

THE APPLICATION OF STATE-OF-THE-ART PETROLEUM TECHNOLOGY TO SHALE OIL REFINING.
R. E. Hildebrand and B. M. Harney. U. S. Department of Energy, ASET/FE, #20
Massachusetts Avenue, N.W., Washington, D.C. 20545

Shale oil offers one of the most promising near term options for providing transportation fuels from non-petroleum domestic resources. The unusually high nitrogen content of shale oil however, presents a significant problem in refining this synthetic fuel to specification products. Under contract to the Department of Energy, Chevron Research Company has successfully applied state-of-the-art hydroprocessing technology to shale oil refining. In addition, Chevron has estimated the economics of hydro-processing shale oil to a variety of product slates. A summary of the technical and economic results of that program will be presented. In a larger scale effort, the Department of Energy and the Department of Defense have a joint program for refining 100,000 barrels of shale oil at an existing Sohio refinery. The status and some results of this program will also be presented. The results of this on-going work indicates that refining of shale oil will be expensive. Consequently, an expanded D.O.E. shale oil refining program is being developed to assure that the cost of refining shale oil is not an impediment to commercialization of the shale resource. The goals of this program will be outlined.

Shale Oil: An Acceptable Refinery Syncrude

H. C. Stauffer & S. J. Yanik

Gulf Science and Technology Company
P. O. Drawer 2038, Pittsburgh, PA 15230

Introduction

Technology for the extraction of oil from shale has been in existence for a very long time. In a less restrictive economic and environmental climate, the production of substantial quantities of shale oil could have been realized rather quickly. It has also been well established that shale oil must be substantially upgraded before any conventional refining processes can be applied.

No refinery has the capability of effectively processing any significant volume of raw shale oil. Therefore, most upgrading studies have two objectives: 1) produce a syncrude that can be pipelined and then refined in an existing facility, or 2) upgrade and refine to a full slate of products at the retort site. In either case, the overall upgrading requirements are substantial and quite similar.

Our upgrading studies were initiated in the 1960's. As a result of our participation in the Rio Blanco Project, these have been updated during the past few years. This paper presents the results of our most recent exploratory studies made to determine 1) the effectiveness of our commercially available hydrotreating technology for upgrading shale oil to a petroleum substitute and 2) the response obtained in conventional downstream refining processes.

Upgrading Routes

In upgrading shale oil for refining purposes, there are two general approaches. In the one most often considered, Figure 1, the raw oil is fractionated to yield a residuum that may be gasified, coked or deasphalted. A heavy gas oil is obtained for hydrocracking or hydrotreating for FCC feed. The furnace oil distillate is hydrotreated to No. 2 fuel (or additional FCC feed) and a naphtha is produced for hydrotreating and catalytic reforming. The syncrude from this route is, essentially, an all-distillate stream, comprised of the reconstituted, hydrotreated fractions.

A more unconventional approach, which avoids much duplication of facilities, is shown in Figure 2. In this route, the whole shale oil is hydrotreated in a modified Gulf Residual HDS Unit. The effluent can be pipelined as syncrude or fractionated and converted to prime products via reforming, hydrocracking and/or FCC. Volumetric yields are higher, by this route, and no residual products need be produced.

Discussion

Shale Oil Quality

Although all our latest pilot plant studies were limited to a single shale oil sample, a number of different oils were examined. Assays for five of these (A thru E) are shown in Table I. These data are indicative of the variation in shale oil composition that can result from differences in retorting modes and oil shale source. Obviously, as retorting technology changes, so can the character of the oil.

Regardless of oil shale source or retorting mode, all the oils are typified by their high hetero-atom content, with nitrogen being the highest, by far. Sulfur content is relatively low in all samples and of no particular concern. As would be expected, the hetero-atom content of the particular fractions varies from sample to sample as do the yields of these fractions. In view of the present trend toward in-situ retorting, the

lower residuum and hetero-atom content of sample E is encouraging. Sample A was used exclusively for all the pilot plant studies herein reported.

Experimental

In order to meet the objectives of this study, with the amount of shale oil available, most of the data was acquired from survey-type runs, using our early exploratory studies as a basis. All the pilot plant work was done in existing facilities normally used for petroleum-based feeds.

Delayed coking runs were made in a 2 gal/hr unit, equipped for downstream fractionation and gas oil recycle.

Catalytic cracking data was obtained in a 1,500 cc/hr, automated riser unit having product fractionation and continuous catalyst regeneration facilities.

Hydrogenation and catalytic reforming runs were also made in automated units, both isothermal and adiabatic. These units are equipped for downstream product fractionation and most have gas scrubbing and recycle systems. All operations were downflow, with combined hydrogen, in catalyst beds ranging from 300 to 2,500 cc.

Only commercially available catalysts were employed, with those for hydrogenation being Gulf formulations. The riser cracking runs were made with an equilibrium catalyst of high zeolite content. A commercially available bimetallic catalyst was used in the reforming studies.

Because of the inherently poor stability characteristics of raw shale oil, it was felt that the problems this could cause during the study could be alleviated by a mild hydrogen pretreatment. Thus, the entire sample was mildly hydrotreated, with the intent of eliminating the most reactive double bonds. Although hydrogen consumption was about 150 SCF/B, except for arsenic removal, the detectable changes in product properties and composition were insignificant. It was concluded that the pretreatment would have no effect on further processing. Thus, the studies were considered to be representative of upgrading a raw shale oil sample.

Delayed Coking of Residuum

Coking of the 960 F+ fraction was done at conditions previously found suitable for shale oil residua and no unexpected problems were encountered. The conventional, relatively mild conditions, with product yields and inspections, are shown in Table II. The liquid products are typical of a coker operation and, of course, very high in nitrogen. The coke is of relatively poor quality, very high in nitrogen content, but low in sulfur and vanadium. Ash content will be a function of the carry-over from the retorting operation. It was observed that the yield structure does not fit that predicted from a petroleum-based correlation. Coke yield was higher while gas and naphtha yields were lower.

Gas Oil Hydrotreating and Catalytic Cracking

The gas oil fraction, 680-960°F, was hydrotreated in two stages to produce feedstocks for catalytic cracking. Products of 0.73 and 0.61% nitrogen were obtained at two severities in the first stage. The higher nitrogen level material served as feed to the second stage. At two severities in this stage, nitrogen content was reduced to 0.28 and 0.10%; the lower level representing 95.9% overall denitrogenation. Yields, operating conditions and product inspections are shown in Table III. For comparison, the properties of a good quality, low nitrogen, petroleum gas oil (PGO) are also shown.

Except for the unique sulfur/nitrogen ratio, the hydrotreated shale oils (HTSO) exhibit no apparent unusual characteristics. As would be expected, however, boiling range does change with denitrogenation severity.

Since the products were not stripped back to feed IBP, they contain increasing amounts of material in the furnace oil boiling range. Based on properties other than nitrogen content, the quality of these synthetic gas oils is equal to or superior than that of many petroleum based FCC feedstocks.

