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DEVELOPMENT AND EVALUATION OF HIGHLY-LOADED COAL
SLURRIES

Phase I Summary Report for the Period October 15, 1977-December 31, 1978

By
R. S. Scheffee

May 1979

Work Performed Under Contract No. AC22-77ET13041

Atlantic Research Corporation
Alexandria, Virginia

U. S. DEPARTMENT OF ENERGY

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DEVELOPMENT AND EVALUATION OF
HIGHLY-LOADED COAL SLURRIES

by R. S. Scheffee

Phase I Summary Report
October 15, 1977 - December 31, 1978

Submitted to:

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Contract No. AC01-77-ET13041

May 1979

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FOREWARD

This is the Phase I Summary Report for DOE Contract AC01-77-ET13041.

This report covers the work performed during the period 15 October 1977 through 31 December 1978. This contract was initiated at the office of Fossil Energy, Washington, DC 20545, under the direction of William Fedarko. The program is currently administered by the Pittsburgh Energy Technology Center, Pittsburgh, PA 15213. Roy Kurtzrock is the DOE program manager. Jim Elmann is the Technical Project Officer.

This program was carried out by the Research and Technology Division of the Atlantic Research Corporation, Alexandria, VA 22314. The program manager was J. D. Martin, Manager, Propulsion Technology Department. The principal investigator was R. S. Scheffee, Chief, Energy Technology Group.

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ABSTRACT

Slurry fuels comprised of either bituminous, subbituminous, or lignite coal, and either aqueous media or emulsions of No. 6 oil in water as the carrier were developed and evaluated at solids loadings up to 70% by weight. Emphasis was placed on aqueous slurries of bituminous coal.

These slurries were developed for use in place of No. 6 oil in oil-fired burners.

High solids loadings were attained by use of bimodal particle size distributions, which are blends of coarse-grind coal (~50-85% -50 mesh) and fine-grind coal (generally 90% -200 mesh). The effect of the blends on slurry viscosity was determined to find the blends that minimize viscosity. The effect of mill conditions on particle size distribution was determined for each coal, using a hammermill pulverizer.

A large number of water-soluble resins were evaluated for effect on slurry stability and viscosity. The best of these was found to be hydroxypropylated corn starch. Slurries based on the use of 3% solutions of the starch in water were prepared with up to 70% by weight bituminous coal and up to 65% subbituminous coal. The slurries are pourable pseudo-plastic fluids having room-temperature viscosities in the range of 550 to 1100 cp at a shear rate of 3000 sec^{-1} , depending on the type of coal, solids loading, and particle size distribution. None of the slurries exhibited hard pack settling, even after room-temperature storage up to 74 days.

Oil-in-water emulsions made with polyethylene glycol (23) lauryl ether as an emulsifier were found to be stable with respect to phase separation when stored at 160°F. Slurries made with these emulsions do not exhibit hard pack settling after one week storage at 160°F.

1.0 PROGRAM INTRODUCTION AND SUMMARY

1.1 Introduction

The objective of this program was to develop and evaluate stable coal slurry fuels for use in No. 6 oil burners. The goals were 70% by weight coal and 3 months stability toward settling.

During the last half of Phase I, program cognizance was transferred from Fossil Energy Research (in Washington, DC) to the Pittsburgh Energy Technical Center. As a result of this action, evaluation of unstable slurries was included in the program. This was in the interest of minimum slurry ingredient cost, and because it is difficult to quantify a priori the cost effectiveness of slurry stability. Consequently, while emphasis was placed on stabilized slurries, the evaluations included a number of unstabilized ones. Stabilities ranged from essentially complete settling in a few hours for most of the unstabilized slurries to essentially no packing after 74 days for the better stabilized ones.

The program is being carried out in two parts. In Phase I, carried out during the calendar year 1978, solids loadings of slurries were maximized for selected coals and carriers, and evaluation was directed toward slurry rheology, stability, and cost. In Phase II, planned for calendar year 1979, combustion of candidate slurries in a LMBTUH fire-tube burner is to be carried out. The results of Phase I are the subject of this report.

1.2 Scope

Aqueous and emulsified carriers were evaluated in this program. The aqueous carriers were primarily solutions of water-soluble resins and/or dispersants in water. Emulsified carriers were oil-in-water emulsions of No. 6 oil in water. As a design point the water content of the slurries was initially constrained to values of 30 and 10% by weight. Thus it is seen that carriers meeting the stated objective of 70% coal in the slurry are comprised of either water or 2/1 mixture of oil and water. As it turned out, slurries containing water contents >30% and <10% were evaluated in the effort to reach the program objective.

Several types of coal were evaluated in this program. These are enumerated below.

1. A clean coal from the Bruceton Experimental Mine.
2. A Pittsburgh Seam bituminous coal from the Bruceton Experimental Mine. This is identified throughout this report as PHS 361.
3. A Wyoming subbituminous coal received from Penn State, identified as PSOC 846.
4. An Iowa subbituminous coal (PSOC-664).
5. A Montana lignite coal (PSOC 837).

Emphasis in the program was placed on slurries of the bituminous coal (PHS 361).

1.3 Program Plan

The technical approach was to develop highly loaded slurries by systematic evaluation of the effect of composition and process variables on slurry rheology, stability, and cost. Toward this end the Phase I program was comprised of a number of tasks: (1) a literature survey; (2) calculations of heating values and costs; (3) evaluation and selection of carriers; (4) evaluation of slurries, and (5) selection and evaluation of candidate slurries. The literature survey was concerned with the state of the art of slurry technology and was carried out at the start of the program. Results of the survey are summarized in Appendix A. Calculations of heating values and cost were carried out to aid in direction and evaluation of the experimental work. The experimental work, Tasks 3, 4, and 5, was concerned with maximizing solids loading and stability, and minimizing viscosity. The control of particle size distribution was used to maximize solids loadings and minimize viscosity. A hammermill was used to pulverize coal and a high shear mixer (Hobart type) for slurry preparation. Viscosity at high shear rates was measured with an extrusion rheometer. Slurry stability was based on carrier composition. Stability was measured with a compound pendulum. Salient features of the technology are presented in Section 2, and experimental results are given in Section 3. Preliminary cost estimates are given in Section 4.

Results of the Phase I effort are summarized as follows:

1. Coal slurry fuels are not new. The earliest patent is 100 years old (issued 1879), and extensive experiments to evaluate slurries of coal and oil as shipboard fuels date from World War I.

2. The interest in coal slurry fuels has historically stemmed from crises: WWI, WWII, the Arab oil embargo, and the diminishing oil supply. The fuels have never gained commercial importance, in spite of several successful demonstration projects, because of the ease of handling of competing fuels (coal, oil, and gas). With the exception of slurries made with very finely pulverized coal ($\frac{1}{4}$ μ diameter), the literature reveals no proven examples of stable slurries, in spite of patent claims to the contrary. In addition to slurry instability (i.e. solids settling), uncertain cost effectiveness has been the second major drawback to the use of these fuels. Historically, the prices of the major fuels have seemed to be low enough to ensure their continued existence and use, and to forestall that of the slurries. These prices are probably just as arbitrary today, but at least seem more predictable and permit more certain estimates of the cost effectiveness of slurries.

3. An important result of the present program was the preparation of stable slurries by use of carriers that have a yield point. These carriers are fluids, technically known as Bingham plastics, or more accurately as Bingham pseudoplastics because generally the viscosities of these fluids were found to decrease with increasing shear rate. A yield point in the range of 5 - 10 dynes/cm² was found to be adequate for preparation of stable slurries.

The best carriers based on water were found to be 3% solutions of hydroxypropylated corn starch (HPCS). This type of resin is particularly useful for coal slurries because it is unaffected by ionic contamination, which is always present in coal/water mixtures.

The best carriers based on No. 6 oil were found to be oil-in-water emulsions made with polyethyleneglycol (23) lauryl ether as an emulsifier. These emulsions resemble mayonnaise in consistency, at high

temperature, and are stable with respect to phase separation when stored at 160°F. The water content of the emulsions was adjusted to be 10% of the total slurry weight. The emulsifier content was one part per hundred of oil plus water, or about 0.5% of the total slurry weight.

4. A second important result of the present program was the preparation of highly loaded slurries by means of bimodal particle size distributions. Blends of coarsely-ground and finely-ground coal are used to obtain desired distributions. In some of the slurries, the coarse size was constrained to 100% -50 mesh to minimize the possible effect of particle size on combustion efficiency. Higher solids loadings were obtained by use of coarse grinds having some of the particles >50 mesh. In all of the slurries, the fines size consist was typically 90% -200 mesh. All grinding was carried out with a hammermill, and is well within the capabilities of other conventional pulverizers. In terms of lower viscosity and high solids loadings, the blends are significantly superior to use of a single "standard" size consist of 80% -200 mesh. Typically, solids loadings can be increased 10-15 percentage points with no increase in viscosity, when the blends are used in place of the standard grind.

5. Emphasis in the present program was placed on slurries of coal in water and various water solutions. The best of these slurries are fluids that are stable toward settling and are significantly more cost-effective than No. 6 oil.

Stable slurries of 65% bituminous coal in an aqueous 3% solution of hydroxypropylated corn starch (HPCS) were prepared with all particles <50 mesh. The coarse/fines weight ratio of 55/45 was found to be the most fluid. These slurries exhibit ~1% settling (by pendulum) after 74 days, and a viscosity of 779 cp @ 3000 sec⁻¹.

Stable slurries of 70% bituminous coal in an aqueous 3% solution of HPCS were prepared with ~15% of the coal particles >50 mesh in size. Here, the coarse/fines weight ratio of 75/45 was the most fluid. These slurries exhibit no settling by pendulum after 73 days, and also have a typical viscosity of 800 cp at 300 sec⁻¹.

Fluid, unstable slurries of 70% bituminous coal in aqueous solutions of dispersants were prepared with the 65 coarse/35 fines blend, all particles <50 mesh. The viscosities of these slurries were the lowest of any of the slurries evaluated in this work.

Stable slurries of 60-65% subbituminous in an aqueous 3% HPSC solution were prepared and evaluated. These slurries could not be loaded as highly as those made up with bituminous coal.

6. Slurries with 50 - 60% bituminous coal were prepared with the emulsified carriers. A limited evaluation indicated that slurries prepared with the emulsion do not hard pack settle, as do those prepared with oil.

7. Preliminary estimates of the cost-effectiveness of slurry fuels were made for selected candidates, based on higher heating value (HHV) and the following prices: \$15/bbl No. 6 oil (144570 BTU/gal); \$30/ton bituminous coal (13460 BTU/lb); 27¢/lb HPSC, and 72¢/lb emulsifier. The relative price of energy, ($\$ \text{ of fuel/MBTU} / (\$ \text{ of oil/MBTU})$) was found to be a good figure of merit for cost-effectiveness. Results based on this parameter are summarized below:

<u>Fuel</u>	<u>Relative Price of Energy</u>
1. No. 6 Oil	1
2. Bituminous Coal	0.46
3. 65% coal + 35% water, an unstable slurry	0.64
4. 65% coal + 35% aqueous solution of 3% HPSC, a stable slurry	0.76
5. 70% coal + 30% aqueous solution of 3% HPSC a stable slurry	0.72
6. 50% coal + 50% oil, an unstable slurry	0.88
7. 50% coal + 50% emulsion	0.96

2.0 TECHNICAL INTRODUCTION

As stated previously, the control of particle size distribution and the use of carriers with yield points were used to develop highly loaded stable slurries. The coal slurry literature is silent on the use of this technology, aside from a brief reference to the use of fluids with a yield point, made by Sheppard in 1921 (see the attached literature review, Appendix A). For this reason, a brief review of the colligative properties of slurries is presented here. Also included is a discussion of theoretical heating values, costs of fuels, and measurement of rheology and stability.

2.1 Particle Size Technology

The development of highly loaded coal slurries is predicated on the use of pulverized coal having a bimodal particle size distribution. The maximum solids loading of slurries occurs when the carrier fills the voids volume (interstices) of the solids. During mixing, the solids assume a random packing configuration, ranging from cubic to rhombohedral, where the voids volume (for spheres of a given size) ranges from 0.48 to 0.26 respectively. The end-of-mix configuration depends on practically everything: (1) type of mixer; (2) mixing time; (3) order of addition of ingredients; (4) size distribution; (5) sphericity and other shape effects; (6) surface forces. These parameters also affect slurry viscosity, and the slurry consistency may range from a free-flowing fluid to a dough or putty. Naturally, viscosity decreases as the amount of carrier exceeds the voids volume, and the slurry is "wet sand" or dry if the amount of carrier is less than voids volume. It is not at all uncommon for a slurry to be dry initially in a mixer and to become fluid with continued mixing as the initial packing assumes its equilibrium configuration (i.e. as voids volume decreases).

When particles have a bimodal size distribution, the fines fit into the interstices of the larger particles, and the equilibrium packing tends toward a rhombohedral configuration. Consequently, less carrier is required to prepare a fluid slurry. The effect on viscosity is pronounced at the high solids loadings, where fluid slurries are prepared with bimodal blends while dry mixes result from a monomodal size distribution. At lower solids loadings, where the carrier exceeds the voids volume with either kinds of particles, the effect of bimodal blends is less pronounced. Thus, at 50% solids, the blends are probably of no value.

Theoretically, if all the fines were spheres of one size and the coarse were spheres of another size, maximum solids loading takes place at a coarse/fines size ratio of ~ 10 , and weight ratio of $\sim 70/30$. This is a familiar problem to workers in the solid propellant industry whose job is to maximize propellant performance (i.e. solids loading) while maintaining processability (i.e. castability). A reading of the coal slurry literature indicates that this practice has not been evaluated in the previous work, which dates to 1879. Generally, past work with coal slurries is based on the use of coal pulverized to a consistency of $\sim 80\%$ through 200 mesh, which is the typical product of pulverizers used for coal-fired steam-raising facilities. While some past work has been concerned with the use of ultra-fine coal ($\sim 1\mu$ MMD, mass mean diameter) in slurries, no attempt was made to blend this coal with larger sizes to gain the benefits of a bimodal size distribution. A literature review of past work with coal slurries, carried out at the onset of this program, and is summarized in Appendix A.

Bimodal particle size distributions are attained in practice by use of the products from two mill runs. Mill conditions can be selected to generate either the fines or the coarse as the product. For the work here, a hammermill pulverizer ("Bantam" Mikropulverizer) was used. Mill conditions of interest are feed size and feed rate, hammer speed, and grate size. In the interest of practicability, two constraints were imposed on the particle sizes. The first was that the fines be limited to the minimum size attainable by the hammermill. The resultant size consistency is typically 90% -200 mesh. Smaller sizes can be attained by jet mills, colloid mills, vibra-energy mills, attriters, etc.), but typically this would be either too energy-intensive, or not amenable to continuous processing on a large scale. The 90% -200 mesh size consist is within the capability of other mechanical mills that are more generally used to pulverize coal, such as the ball-and-race and the ring-roller mills, the cage mill, and the ball mill. The second constraint was that, if possible, the maximum particle size of the coarse be limited to 300μ . This is because the literature reveals that coal slurries made with 80% -200 mesh size consist can be burned fairly successfully in oil burners, and all of this coal is $<300\mu$ in size. As will be shown later, 65% slurries were prepared, satisfying these two constraints. For these slurries all of the

coarse that was $>300\mu$ ($\sim 15\%$ by weight) was removed by sieving and used as mill feed for the fines. (All of the coal is used as feed, either for the coarse or fines mill runs. None is not used.) The 70% slurries required a larger coarse size, and about 15% of the coal particles in these slurries was $>300\mu$.

When coal is milled mechanically, spherical particles of uniform size do not result, of course. A size distribution of irregularly shaped particles results, and the shape of the curve indicates the size range and the mass mean diameter (MMD). Fines of 90% -200 mesh size consist have an MMD value of $\sim 30\mu$, so the rule of thumb of a 10/1 size ratio cannot be attained because the MMD of the coarse cannot be 300μ without an excess of particle $> 300\mu$. Thus, within the operating constraints of the problem, the best size and mass ratios must be found by trial and error. This was the approach taken for each of the coals considered in the program. To generate the fines, the mill was operated at maximum speed with the smallest grate size. Several mill runs were then made at lower hammer speeds and with larger grate sizes to obtain the coarse which was then sieved, as required. Slurries were prepared with the fines and each coarse product at several values of coarse/fines weight ratio. The best coarse and weight ratio(s) were then selected on the basis of minimum values of end-of-mix viscosity.

In general, it was found that the coarse size consist ranged from ~ 50 to 85% -50 mesh; the coarse/fines size ratio was ~ 4 to 7, and the weight ratio was from 55/45 to 75/25. Within these limits on weight ratio, viscosity is fairly constant and at a minimum, while beyond those limits, viscosity increases. Preliminary calculations show that use of the blends to get the bimodal particle size distributions is no more costly than the use of a single size consist of 80% -200 mesh. The energy requirements for the fines (90% -200 mesh) is ~ 20 KWH/ton while that for the coarse is ~ 7 KWH/ton, so that the blends require ~ 10 to ~ 13 KWH/ton, compared to ~ 16 KWH/ton for 80% -200 mesh. The other costs (amortization, maintenance, labor, etc.) are similarly proportioned.

It is possible to conceive of trimodal or even polymodal size distributions as a route to further optimization. However, the results obtained with the bimodals seem to represent satisfactory solutions for

the problem at hand. Further, it is probable that either the greater use of particles >300 μ in size or the use of particles having a size consist smaller than 90% -200 mesh would be required for satisfactory use of the other size distributions. The attendant drawbacks of both requirements seem, at this time, to mitigate against their use, and favor the use of only a bimodal size distribution.

2.2 Carrier Selection Criteria

The development of stable slurries is predicated on the use of carriers that have a yield point. Generically, these fluids are called Bingham plastics. A certain value of stress, called the yield stress, must be exceeded before the onset of fluid motion or before particles can settle in the fluid. The critical value of yield stress to prevent settling is derived from Stokes flow*

$$\tau_y > \frac{D_p g (\rho_s - \rho_l)}{3g_c}$$

where τ_y = yield stress

D_p = particle diameter

ρ_s = particle density

ρ_l = liquid density

g = acceleration due to gravity

g_c = Newtons constant

The standard tests for transportation of materials and equipment require vibration at 1.5gs. Using this value along with 1.26 gm/cc for coal and 1 gm/cc for the carrier (water) gives the curve shown in Figure 1. For suspension of particles up to 300 μ , it is seen that a yield stress of at least 3.8 dynes/cm is required. Aqueous solutions that exhibit a yield point are generally prepared by use of water-soluble resins. Resins specially suited for preparation of Bingham include polyvinyl carboxylic acids, carboxymethyl cellulose, starches and modified starches, and various gums (quar, xanthan, etc.). Many oil-in-water emulsions are characteristically Bingham (e.g. mayonnaise). To prevent phase separation, an emulsifier is generally required.

*S. Charm and W. McComis, Food Technology, 19, 948 (1965).

A summary of other desirable carrier properties is given in Table 1, in approximate order of decreasing importance. These are discussed briefly. (1) yield point is, of course, required for a stable slurry as described above. (2) low cost is of primary importance, but is a relative number. As described in this report later, stable slurries of coal in water are considerably lower in price than oil, in terms of \$/MBTU. However stabilizers can be more costly than the unit cost of continuous mixing unstabilized coal slurries. The approach taken here has been to minimize unit cost to the greatest extent. (3) low chemical, physical, and biological reactivity are all of about equal importance and are required for tractable slurries. (a) Chemical reactivity of the water-soluble resins is manifest primarily as ion sensitivity and acid-catalyzed hydrolysis, both due to leachates generated by slurries of coal in water. Most of the important ionic resins are either destroyed (resulting in permanent viscosity loss) or gelled in ionic media, particularly by polyvalent cations (Ca^{+2} , Fe^{+3} , Al^{+3}). This property is less important when cleaned coal is used, but in general, only non-ionic resins are suitable for use here. All of the naturally-occurring resins, such as the cellulose, starches, and gums, are subject to hydrolysis catalyzed by acid leachates. Depending on the coal and water used to make up the slurries, the carriers may have to be buffered to maintain neutral pH. Of the coals studied to date, only Iowa subbituminous required neutralization. Ammonium hydroxide was used for this purpose, but in retrospect, it is believed that lime ($\text{Ca}(\text{OH})_2$) would be the best choice. Lime is the cheapest base available, and is probably also desirable as a sulfur scavenger. The sulfate is favored thermodynamically as the major combustion product of either Ca or S, depending on stoichiometry. (b) The nature of physical reactivity is due to the surface activity of coal particles. This property has been the subject of most of the past work (see Appendix A) with slurries of coal and oil. The use of lime-rosin soaps and oxidized oils have been two of the primary approaches taken to stabilize coal/oil slurries by coupling the coal to the oil through surface forces of both a physical and chemical nature. Properties (particularly viscosity) of coal/water slurries are also strongly dependent on surface forces. Dispersants, such as the lignin derivatives and other sodium salts of organic sulfonates, are widely

Table 1. Desirable Attributes of Carriers

1. Yield Point
2. Low Cost
3. Low Reactivity
 - a. Chemical
 - b. Physical
 - c. Biological
4. Low Temperature-Sensitivity
5. Pseudoplasticity

used to reduce viscosity of commercially important slurries (e.g., TiO_2 , CaCO_3 , and carbon black). Stable slurries are also prepared with use of dispersants, depending on the size and surface activity of the solids. Generally, stable dispersions of carbon blacks (which are angstrom-size particles), and paint pigments and solids (ca. 1-2 micron size) can be prepared through judicious use of dispersants. It was found here that dispersants reduce slurry viscosity of coal/water slurries by 1-2 orders of magnitude, but also cause rapid and extensive settling. This was probably due to the large particles (up to 300 micron in some slurries) used here. For the problem of stability, physical reactivity was manifest as adsorption of the stabilizing resins on the coal surface. The supernatant in settled slurries is a water-like liquid, rather than the viscous carrier, indicating it contains no resin. Adsorption seems more pronounced for some resins than others, and the amount of XS resin that must be provided to overcome this deficit is determined by trial-and-error. In addition, naturally-occurring resins such as the starches and guar gums exhibit the phenomenon of retrogradation. These solutions are unstable below critical concentrations, resulting in precipitation of the resin. Solutions of unmodified dent corn starch also gel above critical values of concentration. Adsorption is believed to cause sub-critical concentrations of the remainder of the resin in the carrier, resulting in unstable slurries. It is believed that this phenomenon has prevented successful use of unmodified dent corn starch solutions, which are the most cost-effective carriers. Much of the developmental work in this program for stabilizing slurries was spent in solving the problems associated with physical interaction between the coal and the carrier. A second problem of a physical nature is shear degradation. The selection of resins is necessarily limited to those whose solutions do not suffer a permanent viscosity loss when sheared by mixing or pumping. This is to permit processing and mass transfer operations without loss of properties. Most of the polysaccharides satisfy this requirement. (c) All of the modified and unmodified naturally occurring resins are biodegradable, and require a preservative for use. Formaldehyde, at a level of 1000 ppm has been found to be satisfactory. A biocide is also believed required for long-term stability of coal in water. Our data show that part of the coal is biodegradable. (4) Just as important, the solutions should be stable and maintain rheological integrity upon

cyclical exposure to high temperature (160°F) and to freezing temperatures, for protection of the slurry against settling in storage due to exposure to environmental extremes. (5) Pseudoplastics are fluids whose apparent viscosity decreases with shear rate. If the fluid is also a Bingham, the shear stress, τ , is usually defined as a power function of shear rate, $\dot{\gamma}$ (for $\tau > \tau_y$, the yield stress),

$$\tau = K\dot{\gamma}^n \quad (1)$$

where K, n are experimentally derived constants. τ is usually expressed in units of either dynes/cm² or psi; $\dot{\gamma}$ is usually expressed in units of sec⁻¹. For Newtonian fluids, n = 1, and for pseudoplastics, n < 1. By definition, viscosity, μ , is expressed as

$$\mu = \tau/\dot{\gamma} \quad (2)$$

$$= K\dot{\gamma}^{n-1} \quad (2a)$$

Viscosity is expressed in units of poise for $\tau/\dot{\gamma}$ = dynes/cm² sec. The shear rate has order-of-magnitude values of 1 - 10 sec⁻¹ for pouring (from a beaker) or draining in a tank; 10-10² sec⁻¹ for pipe flow and for typical pump suction-side conditions; 10² - 10³ sec⁻¹ for mixing, and 10³ - 10⁴ sec⁻¹ for atomization and centrifugal pumping. It is evident that pseudoplastic fluids having n as close to zero as possible are desirable to minimize viscosity at the various user conditions. Most of the carriers of interest are pseudoplastic to some extent, but most fluids approach Newtonian behavior at the higher shear rates. As a figure of merit, viscosities at 3000 sec⁻¹ have been used to characterize candidate slurries in this report.

2.3 Measurement of Rheological Properties

These measurements, with those of stability, comprised the bulk of the experimental work carried out in this program. The rheological properties of carriers were measured with a rotational viscometer, and those of slurries were measured with an extrusion tube rheometer. Details of the experimental and data reduction procedures are summarized below.

2.3.1 Procedure for Carrier Rheologicals

The tools available for use here were a Brookfield synchro-Lectric viscometer (both RV and LV models), and a Haake Rotovisco viscometer. Both

types are rotational viscometers, based on the use of a rotating spindle in a stationary cup. For cylindrical spindles, the shear stress at the spindle wall, τ_w , is

$$\tau_w = \frac{2T}{\pi D_s^2 L_s} \quad (3)$$

where T = torque

D_s = Spindle diameter

L_s = spindle length, corrected for end effects

Both Brookfield and Haake supply the user with values of full-scale torque, D_s , and L_s . The shear rate in rotational viscometers is a function of shear stress, that can be expressed as an infinite series.* A reduced expression of this function is

$$\dot{\gamma}_w = 4\pi \sum_{i=0}^{\infty} (N/n) TS^{-2i} \quad (4)$$

where $\dot{\gamma}_w$ = shear rate at the spindle wall

N = spindle rotational speed, rpm or rps

$n = \frac{d \log T}{d \log N}$

S = cup-to-spindle radius ratio

and i = dummy summation variable

Values of the ratio N/n are computed at T , TS^{-2} , TS^{-4} , etc. and summed,

$$\dot{\gamma}_w = 4\pi \left[\left(\frac{N}{n} \right)_T + \left(\frac{N}{n} \right)_{TS^{-2}} + \left(\frac{N}{n} \right)_{TS^{-4}} + \dots \right] \quad (5)$$

When $S \gg 1$, which corresponds to the use of a Brookfield in a large container, only the first term in the bracket of (5) is important (the other terms are zeros as $S \rightarrow \infty$ because $S^{-2,4,\text{etc.}} \rightarrow \text{zero}$), and (5) reduces to

$$\dot{\gamma}_w = \frac{4\pi N}{n} \quad (6)$$

A 400 cc beaker gives values of S adequately infinite for use of (6). If n is constant, the use of (6) is straightforward. Viscosity is the quotient of $\tau_w / \dot{\gamma}_w$. In the case of a Bingham fluid, n varies with N : $n \rightarrow 0$ as $N \rightarrow 0$. Thus, n must be computed at each N . Generally a loglog plot of T vs N is required to obtain the derivative.

*

1. Krieger, I.M. and H. Elrod, J. Appl. Phys., 24, 134 (1953)
2. Krieger, I.M., and S. H. Maron, J. Appl. Phys., 23, 147 (1952)
3. *ibid*, J. Appl. Phys., 25, (1954).

The main property of fluids under evaluation here is the yield point, i.e., the value of shear stress at $n = 0$. This condition is not always found on rheograms although it is frequently evident that n is decreasing with shear rate. However, extrapolating the curve to $n = 0$ is not good practice. The rheogram may even be linear (constant n) even though the fluid is an obvious Bingham, and extrapolation to $n = 0$ is not possible. Yield values of fluids reported here were taken from direct readings off a Brookfield by rotating the spindle at the lowest speed (0.5 rpm for the Model RVT), allowing the torque reading to equilibrate, and switching off the instrument. The torque will decrease to a constant, non-zero value if the fluid is a Bingham, and the resulting value can be converted to shear stress by (3), and is taken as the yield value. If the fluid is not a Bingham, the indicator returns to zero. Measurements of yield value (or zeros if the fluid is Newtonian or pseudoplastic) are repeatable and indicate an accuracy of $\sim \pm 5\%$.

The S -values of the Haake are on the order of unity, so that (6) cannot be used, and $\dot{\gamma}_w$ must be derived from (5). Here, a loglog plot of T vs N is required to compute the values of N/n at each value of TS^{-2i} . The equation is general for all values of n and S but is most accurate at high values of N (and T). At low values of T , only two or three terms of (5) may be used without extrapolation, which is not good practice, especially at low T when n is decreasing. Analytical solutions of (5) have been derived* for cases where $\ln S/n < 1$:

$$\dot{\gamma} = \frac{4\pi N}{1 - 1/S^2} \left\{ 1 + k_1 \left(\frac{1}{n} - 1 \right) + k_2 \left[\left(\frac{1}{n} - 1 \right)^2 + \frac{d \left(\frac{1}{n} - 1 \right)}{d \log T} \right] \right\} \quad (7a)$$

$$\text{where } k_1 = \frac{S^2 - 1}{2S^2} \left(1 + \frac{2}{3} \ln S \right) \quad (7b)$$

$$\text{and } k_2 = \frac{S^2 - 1}{6S^2} \ln S \quad (7c)$$

*Metzner, A.B., Advances in Chem. Eng., I, 77 (1956), Ed. by T.B. Drew and J.W. Hoopes, Jr., Acad. Press Inc., N.Y.

