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ROLE OF TEMPERATURE, SOLVENT AND
AGITATION IN COAL DISSOLUTION
AND LIQUEFACTION

Quarterly Report for the Period
December, 1981 - February, 1982

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ABSTRACT

A Plexiglas reactor was constructed and experiments carried out with three mixer configurations in a sand-water system to determine the best mixer configuration and the minimum rpm to produce uniform conditions during coal dissolution.

Coal dissolution experiments on Kentucky No. 9 coal were made with combinations of tetralin and 2-methylnaphthalene to obtain the optimum ratio in the solvent.

The effect of β -naphthol addition to the solvent on the dissolution of Kentucky No. 9 coal was studied.

The effect of holding time at 400°C on the dissolution of Kentucky No. 9 coal in a solvent containing 46.1 wt % tetralin, 46.1 wt % 2-methylnaphthalene, 2.9 wt % γ -picoline and 4.9 wt % β -naphthol was studied.

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SCOPE OF WORK

A systematic study of the roles of temperature, solvent character and agitation in the dissolution and liquefaction of bituminous coal will be conducted. Pulverized bituminous coals will be dissolved and liquefied in a 900 ml reactor at controlled temperature profiles and agitation. Model aromatic, hydroaromatic, monophenol and ring-nitrogen compounds will be used in different proportions to resemble recycle solvents. The proposed maximum temperature will be approximately 400°C. Upon completion of the desired operating conditions, the products will be quenched and the products analyzed. Based on the extent of liquefaction and the distribution and character of the oil, asphaltene and preasphaltene fractions, an understanding will be developed for the chemical structure of the coal and for the role of temperature, solvent character and agitation in coal dissolution and liquefaction.

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SUMMARY

A Plexiglas vessel was constructed to study the effect of three mixer configurations and rotation rate on the suspension of solid particles and the flow patterns within the vessel. The Plexiglas vessel had approximately the same inside dimensions as the coal dissolution reactor. The mixer configurations were: turbine impeller, propeller and turbine impeller/propeller. Experiments were done with the sand-water system.

The turbine impeller/propeller combination was the most effective in dispersing stationary settled sand. It also gave the most intense flow at the reactor walls. Based on the anomalies seen in coal dissolution experiments at different heating rates with different mixing conditions, it was concluded that the heat transfer rate at the inside surfaces of the reactor had the greatest influence on the uniformity of conditions within the reactor. The turbine impeller/propeller combination is best and there is a minimum rotation rate for each reactor heating rate.

Coal dissolution experiments were carried out with different combinations of tetralin and 2-methylnaphthalene. The conversion of Kentucky No. 9 coal to pyridine solubles was a maximum when the weight ratio of tetralin to 2-methylnaphthalene was approximately 1.

Experiments with β -naphthol addition to the solvent indicated some increase in pyridine solubles up to concentrations of 5 wt % β -naphthol in the solvent.

Four runs were made to study the effect of holding time at 400°C on the dissolution of Kentucky No. 9 coal in a solvent containing 46.1 wt % tetralin, 46.1 wt % 2-methylnaphthalene, 2.9 wt % γ -picoline and 4.9 wt % β -naphthol.

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I. AGITATION

During the first quarter it was found that a minimum rotation rate was required to keep the coal suspended in the solvent, to insure good heat transfer at the reactor surfaces and to maintain isothermal conditions within the reactor. At rotation rates below 900 rpm with a 1 1/4-in diameter turbine impeller in the 2.9-in I.D. reactor anomalies were seen which suggested that the contents of the reactor were not uniform.

After a 2-in. diameter propeller was installed immediately above the turbine impeller, the anomalies disappeared at a lower rotation rate than with the turbine impeller alone.

A Plexiglas vessel with a 3.0-in I.D. and the same inside length as the reactor was constructed during the past quarter to examine the mixing within the vessel. The flange on the Plexiglas reactor was made the same thickness and with the same bolt layout as the reactor vessel. The stainless cover flange containing the Magne-Drive stirrer was bolted to the Plexiglas reactor and the system operated at ambient temperature.