The response obtained in fluid catalytic cracking is shown in Table IV. The yield structure produced from the HTSO's is compared with those from the PGO and two stocks which were blends of the PGO with the raw feed to hydrotreating. The HTSO's crack very well up to a nitrogen content of at least 0.28%. Of all the stocks, maximum conversion and gasoline yield was obtained with the low nitrogen HTSO. For the hydrotreated stocks, however, response is nonlinear with nitrogen content. At the 0.61% level, conversion and gasoline yield were much poorer than those obtained with the blended feed at the same nitrogen level. This discrepancy has been attributed to the high basic nitrogen content of the HTSO.

FCC Product Quality

With one exception, adequate octane numbers were obtained with all shale oil-containing feedstocks. All research octane numbers (RON) were 91 or greater except when cracking the low nitrogen HTSO, Table V. In this case, the RON was only 89.2. This gasoline had the highest saturate content and the lowest sensitivity. It was also derived from the most paraffinic feedstock.

Gasoline aromaticity was remarkably constant for all shale oil stocks, hydrotreated or blended, but lower than obtained with the PGO. As feed nitrogen increased, saturate content decreased with a corresponding gain in olefin content. Motor octane numbers obtained from the shale oil stocks were consistently lower than from the PGO. Sensitivity increased with feed nitrogen content. The increase, however, was not as great with the HTSO's as with the blended feeds.

Relative to the gasoline from the PGO, all shale oil stocks gave gasolines of much higher nitrogen content. Of these, the HTSO's gave the lowest values at comparable feed nitrogen levels. For the cycle oils and decanted oils, however, nitrogen contents were higher from the HTSO's than the blended feeds. All available data indicate satisfactory product stability up to a feed nitrogen level of at least 0.3%.

Middle Distillate Hydrotreating

Hydrogenation of the middle distillate fraction, 375-680°F, readily yields a high quality furnace oil product. As shown in Table VI, negligible sulfur content and high cetane index is easily obtained. Compared to petroleum derived furnace oils, however, nitrogen contents are quite high. This can be reduced to a very low level; but, it should not be required except for exclusive use in combustion applications where NO_x emissions are limiting. In all other respects, the combustion characteristics of these fuels are excellent(1) and in many cases superior to No. 2 fuels from petroleum.

Naphtha Pretreating and Reforming

Unlike heavier stocks in which substantial amounts of nitrogen can be tolerated, the naphtha must be essentially nitrogen-free for satisfactory reforming response. As the inspection data show, in Table VI, the nitrogen level is many orders of magnitude greater than typical for most virgin, petroleum-based naphthas. Nitrogen at this high level totally overwhelms the difficulty associated with removal of the remaining hetero-atoms. Figure 3 shows a temperature-space velocity-pressure relationship required to produce a reformer charge of 0.5 ppm nitrogen content. These conditions far exceed typical refinery pretreating severities.

The raw naphtha has a relatively high aromatic content and is very olefinic. About 85% of the hydrogen required is consumed in saturation reactions. The total consumption, 808 SCF/B, is in excess of that required for many gas oil hydrocrackers.

As reformer feed, the treated naphtha inspections show two important points. First, the front-end volatility is very low, indicating a deficiency in C₆ and C₇ hydrocarbons. Second, the ratio of naphthenes to aromatics is exceptionally high. Consequently, the reforming results show quite low benzene and toluene yields and a high hydrogen make.

The quality of the feed, as indicated by its N+2A relationship, is significantly better than would be predicted. Although this simple relationship would indicate reforming susceptibility close to that of a Mideast naphtha, such as Kuwait, its response was actually much closer to that of a good quality domestic naphtha. This is illustrated by the yields obtained and temperature requirements shown in Figures 4, 5 and 6.

Alternate Upgrading Route

The maximum yield case is shown in the alternate approach, Figure 2. In this route, the raw, full-boiling range shale oil is charged to a modification of the Gulf HDS Process. The results shown in Table VIII are for maximizing the yield of FCC feed at the minimum denitrogenation level. The yield of 375°F+ FCC charge is approximately 85% on raw crude and contains 0.38% nitrogen with <1.0 ppm Ni equivalent. Although the 375°F+ material is relatively high in nitrogen, the naphtha is essentially nitrogen-free and can be charged directly to a catalytic reformer.

This is not a limiting case; if the furnace oil fraction is desired for other end uses, the 680°F+ can still be reduced to a satisfactory nitrogen level. The residuum, which has an API gravity higher than that of the crude, may also be more useful in other applications.

Conclusions

For satisfactory hetero-atom removal, particularly nitrogen, and for olefin saturation, hydrogen requirements are substantial. With today's commercially available catalysts, processing severities are high and costly.

With respect to FCC feed, limited quantities of raw shale oil can be tolerated in a refinery crude slate. Handling the 650°F and lighter material would require a hydrotreating capability greater than usually available.

Shale oil fractions when suitably upgraded, are quite amenable to refining in conventional processes. Product yields and quality are comparable to those obtained with a good quality petroleum crude. Upgrading the total shale oil via the modified Gulf HDS Process results in an improved yield structure and a less complex facility.

New catalyst formulations are expected to substantially reduce process severity. This will strongly affect upgrading and refining economics.

Reference

- (1) Dzuna, E. R., "Combustion Tests on Shale Oil Fuels", presented at Central States Section the Combustion Institute, April 1976.

TABLE I
ASSAYS OF RAW SHALE OILS

Sample Source Retort	A Dow Tosco	B Paraho Paraho	C Superior Tosco	D Occidental Tosco	E -- In-Situ
<u>Shale Oil</u>					
Gravity, °API	20.7	20.1	20.7	19.3	25.4
Viscosity, SUS: 130°F	85.7	121.4	105.5	92.7	42.6
Pour, °F	+75	+85	+80	+50	+80
Carbon, wt %	84.52	84.83	84.06	83.97	84.89
Hydrogen, wt %	11.14	11.51	11.27	10.72	11.82
Sulfur, wt %	0.70	0.58	0.77	0.43	0.42
Nitrogen, wt %	1.99	2.04	2.06	1.96	1.62
Oxygen, wt %	1.32	1.24	1.58	1.92	1.09
Arsenic, ppm	13.9	20.9	8.0	32.0	19.0
Ash, wt %	0.20	0.03	0.05	0.06	0.26
<u>Fractions:</u>					
<u>QP-310°F</u>					
Yield, vol %	5.20	1.17	5.08	6.30	3.58
Gravity, °API	53.3	48.0	52.2	52.4	49.6
Carbon, wt %	85.06	84.20	84.11	84.87	85.84
Hydrogen, wt %	13.35	13.03	12.87	12.37	13.02
Sulfur, wt %	0.85	0.81	1.04	0.59	0.69
Nitrogen, wt %	0.25	0.95	0.41	0.30	0.59
Oxygen, wt %	0.52	0.75	0.95	0.69	0.49
Saturates, vol %	28.0	--	26.0	27.0	--
Olefins, vol %	56.0	--	54.0	57.0	--
Aromatics, vol %	16.0	--	20.0	18.0	--
Arsenic, ppm	--	5.2	1.5	3.4	1.6
<u>310-375°F</u>					
Yield, vol %	4.54	1.13	4.58	4.53	3.39
Gravity, °API	44.8	40.7	43.6	42.8	43.0
Carbon, wt %	84.84	83.44	84.36	84.72	84.74
Hydrogen, wt %	12.97	12.68	12.80	12.71	12.67
Sulfur, wt %	0.72	0.52	0.91	0.59	0.55
Nitrogen, wt %	0.65	1.46	0.82	0.79	1.09
Oxygen, wt %	0.70	1.46	1.24	0.87	0.77
Saturates, vol %	25.0	--	25.5	23.5	--
Olefins, vol %	52.0	--	48.0	48.0	--
Aromatics, vol %	23.0	--	26.5	28.5	--
Arsenic, ppm	--	1.8	<0.2	3.9	6.0
<u>375-520°F</u>					
Yield, vol %	12.64	9.60	10.87	13.64	20.49
Gravity, °API	35.0	33.8	34.3	33.0	34.1
Carbon, wt %	84.57	84.09	83.92	84.58	84.94
Hydrogen, wt %	12.32	12.38	12.30	12.02	12.31
Sulfur, wt %	0.64	0.68	0.74	0.39	0.36
Nitrogen, wt %	1.05	1.35	1.25	1.15	1.21
Oxygen, wt %	1.24	1.53	1.70	1.38	0.85
Pour, °F	-45	-30	-35	-55	-30
Aniline Point, °F	82.0	--	73.4	80.0	93.2
Arsenic, ppm	--	24.7	1.8	9.8	1.5