These equations are based on the first few terms of (5). Note that two graphs are required for the derivatives: one graph of $\log T$ vs $\log N$ for n , and a second of $\frac{1}{n} - 1$ vs $\log T$ for the last term in 7a.

The use of the Haake is considerably simplified for constant n . Here the torque can be expressed as a power function of N ,

$$T = T_1 N^n \quad (8)$$

where $T_1 = \text{a constant}$

Solving (8) for N and substituting, (4) becomes

$$\begin{aligned} \dot{\gamma}_n &= 4\pi \sum_{i=0}^{\infty} \left[\frac{1}{n} \left(\frac{T}{T_1} \right)^{1/n} \right]_{TS^{-2i}} \quad (9) \\ &= 4\pi \left[\frac{1}{n} \left(\frac{T}{T_1} \right)^{1/n} + \frac{1}{n} \left(\frac{TS^{-2}}{T_1} \right)^{1/n} + \frac{1}{n} \left(\frac{TS^{-4}}{T_1} \right) + \dots \right] \\ &= \frac{4\pi N}{n} \sum_{i=0}^{\infty} S^{-2i/n} \end{aligned}$$

The sum can be expressed analytically,

$$\sum_{i=0}^{\infty} S^{-2i/n} = \frac{1}{1 - S^{-2/n}}, \quad (10)$$

so that

$$\dot{\gamma}_w = \frac{4\pi N}{n} \left(\frac{1}{1 - S^{-2/n}} \right) \quad (11)$$

when $n = 1$ (Newtonian fluid), (11) reduces to the correction factor supplied in the Haake user's manual.

Because the interest here is finding the yield point and evaluating viscosity near the yield point, where n is not constant and $n \rightarrow 0$, the carriers were evaluated by means of a Brookfield with cylindrical spindles, and a sample size of at least 400 cc.

2.3.2 Procedure for Slurry Rheologicals

Rotational viscometers generally are unsuited for slurries because of cavitation and/or frictional heating at high spindle speeds. Communication with the sponsor indicated that apparent shear rates on the order of 3000 sec^{-1} can be expected at atomizer conditions. An extrusion rheometer is required for flow rates of this magnitude.

The viscosities of several of the most interesting slurries developed here were determined by means of an extrusion rheometer. A description of the experimental procedure is given below.

The equipment was built for evaluation of slurry fuels. It is built of stainless steel and comprised of a cylindrical feed chamber 1.25" Dia. x 6" L, that can be fitted with any of several tubes of various L/D. The objective of the measurements is to determine mass flow rate as a function of feed pressure and tube L/D. A schematic of the equipment is shown in Figure 2. The rheometer is made ready by charging the chamber with the slurry and filling the tube at low pressure, and setting the desired run pressure on the regulator. A switch-actuated relay starts the clock and closes the three-way solenoid valve, pressurizing the chamber to the regulated value. When the switch is off, the clock stops and the solenoid is opened simultaneously, venting the chamber and stopping flow through the tube. Measured data are mass of extrudate, time, and pressure. Accuracy is $\sim 0.01 \text{ gm}$, $\sim 1 \text{ ms}$, and $\sim 0.5 \text{ psi}$ respectively, out of typical values of 10-100 gm, 0.5 to 10 sec, and 10-100 psi respectively. For these tests, tube dimensions were 6.732" L x 0.251" Dia. and 12.745" L x 0.250" Dia., permitting measurements at shear rates up to $\sim 10^4 \text{ sec}^{-1}$. Higher shear rates can be obtained by operating at higher pressures or with smaller tube diameters. The entrance section into the tubes is a sudden contraction from a chamber diameter of 1.250".

From these data, viscosity, μ , is expressed as

$$\mu = \frac{(D\Delta P/4L)}{\frac{3n+1}{4n} \frac{8V}{D}} \quad (12)$$

Figure 2. Extrusion Rheometer Schematic.

where D = tube diameter

ΔP = pressure drop through the tube

L = tube length

V = fluid velocity in the tube

$$n = \frac{d \log (D P / 4L)}{d \log (8V/D)}$$

The numerator of (12) is shear stress at the tube wall, while the denominator is shear rate. The apparent shear rate is expressed as $(8V/D)$. For Newtonian fluids, $n = 1$; the apparent shear rate is the true shear rate. For ease of use, shear stress and shear rate are expressed in engineering units, psi and sec^{-1} respectively. Viscosity is expressed in cp.

For data reduction, the practice was to run the extrusions at several values of pressure (5-10 runs) for each tube L/D . Regression analyses were then carried out on the loglog plots of $D\Delta P_T/4L$ vs $8V/D$ for both tubes, where ΔP_T is the total pressure drop. A test for significance at the 5% level was run with Students t -statistics on the two curves, assuming infinite population. If no significant difference was found, the data were lumped, and the total measured pressure drop was assumed to occur in the tubes. If the difference was found to be significant, then the pressure drop at the entrance (ΔP_E) was computed by extrapolating curves of ΔP_T vs L/D to $L/D = 0$ at constant shear rate. Because the extrapolation is mathematically simple, it can be expressed, for these tubes, as

$$\Delta P_E = 2.11 \Delta P_S - 1.11 \Delta P_L \quad (13)$$

where ΔP_S = total pressure drop in the short tube

and ΔP_L = total pressure drop in the long tube

Both ΔP_S and ΔP_L are computed from the regression curves. Values of ΔP used in (12) are then

$$\begin{aligned} \Delta P &= \Delta P_S - \Delta P_E \\ &= \Delta P_L - \Delta P_E \end{aligned} \quad (14)$$

Data reduction for these slurries was found to be a difficult and sometimes gamey task. A fairly large amount of slurry (500 gm) was made up for the tests, each extrusion run requiring ~50 gm. The 500 gm batch was well-mixed prior to the start of the tests. However, replicate runs indicated variations in mass flow rate of $\sim \pm 10\%$, in spite of the precision in the measurements. This phenomenon is attributed to thixotropy, the time-dependency of shear rate. It is nice if the rheological time constant is either much less than or greater than the characteristic time of an extrusion run. Such was not believed to be the case here, and the result is data scatter. This behavior was particularly evident for slurries containing starch solutions as carriers, and for long tube data. In general, short tube data was well-behaved and repeatable. Primarily because of data scatter in the long tube runs, the differences in shear stress ($\Delta P/4L$) at a given shear rate were generally computed to be not significant. This result would not be unexpected, even with well-behaved long tube data, if the slurry behaves as a fluid. From engineering texts, where entrance loss is generally expressed as $\sim \rho V^2/2 g_c$, values of ΔP_E of only 1.5 - 2 psi are computed for the sudden contraction from 1.25 in. to 0.25 in. diameter, at a shear rate of 3000 sec^{-1} . The total pressure drop at this shear rate is generally on the order of 60 - 80 psi, so a small entrance effect would be expected, requiring precise measurements, and, needless to say, the absence of interfering side effects, such as thixotropy. When tests for significance failed, it was the practice to give most weight to short tube data in constructing rheograms. Viscosities and values of shear stress derived this way may be too high, by as much as 10-15%. Inter-comparisons of a family of slurries are unaffected.

2.4 Measurement of Stability

2.4.1 General

Slurry stability can be detected qualitatively, by eyeball. If it is unstable, any slurry that is fluid enough to pour, and many which are not, will exhibit a supernatant liquid on its surface after a fairly short length of time in storage. This supernatant is clearly evident for both coal/water and coal/oil (and coal/oil/water) slurries which are unstable. A probe of the slurry with a small spatula indicates hard packing or at least a great thickening of the slurry with probe depth. These are

qualitative tests which give good reliable data, and are valid for yes/no decisions. For slurries which are not designed to be stable, no other stability tests are needed.

Slurries which are designed to be stable, and/or slurries which exhibit very low settling rates are difficult to evaluate for stability by such techniques. The appearance of a supernatant may be only condensate as a result of surface evaporation. Hard pack settling may not occur. Variations in viscosity with depth may be measured by probing the slurry with a T-bar spindle, if the drag effects on the shaft are accounted for. However these variations may or may not be attributable to settling. Thixotropy and carrier/particle interactions significantly effect viscosity. Also probing is considered by some workers to be a form of destructive testing, though in the opinion here, it is not very.

For the work here, it was decided to evaluate slurry stability by measuring the location of center of gravity (CG) by means of a compound pendulum. This technique is not novel - it dates to the 1930's - and has several advantages. It is simple, inexpensive, and non-destructive. When used correctly with good tools, it offers very good precision and sensitivity. Like the visual and probe tests, the pendulum gives a yes/no result. If the CG shifts, the slurry is unstable; if CG is unchanged, the slurry is stable.

The compound pendulum method was developed at Kansas State College,* to determine slurry stability by monitoring the change in center of gravity (CG). This device was developed by workers at KSC for evaluation of coal slurry fuels. The period of oscillation of a compound pendulum comprised of a test tube filled with slurry is measured at two values of pendulum length and used to compute center of gravity. A cross-sectional schematic of the set-up is given in Figure 3.

The period of oscillation (the time required to traverse the arc of travel, and return) of a compound pendulum is

$$T^2 = 4\pi^2 I / MgH \quad (15)$$

*McMillen, J.H., L.F. Stutzman, J.E. Hedrick, I&EC Anal. Ed., 13, 477 (1941).

Figure 3. Schematic of Pendulum

where T = period of oscillation, sec
 I = moment of inertia of the pendulum about its axis of support,
 gm cm^2
 M = pendulum mass, gm
 g = acceleration of gravity, cm/sec^2
 H = distance from the axis of support to the center of gravity
of the pendulum

The moment of inertia, I , at H is related to that at the CG, I_o , by

$$I = I_o + MH^2 \quad (16)$$

Referring to the Figure 3, the period, T_2 , about the lower support axis is

$$T_2^2 = \frac{4\pi^2(I_o + MH^2)}{MgH} \quad (17)$$

and about the upper support axis, located a distance h above the lower one, is

$$T_1^2 = \frac{4\pi^2[I_o + M(H+h)^2]}{Mg(H+h)} \quad (18)$$

Subtracting these two equations and solving for H gives

$$H = \frac{T_1^2 h - 4\pi^2 h^2 / g}{(T_2^2 - T_1^2) + 8h\pi^2 / g} \quad (19)$$

Note that H is the CG of the compound pendulum comprised of carriage, tube, and slurry.

The CG of the slurry, X_s , is related to H by the conservation of momentum,

$$M_c X_c + M_s X_s = M(H+y) \quad (20)$$

where

M_c = mass of carriage, including tube.

X_c = distance between slurry surface at the top of
the tube and the CG of the carriage, including tube.

M_s = mass of slurry

X_s = distance between slurry surface at the top of
the tube and the CG of the slurry.

M = total mass of the pendulum

$$= M_c + M_s$$

H = distance between lower support and the CG of the total mass

y = distance between slurry surface at the top of the tube and the lower support.

Thus,

$$X_s = \frac{M_c + M_s}{M_s} (H+y) - \frac{M_c X_c}{M_s} \quad (21)$$

2.4.2 Experimental Procedure

The swing stand was built of steel bar stock and the base from steel plate. A removable harness was machined from aluminum and the supports from case-hardened nails. Both sets of supports were housed permanently in the harness. Glass sample slides were used for the support bearing surfaces. Tall-form 100 cc Nessler tubes were used to house slurry. The harness was held in place with set screws. In storage, the filled tubes are capped with rubber stoppers until ready to use. The harness and supports assembly weighs 63.30 gm; typical tube and fill weights are 80 gm and 135-150 gm respectively.

The experimental procedure was to cast the slurries into the tubes and fasten the harness to the tubes at a point where the initial values of period at the lower supports were at least 2 sec. Measured data included tube weight, fill weight, periods at both supports, and depth of fill (i.e., the column height of the slurry). Periods were measured with a stop watch in a quiet, draft-free room. The time for 10 oscillations was measured, recorded, and divided by 10 to get the period. Three measurements at each support were made for each test, and averaged. Measurements indicate an accuracy of ± 0.1 sec for 10 oscillations, or about $\pm 1\%$ for the upper supports and $\pm 0.5\%$ for the lower supports. For a typical case, this translates to a precision of $\pm 4\%$ in H and $\pm 0.5\%$ in X_s . Experiments have shown an accuracy of $\pm 1\%$ in the CG of the slurry (X_s). Unstable slurries exhibit a CG shift of a few percent: the least stable slurry found in the tests was 65% Pittsburgh seam bituminous (PHS-361) in an aqueous solution of a dispersant, for which extensive settling was observed visually, and for which the Δ CG after 24 hours was measured to be 3.3%.

The period of the pendulum around the upper supports (i.e., with a long stand-off from CG) is insensitive to a CG shift. For 10 oscillations, the total swing time of typically ~ 10 sec. was never observed to vary by more than 0.1 or 0.2 second. When the lower supports are placed (initially) a fraction of an inch above the CG, so that the period is at least 2 sec. per oscillation, the period is very sensitive to a CG shift. For 10 oscillations, and a total initial swing time of >20 seconds, the total time decreases measurably (up to ~ 3 sec) for unstable slurries. As a calibration test, one of the tubes was filled with water and a steel ball having the same diameter as the ID of the tube was suspended in the column of water at various depths by means of a thread. The periods were measured and CG's computed by centroids. A plot of the results as $-\Delta T_2 / \Delta X_s$ vs T_2 is given in Figure 4. The importance of initializing the experiments at high values of T_2 is evident. The bearing surfaces, where the supports pivot, must be as frictionless as possible for accurate data. In the set-up here, no significant change in amplitude was observed over 10 oscillations.

2.5 Theoretical Performance Criteria

2.5.1 Theoretical Values of Flame Temperature and Available Heating Value (AHV)

In the interest of evaluating and comparing fuels, calculations of theoretical flame temperature and combustion product composition were carried out for coal, coal/water slurries, and No. 6 oil, using a computer program on IBM 370 equipment. The calculations were based on adiabatic combustion at one atmosphere, with thermochemical equilibrium. All thermochemical data were from the JANNAF tables. In addition to calculations for adiabatic combustion, the equilibrium values of combustion product composition and enthalpy were computed at 500°F (and one atmosphere pressure) which is assumed to be a nominal stack gas temperature. The difference between the enthalpies of the combustion products at 500°F and the flame temperature is the actual amount of energy extracted from the fuel, and is defined here as the available heating value (AHV). For these calculations, two types of coal were considered: (1) the Pittsburgh seam bituminous (PHS 361), and (2) the Iowa subbituminous (PSOC 664). Analyses of

these coals and the oil (Texaco No. 6) are given in Appendix B. Values of HHV were converted from internal energy of combustion to heat of formation for use in the computer input. The as-received coals were used as the fuels. The ash composition in the coals is not known, so for these calculations the ash was assumed to be comprised of 50% (by weight) SiO_2 + 30% Al_2O_3 + 20% CaO . These are the input values used as constituents of the coal. At the flame temperature, all of the Al_2O_3 is converted to Al_2SiO_5 and the remaining SiO_2 and the CaO appears in the combustion products unchanged. At 500°F, Al_2O_3 again appears as Al_2SiO_5 , while the CaO is converted to CaSO_4 . Values of T_f and AHV were computed for the as-received coal (which includes moisture) and for 75, 70, 65, and 60% by weight slurries of this coal in water, at 0 to 100% XS air. The oil was also evaluated at 0 to 100% XS air. An ultimate analysis was not available for oil, so this fuel was assumed to be CH_2 , in addition to the sulfur. Results of the calculations are given in Table 2 and 3.

The calculations show that T_f decreases with (1) increasing oxidation ratio (XS air), as expected, and with (2) increasing water content, though not by much. This is because proportionately less air is required to burn the slurries than the coal. Most of the heat of combustion is consumed in heating nitrogen to the flame temperature. Most of the energy required to vaporize and heat water is thus offset by the lower air requirement. The flame temperatures of the slurries of interest are about the same as that of oil. The AHV also decreases with XS air, because the total heat capacity of the combustion products decrease with temperature. On the basis of BTU/lb coal, the AHV of the slurries is slightly lower than that of the coal. Referring to Table 2 for example, the AHV of the 70% slurry is 11307 BTU/lb coal. This is 4.5% less than that for the as-received coal (11840). This result was expected. The AHV of the slurries is, of course, proportionately lower than the coal on the basis of BTU/lb fuel. The ratio of AHV/HHV is 0.88 for the coal and 0.83 for the oil. This is because of the higher hydrogen content of the oil, which forms $\text{H}_2\text{O}(\text{g})$.

Table 2. Theoretical Values of Flame Temperature and "Available Enthalpy Values" of Bituminous Coal (PHS 361) Slurries of the Coal and Water, and No. 6 Oil.

Fuel Composition, Wt. %			XS Air, Wt. %	Air/Fuel Mass Ratio	Flame Temp., °F	O ₂ Conc. in Stack Prods., Vol. %	Available Enthalpy*		
Coal	Water	No. 6 Oil					BTU/lb Coal	BTU/lb Fuel	BTU/Ft ³ S.G.
100	-	-	0	10.13	3652	0	11840	11840	46.0
			20	12.26	3330	3.52	11621	11621	37.6
			40	14.15	3013	5.78	11428	11428	32.2
			60	16.21	2717	7.65	11215	11215	27.7
			80	18.23	2479	9.11	11007	11007	24.2
			100	20.26	2279	10.30	10798	10798	21.5
75	25	-	0	7.598	3468	0	11425	8569	42.3
			20	9.195	3141	3.37	11207	8405	34.8
			40	10.61	2838	5.61	11009	8257	29.9
			60	12.16	2572	7.41	10800	8100	25.8
			80	13.67	2352	8.85	10593	7945	22.7
			100	15.20	2168	10.00	10384	7788	20.1
70	30	-	0	7.091	3415	0	11307	7915	41.3
			20	8.582	3089	3.34	11088	7761	34.1
			40	9.905	2792	5.55	10891	7624	29.3
			60	11.35	2532	7.35	10682	7578	25.4
			80	12.76	2318	8.78	10474	7332	22.3
			100	14.18	2141	9.93	10266	7186	19.8
65	35	-	0	6.584	3355	0	11170	7261	40.2
			20	7.969	3028	3.29	10952	7119	33.2
			40	9.198	2739	5.49	10755	6991	28.6
			60	10.54	2486	7.27	10546	6855	24.8
			80	11.85	2278	8.69	10338	6720	21.8
			100	13.17	2108	9.85	10129	6584	17.3
60	40	-	0	6.078	3297	0	11011	6607	38.9
			20	7.356	2959	3.24	10793	6475	32.2
			40	8.490	2679	5.42	10596	6357	27.8
			60	9.726	2435	7.19	10386	6232	24.1
			80	10.94	2233	8.61	10179	6107	21.2
			100	12.16	2071	9.76	9970	5982	18.8
-	-	100	0	14.64	3436	0	-	15337	40.4
			20	17.57	3095	2.32	-	15035	33.3
			40	20.50	2764	5.73	-	14734	28.2
			60	23.42	2496	7.56	-	14433	24.3
			80	26.35	2275	8.99	-	14131	21.3
			100	29.28	2092	10.20	-	13830	18.8

* Heat content of the combustion products above 500°F.
BTU/Ft³ S.G. denotes heat content per ft³ of 500°F stack gas.

Table 3. Theoretical Values of Flame Temperature and Available Enthalpy of Subbituminous Coal (PSOC 664), Slurries of the Coal in Water, and No. 6 oil.

Fuel Composition, Wt %			XS Air, Wt %	Air/Fuel Mass Ratio	Flame Temp. °F	O ₂ Conc. in Stack Gases, Vol %	Available Enthalpy		
Coal (PSOC-664)	Water	No. 6 Oil (Texaco)					BTU lb. Coal	BTU lb. Fuel	BTU Ft ³ S.G.*
100	-	-	0	8.01	3528	0	9079	9079	43.84
			10	8.82	3391	1.46	9108	9108	40.34
			20	9.62	3220	3.0	9026	9026	36.80
			30	10.42	3047	4.34	8943	8943	33.78
			40	11.22	2888	5.47	8861	8861	31.18
			50	12.02	2743	6.46	8778	8778	28.91
			60	12.82	2612	7.35	8696	8696	26.91
75	25	-	0	6.01	3297	0	8664	6498	39.38
			10	6.62	3152	1.38	8694	6520	36.41
			20	7.22	2983	2.85	8611	6458	33.34
			30	7.82	2825	4.14	8529	6397	30.71
			40	8.42	2682	5.23	8446	6334	28.42
			50	9.02	2553	6.20	8364	6273	26.42
			60	9.62	2436	7.07	8281	6211	24.64
70	30	-	0	5.61	3229	0	8546	5982	38.20
			10	6.17	3084	1.36	8575	6000	35.36
			20	6.74	2918	2.81	8493	5945	32.42
			30	7.29	2765	4.08	8410	5887	29.89
			40	7.85	2626	5.17	8328	5830	27.68
			50	8.41	2501	6.12	8245	5772	25.74
			60	8.97	2388	6.99	8163	5714	24.02

Table 3. (Continued)

Fuel Composition, Wt %			XS Air, Wt %	Air/Fuel Mass Ratio	Flame Temp. °F	O ₂ Conc. in Stack Gases, Vol %	Available Enthalpy		
Coal (PSOC-664)	Water	No. 6 Oil (Texaco)					BTU lb. Coal	BTU lb. Fuel	BTU Ft ³ S.G.*
65	35	-	0	5.21	3153	0	8409	5466	36.88
			10	5.73	3006	1.33	8439	5485	34.20
			20	6.25	2844	2.76	8356	5431	31.39
			30	6.77	2697	4.02	8274	5378	28.96
			40	7.29	2563	5.10	8191	5324	26.84
			50	7.81	2443	6.04	8109	5271	24.98
			60	8.33	2334	6.90	8026	5217	23.33
60	40	-	0	4.81	3064	0	8250	4950	35.41
			10	5.29	2917	1.30	8279	4967	32.89
			20	5.77	2761	2.71	8197	4918	30.22
			30	6.25	2620	3.95	8114	4668	27.92
			40	6.73	2493	5.02	8032	4819	25.90
			50	7.21	2377	5.95	7950	4770	24.12
			60	7.69	2291	6.80	7867	4720	22.54
-	-	100	0	14.64	3436	0	-	15337	40.4
			10				-		
			20	17.57	3095	3.32	-	15035	33.3
			30				-		
			40	20.50	2764	5.73	-	14734	28.2
			50				-		
			60	23.42	2496	7.56	-	14433	24.3

* S.G. denotes stack gas at 500°F.

There are two figures of merit that can be derived from these calculations for use in comparing fuels and estimating the effect caused by use of slurry fuel in place of either coal or oil in a given fuel-burning facility. The first is based on constant firing rate, the second is based on constant volumetric flow rate of stack gas.

For the assumption of constant firing rate, the units of AHV are BTU/lb fuel. The mass of slurry fuel required to replace a unit mass of oil is then simply the quotient $AHV(\text{oil})/AHV(\text{slurry})$, and has the units lb slurry/lb oil. Referring again to Table 2 the AHV of oil at 20% XS air is 15035 BTU/lb oil, and that for 70% coal/water slurry is 7761 BTU/lb slurry at 20% XS air. So, $15035/7761 = 1.94$ lb 70% slurry is required to replace the lb. oil. When the substitution of slurry for oil is made, there is an attendant change in the total mass and/or volumetric flow rate of the combustion products through the heat transfer units of the facility. The assumption of constant firing rate is predicated on the capability of the boiler to accommodate these changes in flow rate.

For the second figure of merit, based on constant volumetric flow rate of stack gas, the units of AHV are BTU/ft^3 S.G. (stack gas). Here, it is assumed that the boiler unit cannot accommodate changes in the flow rate of the combustion products. The mass of slurry required to replace a unit mass of oil is computed from the relative unit stack gas volumes, ft^3 S.G./lb slurry or oil. The resulting firing rate is then computed. From Table 2, the AHV values of oil at 20% XS air are 15035 BTU/lb and $33.3 \text{ BTU}/\text{ft}^3$ stack gas. The volume of stack gas generated by a unit mass of oil is thus $15035/33.3 = 451.5 \text{ ft}^3$ S.G./lb oil. Similarly, the volume of stack gas generated by a slurry of 70% bituminous coal in water is $7761/34.1 = 227.6 \text{ ft}^3$ S.G./lb slurry. In order to maintain constant volumetric flow rate of stack gas, a lb of oil must be replaced by $451.5/227.6 = 1.98$ lb 70% slurry/lb oil. The available enthalpy from this much slurry is $1.98 \times 7761 = 15367 \text{ BTU}/\text{lb}$ of oil replaced. The rating of the burner is thus increased by 2.2%. There is also a unique slurry composition that will deliver both the same volumetric flow rate of stack gas and firing rate, depending primarily on the energy of the coal used in the slurry and the air/fuel ratio.

These two figures of merit were used to compare the performance of coal/water and coal/oil slurries with oil. The calculations were based on the use of either PSOC-664 subbituminous or PHS 361 bituminous coal in the slurries, and 20% XS air. Results of the calculations are given in Tables 4 and 5.

The results for the coal/oil slurries are interesting, in light of the assumptions used. For example, consider the first slurry entry in Table 4, the composition of 30% bituminous and 70% oil. On the basis of constant firing rate, the slurry flow rate required to replace the oil is $15035/14011 = 1.07$ lb slurry/lb oil. The amount of oil in this much slurry is $1.07 \times 0.7 = 0.75$ lb oil/lb oil replaced. Thus even though 30% of the oil has been replaced with coal, the amount of oil saved is only 25% because of the higher slurry feed rate. The amount of energy per unit weight of oil is, of course, higher in the slurries: $15035/.75 = 20047$ BTU/lb oil. In the case of constant volumetric flow rate, the results are similar. Referring again to the 30% bituminous + 70% oil slurry, 1 lb of oil is replaced with 1.1 lb of slurry to maintain constant volumetric flow rate of combustion products. The 1.1 lb of slurry contains 0.77 lb of oil. The firing rate however was increased 2.9% by use of the slurry. The amount of energy gained from the oil is therefore $15035 \times 1.029/0.77 = 20,092$ BTU/lb of oil used in the slurry vs 15035/lb oil originally. Either of the assumptions used here do not seem unreasonable as a basis of substitution, so it seems that the use of oil in the slurry is a significant improvement over firing with oil alone, from the standpoint of oil conservation. A similar conclusion is drawn for the slurries made with the subbituminous coal.

Considering next the coal/water slurries, it is seen from Table 4 that the 65-75% slurries are equal to or superior to oil when substituted for oil on the basis of constant volumetric flow rate of combustion products. The 65 and 70% slurries were given greatest emphasis in the experimental program. These slurries are believed to be the most cost-effective slurry fuels. Coal/water slurries made with the Iowa subbituminous coal are significantly inferior to those made with the bituminous, due to its lower heating value and higher water content (and sulfur content).

Table 4.
Comparison of Slurry Fuels with Oil for Slurries Comprised of
PHS-361 Bruceton Bituminous Coal and Either Oil or Water

Fuel Composition, Wt %			A				B					
			Basis: Constant Firing Rate @ 20% XS Air			Relative Fuel Flow			Basis: Constant Volumetric Flow Rate of Stack Gas, Ft ³ /hr. @ 20% XS Air			Relative Fuel Flow
Coal (PHS-361)	Water	No. 6 Oil (Texaco)	AHV (Fuel) BTU/lb Fuel	Rate, lb/lb Oil Total	Coal	Oil	Ft ³ S.G./ Lb Fuel	BTU/ Ft ³ S.G.	Rate, lb/lb Oil Total	Coal	Oil	% Change In Rating
-	-	100	15035	1	0	1	451.5	33.3	1	0	1	0
30	-	70	14011	1.07	0.32	0.75	408.8	34.3	1.10	0.33	0.77	+2.9
40	-	60	13669	1.10	0.44	0.66	394.5	34.6	1.14	0.46	0.69	+4.0
50	-	50	13328	1.13	0.56	0.56	380.3	35.0	1.19	0.60	0.59	+5.2
60	-	40	12987	1.16	0.70	0.46	366.0	35.5	1.23	0.74	0.49	+6.5
70	-	30	12645	1.19	0.83	0.36	351.8	35.9	1.28	0.90	0.38	+7.9
80	-	20	12304	1.22	0.98	0.24	337.6	36.4	1.34	1.07	0.27	+9.5
100	-	-	11621	1.29	1.29	-	309.1	37.6	1.46	1.46	-	+12.9
75	25	-	8405	1.79	1.34	-	241.5	34.8	1.87	1.40	-	+4.5
70	30	-	7761	1.94	1.36	-	227.6	34.1	1.98	1.39	-	+2.2
65	35	-	7119	2.11	1.37	-	214.4	33.2	2.11	1.37	-	0
60	40	-	6475	2.32	1.39	-	201.1	32.2	2.24	1.35	-	-3.3

Table 5.