The mixing of solids and the flow patterns which developed were studied with pulverized coal-water and fine sand-water. The pulverized coal tended to agglomerate in water which made data interpretation difficult. The sand-water system worked well and it was possible to see the distribution of the sand at different rotation rates.

The effect of rotation rate on the distribution of sand in water was studied with the turbine impeller alone, propeller alone and the combination of the turbine impeller and propeller. The results are presented in Figure 1. At each concentration, the rotation rate was determined at which:

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Figure.1. The Effect of Mixer Configuration and Rotation Rate on the Dispersion and Suspension of Sand in the Sand-Water System.

1. The stationary sand pile on the reactor bottom disappeared;
2. The vortex reached the bottom of the reactor and a very small amount of sand rotated in the vortex at the bottom of the reactor;
3. The sand was completely suspended.

The rpm values which gave total suspension of the sand for the turbine impeller and propeller were compared to the rpm values calculated from the Zwietering (1) mixing correlation:

$$\frac{nD^{0.85}}{\nu^{0.1} X^{0.2} (g\Delta\rho/\rho_L)^{0.45} B^{0.14}} = K(T/D)^a \quad (1)$$

where a = constant depending upon type and position of stirrer

B = weight of solids in suspension per weight of liquid

D = stirrer diameter, m

g = acceleration of gravity, m/sec²

K = function depending upon type and position of stirrer

n = stirrer speed, revolutions per sec.

T = vessel diameter, m

$\Delta\rho$ = difference in density between solids and liquid, Kg/m³

ρ_L = liquid density, kg/m³

X = particle size of the solids, m

ν = Kinematic viscosity of the fluid, m²/sec

The results were quite good. Zwietering did not present K functions for combination mixers.

There was no apparent advantage to the turbine impeller/propeller combination in suspending the sand particles but there was a drastic difference in the flow patterns. For the same rotation rate, the flow patterns at the bottom and walls of the reactor were substantially more intense with the turbine impeller/propeller combination than with the turbine impeller alone. The anomalies seen at low rpm with the turbine impeller were apparently associated with insufficient heat transfer at the reactor surfaces and non-isothermal conditions.

A new turbine impeller/propeller combination has been constructed. It will be used in conjunction with two 1/4-in wide baffles located 1/8-in away from the reactor wall. The turbine is 1 7/8-in diameter and contains four 1/2-in wide by 11/16-in long blades. The propeller is 1 7/8-in in diameter and contains four blades at a 45° angle. Each blade is 1/2-in wide by 11/16-in long. The open construction of the turbine should make the propeller more effective. The original impeller partially obstructed the downward flow. Once the series of runs, which are now being conducted with the original turbine impeller/propeller is completed, the new agitation system will be examined in the Plexiglas reactor and then put into use.

II. EFFECT OF SOLVENT, TEMPERATURE AND HOLDING TIME ON THE CONVERSION OF KENTUCKY NO. 9 COAL

Several experimental runs were made with the combined propeller/impeller at 1500 rpm and a constant electrical input to the furnace to give a 6°C/min rate of temperature rise up to the desired temperature. The coal was -100 mesh, +200 mesh Kentucky No. 9 coal from the Fies Mine.

Solvent Effects

Four runs were made with a solvent containing different amounts of tetralin and 2-methylnaphthalene. In each run the reactor contents were heated to 400°C and held for 25 minutes before quenching the reaction products. The results are presented in Figure 2. The conversion of the DMMF coal to pyridine and toluene solubles was obtained by Soxhlet extractions. The highest conversion to pyridine solubles was obtained at 50 wt % tetralin. Additional runs are planned at 35 and 75 wt % tetralin to better establish the sensitivity of the hydroaromatic and aromatic content of the solvent to the conversion to pyridine solubles.

A portion of the reactor contents in each run was filtered at room temperature and toluene added to the extract to precipitate preasphaltenes. Samples of the preasphaltenes were analyzed for carbon and hydrogen. A portion of the reactor contents were Soxhlet extracted with pyridine and the residue vacuum dried for 20 hours at 105°C. A sample of each residue was analyzed for carbon and hydrogen. The results of the analyses are presented in Figure 3.

