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Novel Nanodispersed Coal Liquefaction Catalysts: Molecular Design Via Microemulsion-Based Synthesis

Technical Progress Report
October - December 1992

by

E. Boakye, M. Vittal, K. Osseo-Asare and L. R. Radovic

Department of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

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PROJECT OBJECTIVES

The objective of this project is to pursue the development of highly dispersed and inexpensive catalysts for improved coal solubilization and upgrading of coal liquids. A novel study of the synthesis of liquefaction catalysts of nanometer size is being carried out. It is based on the molecular design of reverse micelles (microemulsions). These surfactant-stabilized, metal-bearing microdrops offer unique opportunities for synthesizing very small particles by providing a cage-like effect that limits particle nucleation, growth and agglomeration. The emphasis is on molybdenum- and iron-based catalysts, but the techniques being developed should also be generally applicable. The size of these very small and monodispersed particles will be accurately determined both separately and after *in situ* and *ex situ* coal impregnation. The as-prepared nanoparticles as well as the catalyst-impregnated coal or char matrix are characterized using a battery of techniques, including dynamic light scattering, x-ray diffraction and transmission electron microscopy. Catalytic activity tests are conducted under standardized coal liquefaction conditions. The effect of particle size of these unsupported catalysts on the product yield and distribution during conversion of a bituminous and a subbituminous coal are being determined.

INTRODUCTION

In the previous quarter, work on the synthesis of molybdenum sulfide in the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion was reported. The alcohol-to-surfactant mass ratio was 2.5. In this quarter, we report the synthesis of molybdenum sulfide in a similar microemulsion system with an alcohol-to-surfactant mass ratio of 3.5. Also presented in this document is the synthesis of molybdenum sulfide in the 0.4 M NP-5/tetralin/ methanol microemulsion system. Other studies reported are the fluorescence spectroscopy of the locale and site of solubilization of the alcohols used as cosurfactants in the above microemulsion systems and the photon correlation spectroscopy of the size of the reverse micelles in the NP-5/tetralin/methanol system.

EXPERIMENTAL

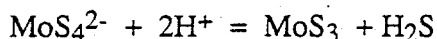
Materials. The following chemicals obtained from Aldrich were used as received: the nonionic surfactant polyoxyethylene(5)nonylphenyl ether (NP-5), ammonium tetrathiomolybdate (99.97%), benzyl alcohol, methanol, 1,2,3,4-tetrahydronaphthalene (tetralin) and tris(2,2'-bipyridyl) ruthenium(II) chloride hexahydrate.

Microemulsion Characterization. The solubilization locales of methanol and benzyl alcohol were determined by fluorescence spectroscopy using a Shimadzu RF-5000 spectrofluorometer. The spectrum was collected in the emission mode with an excitation wavelength of 460 nm. The molecule tris(2,2'-bipyridyl) ruthenium(II) chloride hexahydrate was used as a fluorescence probe. In all cases the concentration of the probe molecule was 1.45×10^{-5} M with respect to 10 mL of microemulsion.

Photon correlation spectroscopy was used to monitor the size of the reverse micelles at various water-to-surfactant molar ratios. The light source of the apparatus was a coherent Innova

70-2 argon ion laser operating at 488 nm. The scattered light was collected at an angle of 45° by a goniometer and was focused on a photomultiplier tube (both from Malvern Instruments). The correlation function was recorded with a Malvern 7032-8 correlator with 264 channels. The hydrodynamic size was calculated with a particle size distribution software also obtained from Malvern Instruments.

Particle Synthesis. The synthesis experiments were conducted at 50 °C. Solutions of 0.4 M NP-5/tetralin/benzyl alcohol and 0.4 M NP-5/tetralin/methanol were first made at room temperature. The alcohol-to-surfactant mass ratios were 3.5 and 2.5, respectively. A number of samples containing a fixed oil-to-surfactant and oil-to-cosurfactant molar ratios with variable amounts of water were prepared. This was followed by adding 36.2 µL of 1.1 M aqueous sulfuric acid to a 10 mL solution of 0.4 M NP-5/tetralin/benzyl alcohol and 0.4 M NP-5/tetralin/methanol microemulsions. The acid-solubilized microemulsion was deoxygenated by bubbling high-purity nitrogen gas through it. This procedure was followed by adding 36.2 µL of 1.25×10^{-2} M ammonium tetrathiomolybdate to the microemulsions. Nitrogen was further bubbled while molybdenum sulfide was being precipitated according to:



The concentrations of the reactant species were as follows: 4×10^{-3} M sulfuric acid and 4.5×10^{-5} M ammonium tetrathiomolybdate with respect to both microemulsions.

Samples for transmission electron microscopy were prepared by directly dropping a very small amount of molybdenum sulfide dispersion on carbon-coated copper grids and drying at room temperature. Particle sizes were determined with a Philips 420 TEM operating at 120 kV with a resolution of 0.6 nm. The diameters of at least 200 particles were measured for each sample to obtain an average particle diameter.

RESULTS AND DISCUSSION

Task 2: Catalyst Characterization

Fluorescence Spectroscopy. It has been reported that short-chain alcohols used as cosurfactants in the formulation of microemulsions partition between the reverse micellar water core and the bulk oil phase (1,2). In addition, Atik and Thomas (3) have shown that additives such as benzyl alcohol and hexanol affect differently the transport of ions between reverse micelles. The rates of ion transport when benzyl alcohol and hexanol were used as cosurfactants were 330 and 7.5, respectively (3). Thus, obviously, the use of methanol and benzyl alcohol will affect differently the rate of ion transport between the reverse micelles and hence the exchange of solubilizates between the water pools.