Comparison of Slurry Fuels with Oil for Slurries Comprised of
PSOC-664 Iowa Subbituminous Coal and Either Oil or Water

Fuel Composition, Wt %			A				B						
			Basis: Constant Firing Rate @ 20% XS Air			Basis: Constant Volumetric Flow Rate of Stack Gas, Ft ³ /hr. @ 20% XS Air							
Coal (PSOC-664)	Water	No. 6 Oil (Texaco)	AHV (Fuel) BTU/lb Fuel	Relative Fuel Flow Rate, lb/lb Oil			Ft ³ S.G./ Lb Fuel	BTU/ Ft ³ S.G.	Relative Fuel Flow Rate, lb/lb Oil			% Change In Rating	
				Total	Coal	Oil			Total	Coal	Oil		
-	-	100	15035	1	0	1	451.5	33.3	1	0	1	0	
30	-	70	13232	1.14	0.34	0.80	389.6	34.0	1.16	0.35	0.81	+2.0	
40	-	60	12631	1.19	0.48	0.71	369.0	34.2	1.22	0.49	0.73	+2.8	
50	-	50	12030	1.25	0.62	0.62	348.4	34.5	1.30	0.65	0.65	+3.7	
60	-	40	11430	1.32	0.79	0.53	327.8	34.9	1.38	0.83	0.55	+4.7	
70	-	30	10829	1.39	0.97	0.42	307.2	35.3	1.47	1.03	0.44	+5.9	
80	-	20	10228	1.47	1.18	0.29	286.5	35.7	1.58	1.26	0.32	+7.2	
100	-	-	9026	1.67	1.67	-	245.3	36.8	1.84	1.84	-	+10.5	
75	25	-	6458	2.33	1.75	-	193.7	33.3	2.33	1.75	-	0	
70	30	-	5945	2.53	1.77	-	183.4	32.4	2.46	1.72	-	-2.6	
65	35	-	5431	2.77	1.80	-	173.0	31.4	2.61	1.70	-	-5.7	
60	40	-	4918	3.06	1.83	-	162.7	30.2	2.78	1.66	-	-9.2	

2.5.2 Comparison of AHV and HHV

The price of energy is the parameter generally used to evaluate fuels, and is generally expressed as dollars per million BTU (MBTU), as calculated by dividing the unit price of the fuel by its higher heating value (HHV). On this basis, the price of energy is \$1.11/MBTU based on bituminous coal rated at 13460 BTU/lb and costing \$30/ton; for oil rated at 144,570 BTU/gal and costing \$15/bbl, it is \$2.47/MBTU. Of course, all of the energy is not extracted from HHV because stack gas temperatures are higher than the boiling point of water. Thus, these prices are only useful for comparisons. The effect of loss of heat of vaporization as well as the effect of air-to-fuel ratio on heat content function is accounted for in the calculation of AHV. On this basis, the prices of energy are \$1.29/MBTU and \$3.02/MBTU respectively for \$30/ton bituminous having AHV = 11621 BTU/lb at 20% XS air and \$15/bbl oil having AHV = 15035 BTU/lb at 20% XS air. These values are seen to be much higher than those based on HHV, and are probably closer to the truth, considering the rigor of the AHV calculation. If stack gas temperatures $< 500^{\circ}\text{F}$ are of interest, the correction to AHV is $\sim 6.5 \text{ BTU}/^{\circ}\text{F}$, as long as the stack gas temperature is $> 212^{\circ}\text{F}$. Thus, for a stack gas temperature of 212°F , increase AHV by 6.5 $(500 - 212) = 1872 \text{ BTU/lb}$ fuel, resulting in 16907 BTU/lb for the AHV of oil, at 20% XS air. Most of the difference between this value and the HHV of oil (18402 BTU/lb) is due to the heat of vaporization of water ($\sim 1300 \text{ BTU/lb}$ oil). The remainder is due to the lowered total heat content function caused by running the calculation at 20% XS air.

The price differences between oil and coal are greater using AHV $(\$3.02 - \$1.29 = \$1.73/\text{MBTU})$ than with HHV $(\$1.36/\text{MBTU})$. This is because oil contains a lot more hydrogen than coal, and the loss due to the unreclaimed heat of vaporization of the resulting water is correspondingly greater. Thus, the price difference based on AHV is 27% greater than that based on HHV. The discrepancy is much less if comparison is made on the basis of relative price, i.e., $(\text{price of fuel, } \$/\text{MBTU})/(\text{price of oil, } \$/\text{MBTU})$. On the basis of HHV, the relative price is 0.449: on the basis of AHV, it is 0.427. The effects of heat of vaporization and XS air that are

accounted for by AHV appear in both the numerator and denominator of the relative price of energy, and the percentage correction to both is about the same. Thus, the errors involved in use of HHV in this expression are compensated for. A similar computation for coal/water slurries indicates comparable agreement. The AHV of a 65% coal/water slurry is 7120 BTU/lb at 20% XS air; its HHV is $.65 \times 13460 = 8749$ BTU/lb fuel (the HHV of water is zero, by definition). Thus the prices of energy of the slurry are \$1.37/MMBTU (AHV) and \$1.11/MBTU (HHV) and the relative price is 0.454 and 0.449 respectively. This is pretty good agreement, amounting to ~ 1 pph, and is due again to the compensating errors of omission in the numerator (no correction for vaporization of the water in the slurry) and the denominator (no correction for vaporization of the water generated by oil combustion). Note again that no vaporization correction for the water content of the slurry is made in computing the HHV of a coal/water slurry.

In the above discussion, only the ingredient costs of the slurries were considered. In practice, the slurry costs are considerably greater because of the cost of manufacturing and the cost of converting an oil burner to burn slurry. Still, the ingredient costs are much higher than the manufacturing and converting costs, and the utility of relative price of energy was found to remain valid. These results are summarized in Section 4 of this report for a number of slurry fuels.

A systematic experimental program was carried out to determine the effect of composition variables on slurry properties. Composition variables were (1) type of coal and coal particle size distribution, and (2) type of carrier and carrier rheology. Slurry properties of interest were rheology, stability, and ingredient cost.

Described here are (1) the results of pulverizing coal with a hammermill pulverizer; (2) the rheological properties of carriers; (3) the rheological properties of slurries; and (4) the measurements of stability.

3.1 Effect of Mill Conditions on Particle Size Distribution

The use of a hammermill ("Bantam" Mikropulverizer) to pulverize coal was evaluated for five different coals. The type and source of the coals is given in Table 6. Analyses of the coals were carried out at Commercial Testing and Engineering Company, Bruceton, and at Penn State University. Results of these are given in Appendix B.

The effect of hammer speed and grate size on particle size distribution was determined for each of the coals. Hammer speed was varied from 1000 to 13,800 rpm, which is the maximum tip speed. Herringbone (HB) grates were used for most work; the range of grate sizes (i.e., slot size) varied from 10 mils (the smallest available size) to 62 mils. Round hole (RD) grates were evaluated to a limited extent. The feed size for all work was -1/2 inch, obtained with a laboratory crusher. Pulverized coal was sieved to determine particle size distribution, using the $\sqrt{2}$ method. The mass mean diameter (MMD) was determined graphically from a plot of log (size) vs cumulative weight percent over size. Results are summarized in Table 7 and graphically in Appendix C.

Particle size increases, generally, with increasing grate size and decreasing hammer speed. It was desired to obtain coarse/fines size ratios as high as possible, up to about 10/1. At the same time, it is not desirable to use particle sizes $> \sim 300\mu$ (50 mesh) because of the anticipated impact on coal combustion (the larger particles take too long to burn to completion, particularly at residence times expected in a heavy oil burner), and on slurry stability (larger particles require greater yield

Table 6. Rank and Source of Coal.

ID	Rank	Source
1. Clean coal from Bruceton Experimental Mine	1. Bituminous	1. Bruceton
2. PHS 361	2. Pittsburgh Seam Bituminous	2. Bruceton
3. PSOC 664	3. Iowa Subbituminous	3,4,5. Penn State University, College of Earth and Mineral Sciences, Coal Research Section
4. PSOC 846	4. Wyoming Subbituminous	
5. PSOC 837	5. Montana Lignite	

Table 7.
Data Summary for Effect of Mill Conditions in Particle Size of Various Coals.

Coal ID	Type of Coal	Hammer Speed, rpm	Grate Data		Sieved Through 50 Mesh	MMD, μ	Size Consist. Wt. %		Coarse/Fines MMD Size Ratio
			Size, mls	Type			+50 Mesh	-200 Mesh	
Clean coal from Bruceton Experimental Mine	Bituminous	13,800	10	HB	no	26	0	94	1.0 (by definition)
		13,800*	27	HB	no	37	0	80	1.4
		3,600	27	HB	no	68	0	54	2.6
		3,600	27	HB	no	140	14.5	31	5.4
		3,600	27	HB	yes	113	0	35	4.4
		2,000	27	HB	no	195	35	31	7.5
		2,000	27	HB	yes	80	0	48	3.1
		1,000	27	HB	no	300	50	24	11.5
		1,000	27	HB	yes	75	0	50	2.9
		3,600	62	HB	no	225	38	18	8.6
		3,600	62	HB	yes	140	0	26	5.4
		13,800	20	RD	no	34	0	84	1.0 (by definition)
		3,600	27	RD	no	90	2.3	44	2.6
		3,600	27	RD	yes	86	0	45	2.5
		3,600	46	RD	no	145	16	26	4.3
		3,600	46	RD	yes	120	0	32	3.5
		3,600	62	RD	no	190	30	19	5.6
		3,600	62	RD	yes	130	0	27	3.8
PHS 361	Pittsburgh Seam Bituminous	13,800	10	HB	no	30	0	90	1.0 (by definition)
		13,800	10	HB	no	36*	0	85*	1.2
		13,800	27	HB	no	50	0.8	77	1.7
		3,600	27	HB	no	148	21	27	4.9
		3,600	27	HB	yes	123	0	33	4.1
		3,600	46	HB	no	215	37	21	7.2
		3,600	46	HB	yes	123	0	33	4.1
		3,600	62	HB	no	173	26	18	5.8
		3,600	62	HB	yes	133	0	24	4.4
PSOC 837	Montana Lignite	13,800	10	HB	no	36	0	84	1.0 (by definition)
		3,600	27	HB	no	183	32	22	5.1
		3,600	27	HB	yes	120	0	32	3.3
		3,600	62	HB	no	345	55	11	9.6
		3,600	62	HB	yes	142	0	26	3.9
PSOC 664	Iowa Subbituminous	13,800	10	HB	no	31	0	90	1.0 (by definition)
		3,600	27	HB	no	145	19	28	4.7
		3,600	27	HB	yes	115	0	36	3.7
		3,600	62	HB	no	220	40	20	7.1
		3,600	62	HB	yes	115	0	34	3.7
PSOC 846	Wyoming Subbituminous	13,800	10	HB	no	37	0	96	1.0 (by definition)
		3,600	27	HB	no	180	26	20	4.9
		3,600	27	HB	yes	135	0	27	3.6
		3,600	62	HB	no	265	45	12	7.2
		3,600	62	HB	yes	145	0	23	3.9

* Feed for all mill runs was -1/2" except for the second 13,800/10 HB mill run with PHS-361, which was the +50 mesh product from accumulated mill runs with this coal at 3600/27 HB.

point, and therefore more stabilizing resin, which is a significant cost item). Since the smallest particle size obtained with the mill is $\sim 30\mu$, and since the distribution is normal, mill runs to obtain coarse sizes resulted in product $>300\mu$. For these reasons, the mill product of many of the runs was sieved through a 50-mesh (297μ) screen. In practice, the +50 mesh product is recycled as feed for the mill runs to make fines. It was found that tractable slurries having solids loading of 65% bituminous coal could be prepared with all product $<300\mu$, at a coarse/fines size ratio of 4.1/1. Slurries containing 70% bituminous were prepared with $\sim 15\%$ of the coal being $>300\mu$. The coarse/fines size ratio was 5.8/1.

When the mill is run at highest speed (13,800 rpm), a product having a fairly narrow size distribution is obtained. For example, with the hammer speed at 13,800 rpm and an HB grate size of 27 mils, the size consist of PHS 361 bituminous coal is 77% -200 mesh, and 54% of the product is -200/+325 mesh ($<74\mu/>44\mu$). The MMD of this product is 51μ . Slower hammer speeds are required to obtain a product with a larger MMD, but this product has a much broader size range. A broad size range is desirable for preparation of highly loaded slurries, because this indicates that both fines and coarse are present in sufficient amounts to permit a "size fit" for good packing. It is hypothetically possible for such a size distribution to be generated by a single mill run. An "accidental" result of this sort was not looked for in the present work. Instead, it was the practice to use blends of mill products to obtain the desired size distributions. An example of this practice is shown in Figure 5. These are curves for PHS-361 bituminous coal pulverized at the following conditions: (1) 13,800 rpm/27HB, which has a size consist of 77% -200 mesh; (2) 3600/27HB; (3) a blend consisting of 55% of 3600/27HB/-50 mesh product and 45% of 13,800/10HB product, which was used to prepare many of the slurries in this program, and (4) a blend consisting of 55% of 3600/62HB product and 45% of 13,800/10HB product, which was used to prepare 70% slurries. The curves for the two blends were constructed from the curves in Appendix C. The two blends show an absence of the relatively sharp inflections found

10³

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Particle Size, Micron

Figure 5
Effect of Blending on Particle Size Distribution
1. BMS 361 Bituminous Coal
2. RB Gales

MMD Line

Summary

Curve No.	Blend Composition Wt. %	Hammer Speed, RPM	Grate Size, Wt/s	Sieved	MMD, μ
1	100	13,800	27	No	50
2	100	3,600	27	No	148
3	55%	3,600	27	Yes	53
4	45%	13,800	10	No	74
	55%	3,600	62	No	
	45%	13,800	10	No	

Cumulative Wt. % Oversize

for the standard grind, and indicate a very wide uniform size distribution. It is instructive to note that the MMD of the blend of curve (3) is 53μ , which is only slightly greater than that of the "standard grind" (50μ , curve 1). Very fluid slurries were prepared with this blend, at 65% solids, while "dry mixes" were obtained with the standard.

3.2 Rheological Properties of Carriers

The most important selection criteria for carriers were yield point, cost, and viscosity. The effective cost of a carrier is the cost of obtaining a given value of yield point, which is the ingredient cost of a slurry divided by yield point. Carriers having low reactivity (see Table 8 and discussion) were selected from product literature, and evaluated as required in slurries. Both aqueous and emulsified carriers were studied. The rheologicals were determined by means of a Brookfield rotational viscometer.

3.2.1 Rheological Properties of Aqueous Gumstocks

The number of water-soluble resins on the market is almost legion. Time and funds prevent an exhaustive evaluation of all of the available resins. A fairly systematic and thorough reading of the technical and product literature, coupled with experimental evaluation of the most promising resins was carried out. A list of resins and properties of interest is given in Table 8. These are representative of the generic products that are commercially available. For each generic type, a number of viscosity grades are available, the highest of which are listed in the table. A number of other generics, such as the agars, algin, gum arabic and other industrial gums were omitted primarily for reasons of cost and availability. The prices of the resins listed in the table were collected at various times during the 1978 calendar year.

The cost effectiveness of the resins was determined by calculating the incremental cost per ton of coal in a 70% slurry. This required an estimate of the effective concentration of resin in the carrier, a number achieved by evaluating the rheological properties of gumstock solutions. The

Table 8. Selected Properties and Product Data of Water-Soluble Resins.

Resin Data			Incremental Cost of a 1% Solution as a Carrier in a 70% Coal Slurry, \$/ton Coal	Estimated Effective Concentration, Wt % of Carrier	Incremental Cost of the Estimated Effective Concentration in the 70% Slurry, \$/ton of Coal	Yield Point, dynes/cm ²	Viscosity μ_{10} , cp	Coefficients n	Ion Sensi- tivity	Reference Table No. in Appendix D	
Generic Name	Trade Name	Manufacturer	Cost, ¢/lb								
Polyvinyl car- boxylic acid	Carbopol 941	B.F. Goodrich	265	22.71	0.2	4.54	16.0	616	-.64	yes	D1
Guar Gum	SC 200	Perney	50	4.29	1.0	4.29	0.9	1863	-.50	no	D2,3
Guar Gum	A40F	Stein-Hall	84	7.20	1.0	7.20				no	D4
Modified Guar Gum	HP11	Stein-Hall	94	8.06	1.0	8.06	0	2272	-.73	no	D5
Xanthan Gum	Kelzan	Kelco	280	24.00	0.5	12.00	1.0	452	-.78	yes	D6,7
Hydroxyethyl Cellulose	Natrosol 250 HHR	Hercules	150	12.86	0.5	6.43	0	215	-.21	no	D8
Carboxymethyl Cellulose	CMC-9H4	Hercules	84	7.20	0.5	3.60	0	188	-.19	yes	D9
Polyacrylamide	Cyanamer P-250	Am. Cy.	1.55	13.29	1.0	13.29	0			no	D10
<u>Starches</u>											
Dent Corn	CP 3005	CPC	7	0.60	3.0	1.80				no	D11,13,14, 15
Waxy Maize	CP 6400	CPC	19	1.63	3.0	4.86	0	69	-.28	no	D12
Hydroxypropy- lated corn starch	Hamaco 267	Staley	27	2.31	3.0	6.94	7	450	-.54	no	D16,17

Notes: $\mu = \mu_{10}(S/10)^n$ μ = viscosity, cp μ_{10} = modified viscosity index, cp
 μ_{10} = viscosity @ 10 sec⁻¹S = Shear rate, sec⁻¹n = viscosity coefficient of
shear rate, dimensionless

The power function is useful only at the higher shear rates of the measurements. See the rheograms for details.

rheograms of these solutions are given in Appendix D, Tables D1-15. Qualitatively, in addition to low cost, the ideal carrier has a yield point $>4 \text{ dynes/cm}^2$, a viscosity of up to a few hundred cp at a shear rate of 10 sec^{-1} (a shear rate that approximates pouring the solutions), and a shear coefficient of viscosity as low as possible.

The results of the above calculations and measurements indicate 3% dent corn starch solutions are the best carriers. It turns out that this concentration is the most stable of this starch in terms of retrogradation. At concentrations $<3\%$, the starch precipitates from solution, while at $>3\%$ the solutions gel, with syneresis. Retrogradation is due to the high amylose fraction of the starch, and can be suppressed by increasing the amylopectin/amylose ratio. An easy way to do this is by blending with waxy maize, which is essentially pure amylopectin. Rheograms of these blends (Figures D13 to D15) indicate the yield point is decreased significantly. Also, the cost effectiveness of the blends is impacted. As shown later in this report, attempts to prepare slurries with 3% dent corn starch solutions failed. While the initial viscosities of the slurries are low, and the slurries are pourable fluids, the viscosities increase with age, and the slurries "set-up" to a solid. This is a second peculiarity of dent corn starch, as well as most underivatized natural gums (including the waxy maize and the guar gums), known as "set back". The starch is adsorbed out of solution onto the coal particle surfaces, and bonds the particles together. For these reasons, tractable slurries could not be prepared with dent corn starch solutions.

The Carbopol resins were found to be too ion-sensitive for use in coal slurries. Gumstock solutions are prepared by neutralizing the organic acids with either a base such as NH_4OH or NaOH , or an amine. The resulting polymeric salt can be destroyed by either an excess of Na^+ or by polyvalent ions. Slurries prepared with these slurries were found to be unstable, indicating that the good yield point of these resins vanishes in the presence of coal.

The two cellulose derivatives were considered in these studies even though they exhibit no yield point, because it was found that highly loaded fluid slurries could be prepared with gumstock solutions of these resins. Although these slurries were unstable, the settling rates were found to be low, and a day or two is required before the onset of hard packing. For this reason the slurries may be considered tractable. The slurries are remixable to original viscosities, indicating the absence of set-back. The highest loadings were attained with hydroxyethyl cellulose solutions.

The only other resin in the list that gives an acceptable yield point is hydroxypropylated corn starch. Although these solutions retrograde at concentrations $< 2\%$ (which are not of interest here due to low yield point; see rheograms, Figure D 16), hydroxypropylation evidently minimizes set back. While slurry viscosity has been found to increase with age, the increases are not great and initial values can be reclaimed by remixing. This characteristic is discussed below. Most of the slurry development work was directed toward use of hydroxypropylated corn starch solutions as the carrier.

3.2.2 Rheological Properties of Emulsions

3.2.2.1 General

These carriers are typically comprised of two to four parts No. 6 oil and one of tap water. The state of aggregation is an emulsion of either oil-in-water (o/w) or water-in-oil (w/o). Because of the mass ratio and the nature of No. 6 oil, the latter occurs naturally, wherein the water is dispersed as droplets in a continuous phase of oil. From the standpoint of high combustion efficiency, w/o emulsions are preferred. Here, it is believed that spray atomization of a w/o emulsion results in the formation of drops comprised of a burning oil surface and a water core. The core vaporizes with near explosive rate, atomizes the remaining oil film, and promotes rapid complete combustion of the resulting atomized oil. A good discussion of the combustion of w/o emulsions was given in the 16th International Combustion Symposium. While there is not general agreement on all effects, the benefits of emulsified fuels are generally accepted. From the standpoint of carrier stability, o/w emulsions are probably superior.

Considerable literature exists for these emulsions, which are used extensively in the food and drug industry (mayonnaise and cosmetics), as well as the paint, plastics, and construction industries for latexes, polymerization, and asphalts. Because the interest here is slurry stability, the use of o/w emulsions was emphasized. Properly prepared o/w emulsions of No. 6 oil in water are Bingham fluids (at 160°F) having the consistency of mayonnaise. Conversely, w/o emulsions of water in No. 6 oil have the consistency of a grease at room temperature, and exhibit no yield point at 160°F.

For both types of emulsions, surfactants are required for stability. Surfactant molecules are comprised of both water-soluble (hydrophilic) and oil-soluble (lipophilic) groups, and to a first approximation the relative activity, size, and number (population) of the groups governs the use of the molecule as an emulsifier. Generally if a surfactant is primarily lipophilic, it functions as a w/o emulsifier, while o/w emulsifiers are primarily hydrophilic. The most convenient procedure for selection of surfactants is by use of HLB criteria, where the HLB number is defined as the "hydrophile-lipophile balance" and is a measure of the relative affinity of the molecule for water and oil. There are several techniques for computing HLB number, based on saponification number, acid number, and oxyethylene content,* and many manufacturers rank their surfactants in this way. The HLB number of surfactants used as w/o emulsifiers is in the range of 3 - 6, and is in the range of 8 - 18 for o/w emulsifiers. A list of surfactants of interest here is given in Table 9. The list is representative, and not complete. A fairly complete listing of the hundreds of products on the market is published yearly.**

A second method of stabilizing emulsions is use of gelling agents. Many water-soluble resins are used for this purpose. Some proprietary oil-soluble resins manufactured by Dow Chemical Co., listed in Table 10, were also evaluated. The third method of stabilizing emulsions is "brute force", by very high shear mixing with a blender or homogenizer.

* Becher, P., "Emulsions: Theory and Practice," ACS Monograph No. 135 Reinhold (NY), (1957).

** McCutcheon's Detergents and Emulsifiers, North American Edition, McCutcheon Div., McCutcheon Publishing Co. (NJ).

TABLE 9.

HLB NUMBERS FOR SELECTED SURFACTANTS

<u>Manufacturer</u>	<u>Surfactant Trade Name</u>	<u>Surfactant Chemical Name</u>	<u>HLB Number</u>
Hodag	AS-6	Proprietary cationic emulsifiers	-
	AS-12	for asphalt (o/w) emulsions	-
ICI	Brij 35	Polyoxyethylene (23) lauryl ether	16.9
	Span 80	Sorbitan monooleate	4.3
GAF	Igepal CA-520	Octylphenoxypoly(ethyleneoxy) ethanol	10.0
	Igepal CO-210	Nonylphenoxypoly(ethyleneoxy) ethanol	4.6
	Igepal CO-530	Nonylphenoxypoly(ethyleneoxy) ethanol	10.8
Alkaril	Alkamuls SMS	Sorbitan monostearate	4.7
	Alkamuls SMO	Sorbitan monooleate	4.3
	Akamuls 400-DD	PEG 400 dioleate	7.8
	Alkasurf LA-3	Linear fatty alcohol ethoxylate	7.8
FVO	Lipal TE 43	Polyoxyethylene Tallow Ester	8.6
	Lipal TE 55	Polyoxyethylene Tallow Ester	11.0
	Dremulse GMO	Glyceryl monooleate	3.4
	Dremulse TP	Glycerol monostearate	3.8
	Dremulse SML	Sorbitan monolaurate	8.6
	Dremulse POE-SMO	Poloxyethylene (20) sorbitan monooleate	15.0
R&H	Triton X-15	Octylphenoxy polyethoxy ethanol	3.6
	Triton X-100	Octylphenoxy polyethoxy ethanol	13.5
American Can	Americo SD-1	Sodium lignin derivative from Kraft paper process.	-

Table 10. Viscosities of No. 6 Oil With Dow Additives.

<u>Additive</u>	<u>Wt. % of Additive</u>	<u>Viscosity, cp</u>	<u>Temperature at Which Viscosity was Measured, °F</u>
None	-	55	139
Dow J-315	3	$220S^{-.27}$	139
Imbiber Beads	2	$1090S^{-0.17}$	139
XVS 00100.00 Gellant	2	177	136

S = shear rate, sec^{-1}

* See also Appendix D, Figures D13 - 15.

Emulsions were prepared by a number of mixing techniques, ranging from simple mixing to homogenization. All mixes were prepared with ingredients at 160°F. As shown below, the best technique for preparation of stable o/w emulsions is by addition of the oil to a solution of the emulsifier in the water in a homogenizer. Measurements of yield point, viscosity, and stability were made, at a storage temperature of 160°F. The rheologicals were measured with a Brookfield RVT viscometer using the appropriate cylindrical spindle. The test for emulsion type was made by observing the behavior of a drop of sample in 25 cc of water. If the drop is miscible, the emulsion is declared to be an oil-in-water (o/w) type. If the drop remains immiscible and forms a streaky smear on the cup wall when the contents are swirled, the emulsion is a w/o type. This is a rudimentary but generally true indication of emulsion type. Emulsions are dispersible in the external phase. A drop of oil in water will form a blot on the container walls, as opposed to a smear, when the contents are swirled.

3.2.2.2 Properties of Emulsions Prepared by Low Shear Mixing

A preliminary set of mixes were made to see if simple mixing could be used to prepare stable emulsions. Water and No. 6 oil emulsify spontaneously by bulk mixing with a paddle or planetary type mixer, or by vigorously shaking the ingredients together. The type of emulsion depends on the oil/water ratio. At an oil/water ratio of 2/1, a Newtonian w/o emulsion is formed, having a viscosity of 2.2 poise at 160°F. This emulsion separates after a few days storage at 160°F, even if prepared in a blender, adding the oil to the water.

A series of emulsions were prepared with a 3% solution of Hamaco 267 (hydroxypropylated corn starch) in water as the aqueous phase, and No. 6 oil containing 0, 2, or 3% Dow XVS (a proprietary oil-soluble polymer). These emulsions were prepared manually, by vigorously shaking the ingredients together. The oil (+ resin)/water (+ resin) ratios were 1/6, 2.5/1, and 2/1. The first of these corresponds to 30% water in a 65% (solids) slurry. These are o/w emulsions, and are unstable in 160°F storage, at all levels of Dow XVS. The second and third correspond to 10% water in a 65 and 70% slurry, respectively. These are w/o emulsions and are also unstable in 160°F storage. When these emulsions are prepared without Hamaco 267. The results are the same.

A second set of mixes was prepared using selected aqueous gum-stocks, un-thickened No. 6 oil, and selected surfactants, at an oil/water ratio = 2. As above, manual mixing was used. The mixture of 2 parts No. 6 oil and 1 part 0.25% Kelzan solution results in an unstable w/o emulsion. The use of Triton X-102 (octylphenoxy polyethoxy ethanol, a non-ionic emulsifier manufactured by Rohm and Haas, HLB = 14.6) in water results in unstable o/w emulsions (i.e., the emulsions "cream" on standing). The use of Brij 35 (ICI, polyoxyethylene (23) laurylether, HLB = 16.9) resulted in stable emulsions in a variety of compositions. In the presence of 0.25% Kelzan, 0.5% HEC, or 0.25% HEC very fluid stable o/w emulsions are obtained (See Figure D-18 and D-19, Appendix D). Without thickeners, a w/o emulsion is formed. Brij 35 is not necessary to form the o/w emulsion in the HEC systems, but its use significantly reduces viscosity. A summary of these results is given in Table 11.