TABLE I (continued)

Sample	A	B	C	D	E
Fractions: (cont'd)					
<u>375-680°F</u>					
Yield, vol %	30.85	28.92	27.37	33.07	51.33
Gravity, °API	29.3	28.4	29.7	27.0	29.5
Viscosity, SUS: 100°F	40.1	42.6	40.2	42.1	39.3
Carbon, wt %	84.56	83.90	84.09	86.00	85.29
Hydrogen, wt %	11.96	11.98	12.01	11.83	12.03
Sulfur, wt %	0.63	0.69	0.70	0.44	0.37
Nitrogen, wt %	1.47	1.60	1.62	1.56	1.47
Oxygen, wt %	1.26	1.27	1.72	1.60	0.75
Pour, °F	+15	+20	+30	+5	+20
Aniline Point, °F	87.1	--	86.0	82.4	102.2
Arsenic, ppm	8.0	23.0	3.8	20.4	5.7
<u>680-960°F</u>					
Yield, vol %	32.57	37.81	31.93	31.73	33.79
Gravity, °API	16.3	18.6	18.6	15.3	20.8
Viscosity, SUS: 210°F	66.4	57.0	56.0	91.0	50.7
Carbon, wt %	85.01	85.11	86.11	85.16	87.02
Hydrogen, wt %	10.93	11.25	11.53	10.96	11.84
Sulfur, wt %	0.60	0.53	0.65	0.36	0.24
Nitrogen, wt %	2.09	1.91	2.08	2.00	1.75
Oxygen, wt %	0.94	0.83	1.18	1.20	0.68
Pour, °F	+100	+100	+100	+85	+105
Aniline Point, °F	126.0	--	111.9	118.4	135.5
Carbon Res, wt %	0.91	0.28	0.41	0.44	0.40
Arsenic, ppm	--	12.8	15.5	29	14
Ni + V, ppm	<0.1	<0.1	0.1	<0.1	<0.1
<u>960°F+</u>					
Yield, vol %	26.84	30.97	31.04	24.37	7.91
Gravity, °API	5.9	11.8	9.2	5.3	6.8
Viscosity, SUS: 250°F	1,159	266	503	3,212	2,216
Carbon, wt %	85.14	84.61	84.81	85.20	84.85
Hydrogen, wt %	10.61	10.64	10.37	9.74	10.24
Sulfur, wt %	0.64	0.53	0.80	0.39	0.58
Nitrogen, wt %	2.84	2.60	2.78	2.95	2.26
Oxygen, wt %	1.34	0.95	1.31	1.20	2.05
Carbon Res, wt %	20.3	12.9	15.8	24.4	18.4
C ₅ Insolubles, wt %	18.1	--	15.4	20.7	18.0
Ash, wt %	0.64	0.05	0.13	0.21	2.28
Arsenic, ppm	--	26.0	7.0	59.0	67.0
Ni, ppm	15	9.2	20.8	32.0	45.6
V, ppm	1.6	0.5	1.8	0.5	22.8

TABLE III
GAS OIL HYDROTREATING

<u>Hydrotreatment</u>	<u>First Stage</u> 680°/960°F	<u>Second Stage</u>		
<u>Feed</u>	Gas Oil	First Stage Product		
<u>Operating Conditions:</u>				
Reactor Press., psig	<-----1,725----->			
Gas Circulation, SCFB	4,000	<----- 8,500 ----->		
Avg. Catalyst Temp., °F	725	720	755	
Space Velocity, vol/hr/vol	1.0	1.0	0.75	
<u>Yields, Wt % of Feed:</u>				
H ₂ (SCFB)	(1,200)	(450)	(630)	
H ₂ S	0.49	0.04	0.04	
NH ₃	2.19	0.55	0.77	
H ₂ O	0.90	-	-	
C ₁ -C ₅	4.08	0.42	1.56	
Total Liquid Product	94.21	99.75	98.70	
<u>Inspections:</u>				
	<u>Gas Oil</u>			<u>PGO</u>
Nitrogen, wt %	2.41	0.61	0.28	0.10
Gravity, °API	13.9	27.4	29.7	31.2
Hydrogen, wt %	10.85	12.56	13.00	13.18
Sulfur, wt %	0.49	<0.05	<0.05	<0.05
Oxygen, ppm	0.80	<100	<100	<100
Viscosity, SUS: 210°F	118.4	41.4	37.7	35.8
Pour Point, °F	+105	+95	+80	+85
Aniline Point, °F	101	174.6	181.9	186.1
Carbon Res., Rams.: wt %	1.34	0.12	0.07	0.05
Calc. Comp., Vol Fraction:				
Aromatics(Ca)	-	0.205	0.170	0.147
Naphthenes(Cn)	-	0.212	0.218	0.220
Paraffins(Cp)	-	0.583	0.612	0.633
Nickel, ppm	<0.1	<0.1	<0.1	<0.1
Vanadium, ppm	<0.1	<0.1	<0.1	<0.1
Distillation, Vac., °F at:				
10%	805	611	517	484
30	869	730	688	661
50	905	784	779	763
70	939	839	843	827
90	989	917	893	870