Figures 1 and 2 represent the fluorescence spectra of tris(2,2'-bipyridyl) ruthenium(II) chloride hexahydrate ($\text{Ru}(\text{Bpy})_3$) in the two microemulsion systems studied at various water-to-surfactant molar ratios. For the purpose of comparison, the fluorescence spectrum of $\text{Ru}(\text{Bpy})_3$ in water is included (dashed lines). As seen in Figure 1, the emission maximum for the methanol-based microemulsion is about the same as that for water (615 nm). However, the spectrum of $\text{Ru}(\text{Bpy})_3$ in the benzyl alcohol-based microemulsion peaks at 625 nm, which is red-shifted compared to that of water. These results suggest that while methanol partitions between the aqueous and the bulk organic phase, benzyl alcohol interacts with the aqueous/organic interface.

The above results are further evidence in support of the work done by Atik and Thomas (3). Benzyl alcohol, assumed to be located at the surfactant interface, causes disruption of the surfactant head groups and thus enhances ion penetration into the reverse micelles. Also, since ions cannot interact with the organic phase, the exchange of ions occurs between reverse micelles only during collision. This means that the rate of ion transport is directly related to the rate of exchange of solubilizates between reverse micelles (K_{ex}). It follows that the K_{ex} for the

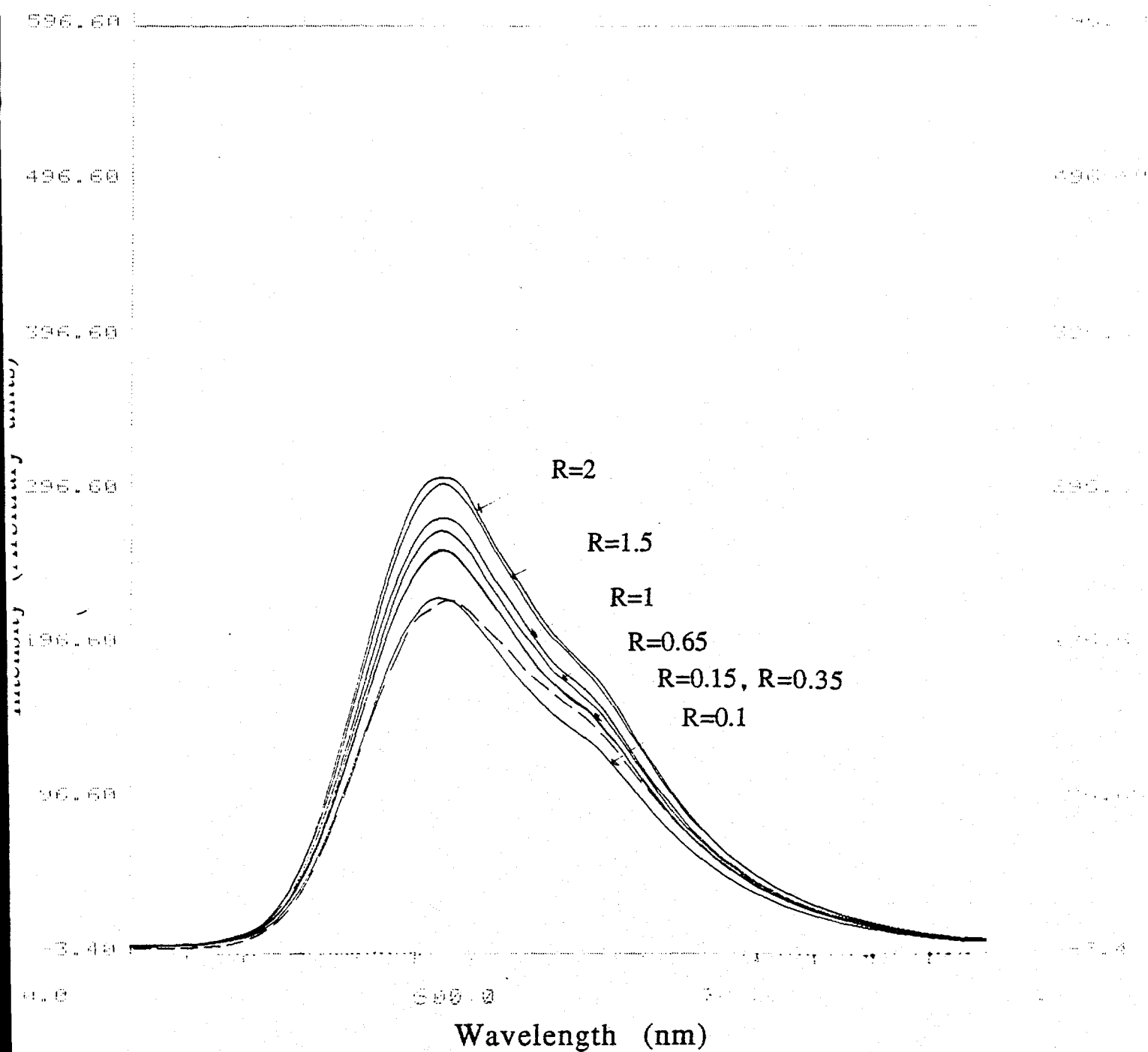


Figure 1. Fluorescence spectra of Ru(Bpy)₃ solubilized in the 0.4 M NP-5/tetralin/methanol/water microemulsion.

