STABILIZING OF SHALE OIL-WATER EMULSIONS BY PENTANE-INSOLUBLE MATERIALS

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INTRODUCTION

Separation of crude shale oil from the water produced during retorting has long been a problem with some shale oils retorted from Green River Formation oil shale of the western United States. In recent work (1) it was reported that shale oil produced from the Paraho retort by the indirectly heated mode could be easily separated from retort water after being heated to 77°C (170°F) and allowed to settle at this temperature for six hours. Conversely, it has been found by the LERC authors that a sample of raw (untreated) crude shale oil produced from Site 9 of the Department of Energy (DOE) in situ retorting project near Rock Springs, Wyoming, was not separated from suspended retort water when heated in a separatory funnel to 82°C (180°F) for a period of 15 hours.

In 1949, a brief study was reported (2) on the removal of suspended solids from N-T-U shale oil by a rotary filter precoated with filter aid. Water that could not be separated from the unfiltered oil by heating was easily separated when the filtered oil was heated to 71°C (160°F) for three hours. It was not determined whether the solids removed by the filter were organic or inorganic.

The Paraho shale oil mentioned above contained only 0.17 weight-percent asphaltenes (1) insoluble in hot heptane, while the in situ shale oil contained over 3.6 percent organic material insoluble in pentane. The present study was undertaken to determine whether the portion of shale oil that is insoluble in normal pentane and other solvents may be responsible for the formation of stable shale oil/water emulsions of in situ shale oil. Greater knowledge of the cause of the emulsions may assist in developing methods of avoiding their formation during retorting or subsequent handling of the oil; it may also help in devising newer and cheaper ways of separating the oil and water phases of emulsions.

EXPERIMENTAL

General Procedure

Pentane-insoluble materials were separated from filtered, dewatered crude shale oil prepared from DOE Site 9 crude oil, and from fractions of the oil. These materials were used as additives for blending in small percentages with light gas oil, dewaxed heavy gas oil, and filtered, dewatered pentane-extracted crude shale oil.

A blend was prepared by mixing a measured weight of additive with 100 ml of oil and stirring the mixture in a beaker at room temperature for 10 minutes with an electric stirrer. Distilled water was added and the mixture was stirred for 10 minutes after which the mixture was transferred to an electrically heated separatory funnel. Amounts of additive ranged from 0.5 to 2.2 weight percent of the oil, and amounts of water ranged from 11.4 to 52.2 percent.

Mixtures in the separatory funnel were heated with an electric jacket to 77°C (170°F), and maintained at this temperature for five hours under a flowing stream of nitrogen. The water and oil phases were drained separately into graduated cylinders and were weighed. A dry ice trap connected by a flexible tube to a water-cooled reflux condenser at the top of the separatory funnel during the

heating period collected vapors leaving the funnel. Only small amounts of water and traces of hydrocarbon too small to separate from the water were collected in the trap.

Preparation of Feeds For Blending With Additives

The first of three feeds for blending with pentane insoluble material was prepared from in situ Site 9 crude by filtering the crude shale oil through 60-to-100 mesh Berkshire sand and number 40 Whatman filter paper. No measure of the solids removed was obtained. Water was eliminated by distillation to a flask temperature of 150°C (302°F)at 40 mm absolute pressure. Oil condensed with the water was separated in a separatory funnel, dried over anhydrous sodium sulfate, and combined with the cooled contents of the distillation flask.

Dried shale oil was stirred with 15 volumes of n-pentane two hours at room temperature and filtered through a medium (M) porosity fritted glass funnel. Pentane was removed from the filtrate by distillation to a flask temperature of 200°C (392°F) at 585 mm mercury absolute, and the pentane-free filtrate was used as a feed for blending with pentane-insolubles in the emulsification studies. The funnel containing pentane-insolubles was vacuum-dried (380 mm absolute) at room temperature to constant weight, and the pentane-insoluble material was used as an additive in the emulsification studies.

The second feed for the blending studies was light gas oil prepared by distillation of raw, wet, unfiltered in situ Site 9 crude shale oil to initial and final column head temperatures of 106°C (223°F) and 200°C (392°F) at 40 mm; these corresponded to 200°C (392°F) and 313°C (595°F) at 760 mm. The light gas oil contained 0.46 weight-percent insoluble in pentane at room temperature (at a pentane:oil ratio of 20:1).

Heavy gas oil, the third feed for the blending studies, was obtained by continued distillation of the crude, after removal of light gas oil, to a column temperature of 300°C (572°F) at 40 mm, corresponding to 431°C (807°F) at 760 mm. To prevent complications during mixing and measuring that would be caused by wax in the heavy gas oil, the oil was dewaxed with a 2:1 acetone-toluene mixture at 0°C. Yield of wax was 11.5 weight percent. The dewaxed oil contained 0.45 weight-percent material insoluble in pentane at room temperature (20:1 ratio).