3.2.2.3 Properties of Emulsions Prepared by High Shear Mixing

The above results indicate that stable emulsions cannot be prepared by low shear mixing, unless the water-phase viscosity is increased. For this reason, a homogenizer (blender) was used to prepare emulsions for the rest of the work. The general practice was to preheat the ingredients to 160°F, and add the oil in a continuous stream to a whizzing solution of surfactant in water. Initial results with the blender indicated that stable emulsions could be prepared without increasing phase viscosity. Consequently, none of the resins were required.

Evaluation of Igepal CA520 and CO530, Americo SD-1, and Brij 35 as emulsifiers was carried out. The first two are aliphatic phenoxy polyethylene glycols having HLB numbers of 10.0 and 10.8 respectively, and are manufactured by GAF. At a level of 2 parts per hundred (pph) of oil + water, emulsions comprised of 2.5 parts oil + 1 part water were found to be unstable. Both separated after overnight storage at 160°F. Both were low-viscosity o/w emulsions.

Americo SD-1 is an anionic dispersant manufactured by American Can. It is a sodium lignin derivative, and contains no sulfur. The effect of oil/water weight ratio, dispersant content, and mixing procedure,

Table 11. Effect of Resins and Emulsifiers on Stability of Selected Emulsions.

ID	679- 57-A	679- 60-A	679- 57-B	679- 60-B	679- 57-C	679- 60-C	679- 57-D	679- 60-D	679- 57-E	679- 60-E	679- 57-F	679- 60-F	679- 57-G	679- 60-G	679- 57-H	679- 57-I	679- 57-J	679- 60-J	165- 64	165- 63	165- 65A	165- 65B	165- 68
1. Water (Parts)	30	30	30	30	30	30	10	10	10	10	10	10	10	10	10	10	10	10	1	1	1	1	1
2. No. 6 Oil (Parts)	5	5	5	5	5	5	25	25	25	25	25	25	20	20	20	20	20	20	2	2	2	2	2
3. Water-Soluble Resins (PPH of Water)																							
Hamaco 267	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3					
Kelzon																			.25	.25			
Natrosol 250 HHR																					.5	.5	.25
4. Oil-Soluble Resins (PPH of Oil)																							
Dow XVS 00100.00			2	2	3	3			2	2	3	3			2	2	3	3					
5. Emulsifier (PPH of Oil + Water)																							
Igepal CA-520		1		1		1																	
Igepal CO-210							1		1		1		1		1		1						
Brij 35																			.17	.33	-	.33	.33
6. Type of Emulsion	o/w	o/w	o/w	o/w	o/w	o/w	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	w/o	o/w	o/w	o/w	o/w	o/w
7. Stability (no separation after 1 wk @ 160°F)	no	no	no	no	no	no	no	no	no	no	no	OK	no	no	no	no	no	OK	OK*	OK*	OK*	OK*	OK*
8. Viscosity, poise, @ 10 sec ⁻¹ , & RT																			9.1	4.2	150	25	6.4

* 1 week stability @ RT.

on rheologicals and type of emulsion was evaluated with this dispersant. Results are summarized in Table 12. See Figures D-20 to D-24, Appendix D, for detailed rheograms. An examination of the rheograms indicates no systematic effect of composition on viscosity, although the 2/1 composition is evidently becoming Newtonian at a shear rate of $\sim 30 \text{ sec}^{-1}$, with a viscosity of ~ 25 poise. The other two are considerably more pseudoplastic. The effect of emulsifier content on rheologicals is shown in Figure D-21. At 2 pph, the emulsion is a non-pourable mayonnaise. At 1 pph, the emulsion is pourable but still has a noticeable yield point. At both concentrations, the emulsions are stable, showing no separation after three weeks storage at 160°F . At 0 pph, the emulsion is a low-viscosity Newtonian, which separates completely to a clear water phase beneath the oil after a few days storage at 160°F . The effect of mixing procedure on rheologicals is shown in Figure D-22. Curve A is the mayonnaise produced by adding oil to the Americo SD-1 solution in the blender. Curve B shows that a low-viscosity Newtonian fluid results when the order of addition is reversed. This is a w/o emulsion and is stable in storage at 160°F . Curve C shows the effect of premixing the ingredients, followed by blending. The result is a mayonnaise similar to that of A, but apparently more pseudoplastic. At the lower shear rates, the two (A and C) are essentially alike. Either premixing followed by high-shear blending, or addition of oil to a highly sheared solution of dispersant in water is required to form the desired emulsion. The effect of mixer type on rheologicals is shown in Figure D-23. Use of a planetary type mixer, such as a Hobart, used at high speed, results in a slightly pseudoplastic, high-viscosity fluid having no yield point. A paddle mixer, such as a Lightnin, results in a low-viscosity pseudoplastic that becomes Newtonian at high shear rates ($>100 \text{ sec}^{-1}$). Evidently, a blender is required to form the mayonnaise. Batch-to-batch variations in rheologicals of emulsions prepared by adding oil to the water/Americo solution in a high speed blender are shown in Figure D-24. Although all of the mixes were similar in appearance, being like mayonnaise, the variations in viscosity can be as much as a factor of 10. Subsequent work with these emulsions as carriers resulted in unstable coal slurries. This is believed

Table 12. Effect of Composition and Process
Variables on Properties of Emulsions
Prepared with Americo SD-1

Mix ID	Emulsion Composition			Type of Mixing	Order of Addition of In gredients	Viscosity @ 10 Sec ⁻¹ , Poise	Type of Fluid	Type of Emulsion
	Oil, Parts	Water, Parts	Americo SD-1, Parts per Hundred of Oil + Water					
<u>Baselines</u>								
400	2	1	2	Blender	O to W	42	Pseudo.	O/W
412	2.5	1	2	"	" " "	80	"	"
415	3	1	2	"	" " "	125	"	"
<u>Effect of Dispersant Content</u>								
420	2	1	1	Blender	O to W	13	Pseudo.	O/W
419	2	1	0	"	" " "	2.2	Newt.	W/O
<u>Effect of Order of Addition</u>								
417	2	1	2	Blender	W to O	3.8	Newt.	W/O
424	2	1	2	"	Premixed	65	Pseudo.	O/W
<u>Effect of Mixer</u>								
413	2	1	2	Paddle	O to W	0.2	Pseudo.	W/O
414	2	1	2	Planetary	" " "	50	"	"
<u>Effect of Batch</u>								
411	2	1	2	Blender	O to W	25	Pseudo.	O/W
421	1	1	2	"	" " "	9.7	"	"
422	1	1	2	"	" " "	6.7	"	"

due to adsorption of the emulsifier out of solution, which breaks the emulsion and results in settling. This is unfortunate because, at 25¢/lb this is the most cost-effective emulsifier.

The use of Brij 35 (ICI), polyethylene glycol (23) lauryl ether (HLB=16.9) as an emulsifier also resulted in stable o/w emulsions having the consistency of mayonnaise. Rheologicals of emulsions are summarized in Table 13. and Figures D-25 and D-26 in Appendix D. These emulsions resulted in more stable slurries, when used as carriers. The unit cost of this soap is 72¢/lb.

3.3 Development and Evaluation of Slurries

3.3.1 General

The objective of the program was to develop stable slurries containing as a goal 70% by weight coal. The technical approach was to use bimodal blends to attain the loadings and minimize viscosity, and to use Bingham fluids as carriers to attain stability. Several different coals were evaluated. These included: (1) a clean bituminous coal from the Bruceton Experimental Mine, which was used in the initial work; (2) a Pittsburgh seam bituminous coal, also from Bruceton, with which most of the work was carried out; (3) a Wyoming subbituminous; (4) an Iowa subbituminous, and (5) a Montana lignite. The last three were received from Pennsylvania State University. The initial goal was to constrain the water content in the slurries to two values: 30% and 10%. Thus in slurries containing 70% by weight coal, it is seen that the two nominal compositions of interest are (1) 70% coal + 30% water, and (2) 70% coal + 20% No. 6 oil + 10% water. As things turned out, stable 70% slurries of coal in water could only be prepared with part of the particles $>300\mu$, although unstable ones were prepared with all particles $<300\mu$. The best loading in a stable coal/water slurry with the small particles was 65%. Calculations of heating values and costs indicate this to be a good candidate fuel. Likewise, the best loading in a coal/oil/water slurry was 65% coal, the remainder being nominally 25% oil + 10% water. The carrier used to prepare stable coal/water slurries was an aqueous solution of hydroxypropylated corn starch. The carriers for stable coal/oil/water slurries were oil-in-water emulsions.

Table 13.

Effect of Emulsion Composition and Temperature on Viscosity
at 10 sec^{-1} of Emulsions Comprised of No. 6 Oil, Water, and Brij 35.

ID	Emulsion Composition			Viscosity, Poise, @ 10 sec^{-1} , @ T =		Stability @ 160°F
	No. 6 Oil, Parts	Water, Parts	Brij 35, PPH Oil + Water	72-75°F	150-160°F	
488	2.5	1	1	20	6.2	OK
455	2.5	1	2	21	11	OK
466	3.0	1	1	34	21	OK
465	3.0	1	2	67	29	OK
490	3.5	1	1	75	21	OK
491	4.0	1	1	54	17	OK

Note: All of the emulsions are Bingham pseudoplastics, having an average exponent of shear rate of ~ -0.7 for use in a power law expression. The viscosity, μ , at any shear rate, S , may be related to the viscosity at 10 sec^{-1} , μ_{10} , by the following estimation:

$$\mu = \mu_{10} (S/10)^{-0.7}$$

As noted above, unstable slurries were also evaluated. The interest here stemmed from the fact that higher solids loadings could be obtained in the unstable slurries, and from the fact that it is not possible (or at least not within the scope of this program) to quantify a priori the cost-effectiveness of stability. Aqueous solutions of hydroxyethyl cellulose were used to prepare 70% slurries which settle slowly, resulting in packing after 1 - 2 days of storage. Aqueous solutions of dispersants, such as the lignin derivatives were used to prepare 70% slurries which settle rapidly, in a few hours. Although both types of slurries are extremely fluid, neither were found to be pumpable: the first because of excessive pressure drop at the entrance to an extrusion rheometer; the second because of no-flow through an extrusion rheometer due to bridging.

Development of slurries proceeded on a trial-and-error basis. Blends of particles were evaluated for effect on viscosity. Slurries having minimum viscosity were then evaluated for stability. Viscosity of developmental mixes was measured at 1 rpm with a Brookfield viscometer fitted with T-bar spindles. Cavitation precluded use of cylindrical spindles for slurries. The instrument constants for converting torque readings with T-bars to viscosity are specific for Newtonians and are not easily correctable (as were those with cylinders) for non-Newtonian fluids. However, as a figure-of-merit, the uncorrected 1-rpm readings were used here for comparative purposes.

The viscosities of candidate slurries, selected because they represent the best we attained with a given coal and carrier, were measured with an extrusion rheometer, and stability was measured with a compound pendulum.

3.3.2 Evaluation of Coal/Water Slurries Containing Clean Coal From the Bruceton Experimental Mine

This was the first batch of coal received for this program and is so-called because of its low sulfur content. It was used in all of the preliminary mixes. Attempts to prepare 60-70% slurries of 80% - 200 mesh coal with aqueous solutions of either 0.2% Carbopol 941, 0.2 - 0.5% Guar gum (Perney, SC 200), 3% unmodified dent corn starch (CPC, CP3005), or

3% waxy maize corn starch (CPC, CP6400) failed, resulting in settling, set-up, and the appearance of a water-like supernatant fluid on the surface of the mixes. These were pint mixes made in a small Hobart mixer. Slurries were stored at ambient in capped pint jars. None of these slurries could be remixed to original values of viscosity. The failure of Carbopols to stabilize slurries is attributed to ionic contamination due to leachates from the coal. Although guar gum solutions do not exhibit much of a yield point, and waxy maize solutions exhibit none, slurries made with either of these solutions or the starch solution all set-up on standing overnight, and exuded a water-like supernatant. This is attributed to the phenomenon known as set-back, which seems to be peculiar to non-derivatized natural gums and resins. Adsorption of the resins from solution bonds particles together in a hard mass, and is self-accelerating because the remaining resin left in solution is too low to prevent retrogradation. At these low resin levels, the appearance of a water supernatant is not believed to be the result of syneresis as much as complete adsorption and precipitation of the resins from solution. Attempts to prepare slurries with 3% solutions of starch and maize, where the starch/maize ratio was varied from 1/1 to 10/1 exhibited in the same results of set-up and water formation.

Fluid slurries were prepared with aqueous solutions of hydroxyethyl cellulose (HEC), xanthan gum, and carboxymethyl cellulose (CMC). Mix data are given in Tables 14 - 16. Although none of these slurries were stable for more than 1 - 2 days, they could be remixed to original viscosities, indicating absence of set-back. In some cases, "remix" viscosities were lower than end-of-mix (original) values, which is attributed to a change in state of aggregation. Entrapped air from original mixing is released on storage, and remixing did not reaerate the slurry. This phenomenon is obviated by vacuum mixing, but this technique was not practiced until later in the program when it was necessitated for preparation of slurries containing hydroxypropylated corn starch solutions which have high yield points.

Coal loadings of 70%, with all particles $<300\mu$ (~50 mesh) were obtained at a 55/45 coarse/fine ratio, using a 0.5% HEC gumstock solution as a carrier. These are fluid pourable slurries. These slurries are

Table 14. Mix Data for Coal/Water Slurries Comprised of Clean Coal From the Bruceton Experimental Mine and Aqueous Solutions of Hydroxyethyl Cellulose (HEC)

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved* Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	HEC	Other			
165-121	65	70/30	113/26	0.5	-	.36	Yes	
-122	65	65/35	113/26	0.5	-	.32	Yes	
-123	65	60/40	113/26	0.5	-	.25	Yes	
-124	65	55/45	113/26	0.5	-	.2	Yes	
-154	70	60/40	140/26	0.5	-	3.26	Yes	
-148	70	55/45	140/26	0.5	-	1.32	Yes	
-151	70	55/45	140/26	0.5	-	1.44	Yes	
-155	70	50/50	140/26	0.5	-	3.35	Yes	
-141	70	55/45	140/-325	0.5	-	0.62	Yes	All fines -325 mesh
-134	70	55/45	140/26	0.5	-	1.2	No	
-140	70	55/45	195/26	0.5	-	1.0	No	
-150	70	55/45	140/26	0.5	.1% Tamol SN	7.82	Yes	
-157	70	55/45	140/26	0.5	.1% Triton X-102	Dry Mix	Yes	

* Sieved coal with MMD = 140 micron is the -50 mesh product of a 3600 rpm/62 HB mill run (see Table 7).

Unsieved coal with MMD = 140 micron is the as-received product of a 3600 rpm/27 HB mill run.

The HEC is Natrosol 250 HHR (Hercules).

Table 15. Mix Data for Coal/Water Slurries Comprised of Clean Coal From the Bruceton Experimental Mine and Aqueous Solutions of Xanthan Gum.

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved* Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Xanthan	Other			
165-112	65	75/25	113/26	.25	.1% Triton X-100	.85	Yes	
-113	65	70/30	113/26	.25	.1% Triton X-100	.58	Yes	
-114	65	65/35	113/26	.25	.1% Triton X-100	.53	Yes	
-115	65	60/40	113/26	.25	.1% Triton X-100	.42	Yes	
-116	65	55/45	113/26	.25	.1% Triton X-100	.41	Yes	
-117	65	50/50	113/26	.25	.1% Triton X-100	.47	Yes	
-118	65	45/55	113/26	.25	.1% Triton X-100	.60	Yes	
-119	65	40/60	113/26	.25	.1% Triton X-100	.63	Yes	
-120	65	35/65	113/26	.25	.1% Triton X-100	1.0	Yes	
-120A	70	55/45	113.26	.25	.1% Triton X-100	Dry	Yes	
-145	70	55/45	140/26	.25	.1% Triton X-100	Dry	Yes	
-144	70	55/45	140/26	.25	.1% Brij 35	Dry	Yes	
-146	70	55/45	140/26	.25	.1% Tamol SN	Dry	Yes	
-158	70	55/45	140/26	.25	-	Dry	Yes	
679-187	65	55/45	120/26	.25	-	.3	Yes	RD grates
-188	65	55/45	130/26	.25	-	.2	Yes	RD grates
-189	65	55/45	130/34	.25	-	.17	Yes	RD grates

*Sieved coal with MMD=140 micron is the -50 mesh product of a 3600 rpm/62HB mill run.

See Table 7 for mill conditions yielding indicated MMD

Xanthan gum is Kelzan (Kelco).

Table 16. Mix Data for Coal/Water Slurries Comprised of Clean Coal From the Bruceton Experimental Mine and Aqueous Solutions of Carboxymethyl Cellulose (CMC)

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved* Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	CMC	Other			
165-162	65	55/45	113/26	0.5	-	1.2	Yes	
-161	65	55/45	113/26	0.5	.1% Triton X-100	0.7	Yes	
-163	65	55/45	113/26	0.5	.1% Tamol SN	3.45	Yes	
-164	65	55/45	113/26	0.5	.1% Triton GR-5M	34	Yes	Not pourable
-165	65	55/45	113/26	0.5	.1% Igepal CA-520	1.0	Yes	Not pourable
-166	65	55/45	113/26	0.5	1.7% Brij 35	0.7	Yes	
-168	65	55/45	113/26	0.4	.1% Triton X-100	0.9	Yes	
-169	65	55/45	113/26	0.3	.1% Triton X-100	0.1	Yes	
-174	65	55/45	113/26	0.2	.1% Triton X-100	0.07	Yes	
-175	65	55/45	113/26	0.1	.1% triton X-100	6.5	Yes	
-170	65	55/45	113/26	0.6	.1% Triton X-100	2.0	Yes	
-167	65	55/45	140/26	0.5	.1% Triton X-100	0.4	Yes	
-153	70	55/45	140/26	0.5	-	8.04	Yes	Dough-like mix

* Sieved coal with MMD = 140 micron is the -50 mesh product of a 3600 rpm/62HB mill run.
See Table 7 for mill conditions yielding indicated MMD
CMC is Cellulose Gum 9H4 (Hercules)

short lived in terms of stability, exhibiting settling after 24 hours, but the high solids loadings may offset instability, in terms of cost effectiveness, at the price of occasional remixing in storage.

This coarse/fines ratio was also found best for slurries made with 0.25% xanthan gumstocks. These slurries could only be loaded to 65% solids; the 70% loadings were dry. It is believed that the gum is gelled by ionic contaminants at the higher loadings.

Similarly, a nearly dry dough-like mix was obtained at 70% solids with 0.5% CMC gumstock. Again, the ion sensitivity of the gum is believed to give this result. This gum, like xanthan, can be gelled by trivalent ions. The 65% slurries were fluid and pourable. The CMC content for minimum viscosity was found to be 0.2% of the carrier. A small amount of wetting agent (Triton X-100, Rohm & Haas) was found to reduce viscosity, but a dispersant (Tamol SN) increase viscosity. This phenomenon was also observed with HEC solutions. As will be shown later, the use of dispersants without resins significantly reduces viscosity.

3.3.3 Evaluation of Coal/Water Slurries Containing Pittsburgh Seam Bituminous Coal (PHS 361)

Most of the work in the program was concerned with developing and evaluating slurries made with this coal. Initial attempts to prepare slurries with solutions of either xanthan gum, CMC, unmodified dent corn starch, or waxy maize all failed because of extreme set-back in storage. This is believed to be due to ionic gellation (with synerisis) of xanthan gum and CMC, adsorption/retrogradation of the starch, and adsorption of the maize. Set-back is manifest as viscosity build-up in storage, generally with little or no settling, and may or may not exhibit synerisis. It must be considered to be a form of slurry instability as serious as settling. Slurries exhibiting set-back cannot be remixed to initial values of viscosity.

Slurries prepared with either hydroxyethyl cellulose solutions ("HEC", Natrosol 250 HHR, Hercules) or solutions of hydroxypropylated corn starch (Hamaco 267, Staley) were found exhibit no set-back. The HEC slurries

are unstable but can be loaded easily to 70% coal. The starch slurries are stable and can be loaded to 70% if part of the coal (~15%) has a particle size $>300\mu$. This requirement was not necessary for HEC slurries. Also, slurries were prepared with dispersants, in place of the resins. Extremely fluid, extremely unstable (with respect to settling) slurries were prepared with dispersants (all coal particles $<300\mu$).

Mix data are presented and discussed below.

3.3.3.1 Evaluation of HEC Solutions as Carriers

Mix data for slurries made with aqueous HEC solutions as carriers are given in Table 17. Most of these slurries were prepared with blends of 123 micron coarse and 30 micron fines, where the coarse is the -50 mesh product of 3600 rpm/27 HB mill runs (the unsieved product is 79% -50 mesh, see Table 7), and the fines are 90% - 200 mesh. It is seen from Table 17 (mixes 208 - 214) that a coarse/fines weight ratio of 65/35 yields minimum viscosity at 70% coal and 0.4% HEC. Variation of HEC content from 0.1 to 0.6% shows that minimum viscosity occurs at 0.5% HEC, at 70% of the 65/35 solids. Note that dry mixes are obtained at 0.1 and 0.2% HEC. These data indicate at least 0.4% and preferably 0.5% HEC is required for fluid mixes. This concentration requirement, and the resultant benefit, is believed to be due to "water binding" by the HEC, which is a euphemism for preferential attraction of water to HEC as opposed to water adsorption onto coal. Although HEC solutions are mildly surface active (the surface tension is ~67 dynes/cm, compared to 70 dynes/cm for water), Triton X-100 (Rohm & Haas) was generally used at the .01% level as a mixing aid. This surfactant decreases surface tension to ~30 dynes/cm at the .01% concentration. It is not really required for small mixes, as shown in the table. The effect of a dispersant, Marasperse CBOs-3 (a sodium lignin sulfonate manufactured by American Can) on viscosity was evaluated at dispersant levels of 0.05 to 1% of the coal (mixes 244, 243, 257, and 258). At low levels, the dispersant increases viscosity. At 1% dispersant, the viscosity is about the same as a mix made with none, in spite of the fact that (as shown later) the use of the dispersant without HEC results in a viscosity of only 0.04 Kp, compared to 0.8 Kp found here. These data are presented

Table 17. Mix Data for Coal/Water Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361) and Aqueous Solutions of Hydroxyethyl Cellulose ("HEC", Natrosol 250 HHR, Hercules).

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	HEC	Other			
679-201	65	55/45	123/30	0.5	-	0.006	Yes	
-210	70	55/45	123/30	0.4	.01% Triton X-100	5	Yes	
-209	70	60/40	123/30	0.4	.01% Triton X-100	2.8	Yes	
-208	70	65/35	123/30	0.4	.01% Triton X-100	0.9	Yes	
-211	70	70/30	123/30	0.4	.01% Triton X-100	1.9	Yes	
-212	70	75/25	123/30	0.4	.01% Triton X-100	1.9	Yes	
-213	70	80/20	123/30	0.4	.01% Triton X-100	2.0	Yes	
-214	70	100/0	123/30	0.4	.01% Triton X-100	6.5	Yes	
-260A	70	65/35	123/30	0.1	.01% Triton X-100		Yes	Dry mix.
-260B	70	65/35	123/30	0.2	.01% Triton X-100		Yes	Dry mix.
-261	70	65/35	123/30	0.3	.01% Triton X-100	26.5	Yes	
-215	70	65/35	123/30	0.5	.01% Triton X-100	0.6	Yes	See No. 208 for .4% HEC
-217	70	65/35	123/30	0.5	None	0.22	Yes	
-216	70	65/35	123/30	0.6	.01% Triton X-100	0.3	Yes	
-264	70	65/35	123/30	0.4	None	~1	Yes	
-265	70	65/35	123/30	0.4*	None	21	Yes	*Natrosol 250 GR; see text
679-219	70	65/35	123/30	0.5	.02% Tritox X-100	0.3	Yes	See 217 and 215 for 0 and 0.01% Triton X-100
-220	70	65/35	123/30	0.5	.04% Triton X-100	0.2	Yes	
-222	70	65/35	123/30	0.5	0.1% Triton X-100	0.6	Yes	

Table 17. (Continued)

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	HEC	Other			
679-218	70	65/35	123/30	0.5	.5% Calgon	0.5	Yes	
-244	70	65/35	123/30	0.5	.05% Dispersant*	5	Yes	*Marasperse CBOs-3 Dispersant concentrations are wt. % of coal.
-243	70	65/35	123/30	0.5	.1% Dispersant*	12	Yes	
-257	70	65/35	123/30	0.5	.5% Dispersant*	13	Yes	
-258	70	65/35	123/30	0.5	1% Dispersant*	0.8	Yes	
679-246	71	65/35	123/30	0.5	-	2.5	Yes	
-247	72	65/35	123/30	0.5	-	13	Yes	
-248	73	65/35	123/30	0.5	-	12	Yes	
686-437	70	55/45	123/50	0.5	-	3.0		
-442	70	65/35	123/50	0.5	-	2.0		
-450	70	75/25	123/50	0.5	-	4.7		
-451	70	85/15	123/50	0.5	-	5.4		

without comment. Failure of the dispersant to reduce viscosity in these slurries indicates an unexpected interaction between the coal surface, dispersant, HEC, and water.

Viscosity increases by about an order of magnitude when coal content is increased from 70 to 71% and by another order at 72%. A few mixes were also made up with 50 micron fines, which are 77% -200 mesh. The viscosity of 70% slurries made with these fines are ~10 times greater than those made with the 30 micron fines.

None of the slurries made with HEC solutions are stable towards settling. The coal settles out slowly, so that remixing must be used for mix uniformity. However, the slurries are of interest because of the high loadings of small particles (all particles are $<300\mu$). The slurries are fluid and pourable at room temperature. It is estimated that recirculation at the rate of 1 or 2 tank volumes per day would be sufficient to maintain uniformity.

Finally, mention should be made here of the results with an extrusion rheometer, reported elsewhere in this report. Viscosities could not be reduced from these tests, because the data indicated that all of the pressure drop occurred at the entrance to the tubes. This is in spite of the fact that the slurries could be easily extruded through the rheometer. It was found that slurry accumulates at the entrance, and it is believed that this build-up causes the abnormally large pressure drops. The diameter ratio of the feed chamber to the tubes was 5/1.

3.3.3.2 Evaluation of Modified Starch Solutions as Carriers

Mix data for slurries made with aqueous solutions of hydroxypropylated corn starch (Hamaco 267, Staley, referred to here as "starch") are given in Table 18. As noted previously, these solutions exhibit yield points, and stable slurries can be prepared. Also, because of hydroxypropylation, set-back was minimized. The starch is cold water soluble. Because of the yield point, vacuum mixing is required. Mixes made at ambient pressure are foams. These foams can be broken by carefully remixing at ambient pressure after 24 hours in storage. However, ease of processing favors use of vacuum mixing. For some reason, vacuum mixing also helped reduce set-back.

Table 18. Mix Data for Coal/Water Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361) and Aqueous Solutions of Modified Corn Starch (Hamaco 267, Staley).