TABLE IV

CATALYTIC CRACKING AT 980°F RISER OUTLET TEMPERATURE-PRODUCT YIELDS

	PGO 0.063	<-----0.10	Hydrotreated 0.28	>-----0.61	<-----PGO + RAW SOGO* 0.29	>-----0.61
Feed						
Nitrogen, wt %						
Product Yields:						
Vol % FF						
Total C ₁ 's	13.0	12.1	11.8	8.1	11.7	10.5
Propane	2.5	2.2	2.1	1.7	2.3	2.6
Propylene	10.5	10.0	9.7	6.4	9.4	7.9
Total C ₂ 's	20.8	20.7	19.1	10.8	18.2	13.3
Isobutane	8.3	7.8	6.2	2.1	6.0	3.4
Normal Butane	2.0	2.0	1.6	0.9	1.6	1.1
Butenes	10.5	10.9	11.2	7.8	10.6	8.8
Debutanized Gasoline:						
C ₆ -430°F TBP	60.6	62.4	60.5	41.7	58.5	50.7
Furnace Oil:						
430°-650°F TBP	11.4	11.8	13.2	19.2	13.5	16.9
Decant Oil:						
650°F+	6.1	5.0	6.2	20.9	8.3	12.7
Total C ₂ + Liquid	111.9	112.1	110.7	100.8	110.2	104.0
Product Yields:						
Wt % FF						
Hydrogen	0.09	0.05	0.09	0.15	0.11	0.13
C ₂ and Lighter	3.0	2.4	2.7	4.4	3.0	3.7
Coke	6.1	4.6	5.1	6.4	5.8	7.9
Conversion: Vol % FF	82.5	83.2	80.7	59.9	78.2	70.4

7680°/960°F shale oil/gas oil

TABLE VI
FURNACE OIL HYDROTREATING

Operating Conditions					
Reactor Press., psig					
Gas Circulation, SCFB					
Avg. Catalyst Temp., °F					
Space Velocity, vol/hr/vol					
Yield, Vol %					
Naphtha-Free Furnace Oil					
Inspections					
Gravity, °API	29.3	99.8	99.0	100.8	99.1
Nitrogen, wt %	1.66	39.7	38.9	37.4	39.1
Sulfur, wt %	0.77	0.038	0.27	0.57	0.17
Hydrogen, wt %	12.09	<0.04	<0.04	<0.04	<0.04
Oxygen, ppm	1.20	13.80	13.54	13.45	13.66
Flash, PM: °F	185	<100	580	1,620	320
Pour Point, °F	+20	182	162	144	170
Cetane Index	41	+10	+10	+20	+10
Aromatics, vol %	-	58.0	56.0	53.5	55.5
Distillation, D86		26.0	36.5	43.5	28.0
°F at:					
10%	453	430	423	426	424
30	493	468	469	475	464
50	534	509	505	511	500
70	574	550	550	554	540
90	612	599	601	606	595

TABLE VII

NAPHTHA PRETREATING AND REFORMING

Operating Conditions	Pretreating		Reforming	
Reactor Press., psig		1,400	<-----325----->	
Gas Circulation, SCFB		8,000	-	
Space Velocity, vol/hr/vol		1.0	<-----1.5----->	
H ₂ /HC, mol/mol		-	<-----7/1----->	
Avg. Catalyst Temp., °F		680	366	880
<u>Yields, wt % of Feed</u>				
H ₂ (SCFB)		(-808)	2.0	2.2
H ₂ S		0.84	-	-
NH ₃		0.69	-	-
H ₂ O		0.61	-	-
C ₁		0.20	1.2	1.4
C ₂		0.02	2.0	2.4
C ₂		0.08	3.8	4.6
C ₃		0.14	5.3	6.2
C ₄		103.0	81.9	78.8
C ₅ + Product (vol %)				
<u>Inspections</u>				
	Feed			
Gravity, °API	47.8	54.7	46.4	44.7
Nitrogen, ppm	5,700	<0.2	-	-
Sulfur, ppm	7,900	<0.5	-	-
Oxygen, ppm	5,400	<100	-	-
Hydrogen, wt %	13.28	14.77	-	-
Bromine Number	66	-	-	-
<u>Hydrocarbon Analysis,</u>				
D1319, vol %				
Saturates	38.0	-	-	-
Olefins	43.5	-	-	-
Aromatics	18.5	-	-	-
D2789, vol %				
Paraffins	-	58.8	44.0	38.7
Monocycloparaffins	-	30.6	3.2	2.7
Dicycloparaffins	-	3.9	0.1	0.1
Alkylbenzenes	-	6.1	50.7	56.7
Benzene	-	0.1	0.9	1.3
Toluene	-	0.6	6.4	7.9
C ₈	-	1.7	13.0	15.5
C ₉	-	3.7	27.8	32.0
Indanes & Tetralins	-	0.4	1.6	1.3
Naphthalenes	-	0.2	0.5	0.5
<u>Octane Numbers:</u>				
Research, Clear	-	29.0	92.9	96.7
Motor, Clear	-	-	82.9	86.0
<u>Distillation, °F at:</u>				
10%	279	262	181	178
30	300	284	-	-
50	316	304	286	282
70	334	325	-	-
90	354	349	358	358

TABLE VIII
UPGRADING FBR RAW SHALE OIL

<u>Operating Conditions</u>		
Reactor Press., psig	2,100	
Gas Circulation, SCFB	5,000	
Avg. Catalyst Temp, °F	750	
Space Velocity, vol/hr/vol	0.5	
<u>Yields, % of HDS Charge</u>		
H ₂ S, wt %	0.72	
NH ₃ , wt %	2.05	
H ₂ O, wt %	1.45	
C ₁ -C ₄ , wt %	2.09	
C ₅ + Syncrude, vol %	102.6	
Chem. H ₂ Consumption, SCFB	1,260	
<u>Inspection:</u>	<u>Feed</u>	<u>Syncrude</u>
<u>Syncrude:</u>		
Gravity °API	20.7	31.5
Nitrogen, wt %	1.99	0.32
Sulfur, wt %	0.70	<0.05
Oxygen, wt %	1.32	0.03
Hydrogen, wt %	11.14	12.84
Pour Point, °F	+75	+70
<u>Fractions:</u>		
<u>Naphtha (C₆-375°F)</u>		
Yield: vol % Syncrude	16.7	
Gravity, °API	53.7	
Nitrogen, ppm	<0.5	
Sulfur, ppm	<0.5	
<u>Furnace Oil (375°-680°F)</u>		
Yield: vol % Syncrude	43.7	
Gravity, °API	36.0	
Nitrogen, wt %	0.23	
Sulfur, wt %	<0.05	
Aniline Point, °F	149	
Pour Point, °F	+10	
<u>Gas Oil (680°-960°F)</u>		
Yield: vol % Syncrude	24.3	
Gravity, °API	27.2	
Nitrogen, wt %	0.43	
Sulfur, wt %	<0.05	
Aniline Pt, °F	189	
Pour Point, °F	+95	
<u>Residuum (960°F+)</u>		
Yield: vol % Syncrude	15.3	
Gravity, °API	22.4	
Nitrogen, wt %	0.68	
Sulfur, wt %	<0.05	
Ni Equiv., ppm	<1.0	