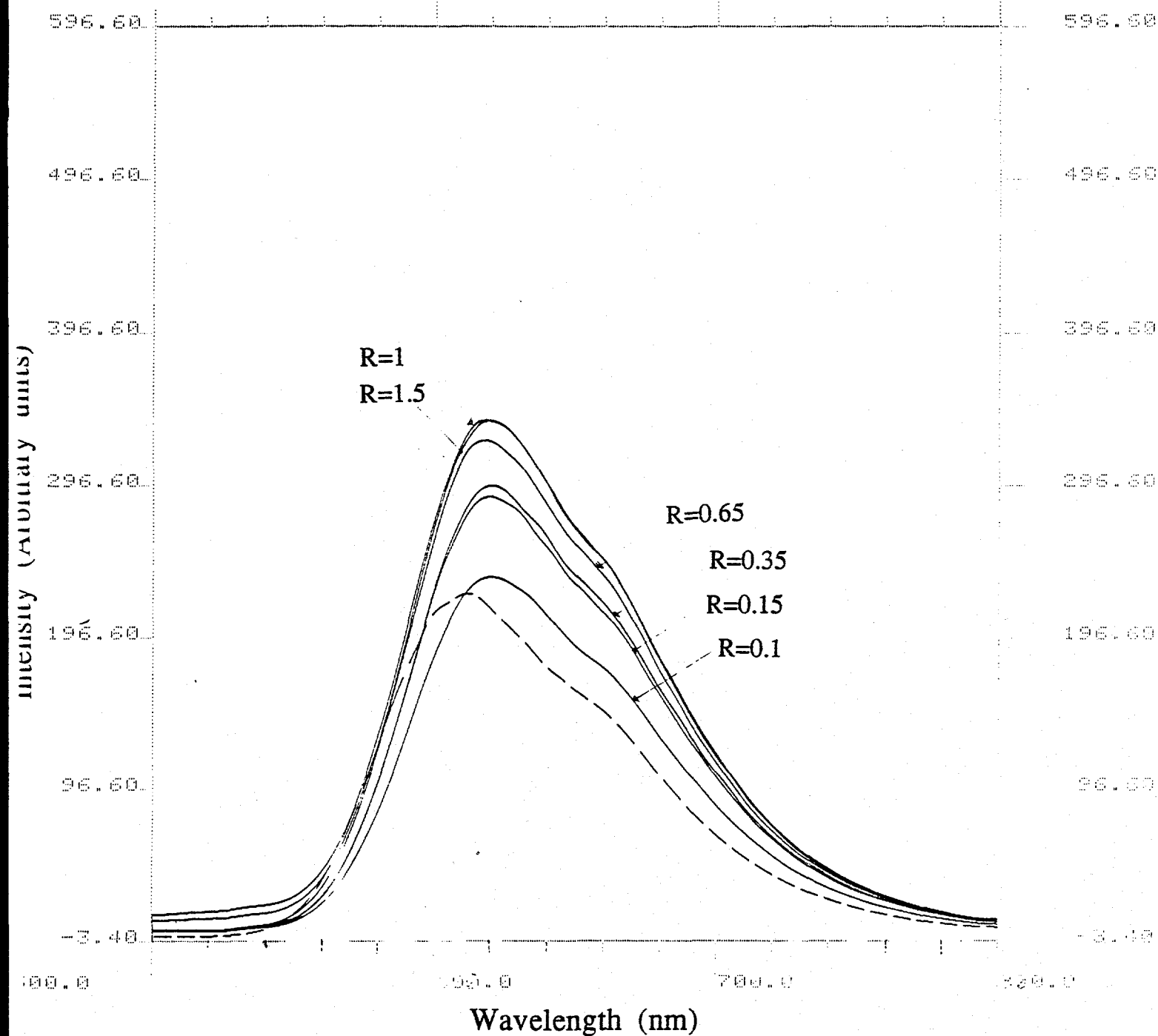


Figure 2. Fluorescence spectra of Ru(Bpy)₃ solubilized in the 0.4 M NP-5/tetralin/benzyl alcohol/water microemulsion.

microemulsion formulated with benzyl alcohol as a cosurfactant is greater than that of hexanol and may be greater than that of methanol.

Photon correlation spectroscopy. We have used photon correlation spectroscopy to monitor the variation of the size of the reverse micelles at various water-to-surfactant molar ratios (R) for the methanol-based microemulsion (see Figure 3). The hydrodynamic diameter of the reverse micelles increases as the water-to-surfactant molar ratio is increased. A similar observation had been made by Robinson et al. (4) for three microemulsion systems: AOT/cyclohexane/water, AOT/toluene/water and AOT/chlorobenzene/water. In a mixture of an apolar organic solvent and a nonionic surfactant such as NP-5, the polar head groups of the amphiphile aggregate to form ionic clusters. With the addition of initial water molecules, interaction with the hydrophilic polar groups of the surfactant via hydrogen bonding leads to the formation of reverse micelles. The addition of more water molecules results in the formation of swollen reverse micelles, the size of which increases with the water content. From Figure 3 it is concluded that the size range is between 4 and 16 nm for R values of 1-8.

At $R < 5$, the hydrodynamic diameter appears to remain constant, which is incorrect, because the size of the micelles is expected to decrease as R decreases. The deviation from the expected values may be due to the nonspherical nature of the micelles at low R values. The photon correlation spectroscopy technique essentially measures the diffusion coefficient of the light-scattered micelles, which in turn is related to the particle size by the Stokes-Einstein equation. Here the assumption is made that the particles are perfect spheres, which may not be true at low R values.

