.	3.034	.192
			5.	3.067	.159
			7.	3.100	.126
		50.	3.	2.858	.368
			5.	2.907	.319
			7.	2.956	.270
		70.	3.	2.714	.512
			5.	2.776	.450
			7.	2.839	.387
	40.0	30.	3.	3.165	.061
			5.	3.198	.028
			7.	3.231	-.005
		50.	3.	3.054	.171
			5.	3.104	.122
			7.	3.153	.073
		70.	3.	2.964	.262
			5.	3.026	.200
			7.	3.089	.137
	60.0	30.	3.	3.296	-.070
			5.	3.329	-.103
			7.	3.362	-.136
		50.	3.	3.251	-.025
			5.	3.300	-.074
			7.	3.349	-.123
		70.	3.	3.214	.012
			5.	3.276	-.050
			7.	3.339	-.113
30.0	4.839	20.0	30.	4.378	.461
			5.	4.411	.428
			7.	4.443	.395
		50.	3.	4.067	.772
			5.	4.116	.723
			7.	4.165	.674
		70.	3.	3.813	1.026
			5.	3.875	.964
			7.	3.938	.901
	40.0	30.	3.	4.509	.330
			5.	4.542	.297
			7.	4.574	.264
		50.	3.	4.263	.575
			5.	4.312	.526
			7.	4.362	.477
		70.	3.	4.063	.776
			5.	4.125	.714
			7.	4.188	.651

COLLOIDAL FUEL COST ESTIMATE FOR 250. KWH/TON GRINDING ENERGY

COST OF OIL		COST OF COAL,	COAL/OIL RATIO,	ELEC. ENERGY COST,	FUEL COST,	NET SAVINGS COMPARED
\$/BBL	\$/MBTU	\$/TON	WT. PERCENT	CENIS/KWH	\$/MBTU	TO OIL, \$/MBTU
(1)	(2)	(3)	(4)	(5)	(6)	(2)-(6)
30.0	4.839	60.0	30.	5.	4.640	.199
				5.	4.673	.166
				7.	4.705	.133
			50.	3.	4.460	.379
				5.	4.509	.330
				7.	4.556	.281
			70.	3.	4.313	.526
				5.	4.375	.464
				7.	4.438	.401
40.0	6.452	20.0	30.	3.	5.721	.730
				5.	5.754	.698
				7.	5.787	.665
			50.	3.	5.276	1.176
				5.	5.325	1.127
				7.	5.374	1.078
			70.	3.	4.911	1.540
				5.	4.974	1.478
				7.	5.036	1.415
		40.0	30.	3.	5.852	.599
				5.	5.885	.567
				7.	5.918	.534
			50.	3.	5.472	.979
				5.	5.521	.930
				7.	5.570	.881
			70.	3.	5.161	1.290
				5.	5.224	1.228
				7.	5.286	1.165
		60.0	30.	3.	5.983	.468
				5.	6.016	.436
				7.	6.049	.403
			50.	3.	5.669	.783
				5.	5.718	.734
				7.	5.767	.685
			70.	3.	5.411	1.040
				5.	5.474	.978
				7.	5.536	.915