Figure 1.
CONVENTIONAL UPGRADING ROUTE

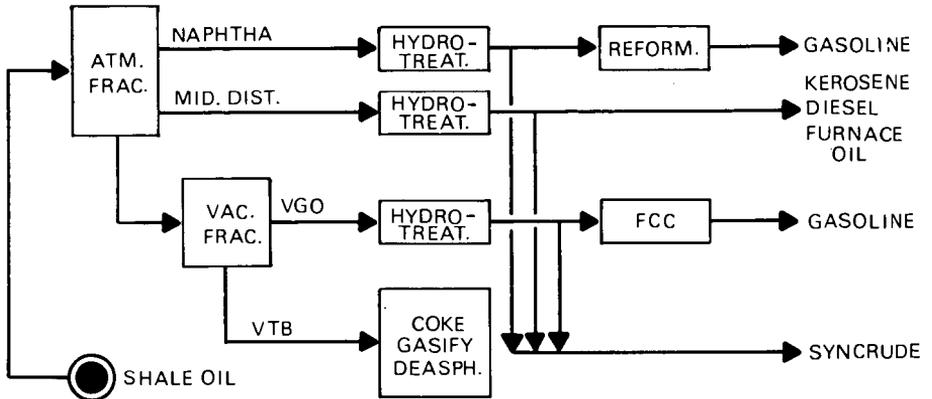


Figure 2.
ALTERNATE UPGRADING ROUTE

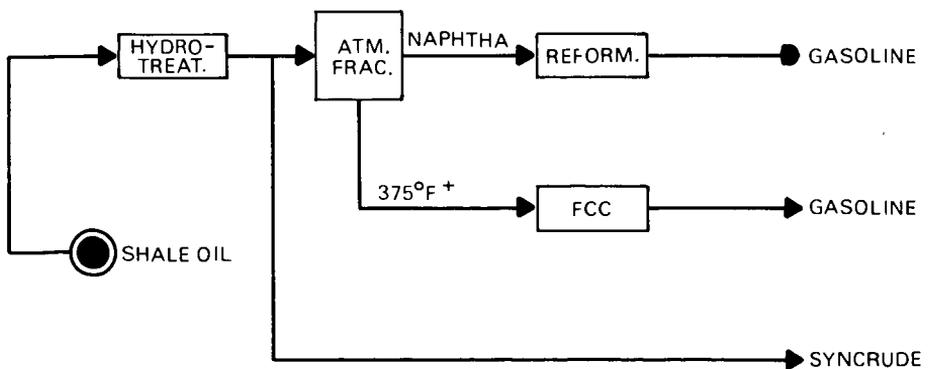


Figure 3
NAPHTHA HYDROTREATING

TEMPERATURE REQUIREMENTS FOR 0.5 ppm N

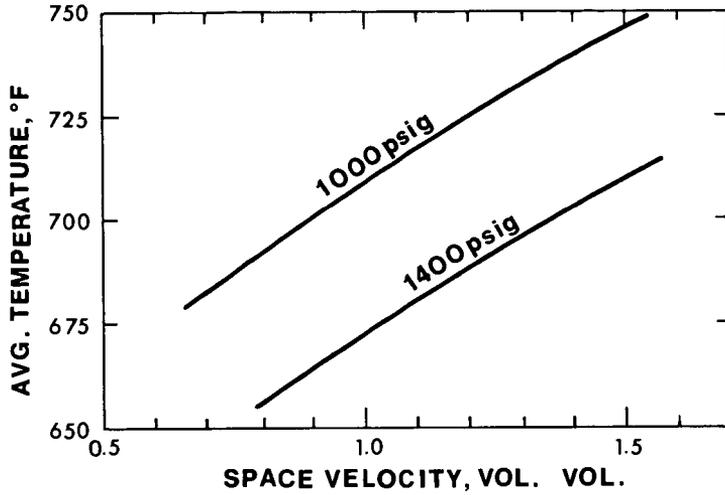


Figure 4
NAPHTHA REFORMING
C₅⁺ YIELD VS OCTANE SEVERITY

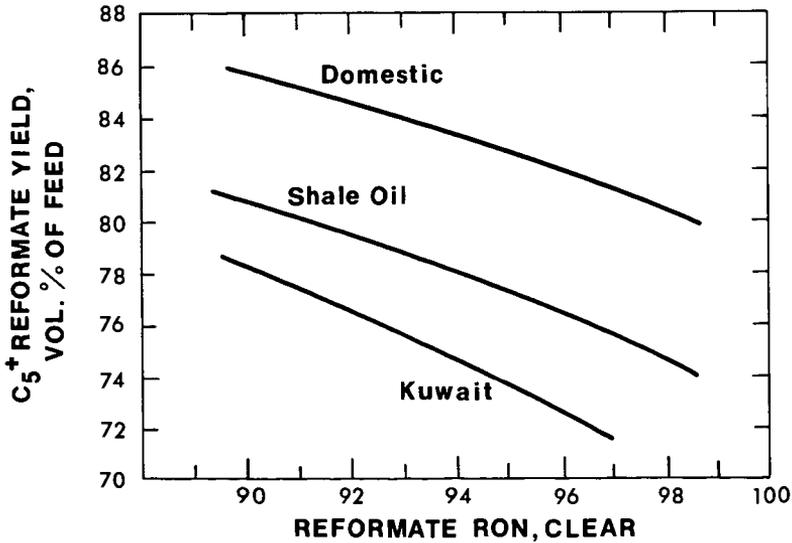


Figure 5
NAPHTHA REFORMING
H₂ PRODUCTION VS OCTANE SEVERITY

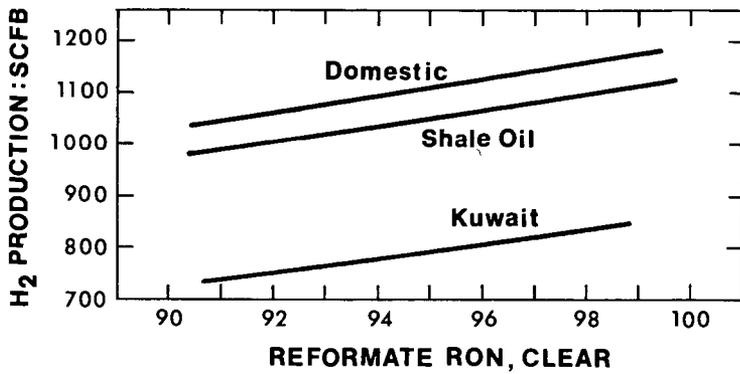
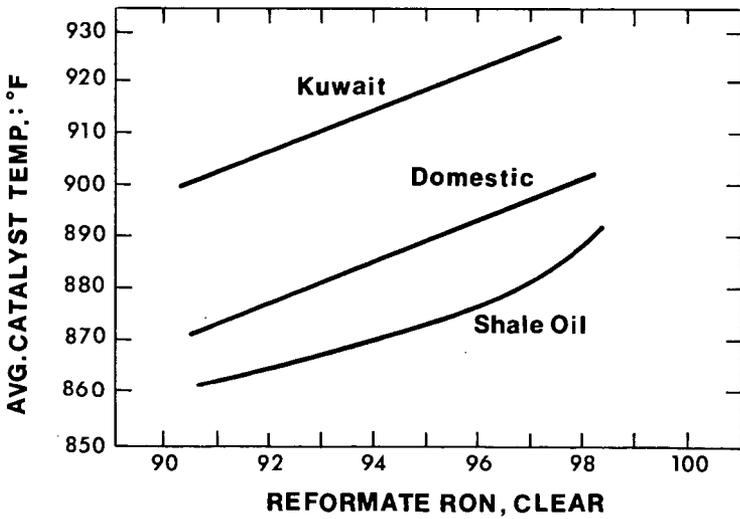


Figure 6
NAPHTHA REFORMING
AVG. CATALYST TEMP. VS OCTANE SEVERITY



ARSENIC AND NITROGEN REMOVAL DURING SHALE OIL UPGRADING

By

D. J. Curtin*, J. D. Dearth*, G. L. Everett
M. P. Grosboll, and G. A. Myers*

Atlantic Richfield Company, 400 E. Sibley Blvd., Harvey, IL 60426,
and *P. O. Box 2819, Dallas, TX 75221

Introduction

Shale oils and shale oil distillates can contain high concentrations of arsenic spread throughout their boiling ranges⁽¹⁾. Arsenic has been shown to rapidly and permanently deactivate commercial hydro-treating catalysts. Even where hydrotreating is not required, arsenic removal may be desirable.