Particle synthesis. Figure 4 presents TEM micrographs of molybdenum sulfide particles synthesized in the 0.4 M NP-5/tetralin/methanol microemulsion. A bimodal distribution is observed for particles made at each R value. Particles in the size range 2-4 nm (primary particles) and 15-50 nm (final particles) were produced. Figure 5 presents a plot of the average particle

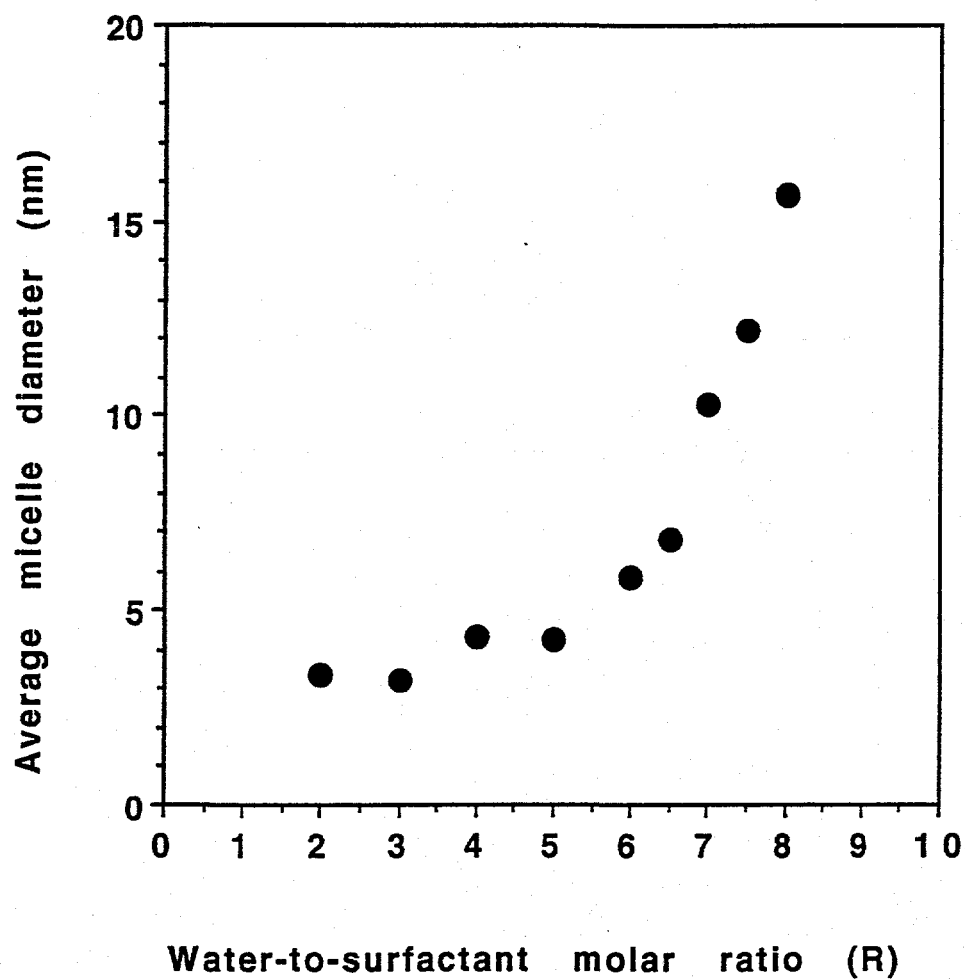
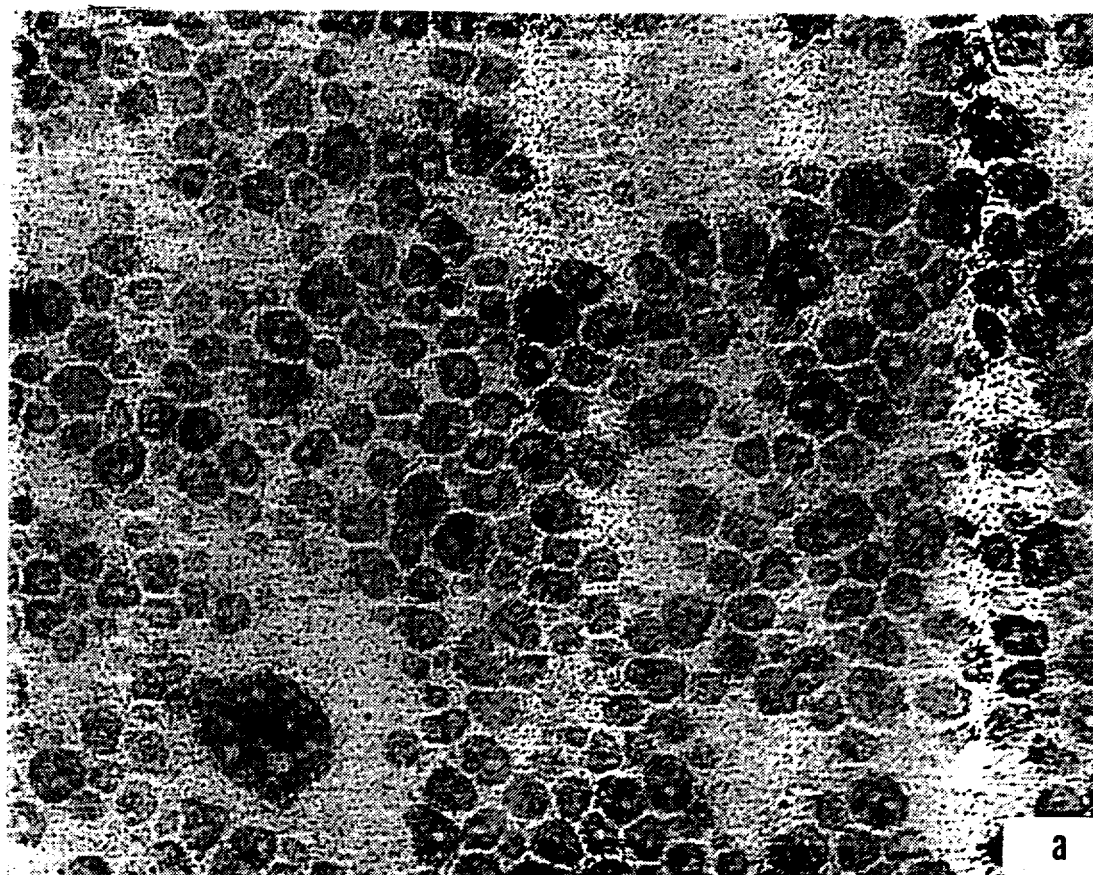
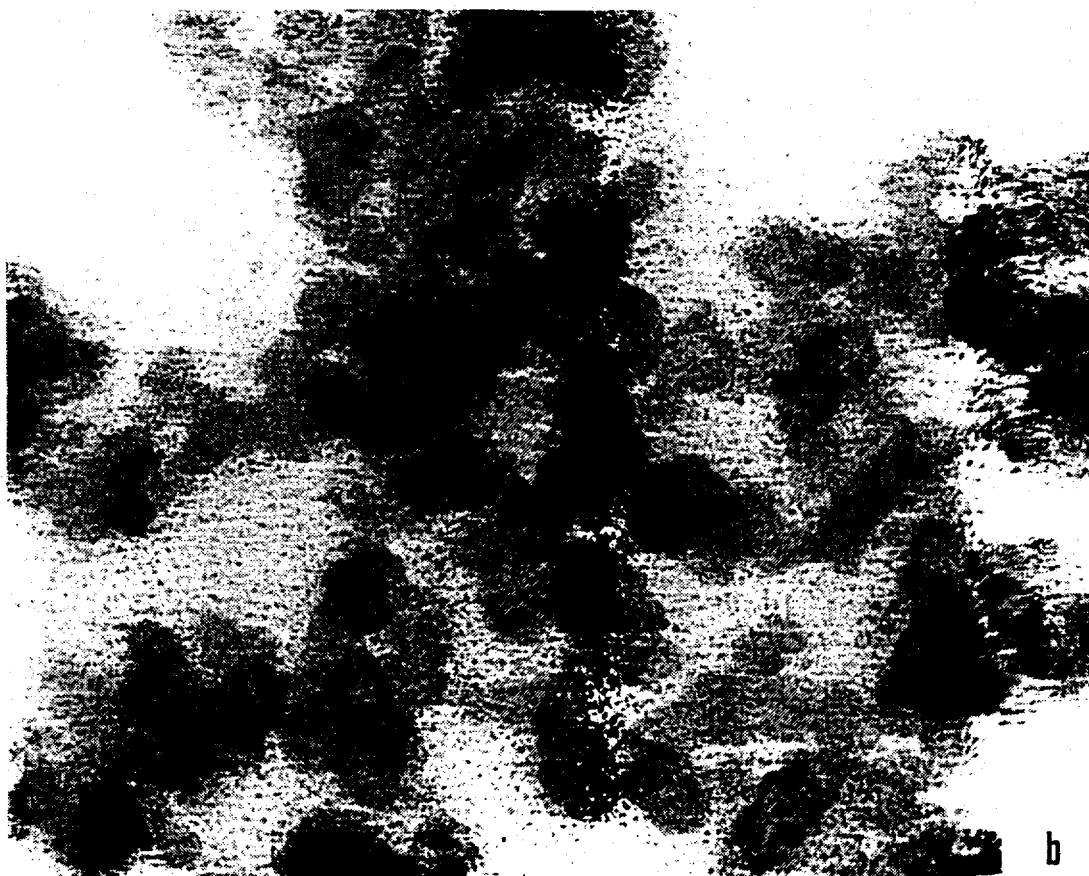