Solvent Tetralin and 2-Methylnaphthalene
Agitation 1500 rpm
Heating Rate 6°C/min to 400°C
Holding Time 25 min at 400°C

Figure 2. The Effect of Tetralin and 2-Methylnaphthalene Concentrations on the Conversion of Kentucky No. 9 Coal

Figure 3. The Effect of Tetralin and 2-Methylnaphthalene Concentrations in the Solvent on the Hydrogen to Carbon Atom Ratio in Preasphaltenes and Pyridine Insoluble Residues.

There is an increase in the atom ratio of hydrogen to carbon in both the preasphaltenes and pyridine insoluble residues as the tetralin content of the solvent is increased. A portion of the increase can be attributed to hydrogenation by the tetralin and the balance attributed to the "antisolvent" property of the tetralin for preasphaltenes and residues. At the higher tetralin concentrations a larger fraction of the preasphaltenes will be insoluble in the liquid phase and they will end up in the residue. The preasphaltenes which are precipitated from the extract by toluene would be expected to have a higher hydrogen to carbon ratio.

Tetralin is expected to act as an antisolvent for the peptization of the preasphaltenes which form initially as the coal is heated above 350° C. If the peptization of the preasphaltenes is inhibited, then some of the preasphaltenes can be converted to pyridine insoluble material before it is converted to asphaltenes and dispersed. This appears to be the case at 100% tetralin where a drop in conversion to pyridine solubles is seen in Figure 2 relative to the conversion at 50% tetralin. It also explains in part the increase in hydrogen to carbon ratio with tetralin concentration in Figure 3.

Runs were made at 375 and 400°C with β -naphthol in tetralin and 2-methylnaphthalene at a mass ratio of 1 to 4 to determine the effect of the β -naphthol on the conversion of the coal to pyridine and toluene solubles. As can be seen in Figure 2, at a 1 to 4 mass ratio of tetralin to 2-methylnaphthalene the sensitivity to the β -naphthol should be clear. The results are presented in Figure 4. At 400°C the coal conversion to Pyridine solubles increases from 75.4 to 82.7 wt % of the DMMF Coal when the β -naphthol content is increased to 5 wt % in the solvent. No

Solvent	Wt Ratio of 2-Methylnaphthalene to Tetralin 4:1 in β -Naphthol
Agitation	1500 rpm
Heating Rate	6°C/min to 400°C
Holding Time	25 min at 400°C

Figure 4. The Effect of β -Naphthol Concentration in a Solvent with a Mass Ratio of 2-Methylnaphthalene to Tetralin of 4:1 on the Conversion of Kentucky No. 9 Coal.

increase is apparent above 5 wt % β -naphthol. The effect on the toluene solubles at 400°C and the pyridine solubles at 375°C is slightly less.

Holding Time Effects

Four runs were made to study the effect of holding time at 400°C on the dissolution of Kentucky No. 9 coal in a solvent containing 46.1 wt % tetralin, 46.1 wt % 2-methylnaphthalene, 2.9 wt % γ -picoline and 4.9 wt % β -naphthol. The solvent appeared to be the optimum solvent based on the work to date. The coal and solvent at a solvent to coal mass ratio of 2.5:1 was heated with a constant electrical input to the furnace to give a temperature rise of 6°C/min. The power is reduced as the contents of the reactor approaches 400°C and the temperature held at 400°C for the desired time and quenched. The stirrer rotation rate was 1500 rpm.

The results are presented in Figure 5. The formation of pyridine soluble material is rapid during the first 10 minutes and then levels off at 89 wt % of the DMMF coal. The formation of toluene soluble material is also rapid during the first 10 minutes but increases slowly afterwards at the reaction conditions.

Changes to the preasphaltenes and the pyridine insoluble residues do occur as the hold time is increased. This is shown by the decrease in the atom ratio of hydrogen to carbon in Table 1. A similar change also occurs with an increased severity of the dissolution conditions, the H:C ratio being higher at 375°C than at 400°C for the same hold time.

Agitation 1500 rpm
Heating Rate 6°C/min to 400°C

Figure 5. The Effect of Hold Time at 400°C on the Conversion of a Kentucky No. 9 Coal in a Solvent Containing 46.1 wt % Tetralin, 46.1 wt % 2-Methylnaphthalene, 2.9 wt % γ -Picoline and 4.9 wt % β -Naphthol.