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Starch	Other			
679-277	65	100/0	123/30	3	.01% Triton X100	13	Yes	
-273	65	85/15	123/30	3	.01% Triton X100	1.4	Yes	
-272	65	80/20	123/30	3	.01% Triton X100	0.85	Yes	
-271	65	75/25	123/30	3	.01% Triton X100	0.86	Yes	
-270	65	70/30	123/30	3	.01% Triton X100	0.93	Yes	
-274	65	65/35	123/30	3	.01% Triton X100	0.60	Yes	
-275	65	60/40	123/30	3	.01% Triton X100	0.46	Yes	
-276	65	55/45	123/30	3	.01% Triton X100	0.42	Yes	
-278	65	50/50	123/30	3	.01% Triton X100	0.3	Yes	
-281	65	45/55	123/30	3	.01% Triton X100	0.85	Yes	
-282	65	40/60	123/30	3	.01% Triton X100	0.70	Yes	
-283	65	35/65	123/30	3	.01% Triton X100	0.65	Yes	
-284	65	25/75	123/30	3	.01% Triton X100	0.65	Yes	
-285	65	20/80	123/30	3	.01% Triton X100	1.05	Yes	
-285	65	15/85	123/30	3	.01% Triton X100	1.45	Yes	
-280	65	0/100	123/30	3	.01% Triton X100	6.5	Yes	Dilatant
-298	65	55/45	123/30	3	0.1% Triton X100	0.32	Yes	
-299	65	55/45	123/30	3	.01% Triton X100	0.39	Yes	Mixed hot (130°F)
-301	65	55/45	123/30	3	-	0.33	Yes	Mixed 30 minutes
-300	65	55/45	123/30	3	.01% Triton X100	0.30	Yes	Mixed 30 minutes
-304	65	65/35	123/30	3	.01% Triton X100	0.50	Yes	Mixed 30 minutes

Table 18 (Continued)

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Starch	Other			
679-305	65	75/25	123/30	3	.01% Triton X100	1.25	Yes	Mixed 30 minutes
-297	65	55/45	123/30	2.5	.01% Triton X100	0.35	Yes	Unstable
-306	70	55/45	123/30	2.5	.01% Triton X100	38	Yes	Unstable
686-363	70	55/45	123/30	2.5	.01% Triton X100 + 1% Tamol SN	1.65	Yes	Unstable
686-365	70	55/45	123/30	2.5	1% Tamol SN	1.5	Yes	Unstable
-389	70	55/45	123/30	2.5	0.5% Tamol SN	3.3	Yes	Unstable
-381	70	55/45	123/30	2.5	2% Americo SD-1	17.5	Yes	Unstable
-382	70	55/45	123/30	2.5	2% Marasperse 52 cp	21.1	Yes	Unstable
-383	70	55/45	123/30	2.5	2% Marasperse CBOs-3	11.7	Yes	Unstable
-384	70	55/45	123/30	2.5	2% Norlig 11	5.5	Yes	Unstable
-385	70	55/45	123/30	2.5	4% Norlig 11	21	Yes	Unstable
679-331	70	55/45	133/30	3	.01% Triton X100	9.1	Yes	
-332	70	65/35	133/30	3	.01% Triton X100	8.2	Yes	
-333	70	75/25	133/30	3	.01% Triton X100	20	Yes	
-334	70	55/45	148/30	3	.01% Triton X100	1.0	No	
-335	70	55/45	173/30	3	.01% Triton X100	0.8	No	
-336	70	65/35	173/30	3	.01% Triton X100	0.4	No	
-337	70	75/25	173/30	3	.01% Triton X100	1.1	No	

Table 18 (Continued)

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Starch	Other			
686-477	65	55/45	123/36	3	.01% Triton X100	0.2	Yes	+50 mesh product from 3600 rpm mill runs was used as feed to make the fines for mixes 477, 478 493, 485, 486, and 487
-478	65	65/35	23/36	3	.01% Triton X100	0.20	Yes	
-493	65	75/25	123/36	3	.01% Triton X100	0.55	Yes	
-485	70	55/45	173/36	3	.01% Triton X100	1.6	No	
-486	70	65/35	173/36	3	.01% Triton X100	2.5	No	
-487	70	75/25	173/36	3	.01% Triton X100	3.3	No	
686-368	65	55/45	123/30	3	.01% Triton X100 + 1% Tamol SN	0.42	Yes	
686-362	70	55/45	123/30	3	.01% Triton X100 + 1% Tamol SN	5.1	Yes	
686-505	65	100%	50	3	.01% Triton X100	3.7	Yes	The coal size consist is 77% -200 mesh

As with HEC solutions, 123 micron coarse and 30 micron fines were used to prepare slurries. The initial work was with 65% slurries, in which the effect of coarse/fines weight ratio on viscosity was evaluated. These results are shown as the first 16 entries in Table 18, and in Figure 6. The minimum viscosity occurs in the range 50/50 to 60/40. The 55/45 ratio was used as a baseline for other work with this coal and resin.

These slurries are pourable fluids. When poured from the mixer bowl to storage jars, the carrier reverts to its plastic state (with its yield point) at rest and the slurry eventually becomes a non-pourable plastic mass. Under very slight agitation the slurry again becomes a fluid exhibiting its original viscosity. Measurements of viscosity at high shear rates reveal values in the range of 500 to 1000 cp at an apparent shear rate of 3000 sec^{-1} , so the slurries are easily pumped fluids. The major operations problem is priming the pump. It is believed that pumps for large tanks may require an auger on the suction side to maintain the prime. Large screw pumps (progressing cavity type) designed for pumping slurries are commercially available with an auger-type suction stage (cf. Moyno).

An attempt to prepare a 70% slurry with a 55/45 ratio of 123 micron coarse and 30 micron fines in a 2.5% starch solution yielded a thick dough-like slurry having a viscosity of 38 Kp. Dispersants were evaluated to reduce viscosity, the most effective being Tamol SN. At levels of 1% in the carrier (3/7% of the coal) the viscosity is reduced to ~1.5 Kp. However, slurries based on 2.5% starch solutions are not, of course, as stable as those based on 3% starch, since the yield point of the former is only 1.2 dynes/cm^2 , which is below the value that is estimated to be necessary for stability. The 70% slurry with 1% Tamol SN and 3% starch (Mix #362) has a viscosity of 5.1 Kp, which is getting pretty thick. Also, the use of a dispersant along with the starch significantly increases cost (Tamol SN costs ~50¢/lb, Hamaco 267 costs ~27¢/lb). The unit cost of starch in a 65% slurry (carrier is 3% starch) is 0.44¢/lb coal. The unit cost of starch and dispersant in a 70% slurry (carrier is 2.5% starch + 1% dispersant) is 0.50¢/lb coal. The unit cost of HEC (at \$1.60/lb HEC) in a 70% slurry is 0.34¢/lb coal (carrier is 0.5% HEC). Slurries made with

10²

Figure 6. Effect of Coarse/Fines Weight Ratio on Slurry Viscosity.

1. 65% PHS 361 Bituminous Coal
2. The carrier is a 3% solution of Hamaco 267 Modified Starch in Water
3. The Coarse/Fines Size Ratio is 123/30, w/w.

10

Slurry Viscosity, Kp (Brookfield, T-Bar @ 1 RPM)

Coarse/Fines Weight Ratio

0.1

80/20

60/40

40/60

20/80

0/100

2.5% starch solutions and 0.5% HEC solutions are roughly comparable in stability (the former is measurably more stable, but also measurably unstable), so the HEC slurries are preferable. It is the opinion here that 3% starch solutions are required for acceptable stability, and that the best way to obtain 70% loadings is through use of larger particles.

Evaluation of coarse sizes of 133 micron, 148 micron, and 173 micron in 70% slurries indicated that viscosity decreases as size increases, as expected. Only one mix was made with 148 micron coarse, and the slurry viscosity was essentially comparable to that made with 173 micron (1.0 Kp vs 0.8 Kp). The 133 micron coarse is the -50 mesh product of a 74% -50 mesh mill product. The 148 and 173 micron coarse are unsieved mill products, and have size consists of 79% -50 mesh and 74% -50 mesh respectively. In 70% slurries having a 65/35 coarse/fines weight ratio, the fraction of coal that is $>300\mu$ is 13.6 and 16.9% for the 148 and 173 micron coarse respectively. The best of the 70% slurries made with these coarse sizes had a viscosity of only 0.4 Kp, which is comparable in fluidity to the best of the 65% slurries, as well as the 70% slurries made with HEC.

When -50 mesh product is used for coarse, as in the 65% slurries, the +50 mesh fraction is accumulated and used as feed to make fines. The fines made with this feed have, oddly, a slightly larger MMD particle size than those made with -1/2 inch feed (36 micron vs 30 micron). Also paradoxically, 65% slurries made with these larger fines have measurably lower viscosities than those made with the smaller fines (0.2 Kp vs 0.42 Kp at 55/45 coarse/fines weight ratio). When 70% slurries are prepared with the larger fines, viscosity increases, as expected. This, of course, is a moot result, since no +50 mesh product would be available for the 70% slurries.

3.3.3.3 Evaluation of Dispersants

To quantify the feasibility of stable slurries, the properties of unstable slurries must be known. These slurries may or may not require a dispersant for fluidity, and continuous recirculation for uniformity. The cost impact of both items (dispersant and recirculation) needs to be computed for comparison with the cost of mixes stabilized with starch. Toward this end, the effect of various dispersants on slurry viscosity was evaluated. The dispersants selected are commercially available products used

for dispersing carbon blacks, clays, pigments, etc., and are listed in Table 19. When used to disperse very small particles, $\sim 1\mu$ in diameter, where surface forces are comparable to or greater than inertial forces, stable colloidal suspensions can be prepared. For the problem at hand, where the MMD of the slurry particles is $\gg 1\mu$, the use of dispersants results in very fluid mixes, having no stability towards settling.

Of the dispersants listed in the table, only Triton X-100 is non-ionic, and functions as a wetting agent. It is a polyethylene glycol (PEG) adduct of octylphenol. The PEG part of the molecule is water soluble while the aliphatic/aromatic part is either oil soluble or is adsorbed onto hydrophobic surfaces. Particles are thus "coupled" to water by the molecules. The other products are either sodium or calcium salts of organic acids, and ionize in solution. Hydrophobic surfaces become polarized and mutually repulsive by adsorption of the organic anions, and slurry (or colloid) is said to be deflocculated (or stabilized). Surface tension is generally unaffected by use of these compounds. Tamol SN is a petroleum derivative, called "a sodium salt of a condensed aryl-sulfonic acid." The products from American Can (Marasperse, Americo and Norlig) are wood derivatives, reclaimed as byproducts from paper manufacturing processes. The Norlig 11, which is the cheapest product, is essentially spent sulfite lignin, the active ingredient of which is the sodium salt of an organic sulfonic acid. The Marasperse products are processed sulfite lignins. Americo SD-1 is reclaimed from Kraft lignin, and contains no sulfur. The sulfur content of the sulfonic acid derivatives described above is typically $\sim 5\%$ by weight. Mix data are summarized in Table 20.

A 55/45 blend of coarse/fines was used for most of the work. At 70% loadings, slurries cannot be made with water as a carrier, or with Triton X-100 as a surfactant. All of the dispersants except Norlig 11 produced very fluid slurries, when used at the proper concentration. Tamol SN seems to be effective at 0.5% by weight of carrier ($\sim 0.2\%$ of coal), while the effective concentration of the others is 1% by weight of carrier. The unit cost of the use of Tamol SN, Marasperse CB)s-3 or 52 cp, or Americo SD-1 at their effective concentrations is $\sim 0.2\text{¢/lb}$ coal. Of these, the most interesting, in the opinion here, is Americo SD-1, because it contains no sulfur. Marasperse C-21, the calcium lignosulfonate is also interesting

Table 19. Properties and Prices of Dispersants

<u>Trade Name</u>	<u>Manufacturer</u>	<u>Generic Name or Type</u>	<u>Bulk Price ¢/lb</u>
Marasperse CBOs-3	American Can	Sodium lignosulfonate	28
Marasperse 52 cp	American Can	Sodium lignosulfonate	22
Marasperse C-21	American Can	Calcium lignosulfonate	12.5
Americo SD-1	American Can	Sodium lignin salt*	25
Norlig 11	American Can	Mixed lignosulfonate	2.1
Tamol SN	Rohm & Haas	Sodium arylsulfonate	49.5
Triton X-100	Rohm & Haas	Octylphenoxy polyethoxy ethanol	39

* Contains no sulfur.

Table 20. Mix Data for Coal/Water Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361) and Aqueous Solutions of Various Dispersants.

Mix ID	Coal Content, Wt. %	Coal Composition		Dispersant Content,* Wt. % of Carrier	End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio				
679-342	70	55/45	123/30	None	-	Yes	Dry mix
-347	70	55/45	123/30	0.1% Triton X-100	-	Yes	Dry Mix
-343	70	55/45	123/30	1.0% Triton X-100	-	Yes	Dry Mix
-349	70	55/45	123/30	0.1% Marasperse CBOs-3	28.5	Yes	Dry Mix
-351	70	55/45	123/30	0.5% Marasperse CBOs-3	3.6	Yes	Dry Mix
-352	70	55/45	123/30	1.0% Marasperse CBOs-3	1.7	Yes	
-355	70	55/45	123/30	2.0% Marasperse CBOs-3	0.04	Yes	
-351	70	55/45	123/30	0.5% Tamal SN	3.6	Yes	
-349	70	55/45	123/30	1.0% Tamal SN	0.02	Yes	
-353	70	55/45	123/30	2.0% Tamal S-N	0.02	Yes	
-356	70	0/100	123/30	2.0% Tamal SN	-	N/A	Dough-like mix
-358	70	55/45	123/30	1.0% Marasperse 52 cp	7.2	Yes	
-357	70	55/45	123/30	2.0% Marasperse 52 cp	0.07	Yes	
-361	70	55/45	123/30	1.0% Americo SD-1	20	Yes	
-359B	70	55/45	123/30	2.0% Americo SD-1	0.03	Yes	
-391	70	55/45	123/30	0.5% Norlig 11	22	Yes	
-388	70	55/45	123/30	1.0% Norlig 11	14	Yes	
-386	70	55/45	123/30	2.0% Norlig 11	3.6	Yes	
-387	70	55/45	123/30	4.0% Norlig 11	23	Yes	
686-379	70	55/45	123/30	2.0% Marasperse C-21	0.11	Yes	

Table 20 (continued)

Mix ID	Coal Content, Wt. %	Coal Composition		Dispersant Content,* Wt. % of Carrier	End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio				
686-380	70	55/45	123/30	3.0% Marasperse C-21	0.18	Yes	
686-510	65	55/45	123/30	None	5.0	Yes	Dilatant
-498	65	55/45	50/30	1.0% Americo SD-1	.0064	Yes	Viscosity measured with cylindrical spindle, T-bar vis. = .016 Kp.
-503	65	100/0	50/30	None	26	Yes	Stiff dilatant mass
-504	65	100/0	50/30	1.0% Americo SD-1	.0095	Yes	Viscosity measured with cylindrical spindle, T-bar vis. = .0088 Kp.
721-68	70	100/0	50/30	1.0% Americo SD-1	-	-	Dry mix.

*Note the dispersant content is expressed as Wt. % of carrier. This is a quirk of the methodology used here. The usual practice is to express dispersant content as wt. % of solids.

because CaSO_4 would be the principal sulfur combustion product at stack gas temperatures, and would be removable. Slurries made with this dispersant are, however, significantly more viscous than those made with the other dispersants, though still very fluid.

At the 65% loadings, coal/water slurries are viscous but may be of interest. With Americo SD-1 at 1% of the carrier, the slurries are extremely fluid. At this loading, a fluid slurry is got with a "standard grind" coal size consist of 77% -200 mesh (mix 504, Table 20), having a viscosity of 9.5 poise. The 70% slurry with this size consist and a 1% aqueous solution of Americo SD-1 as the carrier is a dry mix.

It should be noted that these slurries are extremely unstable with respect to settling. Although the slurries are very fluid, viscosity must be measured immediately after mix preparation. Noticeable settling takes place within an hour after mixing, and hard packing takes place after standing a few hours. The hard-packed slurries can be remixed, with effort, to original consistency.

3.3.4 Evaluation of Coal/Water Slurries Containing Wyoming Subbituminous Coal (PSOC 846)

Evaluation of this coal was limited to slurries containing hydroxypropylated starch solutions. Mix data are given in Table 21. With coarse/fines MMD size ratio of $135\mu/27\mu$, 65% slurries are too viscous for practical use. The 60% slurries are pourable fluids, and the best coarse/fines weight ratio is in the range 55/45 to 75/25. All of the coarse size is the sieved, -50-mesh, product from the mill run that yields 74% -50 mesh. Coal loadings of 65% were obtained in fluid slurries with unsieved coarse having an MMD size 265 micron (55% -50 mesh size consist). At a 55/45 coarse/fines blend, 25% of the coal is $>300\mu$ in a 65% slurry. This coal as well as the other subbituminous and the lignite, is biodegradable and require a preservative for preservation and prevention of outgassing in water slurries. Formaldehyde, at a level of 1000 ppm coal was found satisfactory for preservation. This level of formaldehyde is also used to preserve starch solutions. It is believed that the lower loadings achieved here (relative to bituminous) are due to porosity. As received coal was used, and its moisture content was probably less than the equilibrium value.

Table 21. Mix Data for Coal/Water Slurries Comprised of Wyoming Subbituminous Coal (PSOC 846) and Aqueous Solutions of Modified Corn Starch (Hamaco 267, Staley).

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition, Wt. %		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Starch	Other			
679-287	65	55/45	135/37	3	.01% Triton X100	9.1	Yes	
-288	65	65/35	135/37	3	.01% Triton X100	7.5	Yes	
-289	65	75/25	135/37	3	.01% Triton X100	7	Yes	
-290	65	85/15	135/37	3	.01% Triton X100	7	Yes	
-291	65	100/0	135/37	3	.01% Triton X100	8	Yes	
686-517	60	55/45	135/37	3	.01% Triton X100	0.7	Yes	
-518	60	65/35	135/37	3	.01% Triton X100	0.85	Yes	
-519	60	75/25	135/37	3	.01% Triton X100	0.80	Yes	
679-295	60	100/0	135/37	3	.01% Triton X100	2.4	Yes	
-296	60	0/100	135/37	3	.01% Triton X100	2.9	Yes	
686-370	70	55/45	265/37	3	.01% Triton X100	26	No	
-521	65	55/45	265/37	3	.01% Triton X100	1.8	No	
-522	65	65/35	265/37	3	.01% Triton X100	1.8	No	
-523	65	75/25	265/37	3	.01% Triton X100	2.1	No	
-520	60	55/45	265/37	3	.01% Triton X100	0.26	No	

3.3.5 Evaluation of Coal/Water Slurries Containing Iowa Subbituminous Coal (PSOC 664)

Mix data for these slurries is summarized in Table 22. Very little work was carried out. Slurries of this coal in water have an acid pH (2.6), which were neutralized with NH_4OH . Also, formaldehyde at 1000 ppm coal was added as a preservative. A coal loading of 60% in 3% starch solution is the only composition of interest. This was a fluid pourable stable slurry. All particles in this slurry are $<300\mu$.

Attempts to make 65% slurry with larger coarse (220 micron) did not yield fluid slurries, although they were more tractable than the slurry made with 115 micron coarse. It is believed that this coal is fairly porous, and the particles in the size range studied here act like a sponge, destroying any benefit to be got from size distribution. It seems as though the particles are porous through the entire particle mass. Perhaps high loadings could be attained through use of very large particles where only the surface can interact with the carrier.

3.3.6 Evaluation of Coal/Water Slurries Containing Montana Lignite (PSOC 837)

These slurries were prepared with starch solutions as the carrier. Mix data are given in Table 23. The best solids loading that could be prepared in fluid slurries was only 55%. It is doubtful that coarse/fines blends are of much help here. This coal exhibits the same absorption-like behavior observed for the two subbituminous. Although the use of large coarse lowered the viscosity of 60% slurries significantly, the resultant slurries, with viscosities of 10 Kp, are too viscous for feasibility. At 55% solids, a "standard grind" (e.g. 80% -200 mesh) would probably give as good results as those obtained here with the coarse/fines blends.

These slurries gave picturesque results in storage. All of the slurries were preserved with formaldehyde at 1000 ppm coal except one, which overpressured in storage, rupturing its glass container. All of the slurries exhibited yellow and white precipitates dappled on the surface, in storage. The yellow is believed to be sulfur and the white is believed to be an inorganic salt left by water evaporation. It is not uncommon to find beads of condensate on the jar wall or on the surface of slurries, due to surface evaporation.

Table 22. Mix Data for Coal/Water Slurries Comprised of Iowa Subbituminous Coal (PSOC-664) and Aqueous Solutions of Modified Corn Starch (Hamaco 267, Staley).

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition		End of Mix Viscosity, Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Starch	Other			
679-327	60	55/45	115/31	3	.01% Triton X100	1.4	Yes	Neutralized with NH_4OH
-328	65	55/45	115/31	3	.01% Triton X100	>100	Yes	Neutralized with NH_4OH
-329	60	55/45	115/31	2.5	.01% Triton X100	14	Yes	Neutralized with NH_4OH
-330	65	55/45	115/31	2.5	.01% Triton X100	>100	Yes	Neutralized with NH_4OH
686-374	65	55/45	220/31	3	.01% Triton X100	52	No	Neutralized with NH_4OH
-377	65	55/45	220/31	3	.01% Triton X100 + 1% Tamal SN	70	No	Neutralized with NH_4OH

Table 23. Mix Data for Coal/Water Slurries Comprised of Montana Lignite (PSOC 837) and Aqueous Solutions of Modified Corn Starch (Hamaco 267, Staley).

Mix ID	Coal Content, Wt. %	Coal Composition		Carrier Composition		End of Mix Viscosity Kp	Sieved Coarse	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio	Starch	Other			
679-315	65	55/45	120/30	3	.01% Triton X100	-	Yes	Dry mix
-316	60	55/45	120/30	3	.01% Triton X100	6.2	Yes	Set-back in storage
-318	60	65/35	120/30	3	.01% Triton X100	22	Yes	Set-back in storage
-319	60	75/25	120/30	3	.01% Triton X100	38	Yes	Set-back in storage
-317	60	0/100	120/30	3	.01% Triton X100		Yes	Dry mix
-320	60	55/45	120/30	2.5	.01% Triton X100	20	Yes	Set-back in storage
-321	55	55/45	120/30	3	.01% Triton X100	3.8	Yes	
-322	55	65/35	120/30	3	.01% Triton X100	3.1	Yes	
-323	55	75/25	120/30	3	.01% Triton X100	2.0	Yes	
-324	55	55/45	120/30	2.5	.01% Triton X100	0.68	Yes	
-325	55	65/35	120/30	2.5	.01% Triton X100	2.2	Yes	
-326	55	75/25	120/30	2.5	.01% Triton X100	1.8	Yes	
686-373	60	55/45	345/30	3	.01% Triton X100	9.1	No	
-376	60	55/45	345/30	3	.01% Triton + 1% Tamal SN	10.5	No	

3.3.7 Evaluation of Coal/Oil/Water Slurries Comprised of Pittsburgh Seam Bituminous Coal and No. 6 Oil.

The oil-in-water (o/w) emulsions of No.6 oil, water, and an emulsifier were evaluated as carriers in slurries. Two emulsifiers were evaluated: Amarico SD-1 (Am. Can) and Brij 35 (ICI). Although both form o/w emulsions which have the consistency of mayonnaise and are stable without separation or creaming in 160°F storage, those made with Americo SD-1 were found to break when slurried with coal and stored at 160°F. Those made with Brij 35 seemed more stable in slurries. Results are discussed below.

A preliminary number of slurries were made up with coal and No. 6 oil at coal loadings of 50 - 70%. The mix data are given in Table 24. The slurries were prepared with a "standard grind" coal size consist of 77% -200 mesh and with a 55/45 coarse/fines blend of 123 micron coarse and 30 micron fines. All of the particles in the coarse are <300μ. The data show that, at comparable viscosities, coal loadings with the blend are about 5% greater than those with the standard grind. None of the slurries were stable.

The primary selection criterion for use of emulsions as carriers was to make slurries of coal, oil, and water with a water content of 10% by weight. Thus, at coal loadings of 50, 55, 60, 65, and 70%, the emulsions of interest have oil/water ratios of 4/1, 3.5/1, 3/1, 2.5/1, and 2/1 respectively. The preparation of these emulsions has been discussed previously. Mix data for slurries made with emulsified carriers, for which Americo SD-1 was used as the emulsifier are summarized in Table 25. Slurries were prepared with 50 micron coal (standard grind), a 55/45 blend of 125μ/30μ, and an unsieved 55/45 blend of 173μ/30μ. While the mix data show the beneficial effects of particle size distribution on viscosity, it was noted that none of these slurries were stable. The slurries were prepared at 150°F in a planetary mixer and stored at 160°F in a closed pint jar. The samples were removed from the oven daily and observations of settling were made. All of the samples were found to be unstable with respect to settling, as evidenced by the appearance of a fluid supernatant above hard packing. Inclusion of carbon black as a way to stabilize the emulsion did not stabilize the slurries.

Table 24. Mix Data for Coal/Oil Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361) and No. 6 Oil (Texaco).

Mix ID	Coal Content, Wt. %	Coal Composition		End of Mix Viscosity Kp	Temp, °F	Remarks
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio			
679-341	50	100	50	0.02	134	Coal size consist is 77% -200 mesh
-344	55	100	50	0.11	130	Coal size consist is 77% -200 mesh
-345	60	100	50	0.9	134	Coal size consist is 77% -200 mesh
-360	65	100	50	4.8	146	Coal size consist is 77% -200 mesh
-346	55	55/45	123/30	0.04	136	Sieved coarse (-50 mesh)
-340	60	55/45	123/30	0.17	134	Sieved coarse (-50 mesh)
-339	65	55/45	123/30	1.5	136	Sieved coarse (-50 mesh)
-338	70	55/45	123/30	22	142	Sieved coarse (-50 mesh)

Table 25. Mix Data for Coal/Oil/Water Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361), and O/W Emulsions of No. 6 Oil (Texaco) in Tap Water. Americo SD-1 (Am. Can) is the Emulsifier.

Mix ID	Coal Content, Wt. %	Coal Composition		Emulsion ID	Emulsion Composition				Carbon Black (Regal 400) PPH (O+W)	End of Mix Viscosity Kp	Temp, °F	Sieved Coarse
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio		Oil Parts	Water Parts	Emulsifier,* PPH (O+W)					
686-428	60	100	50	415	3	1	2	-	0.4	150	N/A	
-426	60	55/45	123/30	415	3	1	2	-	0.18	150	Yes	
-427	65	55/45	123/30	412	2.5	1	2	-	6.0	150	Yes	
-429	65	55/45	173/30	412	2.5	1	2	-	0.5	150	No	
-475	60	100	50	471	3	1	1	1	2.4	150	N/A	
-476	60	100	50	472	3	1	1	2	1.6	150	N/A	
-467	60	100	50	460	3	1	2	1	2.0	150	N/A	
-468	60	100	50	459	3	1	2	2	0.75	150	N/A	

* PPH(O + W): Parts per hundred of oil + water

The supernatant is fluid and black in color like oil (as opposed to the rust/brown color of either an o/w or w/o emulsion), and a drop of it swirled in water forms a blot on the cup wall, indicating that it is oil, rather than an emulsion. Evidently the coal is reacting with the emulsion to cause a destruction of its mayonnaise-like properties. It is postulated that the Americo SD-1 is adsorbed out of solution into the coal surface, thereby coupling the water because of its good water-binding property. The result is that both components are removed from the emulsion by adsorption. It is evident from an examination of the entire supernatant that there is no water present, because water here in the absence of the dispersant would appear as a separate layer since such a w/o emulsion is unstable. The miscibility test indicates absence of the dispersant.

From these results, it is believed that an emulsifier having a hydrophobe with a greater affinity for oil than for coal is required to prepare emulsions which are stable in the presence of coal. For this reason, Brij 35 was used to prepare emulsions, as described previously. This emulsifier is described by the manufacturer (ICI) as polyoxyethylene (23) lauryl ether. The hydrophile is a 23-member polyethylene glycol, and the hydrophobe is dodecane (C_{12}). Mix data for use of these emulsions as carriers in slurries are summarized in Table 26. These mixes were prepared at room temperature and stored at 160°F. When first placed in the oven, the mixes foam (they were not vacuum mixed). The foams break easily with remixing and the slurries do not re-foam when returned to storage. Remixing must be rapid because water is volatile at 160°F. The foamed and remixed slurries seem to be relatively stable: none exhibit hard pack settling. Comparing the standard grind and the bimodal blend indicates the latter results in much lower viscosities at 50 and 60% loadings, as expected. The 60% slurries are much more viscous than those prepared with Americo SD-1, but this may be due to latter emulsions having broken. Viscosities of the 65% slurries are comparable with either emulsifier. It is concluded from these data that 60% is the maximum usable loading for all particles $<300\mu$.

Table 26. Mix Data For Coal/Oil/Water Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361), and O/W Emulsions of No. 6 Oil (Texaco) in Tap Water. Brij 35 (ICI) is the Emulsifier.

Mix ID	Coal Content, Wt. %	Coal Composition		Emulsion ID	Emulsion Composition			End of Mix Viscosity Kp	Temp, °F	Sieved Coarse
		Coarse/Fines Wt. Ratio	Coarse/Fines MMD Size Ratio		Oil, Parts	Water, Parts	Emulsifier PPH (o+w)			
686-497	50	100	50	491	4	1	1	0.17	156	N/A
-495	50	55/45	123/30	491	4	1	1	0.06	153	Yes
-482	50	55/45	123/30	466	3	1	1	0.09	160	Yes
-481	50	55/45	123/30	465	3	1	2	0.13	160	Yes
-483	50	55/45	123/30	455	2.5	1	2	0.12	160	Yes
-484	50	55/45	123/30	456	2.5	1	4	0.2	160	Yes
-494	55	55/45	123/30	490	3.5	1	1	0.21	154	Yes
-480	55	55/45	123/30	465	3	1	2	0.33	162	Yes
-470	60	100	50	466	3	1	1	17.5	160	N/A
-489	60	55/45	123/30	466	3	1	1	1.6	160	Yes
-469	60	100	50	465	3	1	2	28.5	160	N/A
-479	60	55/45	123/30	465	3	1	2	1.6	160	Yes
-496	65	55/45	173/30	488	2.5	1	1	7.4	160	Yes
-492	65	55/45	173/30	455	2.5	1	2	4.7	160	Yes

3.4 Measurements of Slurry Viscosity With an Extrusion Tube Rheometer

3.4.1 Results

Rheological properties of slurries made with aqueous 3% solutions of hydroxypropylated corn starch were determined by extrusion tube rheometry for the following solids loadings: (1) 65% and 70% Pittsburgh seam bituminous coal (PHS 361) at coarse/fines size ratios of $123\mu/30\mu$ and $173\mu/30\mu$ respectively, and (2) 60% and 65% Wyoming subbituminous coal (PSOC 846) at coarse/fines size ratios of $135\mu/37\mu$ and $265\mu/37\mu$ respectively. Each composition was evaluated at coarse/fines weight ratios of 55/45, 65/35, and 75/25. Results are summarized in Tables 27 and 28, and the rheograms are given in Appendix D (27 to 34). Shear stress, $\Delta P/4L$ (psi), and viscosity, μ (cp), are expressed as power-law functions of apparent shear rate, $8 V/D$ (sec^{-1}). Values of viscosity at 3000 sec^{-1} are given as a figure-of-merit. The range of shear rate over which these data apply is $\sim 10^2 - 10^4 \text{ sec}^{-1}$. All of these slurries were prepared by vacuum mixing prior to evaluation.