The Nature of Arsenic in Shale Oil

Table 1 shows the arsenic distribution in a raw shale oil. The gas oil fraction contains the highest average arsenic concentration, about 52 ppm. A substantial arsenic peak occurs in the 204-260°C (400-500°F) boiling range. Following this peak, the arsenic concentration decreases. A significant arsenic level is observed in the residuum.

Table 1

Arsenic Distribution in Shale Oil

<u>Boiling Range</u>	<u>Fraction Volume Percent</u>	<u>Arsenic Content ppm</u>
IBP-204°C (IBP-400°F)	18	10
204-482°C (400-900°F)	58	52
482°C (900°F) and heavier	24	38

The distribution of the arsenic throughout the boiling range implies the presence of organic arsenic compounds. Other work reported in the literature confirms that organic arsenic compounds can be present in hydrocarbon fractions formed by the thermal decomposition of naturally occurring organic solids including European brown coal^(2,3,4,5,6,7). The pyrolysis of this coal yields a tar which has a very high arsenic content. Some of the arsenic-containing compounds have been shown to be organic in nature. We also have data which suggest that inorganic arsenic compounds are present.

Many organic arsenic compounds are known to be unstable. Thus it is possible under certain conditions that shale oil samples, including distillates, may lose a significant amount of their arsenic content. Care must be taken not only in sampling but also in storage and handling to maintain representative feedstocks. Over a long period of working with shale oil distillates in the development of the Atlantic Richfield Arsenic Removal and Hydro-treating Process, we have established many techniques necessary to ensure that the arsenic compounds remain representative of those in the commercial feedstock.

The Effect of Arsenic on Hydrotreating Catalysts

Figure 1 shows the effect of arsenic in shale oil on one commercial nickel-molybdenum hydrotreating catalyst. A shale gas oil was passed over the catalyst at 1.5 weight hourly space velocity, 2000 psig, 282°C (720°F), and 1014 m³H₂/m³ (6000 scf H₂/bbl). Initially the arsenic was totally removed from the oil by deposition on the nickel-molybdenum catalyst. When the arsenic level on the catalyst reached 7 weight percent, the arsenic level of the effluent oil increased rapidly.

The hydrodenitrogenation (HDN) activity of the nickel-molybdenum catalyst used in this test charging untreated shale gas oil is plotted in Figure 2. The HDN activity rapidly declined to a point where about 1000 grams of oil had been treated per gram of catalyst. At this point, which corresponds to the point where arsenic began to appear in the effluent oil, the rate of catalyst activity decline became less severe. Arsenic deposition appeared to be a major factor in the catalyst deactivation. This hypothesis was confirmed by an additional test of a fresh sample of nickel-molybdenum catalyst at the same conditions but charging shale gas oil with the arsenic removed. The HDN activity, also shown in Figure 2, declined much less rapidly than was the case when the arsenic-containing raw shale gas oil was treated.

Arsenic Removal from Shale Oil Distillates

Three alternatives were apparent for shale oil hydrotreating. First, one could attempt to develop a hydrotreating catalyst which would be resistant to arsenic poisoning. Our work indicated that existing catalysts with sufficient denitrogenation activity would be poisoned by arsenic due to its strong affinity for metals. A second possibility would be to remove the arsenic deposits from the catalyst during regeneration. Once again our data, later confirmed in tests by other companies, showed that standard regeneration procedures were ineffective in restoring HDN activity to an acceptable level. A third alternative would be to develop a new process to remove arsenic from the oil. In our preliminary studies, we determined that this third alternative was by far the most promising.

Many different arsenic removal process candidates were studied, and sufficient data were developed to permit us to make preliminary design and economic comparisons of the processes. The literature contains a number of patents for removal of arsenic in the parts per billion range from naphthas in order to protect very sensitive reforming catalysts. Unfortunately, such removal processes are apparently not applicable to shale oils with arsenic concentrations of 50 to 60 parts per million. As a consequence, a number of new process ideas were developed. Two processes, caustic washing and fixed-bed guard reactor, emerged from the preliminary evaluation as significantly superior to the others and were selected for further study.

A continuous bench-scale apparatus was constructed for experiments on caustic washing of shale gas oil fractions. As shown by the flow diagram in Figure 3, caustic solution and oil were pumped from storage tanks into a stirred reactor maintained at desired conditions of temperature and pressure. In the reactor a chemical

reaction occurred which resulted in the formation of arsenic compounds which were soluble in the caustic phase. The reactor effluent then flowed into a settler where the two phases were permitted to coalesce and be withdrawn through separate lines. To simulate commercial operation, a portion of the effluent caustic solution was recycled back to the feed tank. From analyses of the individual effluent phases, process conditions were evolved. This system was found to be effective for arsenic removal. Commercial design parameters were obtained from process variable studies, and economics were evaluated.

Figure 4 shows the flow diagram for the experimental guard bed apparatus. Hydrogen and oil were fed at prescribed rates into a packed reactor maintained at appropriate conditions of temperature and pressure. The hydrogen-oil mixture passed down over the catalyst bed and exited from the bottom of the reactor, at which point the gas and liquid phases were separated.

Using the data obtained from the two bench-scale units, we prepared preliminary commercial designs and calculated comparative economics for both processes. Other factors such as process operability and environmental effects were also considered. Based on our studies, the guard bed process was ultimately found to be superior to caustic washing in all three respects.

The development of the guard bed arsenic removal process was complicated by the unconventional nature of the shale oil and of the guard bed catalysts found to be most effective. For example, early catalysts tested, which were inexpensive and commercially available, performed satisfactorily in the process variable studies run to measure the effects of changing temperature and space velocity. However, in extended catalyst aging runs, problems were encountered with catalyst strength. A search for a suitable replacement catalyst was initiated, and a considerable effort was made to test commercial catalysts from a large number of different manufacturers and in several different sizes and physical configurations. Some of the candidates did exhibit performance which was superior to that for the original catalyst, but even the best catalysts did not meet our specifications. Eventually a strong, effective guard bed material was developed which was resistant to shale oil fouling and which will remove a high percentage of arsenic from shale oil distillates even at high levels of arsenic loading. The excellent effectiveness for arsenic removal provides substantial economic benefits. The use of competing materials would result in much larger and costlier processing equipment or a prohibitively high turnaround frequency to renew the guard bed material. This guard bed material, developed in a joint effort with a large catalyst manufacture using commercially projectable techniques, has been used to demonstrate this arsenic removal process for over 1000 hours charging shale gas oils at commercial process conditions. The arsenic removal dearsenation results of this demonstration run are shown in Figure 5.