Figure 3. Photon correlation spectroscopic study of the variation of the hydrodynamic diameter with the water-to-surfactant molar ratio for the NP-5/tetralin/methanol/water.



50nm



50nm

Figure 4. TEM micrographs of molybdenum sulfide particles prepared in the 0.4 M NP-5/tetralin/methanol/water microemulsion system. (a) $D = 2$. (b) $D = 4$.

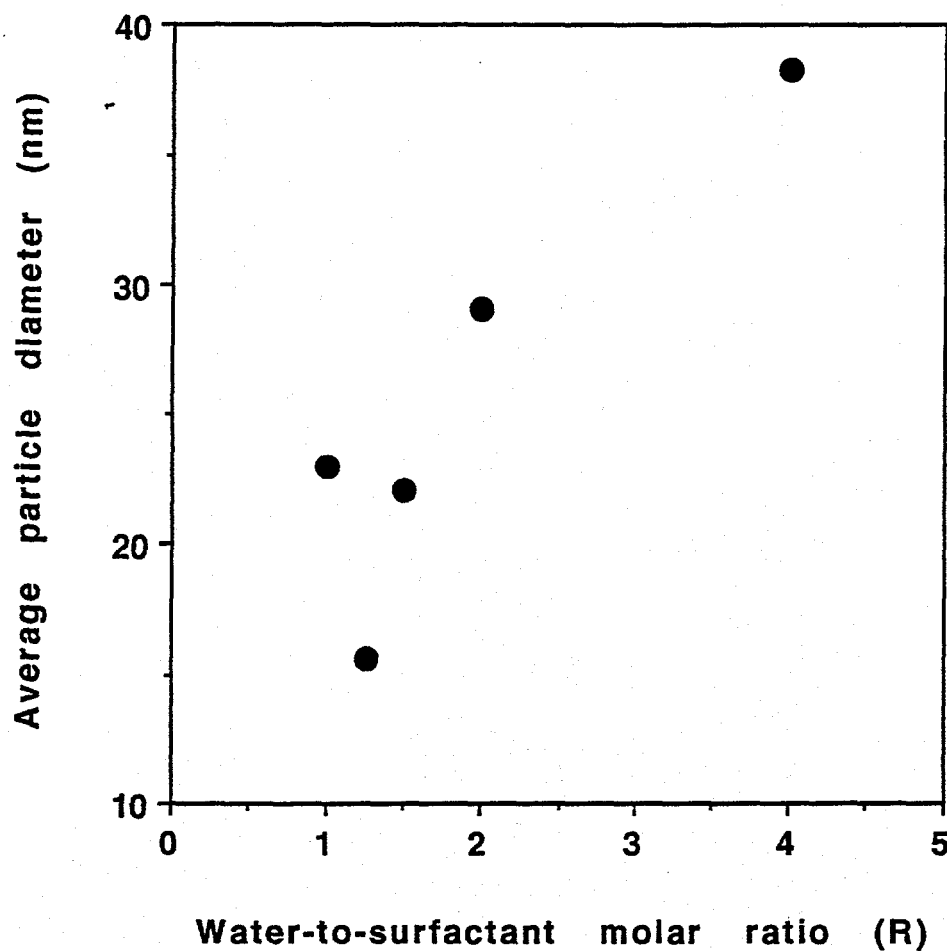


Figure 5. Effect of water-to-surfactant molar ratio (R) on the average molybdenum sulfide particle size for the 0.4 M NP-5/tetralin/methanol/water microemulsion system. $[\text{MoS}_4^{2-}] = 4.5 \times 10^{-5} \text{ M}$; $[\text{H}_2\text{SO}_4] = 4.0 \times 10^{-3} \text{ M}$.

diameter vs. R for the final particles (or aggregates of primary particles). The particle size initially decreases with R (up to $R=1.25$) and then increases with R . This trend is explained by considering the following particle formation and growth scheme (5-7):

- (i) Ammonium tetrathiomolybdate reacts with aqueous sulfuric acid to form molybdenum trisulfide monomer;
- (ii) Before a stable nucleus is formed, a critical number of MoS_3 monomers must combine (5);
- (iii) After a stable nucleus is formed, it can grow by incorporating the molybdate ions from solution (6);
- (iv) As a consequence of intermicellar interactions, primary particles and/or nuclei may aggregate to form bigger particles (7).

In order to generate small and monodispersed particles, it is important that the nucleation and particle growth processes occur on different time scales. To satisfy this condition, it will be necessary to produce a large number of nuclei quickly, i.e., to increase the nucleation rate. An important parameter in connection with the growth mechanism is the average molybdate occupancy number (i.e., the number of tetrathiomolybdate ions per micelle).

The aggregation number decreases as the water-to-surfactant molar ratio decreases. For a fixed volume of microemulsion, it follows that the number of ions per micelle will decrease. For very low R values, relatively few water cores will contain the minimum number of monomers needed to form a nucleus. As a result, the nucleation rate is slow and the remaining ions not utilized in nuclei formation are incorporated into the already formed primary particles and/or nuclei to form bigger particles. As R increases, the aggregation number increases, the micellar concentration decreases, the occupancy number increases and the nucleation rate increases. The observed decrease in particle size with R below $R=1.25$ is due to the increased occupancy number. At $R>1.25$, the occupancy number is relatively high and the formation of smaller particles is expected. Contrary to expectation, however, larger particles were obtained. At $R>1.5$, particle growth via fusion of nuclei or primary particles is more likely, as indicated on the TEM micrograph in Figure 4b. Similar observations have been made in this laboratory (9) during synthesis of

molybdenum sulfide particles in the NP-5/cyclohexane/water microemulsion system, where TEM micrographs showed 5-nm primary particles aggregating to form particles of 80-100 nm.

Figure 6 presents the dependence of the average molybdenum sulfide particle diameter on the water-to-surfactant molar ratio for the 0.4 M NP-5/tetralin/benzyl alcohol system. Figure 7 shows the corresponding TEM micrographs. In contrast to the microemulsion formulated with methanol, the particle size monotonically increases with R . Also, the distribution is monomodal. The increase in particle size with R may be due to particle aggregation, as discussed above.