Table 1. Effect of Hold Time and Temperature on the Atom Ratio of Hydrogen to Carbon in Precipitated Preasphaltenes and in Pyridine Insoluble Residues. The Solvent Contained 46.1 wt % Tetralin, 46.1 wt % 2-Methylnaphthalene, 4.9 wt % β -Naphthol and 2.9 wt % γ -Picoline

Run	Temp	Hold-Time	H/C Atom Ratio	
			Preasphaltenes	Residue
	C	min.		
23	400	0	0.877	0.699
24	400	25	0.814	0.554
26	375	25	0.871	0.576
24	400	25	0.814	0.554

III. CONCLUSIONS

Experiments carried out in a Plexiglas vessel with sand and water revealed that a turbine impeller/propeller combination with the propeller above was the most effective in dispersing the stationary settled sand. It also gave the most intense flow at the reactor walls for a given rpm. Based on the anomalies seen in coal dissolution experiments at different heating rates with different mixing conditions, it was concluded that the heat transfer rate at the inside surfaces of the reactor had the greatest influence on the uniformity of conditions within the reactor. The turbine impeller combination is best and there is a minimum rotation rate for each reactor heating rate.

The conversion of the Kentucky No. 9 coal to pyridine solubles reaches a maximum in a solvent where the weight ratio of aromatic (2-methylnaphthalene) to hydroaromatic (tetralin) components is approximately 1. Conversion increases slightly as the phenolic (β -naphthol) content is increased to 5 wt % in the solvent and appears to reduce conversion at concentrations above 5 wt %. The 2-methylnaphthalene and β -naphthol should tend to peptize and disperse the preasphaltenes as they are produced in coal liquefaction. The tetralin would tend to inhibit peptization and dispersion of preasphaltenes but would be a ready source of protons to stabilize free radicals in preasphaltenes and asphaltenes as they are produced when chemical bonds are broken as the temperature rises and is held above 350°C. Some agitation is required to facilitate mass transfer.

The exact physical state in the solvent-coal mixture during coal liquefaction is not known. Some clue as to phase behavior can be inferred

from solids-liquid separation work on the Kerr-McGee process (2-12). At temperatures above approximately 220°C, two liquid phases exist in the Kerr-McGee process. The less dense phase is the oil and asphaltene-rich phase and the more dense phase is the preasphaltene-rich phase containing most of the carbonaceous and mineral residues. A typical material balance and split for the Kerr-McGee Process is shown in Figure 6. Most of the preasphaltenes exist in the preasphaltene-rich liquid phase with the solids residues. As the temperature rises above 300°C, the solubility of the preasphaltenes in the oil-rich phase should increase. The exact distribution would depend upon the nature of the oil-rich phase and the amount and nature of the solids residues. Agitation disperses the dense preasphaltene-rich liquid phase in the oil-rich phase as an emulsion. Once the agitation is terminated, the two phases separate again.

As coal is converted during coal liquefaction, the distribution of oils, asphaltenes, preasphaltenes and solids change continuously above 350°C as illustrated in Figure 7. One would expect the preasphaltenes and solids in an individual coal particle to resemble the discontinuous phase of an emulsion. The nature of the continuous phase and the temperature would play a dominant role in the distribution of preasphaltenes between the two phases. Agitation also plays a role.

Interestingly, the residues from coal dissolution in 100 wt % tetralin all show evidence of substantial agglomeration of coal particles during the dissolution process. This is further evidence of why there is a drop in conversion to pyridine solubles as the tetralin content of the solvent is increased from 50 wt % to 100 wt % as seen in Figure 2.

Figure 6. Mass Equilibrium Split at Approximately 285°C between Vacuum Still Bottoms and an Aromatic Oil-Like Solvent in the Kerr-McGee Process (2).

Figure 7. Dissolution of Kentucky No. 9 Coal in 46.1 wt % Tetralin, 46.1 wt % 2-Methylnaphthalene, 2.9 wt % γ -Picoline and 4.9 wt % β -Naphthol at a Solvent to Coal Mass Ratio of 2.5 to 1.

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