This process operates over a wide range of pressures, hydrogen partial pressures and temperatures. It can process shale gas oil at high efficiency at required hydrotreating conditions for shale oil.

Pilot Plant Denitrogenation Studies

Experimental

Hydrodenitrogenation studies were performed in a bench scale continuous down-flow packed bed pilot plant unit. Over 60,000 reactor hours of shale oil processing were completed in our studies. Shale oil and hydrogen flowed through the packed bed and then through a high pressure water scrubber for removal of by-product ammonia and hydrogen sulfide gases. The latter stage avoids pilot plant operating problems due to ammonium sulfide formation. Gaseous and liquid products were then separated, metered, and analyzed to permit the determination of yields and weight balances.

Shale oil feedstocks containing both low and high arsenic levels were studied so that the effect on HDN of the arsenic removal co-process could be determined. Shale gas oil and naphtha fractions were treated separately since preliminary investigation showed this to be most economical for commercial applications. The gas oil work is discussed here.

Catalyst Screening

The denitrogenation catalyst activity and stability were shown to have a major impact on the cost effectiveness of the shale upgrading design because reactor investment is a major part of the total plant investment. To assure the selection of the best available catalyst, extensive comparison testing was done. As expected, nickel-molybdenum catalysts were better for HDN than cobalt-molybdenum catalysts. The catalyst chosen was found to have a 10-20 percent higher volume activity on shale oil than the best competitors.

Denitrogenation

An experimental program was conducted to determine the optimum range of processing conditions for achieving the desired low product nitrogen level. Process conditions studied cover a range of temperatures, 371-454°C (700-850°F), and space velocities, 0.5-2.0 (hours)⁻¹, at a reactor pressure found to provide an acceptable aging rate. A pyrolysis shale gas oil produced by a retort operation was tested along with a gas oil from the coking of the bottoms fraction of the pyrolysis oil. A pyrolysis-coker shale gas oil blend with low arsenic content was used for most of the studies, but high arsenic content pyrolysis-coker blends and coker only were also used to establish a feedstock effect.

Denitrogenation data from these tests were used to develop an HDN correlation based on first order kinetics:

$$\ln \frac{N_f}{N_p} = (K_{t,i}) \tau \cdot \alpha \quad 1)$$

where

- N_f = nitrogen content of feedstock, ppm
- N_p = nitrogen content of product, ppm
- $K_{t,i}$ = apparent rate constant at temperature t and with feed i
- τ = space time $\left(\frac{1}{\text{WHSV}}\right)$, where WHSV, the weight hourly space velocity, is defined as the weight of feed per hour per weight of catalyst.
- α = catalyst relative activity

First order kinetics gives a reasonable fit to the HDN data. This is consistent with the observation of McIlvried⁽⁸⁾ and others for the denitrogenation of various materials. Apparent rate constants calculated from equation 1) are plotted in Arrhenius form in Figure 6 showing an apparent activation energy of 26.9 Kcal/gm mole. The higher arsenic level feeds, both pyrolysis-coker blend and straight coker, showed significant HDN activity losses (5-10 percent for the blend and 35 percent for the coker alone). Figure 7 shows the actual denitrogenation data plotted in the form predicted by equation 1). Good agreement between the data and the first order kinetic form is indicated.

Hydrogen Consumption

The hydrogen consumption, calculated from material balance on hydrogen content of feed and product streams, is shown as a function of nitrogen removal in Figure 8. Feeds with higher hydrogen contents tend to consume less hydrogen by an amount approximately equal to the difference in hydrogen contents of the feeds. The range of hydrogen consumption observed for these shale oil HDN tests, 254-304 m³/m³ (1500-1800 scf/b), approach the consumptions obtained in conventional hydrocracking operations.

Aging Studies

A number of catalyst aging runs were made during the process development. One of these was a pilot plant gas oil aging run set up to simulate the production of a low nitrogen level (750 ppm) product from a feed oil containing 21,500 ppm nitrogen. Start-of-cycle process condition needed to achieve this low gas oil nitrogen level was 377°C (710°F).

During the 90-day aging run, the temperature was raised 7°C (13°F) to maintain denitrogenation. After 90 days the temperature was raised to 399°C (750°F), and operated for another 30 days. Only a 1°C temperature increase was required to maintain denitrogenation as shown in Figure 9. These results show that a 1 year cycle or greater is feasible for shale oil upgrading.

Reactor Modeling

In order to screen various reactor designs for a given application, a reactor model which simulates the important design variables was developed. Such a model must predict the required catalyst quantity, and predict yields for each reactor temperature, pressure, and hydrogen rate chosen.

For shale oil hydrotreating, the reactor model must also take into account the effect of arsenic since arsenic is a strong catalyst poison. Even with a guard bed, arsenic is deposited continually throughout the cycle and to compensate for its poisoning effect temperature must be raised to maintain HDN activity. Because of the highly exothermic reaction, many hydrogen quench points, such as shown in Figure 10, or other means of heat removal, are required to control reactor temperature. As the catalyst activity declines, both due to arsenic and time on stream, conversion in each catalyst bed changes. The lower conversion gives less heat release and, therefore, bed temperature must be increased to maintain catalyst activity. This in turn greatly changes the required hydrogen quench after each catalyst bed as the cycle progresses.

The variations are substantial, as illustrated in Figure 11. Since hydrogen quench rate varies significantly with time on stream, the quench system must be designed to handle a wide range of flows. Most conventional hydrotreaters would be unable to handle the quench rate variation along with the high heat release for shale oil processing. Flexibility must also be provided so the reactor inlet temperature can be raised. The model enables the designer to accurately take these effects into account for an optimum design.

The complexity in modeling arises when attempting to simultaneously take into account the effect on conversion of temperature, WHSV per bed and arsenic, when the amount of arsenic laydown itself is a function of WHSV and temperature. The actual system is further complicated in that the catalyst ages with time on stream as well, even if no arsenic were present.

For each catalyst bed the model does the following:

- o Calculates the severity and conversion.
- o Predicts yields including H₂ consumption needed to estimate the exothermic heat of reaction.
- o Performs heat balances to predict outlet temperature and quench rates.
- o Predicts HDS, HDN, hydrocracking, aromatic saturation, and olefin saturation.
- o Predicts catalyst activity as a function of arsenic and time on stream.

Design Studies

With such a model, the overall shale upgrading process can be optimized. Since arsenic removal and HDN are highly interdependent, the reactor design needs to be studied in order to minimize overall processing costs.

One use of the model is to determine the optimum conditions for arsenic removal since any arsenic leakage directly affects the required severity and cycle life for HDN. As the arsenic removal is increased via increased guard reactor size, capital costs increase but catalyst usage decreases. The optimum design for HDN can be found using the model. Conditions are chosen so arsenic removal and coke deposition are balanced to minimize costs.