An interesting question that needs to be addressed is why small particles, in the range 2-4 nm, can be made in the methanol-based microemulsion but not in one in which benzyl alcohol is the cosurfactant. This issue can be resolved by considering the fluorescence studies and the work of Atik and Thomas (3). While methanol partitions between the water pools and the organic phase, benzyl alcohol interacts with the surfactant head group and hence facilitates the transport of ions between the micelles. Further, it is concluded that because of this effect, K_{ex} for microemulsions formulated with benzyl alcohol will be greater than that of the microemulsion formulated with methanol. For the effectiveness of a process in which a critical number of monomers must combine to form a stable nucleus, the monomers must be retained in a specific micelle for a sufficiently long period of time. If the inter-micellar exchange of solubilizates is very rapid, then the monomers will be redistributed in other micelles before nucleation can occur. Consequently, increasing the value of K_{ex} , e.g., for the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion, may result in fewer nuclei being formed and smaller particles being made. Also, as K_{ex} increases, the probability of exchange of solute species between the micelles increases. As a result, particle aggregation will increase and relatively large particles will be made.

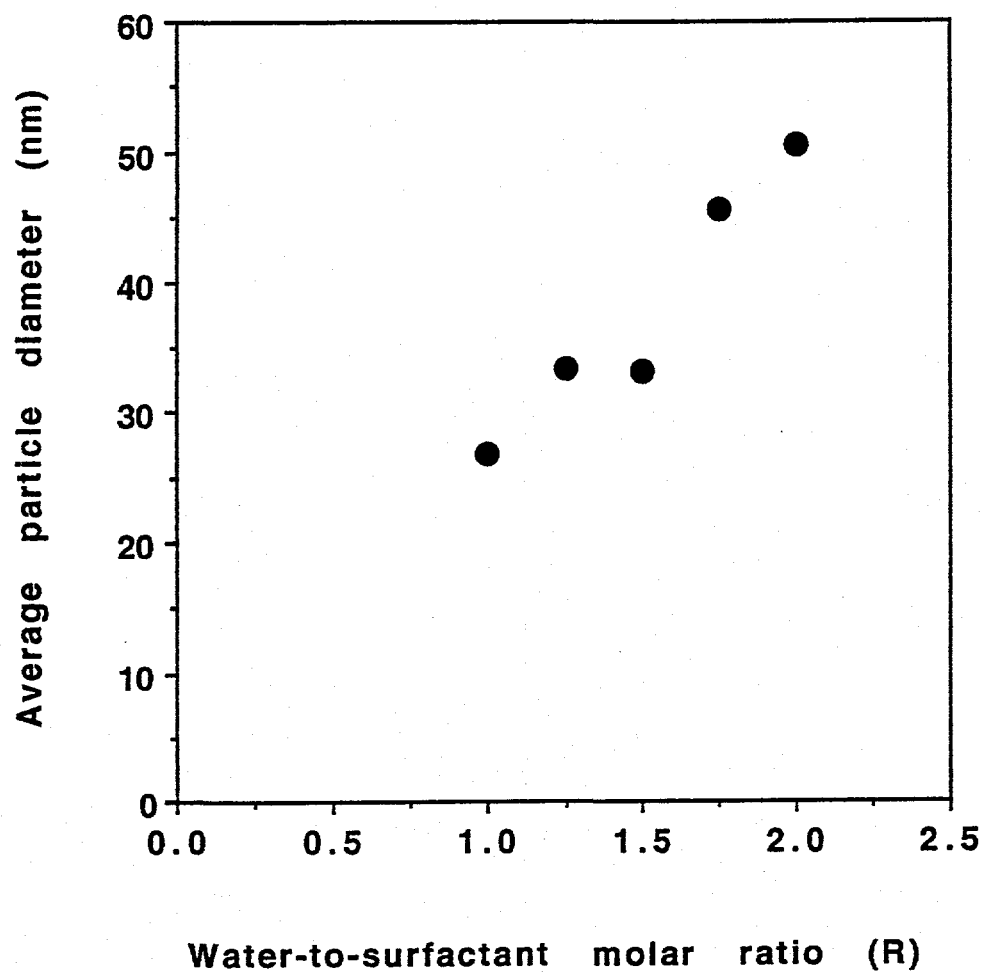


Figure 6. Effect of water-to-surfactant molar ratio (R) on the average molybdenum sulfide particle size for the 0.4 M NP-5/tetralin/benzyl alcohol/water microemulsion system. $[\text{MoS}_4^{2-}] = 4.5 \times 10^{-5} \text{ M}$; $[\text{H}_2\text{SO}_4] = 4.0 \times 10^{-3} \text{ M}$.