Preparation of Pentane-Insoluble Additives Mixed Into Feeds

Four pentane-insoluble materials were used in the study. These included two different insoluble portions of the filtered, dried in situ crude oil prepared by extraction of the dried crude with different pentane:oil ratios; the pentane-insoluble portion of the vacuum distillation residuum from the raw, wet, unfiltered crude; and the pentane-insoluble portion of solids filtered from the same raw crude with a 325-mesh screen. Properties of all insoluble fractions are shown in table 1.

Preparation of the insoluble portion of the filtered, dried crude at a 15:1 pentane:oil ratio has been described. The insoluble portion amounted to 3.6 weight-percent of the dry, filtered crude. A second insoluble portion was also prepared at a 40:1 extraction ratio and was used in one emulsification experiment. It was 2.8 weight-percent of the dry crude.

Distillation residuum from the previously-discussed distillation of light and heavy gas oils from raw crude oil was extracted with pentane at a solvent:oil ratio of 20:1, yielding 24.2 weight-percent of the residuum or 3.8 percent of the dry crude as pentane-insoluble material that was used in emulsification studies. Properties of this material are also shown in table 1.

The fourth pentane-insoluble material was prepared from solids that were separated from Site 9 crude oil by screening the crude at 65°C through a 325-mesh stainless steel standard Tyler sieve. Prior to screening, the sample of raw, wet crude had been heated at 77°C (170°F) in a separatory funnel for five hours with no separation of water. The same sample was filtered through the 325-mesh screen, removing 3.5 weight-percent of the wet oil (4.9 percent, dry oil basis) as "gunk" on the screen.

Solids separated on the 325-mesh screen were extracted with pentane (15:1 weight ratio), yielding 26.5 percent material (1.3 percent of the dry crude) insoluble in pentane. When the filtered oil was replaced in the separatory funnel and heated to 77°C, water quickly separated. Water measured at the end of five hours was 29.2 weight-percent of the original wet crude. Subsequent testing for water in the dewatered oil by the ASTM distillation method (D-95) showed less than 0.05 weight-percent water in the oil.

In addition to emulsification tests made with the pentane-insoluble materials, tests for comparison purposes were made with the pentane-soluble portion of the sand-and-paper filtered dried crude and with the pentane-soluble portion of the distillation residuum (see table 2). Tests also were made with toluene-soluble and toluene-insoluble portions of pentane-insoluble material from the screen-filtered solids, and with chloroform-soluble, pentane-insoluble portion. All tests with materials separated from the wire-screen-filtered crude are shown in table 3.

Results and Discussion of Experiments

Effect of Additives From Residuum and Filtered Crude on Filtered, Pentane-Extracted Crude

Experiments A through G were made with the pentane-soluble portion of crude shale oil that had been filtered through sand and filter paper.

When distilled water alone was mixed with the pentane-soluble portion of sand and paper-filtered crude in experiment A (table 2) the oil and water phases separated in a few minutes with a clear, sharp interface. Heating was continued for the scheduled five hours, at the end of which some loss in weight of the oil was found to have occurred. Part of the loss was the result of vaporization, as shown by some condensate in the dry ice trap; part of it may have been the result of some of the oil being dissolved in the water phase.

In experiments B, C, and D, pentane-insoluble material from the vacuum distillation residuum was added to samples of the same pentane-soluble filtered crude used in experiment A. Addition of 0.5, 1.0, and 2.0 percent pentane-insoluble to the pentane-soluble-oil before mixing with water caused the oil phases to pick up increasingly larger percentages of water that did not separate from the oil phase after settling five hours at 77°C. No individual droplets of water were discernible in the oil phases. The oil phase from experiment D, in which 2.0 percent pentane-insoluble additive was used, gained 48.8 weight percent (including the 2.0 percent additive), based on the weight of the original oil.

The ash content of the pentane-insoluble material from the distillation residuum was only 1.02 percent. In a 2.0 percent blend of the pentane-insoluble material with filtered crude, the pentane-insoluble would contribute only 0.02 percent ash to the blend. It appears that the inorganic material played little part in the formation of the emulsions.