For slurries containing the bituminous coal, it was found that viscosity (μ_{3000}) decreases with coarse/fines weight ratio in 65% slurries, to a minimum of ~ 800 cp at a weight ratio $< 75/25$. However, in 70% slurries μ_{3000} decreases with increasing coarse/fines weight ratio to a minimum of 571 cp at weight ratio of 75/25. For slurries containing the subbituminous coal, minimum μ_{3000} is found at a coarse/fines weight ratio of 65/35 for both the 60 and 65% loadings, being 643 cp at 60% and 632 cp at 65%. All of these slurries are pseudoplastic in this range of shear rates, particularly those made with the subbituminous coal.

The range of values of μ_{3000} is seen to extend from a low of 571 cp to 1137 cp. There is a significant effect of particle size distribution (i.e., coarse/fines weight and size ratios) on viscosity, though not necessarily predictable. With one exception, the highest values of coarse/fines weight ratios (i.e., 75/25) results in the most pseudoplastic slurries (i.e., minimum values of n , the exponent of apparent shear rate, decreasing values of which correspond to increasing pseudoplasticity). The exception was the 60% subbituminous slurry. Minimum n occurred at a 65/35

Table 27. Summary of Rheological Properties of Coal/Water Slurries Containing Pittsburgh Seam Bituminous Coal (PHS 361)

Mix ID	Slurry Composition, Wt. % (A)					Coal Composition Wt. % of Coal With Indicated MWD Particle Size (μ)			Weight - Avg. Coal Particle Size, μ	Wt. % of Coal That is >300μ	End of Mix Viscosity, Brookfield T-Bar at 1 RPM, Kp	Rheological Constants (B)			
	Coal	Water	Modified Starch	Wetting Agent	Biocide	173	123	30				τ ₁ , Psi	μ ₁ , cp	n	η ₃₀₀₀ cp
438	65	33.9	1.05	0.0035	0.035		55	45	53	0	0.31	7.88·10 ⁻⁴	5050	0.77	801
478A	65	33.9	1.05	0.0035	0.035		65	35	67	0	0.79	2.58·10 ⁻⁴	1740	0.90	781
491A	65	33.9	1.05	0.0035	0.035		75	25	85	0	0.50	2.28·10 ⁻³	13900	0.66	914
430	70	29.1	0.9	0.003	0.03	55		45	74	14.3	0.57	4.26·10 ⁻⁴	2840	0.88	1090
411	70	29.1	0.9	0.003	0.03	65		35	100	16.9	0.50	3.21·10 ⁻⁴	2140	0.88	819
435	70	29.1	0.9	0.003	0.03	75		25	125	19.5	0.59	8.56·10 ⁻⁴	5370	0.72	571

(A) 1. Modified starch is hydroxypropylated corn starch (Hamaco 267, Staley)

2. Wetting agent is Triton X-100 (Rohm and Haas)

3. Biocide is formaldehyde

(B) 1. $\tau = \tau_1 S^n$, psi

2. $\mu = \mu_1 S^{n-1}$, cp

3. S = apparent shear rate, sec^{-1}

= $8 V/D$ for tubes

V = fluid velocity

D = tube diameter

4. μ_{3000} = viscosity, cp, @ $S = 3000 \text{ sec}^{-1}$

Table 28. Summary of Rheological Properties of Coal/Water Slurries Containing Wyoming Subbituminous Coal. (PSOC 846).

Mix ID	Slurry Composition, Wt. % (A)					Coal Composition Wt. % of Coal With Indicated MMD Particle Size (μ)			Weight - Avg. Coal Particle Size, μ	Wt. % of Coal That is >300μ	End of Mix Viscosity, Brookfield T-Bar at 1 RPM, Kp	Rheological Constants (B)			
	Coal	Water	Modified Starch	Wetting Agent	Biocide	265	135	37				τ ₁ Psi	μ ₁ cp	n	η ₃₀₀₀ cp
517	60	387	1.2	0.004	0.1		55	45	67	0	0.7	1.38·10 ⁻³	8690	0.72	924
518	60	287	1.2	0.004	0.1		65	35	80	0	0.85	1.75·10 ⁻³	10600	0.65	643
519	60	387	1.2	0.004	0.1		75	25	95	0	0.8	1.09·10 ⁻³	6940	0.75	938
521	65	33.85	1.05	0.0035	0.1	55		45	92	25	1.85	2.84·10 ⁻³	17300	0.66	1137
522	65	33.85	1.05	0.0035	0.1	65		35	130	29	1.89	4.04·10 ⁻³	23200	0.55	632
523	65	33.85	1.05	0.0035	0.1	75		25	175	34	2.1	9.92·10 ⁻³	54800	0.50	1000

(A) 1. Modified starch is hydroxypropylated corn starch (Hamoco 267, Staley)

2. Wetting agent is Triton X-100 (Rohm and Haas)

3. Biocide is formaldehyde

(B) 1. $\tau = \tau_1 S^n$, psi

2. $\mu = \mu_1 S^{n-1}$, cp

3. S = apparent shear rate, sec^{-1}

= $8 V/D$ for tubes

V = fluid velocity

D = tube diameter

4. η_{3000} = viscosity, cp, @ $S = 3000 \text{ sec}^{-1}$

coarse/fines weight ratio. The coarse/fines size ratio in this slurry was also the lowest of all those evaluated. This observation seems academic, however. The slurries exhibiting minimum viscosity were not necessarily the most pseudoplastic.

Attempts to measure viscosity of slurries based on HEC solutions were unsuccessful. These slurries are not thixotropic, and the data were well-behaved, but indicated that all of the measured pressure drop occurred at the entrance. This is in spite of the fact that the slurries are fluid and easy to extrude. Examination of the feed chamber after extrusion runs indicated considerable accumulation of material at the tube entrance. The follower plate in the feed chamber could not be seated to extrude this material. Evidently, these slurries behave as free-flowing powders rather than fluids, and exhibit bridging at entrances or other sudden changes in cross-section.

Slurries based on solutions of dispersants, although very fluid, could not be evaluated in our test equipment because of too-rapid settling. A well-stirred feed chamber is required for these slurries.

The slurry (Mix ID 510) comprised of 65% Pittsburgh seam bituminous coal (PHS 361) at a coarse/fines size ratio of 123 μ /30 μ and weight ratio of 55/45 in a water carrier containing neither dispersants nor resin was evaluated with partial success. This slurry does not settle as fast as those with dispersants. All the data were scattered around the short tube line, and indicate a surprisingly pseudoplastic fluid, for which

$$\frac{\Delta P}{4L} = 1.81 \times 10^{-3} \left(\frac{8V}{D} \right)^{0.68} \text{ psi,}$$

$$\mu = 11142 \left(\frac{8V}{D} \right)^{-0.32} \text{ cp,}$$

and $\mu_{3000} = 860 \text{ cp.}$

3.4.2 Discussion

1. No correlation was found between T-bar viscosities and those from the extrusion rheometer. This was to be expected. As noted previously,

the T-bar values are uncorrected for non-Newtonian flow, and are at extremely low shear rate, estimated to be $\ll 1 \text{ sec}^{-1}$. Probably, if some of the mixes found to be very viscous with the Brookfield had been evaluated in the extrusion rheometer, a qualitative correlation could be found.

2. The use of Bingham fluids as carriers is believed to improve the flow properties of slurries, especially highly loaded ones. At high solids loadings, slurries in flow tend to behave as flowing powders. At sudden contractions or sudden increases in shear rate either bridging or high pressure drops occur. Bridging stops the flow, resulting in extrusion of the carrier through the packed bed of solids. Both phenomena have been observed here in work to evaluate unstable slurries. 70% slurries of coal in a water solution of a dispersant exhibit very low apparent viscosities ($< 0.1 \text{ Kp}$) at very low shear rates (Brookfield viscometer fitted out with T-bar spindles), yet cannot be poured from a beaker because of bridging. Also, extrusion rheometry of 70% slurries of coal in a 0.5% solution of hydroxyethyl cellulose in water reveal pressure drop through the instrument to be independent of tube length, indicating that all of the pressure drop occurs at the entrance to the tubes. This is in spite of the fact that the slurries are pourable fluids of low apparent viscosity. When slurries are prepared with a carrier that has a yield point, the entrance effects of the extrusion rheometer are found to be negligible, in keeping with predictions from engineering equations for fluid flow at sudden contractions. It is concluded that the yield point causes the slurry to behave as a fluid in flow conditions. It seems that a yield point is necessary for the preparation of tractable (i.e., pumpable as well as stable) slurries. Possibly, the yield point prevents flow separation and permits the particles to be carried along at the same velocity as the carrier. The most economical way to prepare Bingham fluids is by use of resins. The use of very finely ground coal ($\sim 1-2 \mu \text{ MMD}$) to form a lyophobic dispersion where surface forces predominate, would also behave as a Bingham fluid.

3. Finally, the importance of vacuum mixing must be emphasized. Carriers that have yield points result in foamy slurries with ambient-pressure mixing. Slurries in this state of aggregation are compressible. Because of the way an extrusion rheometer works, compressibility is manifest in the reduced data as a ΔP_E , which is in actuality an entrance length

effect. These values of ΔP_E are a significant fraction of the total, amount- to 15-30% ΔP_T , and therefore result in too-small values of $D\Delta P/4L$ and μ . Vacuum mixing has not been found to be necessary for slurries made with carriers that have no yield point, but is good practice.

3.5 Measurements of Slurry Stability

3.5.1 General

Samples were prepared and stored and measurements of CG were taken at given time intervals in storage. Following these tests, measurements of the supernatant that had accumulated on the samples during storage were made, and the samples probed with a thin rod to qualitatively assess the presence of settling. The samples were not probed until the end of time-in-storage, which was generally 1 or 2 months. All three parameters were used in evaluating the slurries.

During the course of these tests, it was observed that the column length of slurry decreased with time. This shrinkage amounts to 1-2% of the initial column length (or volume) over the period of 1-2 months storage, and is evidenced not only by measurements of column length, but also by significant decreases in period (T_2) around the lower pendulum supports. For this reason, normalized values of CG were used, and the results expressed in terms of X_s/L_s , where L_s = slurry column length. The normalized CG shift, ΔCG_n , was expressed as

$$\Delta CG_n = \frac{(X_s/L_s) - (X_s/L_s)_o}{(X_s/L_s)_o} \quad (22)$$

where $(X_s/L_s)_o$ is the initial value, at zero time. Theoretically, X_s/L_s is always 0.5 for a freshly cast slurry and for stable slurries, and this was found to be the case in these measurements, to an accuracy of $\pm 1\%$. Thus as a figure of merit, any slurry was accepted as stable if

$$\Delta CG_n < \pm 1\% \quad (23)$$

It is believed that shrinkage is caused by outgassing of the slurry with time, caused by slight biological degradation of the coal. This reaction takes place in a closed container, because the tubes were corked in storage, with a build-up in pressure. The resultant biodegraded

slurry is porous and compressible. Some of the more reactive coals popped their corks in storage at ambient temperature. The final slurries were prepared with enough preservative (formaldehyde) to prevent this from happening, and to enable practical use. However, all of the tubes exhibited the presence of pinhead-sized gas bubbles indicating that slight degradation was present in these slurries.

It is the opinion here that the coal degradation with consequent slight gas evolution seriously compromises the results of these stability tests because of the effect of the third component (the gas) on $\Delta C G_n$. If the gas bubbles are unevenly distributed throughout the column of slurry, their presence can mask settling. If the gas is uniformly distributed, then its effect on $\Delta C G_n$ is obviated. When gas bubbles are observable, they appear to be uniformly distributed and of uniform size. They can only be observed, when/if they appear, on the tube walls, so this observation is qualitative. The pendulum test results presented below are interpreted on the basis of no effect of coal degradation on $\Delta C G_n$.

3.5.2 Experimental Results

Values of X_s/L_s were measured for the first few days of storage and periodically thereafter, in some cases up to 74 days. With the exception of two slurries, all of the coal/water slurries contained a 3% hydroxypropylated corn starch solution as the carrier. The two exceptions were a two-component slurry of 65% coal in water, and a slurry of 65% coal in aqueous dispersant solution. Slurries of coal in oil and coal in emulsified carriers were also evaluated. The results are summarized in Tables 29, 30, and 31.

Values of $\Delta C G_n$ at the longest time interval in storage for which measurements were taken are given along with estimates of the maximum storage time during which stability ($\Delta C G_n < \pm 1\%$) is maintained. Also given are measurements of supernatant volume, in units of volume % of total volume (supernatant + slurry). In most cases, these are small values, and are believed to be condensate from surface evaporation. At the end-of-storage-time, the slurries were probed with a long narrow rod ($\sim 1/16$ " diameter) for a qualitative assessment of general settling and for evidence

Table 29. Summary of Stability Data for Slurries Comprised of Pittsburgh Seam Bituminous Coal (PMS 361) and Aqueous Carriers: The Stability Criterion is Normalized Center of Gravity Shift, ACG_n .

Tube ID	Mix ID	Slurry Composition, Wt. %*						Coal Composition, Wt. % of Coal with Indicated MMD Particle Size (μ)					Wt. - Average Coal Particle Size, μ	Wt. % of Coal That is $>300\mu$	End of Mix Viscosity Kp	Days in Storage	ACG_n %	Super-natant Vol. %	Evidence of Settling from Probe	
		Coal	Water	Modified Starch	Dispersant	Wetting Agent	Biocide	173	123	50	30	36							Hard Pack	General Settling
30	504	65	34.35	-	0.65	-	-			100			50	0	0.0095	1	3.3	22	Yes	Yes
31	510	65	35	-	-	-	-		55		45		53	0	5.0	1	0.8	4.3	No	Yes
12	445	65	33.9	1.05	-	.0035	.035		55		45		53	0	0.25	74	1.0	1.5	No	Yes
27	438	65	33.9	1.05	-	.0035	.035		55		45		53	0	0.31	45	0.4	2.8	No	Yes
16	446	65	33.9	1.05	-	.0035	.035		65		35		67	0	0.57	74	2.3	1.4	No	Yes
17	524	65	33.9	1.05	-	.0035	.035		65			35		0		32	1.6	0.92	No	Yes
25	478A	65	33.9	1.05	-	.0035	.035		65			35		0	0.15	45	0	4.6	No	Yes
17	447	65	33.9	1.05	-	.0035	.035		75		25		85	0	0.79	74	-2	1.7	No	Yes
18	447	65	33.9	1.05	-	.0035	.035		75		25		85	0	0.79	70	1.0	1.2	No	Yes
18	493A	65	33.9	1.05	-	.0035	.035		75			25	85	0	0.50	45	-0.4	6.0	No	Yes
29	430	70	29.1	0.9	-	.003	.03	55			45		74	14.3	0.57	38	-4	3.4	No	Yes
12	430	70	29.1	0.9	-	0.003	0.03	55			45		74	14.3	0.57	48	0.0	3.4	No	Yes
19	439	70	29.1	0.9	-	0.003	0.03	55			45		74	14.3	0.57	73	-8	2.8	No	Yes
20	439	70	29.1	0.9	-	0.003	0.03	55			45		74	14.3	0.57	73	1.0	2.4	No	Yes
33	411	70	29.1	0.9	-	0.003	0.03	65			35		100	16.9	0.50	48	-0.2	4.5	No	Yes
10	440	70	29.1	0.9	-	0.003	0.03	65			35		100	16.9	0.50	73	0.6	1.9	No	Yes
35	415	70	29.1	0.9	-	0.003	0.03	75			25		125	19.5	0.59	43	-0.8	5.8	No	Yes

*1. Modified starch is hydroxypropylated corn starch (Hamaco 267, Staley)

2. Dispersant is America SD-1 (Am. Can)

3. Wetting Agent is Triton X-100 (Rohm & Haas)

4. Biocide is formaldehyde

Table 30. Summary of Stability Data for Slurries Comprised of Wyoming Subbituminous Coal and 3% Aqueous Solutions of Modified Starch.

Tube ID	Mix ID	Slurry Composition, Wt. %*					Coal Composition, Wt. % of Coal With Indicated MMD Particle Size(μ)			Wt. % of coal that is $>300\mu$	End of Mix Viscosity Kp	Days in Storage	ΔCG_n	Super-natant Vol. %	Evidence of Settling From Probe		
		Coal	Water	Modified Starch	Wetting Agent	Biocide	265	135	37						Hard Pack	General Settling	
1	517	60	38.7	1.2	.004	.1		55	45	67	0	0.7	46	0.8	3.0	No	No
8	519	60	38.7	1.2				75	25	95	0	0.8	46	-0.2	0.92	No	No
9	520	60	38.7	1.2			55		45	92	0	0.26	46	0.4	1.3	No	No
21	521	65	33.8	1.05	.0035	.1	55		45	92	25	1.85	46	0.8	0.43	No	No
22	522	65	33.8	1.05			65		35	130	29	1.80	46	0.7	3.2	No	No

1. Modified starch is hydroxypropylated corn starch (Hamaco 267, Staley)
2. Wetting agent is Triton X-100 (Rohm and Haas)
3. Biocide is formaldehyde.

Table 31. Summary of Stability Data for Slurries Comprised of Pittsburgh Seam Bituminous Coal (PHS 361) and Either No. 6 Oil or Emulsions of No. 6 Oil in Water.

Tube ID	Mix ID	Slurry Composition, Wt %						Coal Composition, Wt. % of Coal Indicated MMD			Weight Average Coal Particle Size (μ)	End of Mix Viscosity		Days in Storage @ 160°F	ΔCG _n %	Evidence of Settling From Probe	
		Coal	Oil	Water	Brij 35	Particle Size(μ)			KP	@ T, °F		Hard Pack	General Settling				
						123	50	30									
5	341	50	50	-	-	100			50	0.02	136	7	1.8	Yes	Yes		
6	497	50	39.6	9.9	0.5	100			50	0.17	156	5	-0.6	No	Yes		
14	495	50	39.6	9.9	0.5	55	45		53	0.06	153	7	3.1	No	Yes		
3	346	55	45	-	-	55	45		53	0.04	136	7	2.2	Yes	Yes		
11	494	55	34.65	9.9	0.45	55	45		53	0.21	154	7	3.1	No	Yes		
34	489A	60	29.7	9.9	0.4	55	45		53	1.6	154	7	1.4	No	Yes		

of hard packing. Slurries for which hard pack settling has occurred cannot be probed beyond the depth of the packing. Slurries which have undergone general settling but not hard packing exhibit increasing viscosity with probe depth.

3.5.2.1 Coal/Water Slurries containing Pittsburgh Seam Bituminous Coal (PHS-361)

The results for coal/water slurries containing PHS-361 bituminous coal are given in Table 29. The first entry is a slurry comprised of 65% coal pulverized to a size consist of 77% -200 mesh ($MMD = 50\mu$) and a 1% solution of Americo SD-1 in water. This is a very fluid slurry, and a very unstable one as the data show. Hard pack settling is found after 1 hour storage. Hourly readings were taken for this and the next slurry in the table, which is a 65% slurry with a bimodal size distribution in water. The viscosity of this slurry is high, and the stability is not too bad, considering the fact that no stabilizer was used.

The remainder of the slurries in the table were made with the aqueous starch solution. The coal loadings evaluated were 65 and 70%, at coarse/fines (C/F) weight ratio of 55/45, 65/35, and 75/25. Considering first the 65% slurries made with a C/F size ratio of $123\mu/30\mu$, good stability was found at the 55/45 and 75/25 weight ratios. Two of these slurries (438 and 437) showed essentially no CG shift. A probe of these slurries indicated, however, a general thickening with probe depth, and is evidence of settling. It should be noted here that when the slurries are probed, the stiffest part of the slurry is at the top. All of the slurries exhibit a small amount of supernatant, which is believed to be condensate from evaporation from the top centimeter or so of slurry volume. This "dried-out" volume is stiff to the probe. The thickening that is felt with probe depth is not great, but is easily perceptible. It should be recalled that these slurries are "loaded-to-the-limit", and that a slight change in solids loading that may be due to settling can result in a large increase in viscosity. None of these slurries exhibited hard pack settling.

The 65% slurries made with 36 micron fines exhibited inconsistent results. These slurries were prepared with C/F at ratios of 65/35 and 75/25. The fines are the result of using +50 mesh product from 3600 rpm

mill runs as the feed in a 13800 rpm mill run. One of the 65/35 C/F mixes (524) showed a significant ΔCG_n , similar to that found with 30 micron (mix 446). A second 65/35 C/F mix (478A) showed no CG shift, but a significant supernatant. Similar results were got for a 75/25 C/F mix (493A). None of these mixes exhibited hard packing, but all exhibit some general settling. The mixes may be considered similar in behavior to those made with 30 micron fines, but the appearance of a large supernatant in the two mixes noted above is puzzling.

The 70% slurries were all made with a C/F size ratio of $173\mu/30\mu$. In terms of ΔCG_n , all of these slurries are considered stable, with the 55/45 C/F weight ratio looking best. With the probe, all of these slurries exhibited some settling, none hard packed. The appearance of a supernatant seems more pronounced for these slurries than for the 65% slurries. It is possible that these compositions are more susceptible to "drying out".

All of these slurries, both 65 and 70%, evidenced slight out-gassing to varying extents, in the form of small uniformly distributed bubbles at the tube wall.

The following mixes were subjected to 1.5 gees vibration @ 60 Hz for 24 hours: (1) Mix 438 (65% coal, C/F = 55/45 weight ratio); (2) Mix 524 (65% coal, C/F = 65/35 weight ratio, = 123/36 size ratio); (3) Mix 493A (65% coal, C/F = 75/25 weight ratio, = 123/36 size ratio); (4) Mix 430 (70% coal, C/F = 55/45 weight ratio); (5) Mix 431 (70% coal, C/F = 65/35 weight ratio), and (6) Mix 435 (70% coal, C/F = 75/25 weight ratio). None of the slurries showed significant ΔCG_n values after vibration.

The data for these slurries indicates, from the pendulum tests, that a 55/45 coarse/fines size ratio is preferred for maximum stability. The probe indicates qualitatively that all of the slurries settled to some extent, but that none exhibited hard pack settling.

3.5.2.2 Coal/Water Slurries Containing Wyoming Subbituminous Coal (PSOC 846)

All of these slurries were made with the 3% starch solutions as the carrier. Only five slurries were evaluated. Results are given in Table 30. All of the slurries are seen to be stable in storage, not only from pendulum tests but also from the probe.

All of these slurries were made with a formaldehyde content of 1000 ppm of total weight, as opposed to 1000 ppm of carrier as practiced for the bituminous slurries. This is because it was noticed in preliminary tests that extensive outgassing occurred. In early tests, slurries made with the lower biocide level could not be stored in the tubes more than a few days without "popping their corks". When this happened, the slurry expanded and literally grew out of the tube, generally uniformly, sometimes explosively. Even at the higher biocide level used in these compositions, extensive outgassing in the form of randomly not uniformly distributed bubbles, which were not as small as those observed on the tube walls of bituminous slurries. Because of the nature of outgassing observed here, not much confidence is placed in the pendulum results. However, the probe indicated the slurries to be smooth, uniform, and not at all grainy (in spite of the large coarse size used in 65% slurries), and no evidence of settling was detected. All of these slurries exhibited a bad odor, as further evidence of biodegradation. It seems that the biological activity of these slurries contributed in some way to stability towards settling. Interesting.

3.5.3.3 Slurries Containing Oil

These slurries were made with PHS 361 bituminous coal at loadings of 50, 55, and 60%. The carrier was either No. 6 oil or an o/w emulsion of No. 6 oil in water with Brij 35 as the emulsifier. The water content was maintained at 10% by weight of slurry. Results are given in Table 31.

With the exception of Mix 497, all showed significant values of ΔCG_n after 7 days storage at 160°F. Mix 497 is comprised of 50% coal (70% -200 mesh) in an emulsified carrier. None of the slurries in emulsified carriers exhibits a supernatant, but all exhibit general settling when probed, though not hard packing. Slurries made with only oil as a carrier settled to hard packing.

These results are seemingly contradictory, and are believed to be due to the movement of entrained air in the mixes made with the emulsified carriers. These compositions were not vacuum mixed because at the mix temperature (150 - 160°F) the vacuum required to deareate the mix

results in excessive vaporization of water. Consequently, entrained air was present in the mixes when loaded into the tubes. When stored at 160°F, the mixes are fluid enough for air to work its way up the tubes, and affect measurement of center of gravity. This is a postulated mechanism, that is inferred from the observations of the effects of outgassing found for the aqueous carriers. It is possible, of course, that this phenomenon did not occur, and that the cause of instability was loss of yield point, though it does not seem that demulsification occurred. No evidence of phase separation was found. If so, it is possible that the oil droplet size is increased by interaction with coal, as though the emulsion is de-mixed to a coarse state of aggregation, with loss of rheologicals; a possible fix would be increased emulsifier content.

The cost of using slurry fuels in place of oil is the sum of the ingredient costs, the cost of processing the fuel, and the cost of using it. While critical calculation of these costs is beyond the scope of this program, still, the costs of the fuels, expressed as the price of energy, \$/MBTU, is the most important property of the fuels. Fortunately, a number of papers have been published lately, some very recently, which address this problem.* The following calculations are based on the costs figured by George and Bergman⁽²⁾. These workers estimate the slurry mixing costs to be \$1.66/bbl, based on a 20,000 ton per day plant, 100% equity financed, and 18% discounted cash flow rate (DCF). The mixing costs are comprised of materials storage, handling, and inventory, grinding, mixing, general and administrative charges, and power. For the purposes here, the density of coal/water slurries is taken to be 10 lb/gal, and that for coal/oil slurries to be 9 lb/gal. The price of the fuel is thus the cost of ingredients plus the \$1.66/bbl charge. The cost of using the fuel is based on the modifications and operating costs of oil-fired boilers, primarily alterations to the firing systems, the use of NaHCO_3 as a sulfur scavenger, and the installation and use of a baghouse for fly ash removal. George and Bergman estimated the price differentials of the slurry fuels (compared to oil) as a function of boiler size (in 1000 lb steam/hr) that are required to offset these initial and operating plant costs. For an 18% DCF, the differentials range from .8 - 1 \$/MBTU at 10^5 lb steam/hr to .35 - .45 \$/MBTU at 5×10^5 lb to .25 - .3 \$/MBTU at 106 lb steam/hr depending on load factor. These workers based their estimates on HHV.

For the problem at hand, the price of energy was based on ingredient prices plus a charge of \$1.66/bbl. The ingredient prices used here are listed in Table 32. Fundamental to these calculations are the assumed prices of the coals, which seem to be representative at this time, and that of oil, which is moving fast at this time. The prices of the other ingredients seem considerably more stable. Results of the calculations are discussed below.

- *1. Bergman, P.D., et al, "Economic Considerations for Industrial Firing of Coal-Oil Mixtures", Proc. 1st Int. Symp. on Coal-Oil Mixture Combustion (1978).
2. George, T.J., and Bergman, P.D., "Economics of Coal-Oil Mixtures," Proc. of Industrial Coal Utilization Symp., PETC (1979).
3. Dingo, T.T., "An Industrial Viewpoint of Coal-Oil Mixtures," ibid.

Table 32. Unit Costs of Fuels and Slurry Ingredients

<u>Fuel or Ingredient</u>	<u>Higher Heating Value (HHV), BTU/lb</u>	<u>Unit Cost</u>
1. No. 6 Oil (Texaco)	18402 (144570 BTU/gal)	\$15/Bbl.
2. Pittsburgh Seam Bituminous Coal (PHS 361)	13460	\$30/ton
3. Iowa Subbituminous Coal (PSOC 664)	10470	\$20/ton
4. Wyoming Subbituminous Coal (PSOC 846)	10689	\$20/ton
5. Montana Lignite (PSOC 837)	8091	\$10/ton
6. Modified Starch (Hamaco 267)	8840	27¢/lb
7. Dispersant (Americo SD-1)	7103	28¢/lb
8. Emulsifier (Brij 35)	12507	72¢/lb
9. Wetting Agent (Triton X-100)	13207	70¢/lb
10. Formaldehyde	7582	16¢/lb

4.1 Calculations

Results of calculations are summarized in Table 33. The results of interest are the Δ values which are the differences between the oil and slurry fuel costs, \$/MBTU (HHV). The first two sets are bituminous coal/water slurries, the first unstabilized and the second stabilized with modified starch. The unstabilized coal/water slurries are seen to be the lowest cost fuels in the table. The stabilized coal/water slurries are also very low in cost, and present considerable improvements in handling properties. These latter slurries are probably cost effective at boiler sizes down to 2×10^5 lb steam/hr. The third set of fuels are unstabilized coal/oil slurries and it is seen that the state-of-the-art composition (50% coal) is only marginally feasible and only at the largest boiler size. The use of bimodal size distributions to increase the coal loadings considerably improves the cost status of this fuel. The stabilized coal slurries based on o/w emulsions (the ID 4 fuels) all seem to be too costly for use, even at 60% coal. The fuel costs of the coal/water slurries based on sub-bituminous coal are not as low as those based on bituminous. For these slurries, it is interesting that at a comparable coal loading of 60%, this slurry is more expensive (\$/MBTU) than the unstabilized coal/oil slurry (compare 5B and 3C). This is because of the proportionately higher stabilizer concentration and cost.