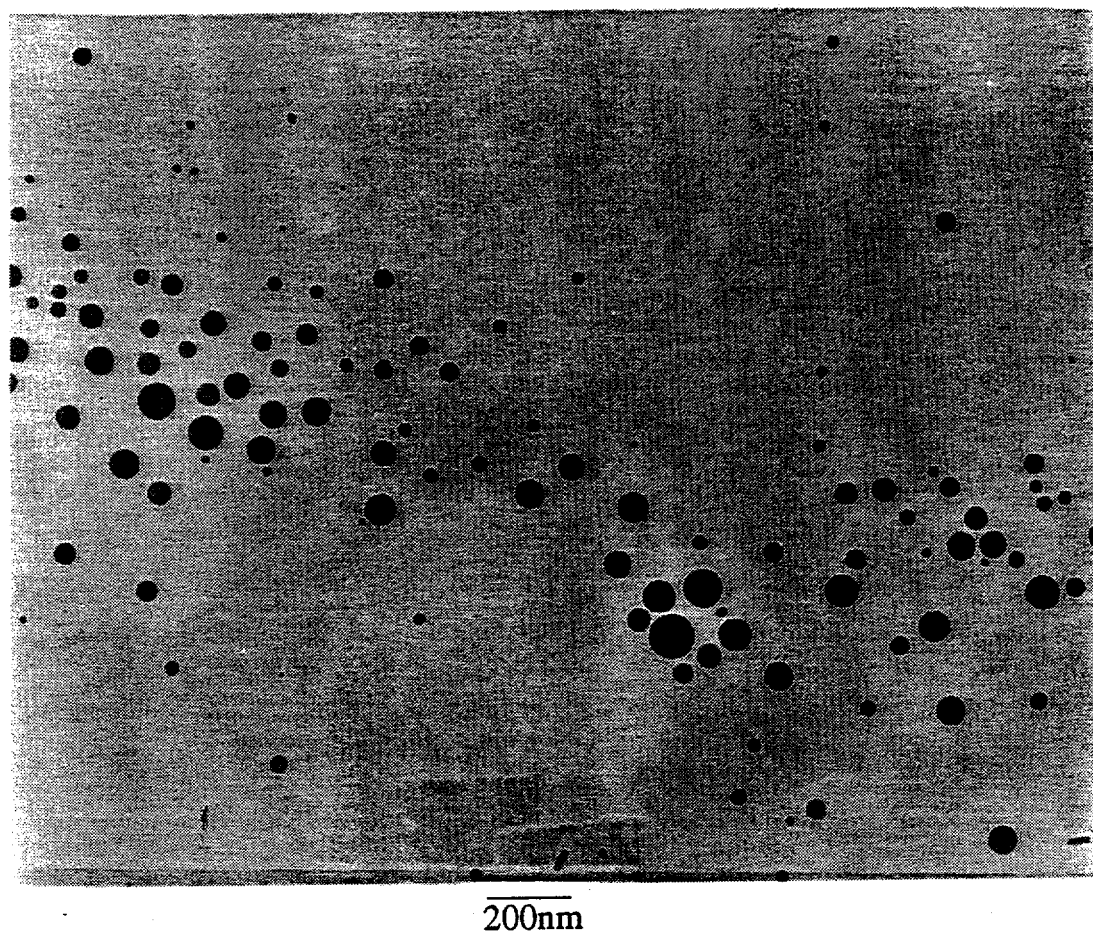


Figure 7. TEM micrograph of molybdenum sulfide particles prepared in the 0.4 M NP-5/tetralin/benzyl alcohol microemulsion system. $R = 1.75$

Task 3: Catalyst Testing

As stated in our previous quarterly report, microemulsion-based catalysts can be used conveniently to study both the influence of catalyst loading and catalyst particle size on the coal liquefaction process. To study the former, the NP-5/tetralin/benzyl alcohol microemulsion formulated with $R=2$ (see Task 2) was chosen, with an average size of particle aggregates of ~ 40 nm. A series of blank experiments was also identified as being necessary to account for solvent effects that are inevitably introduced (at this stage). All tests were carried out at 350°C and 1000 psi H_2 for 30 min. The products were then extracted with THF; the total conversion was calculated from the weight of the THF-insoluble residue, and reported on a daf basis.

The results with a subbituminous coal (PSOC 1401) are reported in Table 1. It was found that the distinction between the catalyzed and the uncatalyzed reaction virtually disappeared as the molybdenum loading increased, owing perhaps to the overwhelming effect of the solvent. Also, the presence of benzyl alcohol (as much as 40% by weight in the microemulsion) may promote retrogressive reactions (10) and mask or suppress the catalytic effect.

Identical experiments were performed with a bituminous coal (DECS-6). The results are reported in Table 2. A modest improvement in total conversion seems to result when the catalyst loading is increased to 100 ppm Mo. It is interesting to note also that the total conversion does not change as the solvent-to-coal ratio increases.

Evidently, these preliminary results emphasize the previously well documented distinct liquefaction behavior of coals of different rank. Experiments are in progress to determine separately the yields of oils and asphaltenes.

Table 1. Liquefaction behavior of a subbituminous coal (PSOC 1401) in the presence of a microemulsion-based catalyst (NP-5/tetralin/benzyl alcohol).

Test No.	Amount of μ E added* (grams)	Catalyst loading (ppm Mo)	Total conversion** (%)
LT 15	2.8457	25	31.3
LT 16	5.4948	50	37.4
LT 17	10.9707	100	43.1
LT 18	16.7763	150	45.4
LT 19	2.8694	0	14.8
LT 20	5.5570	0	28.6
LT 21	10.9954	0	45.3
LT 22	16.8048	0	48.7

* μ E = microemulsion; either blank (19-22) or metal-loaded (15-18).

**T= 350 °C, P=1000 psi H₂ (cold), 30 min; based on mass of THF-insoluble residue, daf basis.

Table 2. Liquefaction behavior of a bituminous coal (DECS-6) in the presence of a microemulsion-based catalyst (NP-5/tetralin/benzyl alcohol).

Test No.	Amount of μ E added* (grams)	Catalyst loading (ppm Mo)	Total conversion** (%)
27	3.4303	0	60.0
28	6.7962	0	61.3
29	13.4341	0	60.4
30	26.5506	0	59.4
31	3.3374	25	61.1
32	7.3835	50	62.0
33	13.6444	100	67.3
34	27.2218	200	68.6

* μ E = microemulsion; either blank (27-30) or metal-loaded (31-34).

**T= 350 °C, P=1000 psi H₂ (cold), 30 min; based on mass of THF-insoluble residue, daf basis.

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