In experiments E, F, and G, 1.0 weight-percent pentane-insoluble from the sand-filtered crude was added to the pentane-soluble crude before it was mixed with water. In experiment F, the oil was heated to 100°C before the pentane-insoluble was added, and was maintained at this temperature for one hour, with stirring, after the addition to promote solution of the additive in the oil before water was added. Pentane-insoluble that was separated from the raw, filtered crude with a solvent:oil ratio of 40:1 was used in experiment G. In each of these

three experiments, a small loss in weight of the oil phase occurred, indicating no emulsion-forming tendency for the pentane-insoluble from the filtered crude under the conditions used.

Effect of Additives From Residuum and Filtered Crude on Gas Oils

When 2.2 percent of the pentane-insoluble from the filtered crude was mixed with dewaxed heavy gas oil and the mixture was heated to 320°C for one-half hour before the addition of water, the oil phase gained 8.8 percent in weight (experiment H). This contrasts with a recovery of only 98.4 weight-percent in the oil phase when the heavy gas oil alone was heated to 320°C before mixing with water (experiment Y). The results show an emulsifying effect for the pentane-insoluble from the filtered crude after it was heated. (Compare experiments E, F, and G in which it was not heated.)

Both experiments J and K of table 2 show that the pentane-soluble portion of the distillation residuum displayed little or no effect as an emulsifying agent either at room temperature or after being heated in gas oil at 320°C.

Experiments M, N, and O show that pentane-insoluble material from vacuum distillation residuum displayed very great emulsion-forming tendency when mixed in light gas oil; but pentane-soluble material from the same source displayed little or no such tendency.

Effect of Additives From Suspended Solids on Gas Oils

Data in table 3 show that the pentane-insoluble part of solids separated from the raw crude with 325-mesh screen displayed strong emulsifying power for water when mixed in light gas oil. (Compare experiment P with M in table 2).

A portion of these pentane-insoluble solids was extracted with toluene (15:1 weight ratio) to produce a toluene-soluble solid and a toluene-insoluble solid. The soluble portion did not show any emulsifying effect when mixed in light gas oil at room temperature (experiment Q) but the insoluble portion showed a strong emulsifying effect (experiment V). When the soluble portion was added to heavy gas oil and heated to 320°C for one-half hour, it showed a strong emulsifying effect (experiment R).

The pentane-insoluble, toluene-insoluble material was extracted with chloroform, also producing soluble and insoluble solids. The soluble portion did not display any emulsifying effect when mixed with light or heavy gas oils at room temperature (experiments S and T); however, when it was added to heavy gas oil and heated to 320°C for one-half hour before the addition of water, it showed strong emulsifying power (experiment U). The chloroform-insoluble portion showed strong emulsifying power when mixed in light gas oil at room temperature (experiment X).

SUMMARY AND CONCLUSIONS

Pentane-insoluble material from vacuum distillation of in situ crude shale oil, and pentane-insoluble material separated from the crude with a 325-mesh screen were found to be strong emulsifying agents for shale oil/water mixtures. The toluene-soluble and chloroform-soluble portions of pentane-insoluble material separated from the crude with the screen did not promote emulsions when mixed in gas oils at room temperature, but when heated to 320°C for one-half hour with the oil they acted as strong emulsifying agents.

The study showed that certain parts of the oil have little emulsifying power when mixtures containing them are kept at low temperatures, but display strong emulsifying power when the mixtures are heated to 320°C. This finding suggests the possibility that cooling the freshly-retorted oil as rapidly as possible after it is retorted may be a method of decreasing the formation of emulsions.

Several possibilities suggest themselves concerning why the solvent-soluble materials act as emulsifying agents after they have been heated to 320°C in gas oil, but no conclusions have been drawn. These soluble materials were all separated from the insoluble materials by filtration through a fritted-glass funnel during their preparation. This fact is further evidence that a large proportion of the emulsions in shale oil are caused by organic emulsifying agents; however, it does not entirely rule out the possibility that inorganic materials also play a part in the formation of some emulsions.

Filtering the raw, wet crude oil through a 325-mesh screen was an effective method of breaking the oil/water emulsion so the water would easily settle out with the application of moderate heat; however, the oil used was over a year old at the time of filtering. The method should be tested on several freshly-retorted crude oils to determine its effectiveness.

LITERATURE CITED

1. Sullivan, R. F., and Stangeland, B. E. Catalytic Hydroprocessing of Shale Oil to Produce Distillate Fuels. Presented before Div. of Petr. Chem., ACS, 174th National Meeting, Chicago, IL, Aug. 28-Sept. 2, 1977.