The costs and Δ values were also computed using AHV as a basis. The AHV values used here are based on 20% XS air. These costs are higher, reflecting the loss of latent heat and lower flame temperatures (i.e. lower total heat content of combustion products), as expected. However, the Δ values are also higher, and are believed to be more representative of the real cost savings to be realized. These values indicate that the stabilized 70% coal/water slurry (2B) may be usable in boiler sizes down to 10^5 lb steam/hr. Finally, the relative price of energy, based on HHV, is tabulated for each fuel.

The calculations indicate that the bituminous coal/water slurries are the lowest cost fuels. It is estimated that the stabilized slurries are more tractable, because the cost of continuous circulation in storage

Table 33. Comparison of Estimated Fuel Costs With Oil.

Fuel ID	Slurry Composition, Wt. %									Cost of Ingrid. c/lb	Processed Price, c/lb	Fuel Heating Values, BTU/lb		Fuel Costs* Based on HHV		Fuel Costs* Based on AHV		Relative** Price of Energy
	Coal	Coal/ID	No 6 Oil	Water	Mod. Starch	Wetting Agent	Disper-sant	Biocide	Emul-sifier			HHV	AHV	Cost, \$/MBTU	Δ HHV	Cost \$/MBTU	Δ AHV	
1-A	65	Pitt. Bit.	-	35	-	-	-	-	-	0.975	1.370	8750	7120	1.57	.90	1.92	110	.64
B	65	"	-	34.35	-	-	0.65	-	-	1.157	1.552	8795	7170	1.76	.71	2.16	86	.71
C	70	"	-	29.3	-	-	0.7	-	-	1.246	1.641	9470	7760	1.73	.74	2.12	91	.70
2-A	65	"	-	33.9	1.05	0.0035	-	0.035	-	1.266	1.661	8840	7220	1.88	.59	2.30	72	.76
B	70	"	-	29.07	0.90	0.0030	-	0.030	-	1.300	1.695	9500	7860	1.78	.69	2.16	87	.72
3-A	50	"	50	-	-	-	-	-	-	3.023	3.462	15930	13330	2.17	.30	2.60	43	.88
B	55	"	35	-	-	-	-	-	-	2.870	3.309	15685	13160	2.11	.36	2.51	51	.85
C	60	"	30	-	-	-	-	-	-	2.718	3.157	15435	12985	2.04	.42	2.43	59	.83
4-A	50	"	39.6	9.9	-	-	-	-	0.5	2.910	3.349	14080	11720	2.38	9.2	2.85	17	.96
B	55	"	34.65	9.9	-	-	-	-	0.45	1.724	3.163	13835	11545	2.29	18	2.74	28	.93
C	60	"	29.7	9.9	-	-	-	-	0.4	1.538	2.977	13590	11360	2.19	28	2.62	40	.89
5-A	60	Wyo. Sub	-	38.7	1.2	0.004	-	0.1	-	0.968	1.363	6520	5020	2.09	38	2.72	31	.85
B	65	"	-	33.85	1.05	0.004	-	0.1	-	0.978	1.373	7040	5530	1.95	52	2.48	54	.79
Baseline			100							4.546	4.546	18400	15035	2.47	0	3.02	0	1

* Δ_{HHV} = Oil Cost - Fuel Cost, \$/MBTU of HHV Δ_{AHV} = Oil Cost - Fuel Cost, \$/MBTU of AHV** Relative price of energy is $\frac{\$ \text{ of fuel/MBTU (HHV)}}{\$ \text{ of Oil/MBTU (HHV)}}$

was not included in these calculations. Inclusion of this item would necessarily increase the costs of the unstabilized coal/water slurries probably to the levels of the stabilized ones. This item must also be considered in judging the feasibility of the unstabilized coal/oil slurries.

CONCLUSIONS

From the results of this program, the following conclusions are drawn:

1. Fluid coal/water slurries containing up to 70% bituminous coal are technically feasible.
2. Hydroxypropylated corn starch is an effective stabilizer for coal/water slurries.
3. Coals are chemically and physically reactive, and are biodegradable.
4. Of the two coals evaluated in coal/water slurries, the more biologically degradable one (a Wyoming subbituminous) seemed to be more stable.
5. None of the stabilized coal/water slurries exhibited hard-pack settling.
6. All of the stabilized bituminous coal/water slurries exhibited some settling when probed.
7. None of the stabilized subbituminous coal/water slurries exhibited settling when probed. All were biodegraded.
8. None of the coal/emulsion slurries exhibited hard pack settling when probed.
9. All of the coal/emulsion slurries exhibited some settling when probed.
10. The compound pendulum is an accurate and sensitive tool for measuring settling by means of shift in center of gravity, but outgassing caused by biodegradation of the coal interferes with interpretation of results.
11. The use of bimodal size distributions is the only way to obtain high solids loadings, in the neighborhood of 70% by weight.
12. The grinding (+ classifying) costs for preparation of a bimodal blend is estimated to be about the same as that for a "standard" size consist (~80% -200 mesh).

13. A carrier having a yield point is required for stability.

14. A carrier having a yield point seems to be required for good flow properties in slurries.

15. All of the slurries have lower values of price of energy, \$ fuel/MBTU, than No. 6 oil. The price of stabilized coal/water slurries is about 75% that of the oil.

APPENDIX A
LITERATURE REVIEW OF COAL SLURRY TECHNOLOGY

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APPENDIX A

LITERATURE REVIEW OF COAL SLURRY TECHNOLOGY

1.0 INTRODUCTION AND SUMMARY

There exists an extensive body of literature pertaining to the preparation and use of coal slurry fuels, dating back nearly 100 years (1). Excellent reviews of the literature were published in 1921 by Sheppard (6), 1936 by Manning and Taylor (13), and in 1942 and 1946 respectively by Schroeder (16) and Jonnard and coworkers at Kansas State College (20). These reviews also contain details as well as results of the major combustion experiments carried out with coal slurry fuels. Initially (before and during World War I) the fuels were developed as a low-cost substitute for oil, and as a safe substitute for both oil (slurry fires can be doused with water because the density is >1) and coal (elimination of the danger of spontaneous combustion in storage). Also, some slurry compositions have a volumetric heating value (BTU/unit volume) greater than that of oil. It is evident however, from a reading of these articles as well as others of that time and up to the present, that the interest in coal slurry fuels has always been a response to a prevailing national emergency, specifically: World War I, World War II, and the oil embargo crisis. In each case, the threat to fuel oil supplies was the driving force to develop coal slurry fuels. During World War I, this activity was supported by the Submarine Defense Association, a consortium of approximately 100 firms engaged in shipping, oil, exporting, etc., formed for the purpose of combating the German submarine threat to (their) world trade (4,6). Some of the firms in SDA were Cunard, Standard Oil of New Jersey, the Texas Company, United Fruit Company, and the Armour Grain Company. Evaluation of coal slurry fuels was carried out under the direction of L. W. Bates who was the Engineering Chairman of SDA. During World War II, the development and evaluation of coal slurry fuel was carried out at the Bureau of Mines (19)

and at Kansas State College (20). At the present time, R & D work is supported by DOE.

With the passing of each emergency, or with the resolution of the fuel oil supply threat, development of coal slurry fuels abated. This is particularly true only of the national situations after the two world wars. At the present time, considerable R&D is in progress. This seems to be because the two problems of slurry stability and economics have never been satisfactorily resolved, notwithstanding the many claims for both that have been put forth by workers in the field. Conversely, the combustion of coal slurry fuels has been considerably more successful. Nearly all the workers have used unmodified No. 6 oil burners for slurry combustion, and in general little or no difficulties were found for combustion of these fuels. In particular, no erosive damage or fouling of boiler surfaces and convection passes has been observed. Air atomizers are generally preferred to steam atomizers, to prevent clogging.

Coal slurry fuels have also been developed specifically to increase radiant heat transfer rates in open hearth furnaces. Generally, this work has concentrated on the use of low solids loadings in the fuels. Results indicate significant reductions in fuel consumption rates are obtained, for a given heating rate, for slurry compositions containing up to 10% by weight pulverized coal. As above, unmodified No. 6 oil burners have been used in all evaluation tests.

Past development efforts date from 1917 to the present and have involved the use of full scale equipment (boilers rated from 1000 to 15000 lb fuel/hr) for evaluation of coal slurry fuels. In the recent tests (1977) by workers at GM Corporation (25) over 250,000 gallons of ~45% coal/oil slurry fuel was fired in a two-month series of tests.

All of the literature reveals two serious drawbacks to the use of coal slurry fuels. These are instability (i.e. solids settling) and cost. Practically all of the literature pertaining to coal slurry fuels is directed in some way to improving slurry stability, generally through the use of thickened carriers (usually No. 6 oil) or through the use of either small solids particle sizes (one micron diameter down to colloidal

sizes) or solids loadings of $\sim 50\%$ to promote hindered (vs free) settling. Other workers, particularly those only interested in improving radiation rates, circumvent the stability problem by mixing (i.e. recirculating) the fuel while in storage. Between laboratories, there is little or no commonality in the test procedures for stability, or even in the definition of stability. Stability criteria have yet to be quantified. The most severe stability tests were employed by workers at Bethlehem Steel Corp. (22) who centrifuged samples at 200 g's for 4 hours. They found stable slurries ($\sim .5\%$ settling) at 45% solids loading of coal ground to 1.1 μ diameter in a fluid energy mill. The carrier was unmodified No. 6 fuel oil. This ranks as one of the best examples of stable slurries found in the literature.

For maximum stability in storage and minimum viscosity in flow, the importance of a Bingham pseudoplastic as the carrier fluid was recognized early (6). However, none of the literature addresses the development of carrier fluids having these properties. Nor are the properties of slurries correlated with carrier properties. Similarly, the effect of particle size distribution on solids loading and slurry viscosity vs solids loading is not addressed systematically in the literature, except for the accidental effects of particle size distribution produced by a given grinding operation. The use of grinding operations that produce a bimodal particle size distribution wherein the interstices of the larger particles are filled with the smaller ones has not been evaluated. Workers at Kansas State College (20) tried blends of -200 mesh, -200/+325 mesh, and -325 mesh in a preliminary effort to increase packing fraction and minimize settling by filling the voids between the larger particles with the small particles. These however can be shown to be the incorrect size ratios to use for maximum packing. Neither has the use of grinding operations to produce particles having maximum sphericity been evaluated as a technique to minimize particle surface (wetted) area and thus maximize fluidity.

The cost picture of coal slurry fuels is about as murky as stability. Predictably, most workers with these fuels claim slurries to be cost

effective. However, their estimates are of the back-of-the-envelope sort made by expert chemists at best, and not by engineering experts in the field of plant design and economics. The most erudite studies (13,20) indicate the economics are marginal and depend strongly on the differences in oil and coal prices (\$ per BTU) which vary in a complex way with geographic location, calendar time, and market forces. None of the literature contains a detailed engineering analysis of the manpower/power/equipment/facilities requirements for manufacture and use of the slurries. The most pessimistic estimates of coal slurry fuel economic feasibility are to be found in the GM study (25), who conclude that the purchase price of oil must be 2.5 to 3 times that of coal if a 50% slurry based on emulsified oil is to be economical to industrial users (capacities $<10^6$ lb/hr steam) converting from oil to slurry. These estimates include amortization, taxes, and projected inflation rates but do not include the effects of improved radiation heating rates gained by the use of slurry fuels. The detailed engineering basis for their estimates is not given.

In summary, it is estimated that as of this writing, and within the present state of the art, the stability and economics of coal slurry fuels is marginal at best. Higher solids loadings are required to obtain favorable economics. Stability should also be favored by higher solids loadings as well as the use of a Bingham plastic for the carrier. For minimum slurry viscosity, the carrier should also be pseudoplastic.

2.0 Preparation of Coal Slurry Fuels

Coal slurry fuels typically contain 30 - 50% by weight pulverized coal (generally 80 to 90% -200 mesh) with the remainder being No. 6 fuel oil. In most cases the oil is thickened to prevent or reduce settling. Nearly all of the literature pertains to the use of coal slurries as fuel, although some of the more recent work considers the use of coal slurry as gasifier feed and for pipeline transport of coal (26).

Initially, the slurries were referred to as "colloidal fuels"(4) ("Fließkohle" in Germany (10)) even though everyone recognized that the suspensions were anything but colloids (27). This terminology prevailed

until the end of World War II (20) though some suggested the name "oil-coal fuel" (10). In 1965, workers at Bethlehem Steel Corporation developed a product they called "liquid carbon", which contained coal ground to $\sim 1\mu$ (22). The latest entry is "COM", which stands for "coal-oil mixture" (25). For the purposes of this report, and further ones issued for this program, the coal slurry fuels will be referred to as "coal slurry fuels."

The processing operations involved in preparing coal slurry fuels are: (1) coal preparation, i.e. drying and grinding; (2) carrier thickening (if necessary), and (3) mixing. Generally, workers in the field dry the coal prior to grinding to reduce power consumption and cost of grinding. Some of the early workers pulverized to colloidal dimensions in colloid mills (see the review by Manning and Taylor (13)), but the cost of such an operation was found to be prohibitive. Most workers used a ball mill, pulverizing the coal generally to $\sim 80\%$ through 200 mesh. Ball milling is generally considered to be one of the most economical operations for pulverizing, typically yielding ~ 150 lb/Hp-hr of -200 mesh product. At this rate, the energy consumed in grinding is $\sim 0.6\%$ of the heating value of the coal (assuming a heating value of 12,500 BTU/lb of coal and overall electrical power use efficiency of 20%). The use of a fluid energy mill has been evaluated for grinding to $\sim 1\mu$ (22). Mill grinding rates of 1 pound coal/1.5 lb high pressure steam were measured. This translates to ~ 1 lb coal/Hp-hr assuming 70% conversion of heat of combustion to the steam, so that the energy used in grinding is $\sim 20\%$ of the heating value of the coal, which must be considered too energy-intensive. Hammer mills and bowl mills, which have a little lower capacity (~ 100 lb/Hp-hr) than ball mills, are also used for coal grinding. The former is not often used nowadays because of vulnerability to scrap iron and subsequent down time and maintenance. It is of interest to note here that no data was found in the literature concerning the preparation of coal slurry fuels with controlled particle size distribution. Generally, slurry rheology and stability has only been correlated with size range (80% -200 mesh, 98% -200 mesh, 1.1μ , etc.) or at best with a too-broad definition of size distribution (30% -200 mesh, 50% -325 mesh, etc.). No work has been carried out to optimize slurry properties by systematic control of particle size and distribution.

For mixing, propeller type mixers are most commonly used for coal slurry fuel preparation in processes up to pilot plant scale (20). For plant scale work, compound propeller type mixers are used. The energy requirements for these types of mixers are essentially negligible, amounting to ~ 0.5 Kw-hr/ton of fuel mixed. With the operations for grinding (and therefore coal particle size) constrained by economics, and mixing of negligible research interest, essentially all work in the field of coal slurry preparation has been concerned with carriers. The carrier of choice has been No. 6 oil, thickened by various techniques to prevent coal settling and thereby provide a stable slurry, and yet result in a low-viscosity slurry for ease of pumping and atomization. While these two requirements may seem mutually exclusive, they can both be met by use of a Bingham pseudoplastic fluid, i.e., a fluid having a definite yield point and apparent viscosity which decreases with increasing shear rate. Yield values of ~ 3.5 dynes/cm² are generally considered adequate for slurry stability in most user environments. A typical pseudoplastic fluid will exhibit a viscosity index, n , of shear rate, S sec⁻¹, in the range 0.5 to 1,

where

$$\mu = \mu_1 S^{n-1}$$

and μ = viscosity, arbitrary units

μ_1 = viscosity at $S = 1$ sec⁻¹

The need for these carrier properties was recognized very early, in 1921, by Sheppard (6). Oddly, this seems to be the only reference in the coal slurry literature for this requirement. No work has been done to systematically evaluate the effect of carrier rheology on slurry properties.

2.1 Carrier Thickening Techniques

The techniques that have been used for thickening No. 6 oil are:

1. The use of no thickeners
2. The use of soaps
3. The use of peptizers
4. The use of emulsions

Results are discussed briefly below.

2.1.1 The Use of No Thickeners

A significant amount of work has been directed toward developing stable coal slurry fuels using no thickeners. The stabilization techniques take about every form imaginable. The first reported work on coal slurries is the patent of 1879 by Smith and Munsell (1) who mixed equal volumes of pulverized coal and oil. They are silent on particle size and stability.

Kern (8) made porous coal powder by grinding the coal (-200 mesh), mixing with water, rapidly heating the mass to 550°C, cooling in the absence of air, regrinding to 200 mesh, and mixing with oil to form a slurry. The author claims it is stable but doesn't prove it. The porous coal floats on oil, and any instability would be manifest in flotation rather than settling. This coal product is known here as "pop coal".

Flagg (18) describes firing an open hearth furnace at the American Rolling Mill Company with a slurry of 5% coal in oil (type not stated). For an equivalent heating rate with oil, a 10% drop in fuel consumption rate was found. No observations of stability or coal particle size are reported.

Barkley, et al (19) found the compositions 40% coal (98-99% -230 mesh)/60% No. 6 oil to be stable. Sieve analysis of coal ground to this size showed most (75 to 93%) to be -325 mesh. In tests at an Atlantic Refining Company boiler plant (45-50 gph), boiler efficiencies using this fuel were found to be lower than with use of No. 6 alone, a result that disagrees with other workers who have evaluated coal slurry fuel combustion. Firing of a larger boiler (90 gph) at the Cambria Silk Hosiery Company produced the same efficiency as with No. 6 oil.

Rudzki, et al (22) show that very stable slurry can be made of 50% loadings of $\sim 1\mu$ MMD (mass median diameter) coal, because settling is hindered, and Stokes flow is obviated. Rudzki, et al pulverized the coal to 1.1μ MMD by means of a fluid energy mill using steam as the grinding medium. The mixtures of this fine-particle coal in No. 6 oil were called "liquid carbon". A pilot plant was built and 250,000 gallons of "liquid

carbon concentrate" (45% coal) was prepared. No settling was observed in this composition. The concentrate was diluted to coal concentrations of 20 and 30% for use as fuel in a series of open hearth furnace trials using two 240-ton furnaces. A total of 592 heats were run with these two compositions, and No. 6 fuel oil for comparison, at comparative heating rates. Results showed lower fuel rates of .36 MBTU/ton steel and .28 MBTU/ton steel for the 30% and 20% compositions respectively. These results are in agreement with those of Flagg.

Workers at Kansas State College (20) burned 10,000 gallons of 40% coal slurry in No. 6 oil in a 300 Hp steam generator during the period March 1943 - March 1944. The coal size was 92% -200 mesh. No stabilizer was used and no settling problems were observed. After all the fuel had been burned, inspection of the furnace showed no slag accumulation in the convection passes or boiler surfaces. The slurry flames were noticeably larger than oil flames and the boiler performance was superior. The average steam raising efficiency was 130% of rated capacity. Steam atomizing burners were used and the slurry fuel was only partially preheated (to 180°F vs 200-220°F in oil alone) to prevent clogging due to overheating.

2.1.2 Soaps

Bates (4, 5) describes the use of lime rosin soaps to thicken No. 6 oil for use as a carrier in coal slurry fuels. These soaps are referred to as "fixateurs" in the literature, and function as a colloid when dispersed in oil and exhibit a stabilizing effect on admixed coal particles apparently by adsorption. Boiler tests were run on the USS Gem during April - July 1918 in Long Island Sound. Approximately 10,000 lbs of a 31% coal slurry in No. 6 oil stabilized with 1% lime rosin soap was burned in four test runs at ~ 1000 - 1500 lb/hr (2-3 hr per run). Steam raising efficiencies of 65-91% were reported. No difficulties were reported. A second series of tests were run with boilers at the Standard Oil Refinery in Brooklyn. This fuel resulted in a heating rate comparable to No. 6 oil. Firing rate was 1286 lb fuel/hr.

The use of a sodium salt of a saponifiable oil-soluble acid is proposed by Burwell for use as a fixateur (7). The acid is prepared by high-temperature (120-140°C) aeration of 36-40° Be oil.

The workers at Kansas State College (20) evaluated 148 soaps, which they call surface active agents, as stabilizers of coal slurries in oil. A product called "spent alkylation acid catalyst" was most effective. This is a tarry product from the butane-isobutylene reaction process for the manufacture of isooctane aviation gasoline.

2.1.3 Peptizers

Peptizers and tars and middle fractions obtained from tar distillation, coal tars, and water-gas tars. Addition of tars to coal and oil slurry partly dissolves the coal and stabilizes the slurry. Manning and Taylor (13) also report that aeration of oil forms oxidation products which function as peptizers upon subsequent admixture with pulverized coal, and form stable suspensions. Stable slurries require high tar contents, ranging from 5 - 20% of the mix. The pioneering work with peptized coal slurry fuels was carried out by Sheppard in 1921 (6), who concluded that peptization is difficult to apply generally because it depends on the volatiles content of coal. A fairly impressive experiment with a peptized coal slurry fuel was carried out in 1932. The Cunard Ship Scythion, fueled with 150 tons of 40% coal slurry fuel using cracked No. 6 oil containing at least 5% carbon, made a round trip between Liverpool to New York. The burners suffered intermittent clogging and an intermittent steam purge was used for cleaning (13,16).

A second test firing with peptized slurry was reported by Sheppard (6), using the same boiler at the Standard Oil Refinery in Brooklyn that was used for evaluation of soap-stabilized slurry. This was a 30% coal slurry stabilized with 12% tar oil and 1.2% lime rosin soap. Steam raising efficiency was comparable to No. 6 oil. Firing rate was 1076 lb slurry fuel/hr.

2.1.4 Emulsions

Oil in water emulsions have been used as carriers for coal slurry fuels, the carrier is a mayonnaise-like fluid. First use of stabilization by emulsification was reported in 1922 by Greenstreet (2). The sodium salt of a fatty acid was used as the emulsifier in the composition 23.1% coal + 69.9% oil (22° Be) + 1.4% emulsifier + 5.6% water.

Results of an extensive evaluation of an emulsified coal slurry fuel has recently been reported by GM (25). The emulsifier was a proprietary product of the Tretolite Div. of Petrolite Corp. The carrier was an emulsion of No. 6 oil in water. During Phase I of the program 60,000 gal of slurry was prepared and burned in a boiler rated at 96,000 lb steam/hr. The boiler was outfitted with No. 6 oil atomizers rated at 16 gph each. The slurry composition was 35% coal + 59% No. 6 oil + 5.25% water + 0.75% emulsifier. The coal was "pre-ground, bagged", assumably -200 mesh, although no size analysis was given. The slurry was prepared in a pilot plant and was found to be unstable. Analysis showed that the coal content in the slurry fed to the boiler was 28%. Boiler tests showed best performance with an air-atomizing nozzle, and no evidence of slagging or ash buildup in the boiler or passages. No efficiency data were taken. During Phase II of the program 250,000 gallons of a 50% coal + 43.3% No. 6 oil + 6.5% water + 0.2% emulsifier (Drew - 5200 additive) were prepared and burned. Settling was also observed for this slurry. The average coal content in the slurry fed to the boiler was 45.3%. This settling seems to have been caused by high storage temperature, which was maintained at 170-180°F for the boiler runs. (Settling was also observed in transportation tests of 6000 gal 985 miles via tank truck (~4% settling in two days). The temperature of the slurry in the truck was maintained at 135-150°F). The boiler results for combustion of this slurry were comparable to those of Phase I. The peak boiler efficiency was measured to be 75% compared to 85% with No. 6 oil. As noted previously, other workers have reported increases in boiler efficiency when slurry fuel is substituted for No. 6 oil.

An emulsion of 44.5% coal + 33.3% No. 2 oil + 22.2% water was prepared ultrasonically (20-22 KHz) by Cottell (24). The power input requirements are ~38 to 54 watts/cc of slurry, or approximately 25 HP/lb. Mass flow rates are not given by the patent, so computation of energy requirements is not possible.

3.0 Summary of Historically Valuable Reviews

The review by Manning and Taylor (13) thoroughly covers the state-of-the-art of coal slurry fuel technology from 1879 to 1936. Included in their review is a tabulation of the extant patent literature pertaining to the subject.

The work at Kansas State College (20) during the war years of World War II not only includes much original experimental data and an excellent treatise on laboratory techniques for evaluation of slurry stability, but also an exhaustive bibliography of the coal slurry literature to 1946.

These sources, coupled with the reviews by Sheppard (6), of Eastman Kodak in 1921, and Schroeder (16) of BuMines in 1942, and the review covering the period from World War II to 1965 by Rudzki, Pease, and Weidner of Bethlehem Steel (22) give the reader an essentially complete picture of the art of coal slurry fuels.

3.1 Review of Combustion Experiments With Coal Slurry Fuels

All of the workers who have evaluated coal slurry fuel combustion have used conventional unmodified No. 6 oil burners. Little or no difficulties have been observed. The use of these fuels did not damage or foul the boiler surfaces. Increased heating rates (over No. 6 oil alone) were found by several workers, and this was attributed to increased radiation heat transfer from the slurry flames. Only the workers at GM reported difficulty with ignition and low values of heating rates (25), and this is probably due either directly or indirectly to the use of emulsified carriers. In general, the results have indicated that air atomizers are superior to steam atomizers in terms of trouble-free operation. The use of steam apparently causes partial vaporization or breakdown of the carrier, leading to nozzle clogging. In summary, the combustion of coal slurry fuels can be carried out in unmodified No. 6 oil burners. The combustion is as clean and trouble-free (in terms of fouling the boiler surfaces) as is No. 6 oil. For a given mass flow rate of fuel, coal slurry fuels are superior to No. 6 oil in heating rate. A summary of the results of combustion experiments with coal slurry fuels is given in Table A1.

Table A1. Chronological Summary of Coal Slurry Combustion Experiments

<u>Date of Expmnt</u>	<u>Source</u>	<u>Remarks on Experimental Set-up</u>	<u>Significant Results</u>
1906-1907	28	Combustion of a "wet sand" mix of oil and coal in a water boiler tube rated @ ~ 1000 lbs steam/hr. The slurry composition is not stated. The slurry was conveyed to the furnace via screw conveyer.	Found heating rates comparable to the best ever made on water tube boilers.
Apr. 18-June 22, 1918	4,6	<u>Slurry Comp.</u> : 31.2% Pocohantas (98% -200 mesh) 1% Lime-rosin "fixateur". No. 6 oil carrier. <u>Facilities</u> : USS "Gem" cruise trials in Long Island Sound <u>Eqmt</u> : Steam boiler (10-20,000 lb 212°F steam/hr, or ~ 1000-1500 lb fuel/hr). No. 6 oil atomizers.	Four firings, 0.67, 2, 2.25 and 3.2 hrs. run time, giving evap. eff. of 92, 66, 71, and 84% resp. vs 70-80 for oil. No fouling or comb. diff. were encountered. No stability problems were reported.
1919	6	<u>Slurry Comp</u> : 30% coal (mixed types) 1.2 - 1.5% lime-rosin "fixateur" + 12% coal tar, No. 6 oil carrier <u>Facilities</u> : Standard Oil Refinery at Brooklyn, N.Y. <u>Eqmt</u> : "Tubular return" boilers rated @ 403 Hp. (16,000 to 17,500 lb 212°F steam/hr or 1100-1300 lb fuel/hr). No. 6 oil atomizers.	Two firings of 8 hrs duration each. Evap. eff = 77 and 85% vs 73-80 with No. 6 oil.
1922	13	<u>Slurry Comp</u> : 60% "Elsecar coal dust" + 40% "fuel oil" <u>Facilities</u> : Locomotive boiler, Great Central Railway	72% overall efficiency
July 1932	13	<u>Slurry Comp</u> : 40% coal (-200 mesh) + 60% No. 6 oil (cracked fuel oil with carbon residue content > 5%) <u>Facilities</u> : Cunard Ship "Scythia", Round trip between Liverpool and New York <u>Eqmt</u> : One of the twelve boilers on board the ship was fired with slurry fuel.	150 tons of slurry fuel was used. No stability problems were encountered. Burners required more frequent cleaning than with use of No. 6 oil. The steam output from the boiler was comparable to those using No. 6 oil.

Table A1. (continued)

<u>Date of Expt.</u>	<u>Source</u>	<u>Remarks on Experimental Set-up</u>	<u>Significant Results</u>
1932	13	<u>Slurry Comp:</u> "Fliesskohle", 55% "powdered coal" (-200 mesh)+ 45% tar oil (Anthracene Type) <u>Facilities:</u> Tests conducted in Germany <u>Eqmt:</u> "Cornish type" boiler	No stability problems. Thermal efficiencies of 70.5 and 74.7% were measured.
1935	13	<u>Slurry Comp:</u> 50/50 mixture of coal and oil ground together <u>Facilities:</u> Demonstration firing in a vertical boiler 6' dia x 12' high. <u>Eqmt:</u> Specially designed air atomizing burner.	No smoke or grit was observed at the stack. No other performance data available.
1936	13	Reported by W. H. Martin <u>Slurry Comp:</u> Fliesskohle <u>Facilities & Eqmt:</u> 80 hp diesel engine. Nozzle dia = 0.5 mm.	Slurry ignition P is 23 atm vs 28 atm for oil or coal dust. Max P _c is 47-49 atm with slurry vs 41-42 atm with oil. Knock is more pronounced but exhaust was "as clean as with oil".
July 22-Aug. 14, 1942	16	Expts by A. Butcher, Gulf Oil Corp. <u>Slurry Comp:</u> Up to 43% coal + No. 6 oil Coal is 99% -100 mesh, 58.5% -325 mesh. <u>Facilities:</u> Test plant assembled at Pittsburgh refinery. <u>Eqmt:</u> 100 gpm boiler (~ 3250 ft ² heating area)	No stabilizer was used so mix was continuously recirculated. Satisfactory combustion was observed with steam atomizers but no heating rates were reported.
1944	18	<u>Slurry Comp:</u> 5% coal in No. 6 oil. Mesh size not stated. No stabilizer used. <u>Facilities:</u> Open hearth furnace at ARMCO (American Rolling Mill Co.) <u>Eqmt:</u> Standard No. 6 oil-burning equipment rated at 340 gph.	Fuel rate is 10% less than No. 6 oil for same heating rate.

Table A1 (Continued)

<u>Date of Expt</u>	<u>Source</u>	<u>Remarks on Experimental Set-up</u>	<u>Significant Results</u>
1944	19	<p><u>Slurry Comp:</u> 40% coal (99% -230 mesh + No. 6 oil. No stabilizer is used.</p> <p><u>Facilities:</u> Batch mixing 5000-7000 gal by means of 9000 gph recirculating pump; feed coal into suction side of pump; recirculate to mix.</p> <ol style="list-style-type: none"> 1. Atlantic Refining Co. Boiler plant, 151 Hp 2. Cambria Silk Hosiery Co., Phila. PA 150 Hp boiler. 3. National Airoil Burner Co., Phila., PA. 90 Hp boiler. 	<p>Found 10% settling in 6-12 days in lab tests. In user tests, 1500 gal was placed in a delivery tank truck, driven on hwy 9 hrs for 150 miles, allowed to stand 8 wks. No settling occurred.</p> <p>Found 79.5-80.5% boiler efficiency vs 81.2 with oil. This was within exptl error. A steam atomizer using 2/3 more steam than oil was used to burn the slurry. No clogging was found.</p> <p>Difficult pumping and ignition found in facility 3.</p>
1965	22	<p><u>Slurry Comp:</u> "Liquid Carbon", coal is 1-4μ MMD. Carrier is No. 6 oil. No stabilizer.</p> <p><u>Facilities:</u> Pilot Plant at Bethlehem Steel Corp. Two 240-ton open hearth furnaces. Used fluid energy mill to pulverize coal.</p>	<p>Found stable slurry @ 45% 1.3μ coal. Prepared 250,000 gal 45% 3μ slurry. Fired 592 heats for comparison of 20 and 30% slurry (made by dilution of 45% slurry) with No. 6 oi.</p> <p>Found shorter heat times, higher production rate and lower fuel rate with both slurries vs oil. No settling problems in storage, transportation, and use.</p>
1976-1977	25	<p><u>Slurry Comp:</u> Phase I, nominal 35% -200 mesh in emulsified No. 6 oil. Phase II, nominal 50% coal in emulsified No. 6 oil.</p> <p><u>Facilities:</u> Pilot plant for Phase I is 1400 gph capacity. For Phase II, capacity in 1000 gph.</p> <p>Phase I and II boiler capacity is 120,000 lb/hr of 250 psia steam.</p> <p>Both steam and air atomizing nozzles were used</p>	<p><u>Phase I:</u> 60,000 gal of 35% slurry was burned in Phase I. This slurry was not stable, ave. coal content = 28%. No measurements of boiler effi. were made. Post firing inspection showed boiler was as clean as if No. 6 oil had been used. Air atomizer was preferred.</p> <p><u>Phase II:</u> 250,000 gal 50% slurry was burned. A different emulsifier was used to prepare this slurry, but instability was found, with ave. coal content = 45.3%. Best boiler eff. meas. was 75% $\pm$ 10% vs 85% with No. 6 oil.</p>

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APPENDIX B

Analyses of Coal and Oil

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COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 228 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 AREA CODE 312 726-8434

March 7, 1978

Atlantic Research Corporation
Alexandria, Virginia

MAIL ADDRESS
1821 LINDSAY AVE.
NORFOLK, VA. 23504
PHONE: 804-622-3051

Sample Identification
by **Yourselves**

Your NO. 289-68-3

Kind of sample Clean coal from Bruceton
reported to us Experimental Mine

Purchase Order NO. 13615

Sample taken at

Analysis made in accordance
with ASTM Specifications.

Sample taken by

Date ~~sampled~~ Rec'd: 1-24-78

Analysis report no. **N-75574-4**
PROXIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	2.13	xxxxx
% Ash	3.53	3.61
% Volatile	33.11	33.83
% Fixed Carbon	61.23	62.56
	<u>100.00</u>	<u>100.00</u>
Btu	14330	14642
% Sulfur	.69	.71

FUSION TEMPERATURE OF ASH

	<u>Reducing</u>	<u>Oxidizing</u>
Initial Deformation		
Softening (H=W)		
Softening (H=½W)		
Fluid		

H is Cone Height
W is Cone Width

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

R. Shepherd
R. Shepherd, Jr., Vice President Eastern & International Divisions

BILLINGS, MT. • BIRMINGHAM, AL. • CHARLESTON, W.V. • CLARKSBURG, W.V. • CLEVELAND, OH. • DENVER, CO. • GOLDEN, CO. • HENDERSON, KY. • MIDDLESBORO, KY. • NORFOLK, VA. • SOUTH HOLLAND, IL. • VANCOUVER, B.C. CAN.

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 228 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 726-8434

March 7, 1978

Atlantic Research Corporation
Alexandria, Virginia

MAIL ADDRESS
1831 LINDSAY AVE.
NORFOLK, VA. 23504
PHONE: 804-622-3051

Sample Identification
by Yourselves

Your NO. PSOC 664

Kind of sample Iowa Subbituminous from
reported to us Upper Seam; Star Coal Co.,
Pella, IA

Purchase Order NO. 13615

Sample taken at

Analysis made in accordance
with ASTM Specifications.

Sample taken by

Date sample ~~xxxxxx~~ Rec'd. 1-24-78

Analysis report no. N-75574- 1
PROXIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	6.40	xxxxxx
% Ash	10.29	10.99
% Volatile	37.81	40.40
% Fixed Carbon	45.50	48.61
	<u>100.00</u>	<u>100.00</u>
Btu	11512	12299
% Sulfur	6.68	7.14

FUSION TEMPERATURE OF ASH

	<u>Reducing</u>	<u>Oxidizing</u>
Initial Deformation		H is Cone Height
Softening (H=W)		W is Cone Width
Softening (H=½ W)		
Fluid

Charter Member

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

R. Shepherd
R. Shepherd III, Vice President Eastern & International Divisions

BILLINGS, MT. • BIRMINGHAM, AL. • CHARLESTON, W.V. • CLARKSBURG, W.V. • CLEVELAND, OH. • DENVER, CO. • GOLDEN, CO. • HENDERSON, KY. • MIDDLESBORO, KY. • NORFOLK, VA. • SOUTH HOLLAND, IL. • VANCOUVER, B.C. CAN.

Analyses of Iowa Subbituminous Coal
(PSOC-664)*

A. Ultimate Analysis (Dry Basis)

<u>Parameter</u>	<u>Wt %</u>
Carbon	63.91
Hydrogen	4.61
Nitrogen	1.06
Chlorine	0.07
Sulfur	8.11
Oxygen	8.08 (by difference)
Ash	14.16

B. Proximate Analysis (As Received)

<u>Parameter</u>	<u>Wt %</u>
Moisture	10.86
Ash	12.62
Volatile	36.23
Fixed Carbon	40.29
Heating Value (BTU/lb)	10470
Wt. % Sulfur	7.23

*
C.P. Dolsen, Pennsylvania State University, College of
Earth and Mineral Sciences, Private Communication.

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 228 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 AREA CODE 312 726-8434

March 7, 1978

Atlantic Research Corporation
Alexandria, Virginia

MAIL ADDRESS
1831 LINDSAY AVE.
NORFOLK, VA. 23504
PHONE: 804-622-3051

Sample identification
by **Yourselves**

Your NO. PSOC 846

Purchase Order NO. 13615

Analysis made in accordance
with ASTM Specifications.

Kind of sample reported to us Wyoming Subbituminous from
Brooks Seam, Section 10 Pit;
Energy Development Co.,
Hanna, WY

Sample taken at

Sample taken by

Date sampled ~~xxxxxx~~ Rec'd. 1-24-78

Analysis report no. **N-75574- 3**
PROXIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	8.64	xxxxxx
% Ash	13.05	14.28
% Volatile	31.92	34.94
% Fixed Carbon	46.39	50.78
	<u>100.00</u>	<u>100.00</u>
Btu	10524	11519
% Sulfur	.50	.55

FUSION TEMPERATURE OF ASH

	<u>Reducing</u>	<u>Oxidizing</u>
Initial Deformation		
Softening (H=W)		
Softening (H=1/2 W)		
Fluid		

H is Cone Height
W is Cone Width

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

R. Shepherd
R. Shepherd II, Vice President Eastern & International Divisions

BILLINGS, MT. • BIRMINGHAM, AL. • CHARLESTON, W.V. • CLARKSBURG, W.V. • CLEVELAND, OH. • DENVER, CO. • GOLDEN, CO. • HENDERSON, KY. • MIDDLESBORO, KY. • NORFOLK, VA. • SOUTH HOLLAND, IL. • VANCOUVER, B.C. CAN.

Analysis of Wyoming Subbituminous Coal (PSOC 846)*

A. Ultimate Analysis (Dry Basis)

<u>Parameter</u>	<u>Wt%</u>
Carbon	69.87
Hydrogen	4.90
Nitrogen	1.05
Chlorine	0.05
Sulfur	0.51
Oxygen	14.57 (by difference)
Ash	9.05

B. Proximate Analysis (As Received)

<u>Parameter</u>	<u>Wt%</u>
Moisture	9.88
Ash	8.16
Volatile	28.49
Fixed Carbon	53.47
Higher Heating Value	10689 BTU/lb
Sulfur	.46

* C. P. Dolsen, op. cit.

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 228 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 728-8434

March 7, 1978

Atlantic Research Corporation
Alexandria, Virginia

MAIL ADDRESS
1831 LINDSAY AVE.
NORFOLK, VA. 23504
PHONE: 804-622-3051

Sample identification
by **Yourselves**

Your NO. PSOC 837

Purchase Order NO. 13615

Analysis made in accordance
with ASTM Specifications.

Kind of sample reported to us Montana Lignite from Fort Union
Formation, Pust Bed, Breezy
Flat Deposit; Knife River
Coal Mining Co., Bismark, ND

Sample taken at

Sample taken by

Date sampled ~~XXXXXX~~ Rec'd. 1-24-78

Analysis report no. N-75574-2 PROXIMATE ANALYSIS

	<u>As received</u>	<u>Dry basis</u>
% Moisture	24.84	XXXXXX
% Ash	4.15	5.52
% Volatile	39.20	52.15
% Fixed Carbon	31.81	42.33
	<u>100.00</u>	<u>100.00</u>
Btu	8412	11192
% Sulfur	.47	.63

FUSION TEMPERATURE OF ASH

	<u>Reducing</u>	<u>Oxidizing</u>
Initial Deformation		
Softening (H=W)		
Softening (H=½W)		
Fluid		

H is Cone Height
W is Cone Width

Charter Member

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

R. Shepherd
R. Shepherd, Vice President Eastern & International Divisions

BILLINGS, MT. • BIRMINGHAM, AL. • CHARLESTON, W.V. • CLARKSBURG, W.V. • CLEVELAND, OH. • DENVER, CO. • GOLDEN, CO. • HENDERSON, KY. • MIDDLESBORO, KY. • NORFOLK, VA. • SOUTH HOLLAND, IL. • VANCOUVER, B.C. CAN.

Analysis of Montana Lignite Coal (PSOC 837)*

A. Ultimate Analysis (Dry Basis)

<u>Parameter</u>	<u>Wt%</u>
Carbon	57.81
Hydrogen	4.25
Nitrogen	0.77
Chlorine	0.04
Sulfur	0.59
Oxygen	20.84 (by difference)
Ash	15.70

B. Proximate Analysis (As Received)

<u>Parameter</u>	<u>Wt%</u>
Moisture	16.83
Ash	13.06
Volatile	22.72
Fixed Carbon	47.39
Higher Heating	
Value	8091 BTU/lb
Sulfur	0.46

* C. P. Dolsen, op. cit.

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 328 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 738-8434

PLEASE ADDRESS ALL CORRESPONDENCE TO
1 VAN DRUNEN ROAD, SOUTH HOLLAND, ILLINOIS 60473

OFFICE TEL (312) 264-1117

Jan. 18, 1978

ATLANTIC RESEARCH CORPORATION
7511 Wellington Road
Gainesville, Virginia 22065

Sample identification
by
Atlantic Research Corp.

Kind of sample
reported to us

No. 86861

Sample taken at

#6 Fuel Oil Texaco

Sample taken by

Atlantic Research Corp.

Sample No. 267-67-1
(combustible liquid)

Date sampled

Analysis report no. 71-11532

GRAVITY:

Specific at 60/60°F ----- 0.9433
Lb per gal at 60°F ----- 7.856
°API ----- 18.5

HEATING VALUE:

Btu per lb ----- 18402
Btu per gal at 60°F ----- 144570

SULFUR CONTENT, Bomb Method ---- 0.60% by wt

VISCOSITY AT:

122°F Saybolt Furol ----- 57.3 Seconds
122°F Kinematic ----- 119 Centistokes

WATER by Distillation ----- 0.5% by vol

SEDIMENT by Extraction ----- 0.01% by wt

TOTAL Water and Sediment by
Distillation & Extraction ---- 0.51%

FLASH POINT, Pensky-Martens ---- 220°F

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

R. A. HOUSE, Manager, Midwest Division

RAH:lf

Charter Member

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES

PHS #361
Test No. 1545

COAL-ANALYSIS REPORT

Lab. No. K-33588

Sample of Coal (Raw Head, 3A) From Coal Preparation Can No. _____

Operator Pittsburgh Mining Mine Bruceton Bed Pittsburgh
Research Center (Experimental)

State Penna. County Allegheny Town Bruceton

Date of sampling 1/24/74 Date of Lab. sampling 2/6/74 Collector H. H. Hensley

AIR-DRY LOSS		COAL (Air dried)	COAL (As received)	COAL (Moisture free)	COAL (Moisture and ash free)
Proximate Analysis	Moisture		2.9		
	Volatile matter		35.7	36.7	39.9
	Fixed carbon		53.7	55.4	60.1
	Ash		7.7	7.9	
			100.0	100.0	100.0
Ultimate Analysis	Hydrogen		5.3	5.1	5.5
	Carbon		75.5	77.7	84.4
	Nitrogen		1.5	1.5	1.7
	Oxygen		8.9	6.7	7.2
			(1.10)	(1.13)	(1.23)
	Sulfur		1.1	1.1	1.2
	Ash		7.7	7.9	
			100.0	100.0	100.0
British thermal units			13460	13860	15050

Fusibility of Ash, temp. ° F.: Initial Deform. 2580 Softening 2630 Fluid 2680

SULFUR FORMS:	Sulfate	Pyritic	Organic
As-received	0.01	0.55	0.55
Moisture-free	0.01	0.56	0.56
M. and ash-free	0.01	0.61	0.61

% As-received: Equilibrium Moisture 2.41
Chlorine 0.09

% Na₂O in ash 0.4

Hardgrove Grindability index 56.

Free-swelling index No. 8

Date February 23, 1974

Forrest E. Walker
Chemist-in-Charge Coal Analysis

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APPENDIX C

PARTICLE SIZE DISTRIBUTION CURVES

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Figure (3-1)

Effect of Mill Conditions on Particle Size

1. Clean Coal from Bruceton XPTL Mine
2. 10 HB Grates
3. All Product >50 Mesh Removed

SUMMARY

Crate Size Mil.	Hammer Speed, RPM	MMD μ
10HB	13,800	26
27HB	13,800	37
27HB	3,600	68
27HB	3,600	113
27HB	2,000	80
27HB	1,000	75
62HB	3,600	140

3

2

10²

9

8

7

6

5

4

3

2

1

0

0

10

20

30

40

50

60

70

80

90

100

110

120

130

140

150

160

170

180

190

200

210

220

Particle Size, Micron

MMD Line

3600/27HB

2500/27HB

1000/27HB

3600/62HB

6200/27HB

13.8K/27HB

13.8K/10HB

-2-

Cumulative Wt % Over Size

10³

Figure C2-A

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Clean Coal From Bruceton APTG Mine
2. RD Grates

SUMMARY

Grate Size Mils	Hammer Speed, RPM	MMD μ	Wt % >50 Mesh
20RD	13,800	34	0
27RD	3,600	90	2.3
46RD	3,600	145	16
62RD	3,600	190	30

10³

Figure C2-R

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Clean Coal From Bruceon Experimental Mine
2. RD Grates
3. All Product >50 Mesh Removed

SUMMARY

Grate Size Mils	Hammer Speed, RPM	MMD, μ
20RD	13,800	34
27RD	3,600	86
46RD	3,600	120
62RD	3,600	130

10²

Particle Size, Micron

MMD Line

-4-

10

Cumulative Wt. % Over Size

10³

Figure C3-A

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. PHS 361 Bituminous Coal
2. HB Grates

SUMMARY

Crate Size Mils	Hammer Speed, RPM	MMD μ	Wt. % >50 Mesh
10HB	13,800	30	0
10HB(A)	13,800	36	0
27HB	13,800	50	0.8
27HB	3,600	148	21
46HB	3,600	215	37
62HB	3,600	173	26

10³

Figure C3-B

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. PHS 361 Bituminous Coal
2. HB Grates
3. All Product >50 mesh removed

SUMMARY

Grate Size Mils	Hammer Speed, RPM	MMD μ
10HB	13,800	30
27HB	13,800	50
27HB	3,600	123
62HB	3,600	133

10²

Particle Size, Micron

13.8K/27HB

3600/27HB
3600/46HB

3600/62HB

13.8K/10HB

MMD Line

-6-

Cumulative wt. % Over Size

10³

Figure C4-A

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Montana Lignite (FSOC 837)
2. MR Crates

SUMMARY

Grate Size Mils.	Hammer Speed, RPM	MMD, μ	Wt. % >50 Mesh
10HB	13,800	36	0
27HB	3,600	183	30
62HB	3,600	345	55

FIGURE C4-B

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Montana lignite (PSOC 837)
2. EB Grates
3. All Product >50 Mesh Removed

SUMMARY

Grate Size Mils	Hammer Speed, RPM	MMD μ
10HB	13,800	30
27HB	3,600	120
62HB	3,600	142

10³

FIGURE C5-A

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Iowa Subbituminous (PSOC 664)

2. HB Grates

SUMMARY

Grate Size	Hammer Mile. Speed, RPM	MMD μ	Wt. % >50 Mesh
10HB	13,800	31	0
27HB	3,600	145	19
62HB	3,600	220	40

10³

FIGURE C5-B

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Iowa Subbituminous (PSOC 664)
2. HB Grates
3. All Product >50 Mesh Removed

SUMMARY

Grate Size Mils	Hammer Speed, RPM	MMD μ
10HB	13,800	31
27HB	3,600	115
62HB	3,600	115

10³
10

FIGURE C6-B

EFFECT OF MILL CONDITIONS ON PARTICLE SIZE

1. Wyoming Subbituminous (PSOC 846)
2. HB Grates
3. All Product >50 Mesh Removed

SUMMARY

Grate Size Mils.	Hammer Speed, RPM	MPD, μ
10HB	13,800	37
27HB	3,600	135
62HB	3,600	145

10³

9

8

7

6

5

4

3

2

1

0

0

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

Figure C6-3

Effect of Blending on Particle Size

1. Wyoming Subbituminous Coal (PSOC-846)
2. HA Grates
3. Blends of 265 μ Coarse and 37 μ Fines
4. See Figure C6-A for Basis

SUMMARY

Coarse/Fines Wt. Ratio	MMU, μ	Wt. % >50 Mesh
55/45	92	25
65/35	130	29
75/25	175	34

10²

9

8

7

6

5

4

3

2

1

0

0

1

2

3

4

5

6

7

8

9

10

11

12

Particle Size, Micron

MMD Line

75/25

65/35

55/45

-16-

10

156

Cumulative Wt. % Oversize

APPENDIX D

Rheograms

- Figures 1 - 17: Gumstocks
- Figures 18 - 26: Emulsions
- Figures 27 - 38: Slurries (by Extrusion
Rheometry)

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INDEX AND SUMMARY OF DATA

<u>Composition</u>		<u>Viscosity @ 10 Sec⁻¹, cp</u>	<u>Figure No.</u>
<u>A. Aqueous Carriers</u>			
1.	.2% Carbopol 941	600	D1
2.	.5% Guar Gum (SC 200)	240	D2
3.	1.0% Guar Gum (SC 200)	1800	D3
4.	0.5% Modified Guar Gum (HP 11)	290	D4
5.	0.25% Xanthan Gum (Kelzan)	125	D5
6.	0.5% Xanthan Gum (Kelzan)	450	D6
7.	0.5% Hydroxyethyl Cellulose (Natrosol 250 HHR)	220	D7
8.	0.5% Carboxymethyl Cellulose ((H4)	195	D8
9.	3.0% Dent Corn Starch (CP3005)	225	D9
10.	3.0% Waxy Maize Starch (CP6400)	69	D10
11.	3.33% CP3005 + 1.67% CP6400	775	DIIA
	2% CP3005+1% CP6400	75	D11C
12.	3% Modified Corn Starch (Hamaco 267)	450	D16
<u>B. Oil Carriers</u>			
1.	No. 6 Oil @ 150°F	50	D12
2.	3% J-315 (Dow) @ 136°F	130	D13
3.	2% Imbiber Beads (Dow) @ 142°F	740	D14
4.	2% XVS (Dow) @ 136°F	180	D15
<u>C. Emulsified Carriers</u>			
1.	2 oil + 1 water (w/o) @ 150°F	150	D12
2.	2 oil + 1 water (0.25% Kelzan) + 1 PPH Brij 35 @ RT	190	D18
3.	2 oil + 1 water (0.25% HEC) + 1 PPH Brij 35 @ RT	320	D19
4.	2 Oil/1 Water + 2 PPH Americo SD-1, @ 150°F	4100	D20
5.	2 oil/1 water + 1 PPH Americo SD-1, @ 150°F	1300	D21
6.	3 Oil/1 Water + 1 PPH Brij 35 @ RT	3400	D25
	3 Oil/1 Water + 1 PPH Brij 35 @ 150°F	2100	D26

<u>Composition</u>		<u>Viscosity @ 10 Sec⁻¹, cp</u>	<u>Figure No</u>
<u>C. Slurries</u>			
1.	65% Bituminous (Coarse/Fines = 55/45)		D27
2.	65% Bituminous (Coarse/Fines = 65/35)		D28
3.	65% Bituminous (Coarse/Fines = 75/25)		D29
4.	70% Bituminous (Coarse/Fines = 55/45)		D30
5.	70% Bituminous (Coarse/Fines = 65/35)		D31
6.	70% Bituminous (Coarse/Fines = 75/25)		D32
7.	60% Subbituminous (Coarse/Fines = 55/45)		D33
8.	60% Subbituminous (Coarse/Fines = 65/35)		D34
9.	60% Subbituminous (Coarse/Fines = 75/25)		D35
10.	65% Subbituminous (Coarse/Fines = 55/45)		D36
11.	65% Subbituminous (Coarse/Fines = 65/35)		D37
12.	65% Subbituminous (Coarse/Fines = 75/25)		D38

Figure D1. Rheogram of 0.2% Carbopol 941
(Neutralized with NH_4OH) in Tap Water.

Figure D2. Rheogram of 0.5 % Guar Gum (SC200)
in Tap Water.

Figure D3. Rheogram of 1% Guar Gum (SC200)
in Tap Water

Figure D5. Rheogram of 0.25% Xanthan Gum (Kelzan) in tap water.

Figure D6. Rheogram of 0.5% Xanthan Gum
(Kelzan) in Tap Water.

Figure D7. Rheogram of 0.5% Hydroxyethyl Cellulose
(Natrosol 250 HHR) in Tap Water

Figure D8. Rheogram of 0.5% Carboxymethyl Cellulose
(Cellulose Gum 9H4) in Tap Water.

K₊ LOGARITHMIC
3 X 3 CYCLES
46 7400
MADE IN U.S.A.
KEUFFEL & ESSER CO.

Figure D113. Rheogram of 2.67% GF3000 and 1.33% CP6400 in Tap Water

Figure D14. Rheogram of 2% Imbibor Beads (Dow)
in No. 6 Oil: $T = 142^{\circ}\text{F}$

Figure D15. Rehogram of 2% XVS Resin (Dow) in No. 6
Oil: $T = 136^{\circ}\text{F}$

Figure D16. Rheograms of Hamaco 267 Solutions

Figure D17. Effect of Storage at 160°F on Viscosity of 3% Hamaco 267 Solution.

Figure D18. Rheograms of O/W Emulsions Comprised
of No. 6 Oil, Water, Kelzan, and Surfactant.

Figure D19. Rheograms of O/W Emulsions Comprised of No. 6 Oil, Tap Water, Hydroxyethylcellulose, and Surfactant.

Figure D20. Effect of Oil-Water Ratio on Viscosity of Emulsions Comprised of No. 6 Oil, Tap Water, and Americo SD-1.

Figure D21. Effect of Emulsifier Content on Viscosity of Emulsions
Made of 2 Parts No. 6 Oil + 1 Part Water.

Figure D22. Effect of Blending Procedure on Viscosity of Emulsions Composed of 2 Parts No. 6 Oil + 1 Part Tap Water + 2 PPH (total) Americo SD-1.

Figure D23. Effect of Mixer Type on Viscosity of Emulsions Comprised of 2 Parts No. 6 Oil, 1 Part Tap Water and 2 PPH (Total) Americo SD-1.

Figure D24. Batch-to-Batch Variation of Viscosity of Emulsions Comprised of 2 Parts No. 6 Oil + 1 Part Tap Water + 2 PPH (Total) Americo SD-1.

Effect of Oil/Water Ratio on Viscosity at 72-75°F of O/W Emulsions Comprised of No. 6 Oil, Water and Brij 35. Emulsifier Content is One Part per Hundred of Oil + Water.

Effect of Oil/Water Ratio on Viscosity at 150-160°F of O/W Emulsions Comprised of No. 6 Oil, Water, and Brij 35. Emulsifier Content is One Part per Hundred of Oil + Water.

Figure D27. Rheogram of Mix 438 (Table 27)
65% Bituminous (C/F = 55/45)

Figure D28. Rheogram of Mix 478A (Table 27)
65% Bituminous (C/F = 65/35)

Figure D29. Rheogram of Mix 493A (Table 27)
65% Bituminous (C/F = 75/25)

Figure D30. Rheogram of Mix 430 (Table 27)
70% Bituminous (C/F = 55/45)

Figure D31. Rheogram of Mix 431 (Table 27)
70% Bituminous (C/F = 65/35)

Figure D32. Rheogram of Mix 435 (Table 27)
70% Bituminous (C/F = 75/25)

Figure D33. Rheogram of Mix 517 (Table 28)
60% Subbituminous (C/F = 55/45)

Figure D34. Rheogram of Mix 518 (Table 28)
60% Subbituminous (C/F = 65/35)

Figure D35. Rheogram of Mix 519 (Table 28)
60% Subbituminous (C/F = 75/25)

Figure D36. Rheogram of Mix 521 (Table 28)
65% Subbituminous (C/F = 55/45)

Figure D37. Rheogram of Mix 522 (Table 28)
65% Subbituminous (C/F = 65/35)

Figure D38. Rheogram of Mix 523 (Table 28)
65% Subbituminous (C/F = 75/25)