2. Secretary of the Interior. Synthetic Liquid Fuels. Annual Report for 1949, Part II. BuMines RI 4652, 70 pp.

TABLE 1. - Properties of Pentane-Insoluble Fractions From Filtered, Dried In Situ Crude

	Source			
	Distillation Residuum	Filtered Crude		+325 Mesh From Raw Crude
Extraction ratio	20:1	15:1	40:1	10:1
Wt. % of dry crude (as pentane insoluble)	3.8	3.6	2.8	1.3
Carbon, wt.%	78.80	79.76	78.76	71.42
Hydrogen, wt. %	7.63	8.09	7.66	6.77
Nitrogen, wt. %	3.59	3.95	4.53	4.26
Sulfur, wt. %	1.42	2.78	3.18	7.15
Oxygen + mineral (by diff.)	8.56	5.42	5.87	10.40
C/H wt. ratio	10.32	9.86	10.28	10.55
Ash, wt. %	1.02	0.82	1/	1/
Mol. wt.	1000	457	1235	948

1/ Not yet available.

TABLE 2. - Emulsion-Forming Tendency of Pentane-Soluble or Insoluble Additives When Blended With Feeds Prepared From Shale Oil

Experiment Identif.	Feed for Blending	Source and Type of Additive	Percent Mixed in Oil: Additive, Wt.% of Oil	Percent Mixed in Oil: Water Used, Wt.% of Oil	Oil Phase[1/] Wt. % of Raw Oil
A	Pentane sol. from filtered crude.	None used.	0.0	11.4	97.9
B	Pentane sol. from filtered crude.	Vac. distn. res. Pentane insol.	0.5	11.4	102.6
C	Pentane sol. from filtered crude.	Vac. distn. res. Pentane insol.	1.0	33.7	113.8
D	Pentane sol. from filtered crude.	Vac. distn. res. Pentane insol.	2.0	51.2	148.8
E	Pentane sol. from filtered crude.	Filtered crude. Pentane insol.[2/]	1.0	33.5	97.0
F	Pentane sol. from filtered crude.	Filtered crude. Pentane insol.[3/]	1.0	33.4	98.5
G	Pentane sol. from filtered crude.	Filtered crude. Pentane insol.[3/]	1.0	33.9	97.1
H	Dewaxed heavy gas oil.	Filtered crude. Pentane insol. (Mix heated to 320°C.)	2.2	49.6	108.8
J	Dewaxed heavy gas oil.	Vac. distn. res. Pentane soluble.	2.0	49.6	100.7
K	Dewaxed heavy gas oil.	Vac. distn. res. Pentane soluble. (Mix heated to 320°C.)	2.0	49.7	101.0
L	Dewaxed heavy gas oil.	Vac. distn. res. Pentane insol.	2.0	50.6	126.9
Y	Dewaxed heavy gas oil.	None used. Heated to 320°C.	0.0	33.5	98.4
M	Light gas oil.	None used.	0.0	35.2	98.6
N	Light gas oil	Vac. distn. res. Pentane soluble	2.0	51.7	101.5
O	Light gas oil.	Vac. distn. res. Pentane insol.	2.0	52.0	140.5

1/ After heating 5 hours at 77°C.
2/ Pentane-insoluble powder (15/1) stirred into oil while oil heated at 100°C.
3/ From extraction of filtered crude at 40/1 solvent/oil ratio.

TABLE 3. - Emulsion-Forming Tendency in Shale Oil of Portions of Solids Filtered From In Situ Crude With 325-Mesh Screen

Experiment Identif.	Oil Used	Additive Mixed in Oil	Additive, Wt. % of Oil	Water Added, Wt. % of Oil	Oil Phase[1/], Wt. % of Original Oil
P	LGO[2/]	Pentane-insoluble portion.	2.0	52.1	132.4
Q	LGO	Pentane-insoluble, toluene-soluble portion.	2.0	51.8	98.8
R	HGO[3/]	Pentane-insoluble, toluene-soluble; oil-additive mix heated ½ hr. at 320°C.	2.0	49.5	138.0
S	LGO	Pentane-insoluble, toluene-insoluble, chloroform soluble.	2.0	52.0	100.5
T	HGO	Pentane-insoluble, toluene-insoluble, chloroform soluble.	2.0	50.0	100.5
U	HGO	Pentane-insoluble, toluene-insoluble, chloroform soluble. Mix heated ½ hr. at 320°C.	2.2	49.8	136.5
V	LGO	Pentane-insoluble, toluene-insoluble portion.	2.0	52.2	121.1
W	Crude	No additive. Water only, mixed with wire-screen-filtered dewatered crude.	0.0	50.9	98.3
X	LGO	Pentane-insoluble, toluene-insoluble, chloroform insoluble portion.	2.0	52.1	120.4

1/ After heating 5 hours at 77°C.
2/ LGO is light gas oil.
3/ HGO is heavy gas oil.