The model has been used for two commercial designs, one for Colony Development Operation, a joint venture of which Atlantic Richfield is the operator, and another for a client of this shale oil hydro-treating technology.

Literature Cited

1. Burger, E. D., D. J. Curtin, G. A. Myers and D. K. Wunderlich, "Prerrefining of Shale Oil", Am. Chem. Soc., Div. Pet. Chem., Aug. 24-29, 1975.

2. Svajgl, O., Collection Czech Chem. Commun., 24, 3829 (1959).
3. Ibid., 28, 11 (1963).
4. Svajgl, O., Freiberger Forschung-H, A340, 89 (1964).
5. Svajgl, O., Scientific Papers of the Institute of Chemical Technology. Prague; Tech. of Fuels, 7, 187 (1965).
6. Ibid., D13, 163 (1967).
7. Svajgl, O., Sbornik praci z vyzkumu chernicke ho vyuziti, dehtu a ropy, 8, 83 (1968).
8. McIlvried, H. G., "Kinetics of the Hydrodenitrication of Pyridine", Industrial Engineering Chemistry, Process Design and Development, 10, 1, 125-130 (1971).

FIGURE 1
ARSENIC IN HYDROTREATED PRODUCT OIL

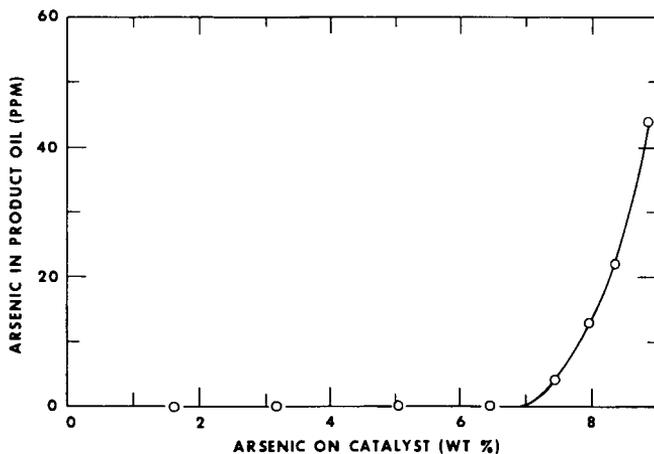


FIGURE 2
 CATALYST ACTIVITY OF A NICKEL-MOLYBDENUM
 CATALYST TREATING SHALE OIL

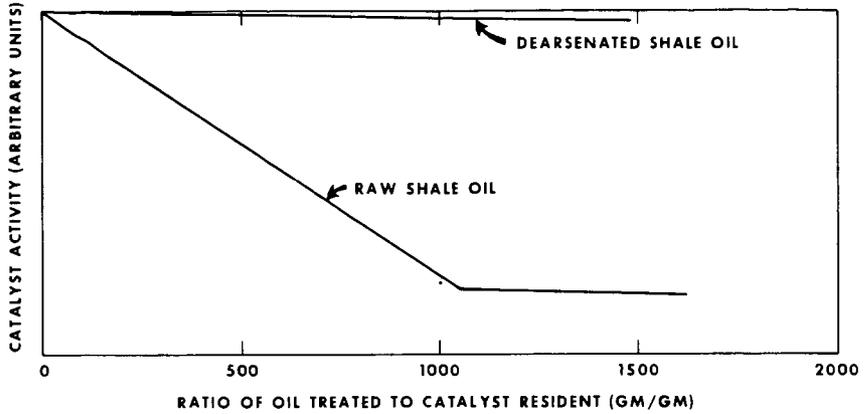


FIGURE 3
 CONTINUOUS CAUSTIC SODA WASH APPARATUS (WITH RECYCLE)

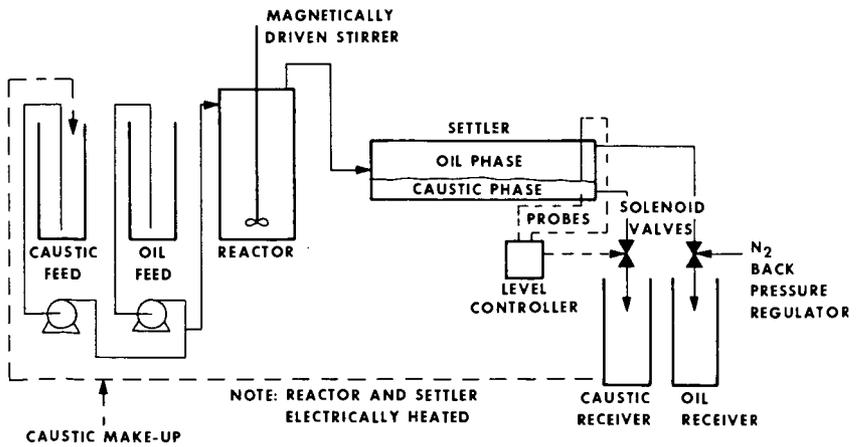


FIGURE 4
 FLOW DIAGRAM FOR EXPERIMENTAL GUARD BED SYSTEM

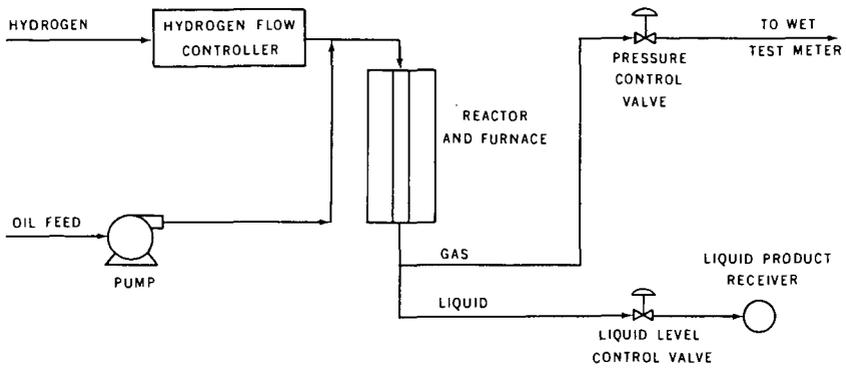
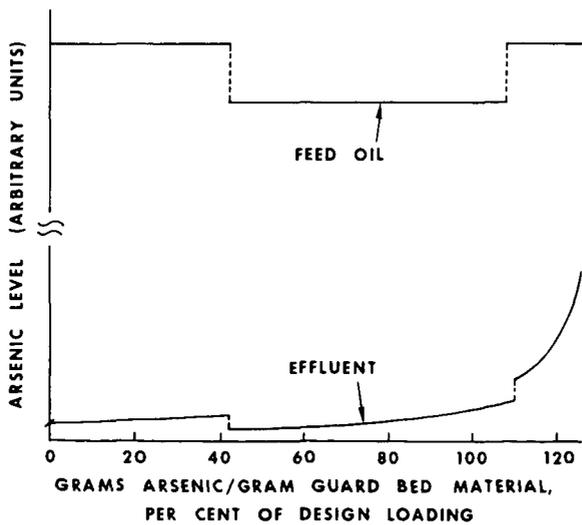


FIGURE 5
 ARSENIC REMOVAL DEMONSTRATION RUN RESULTS



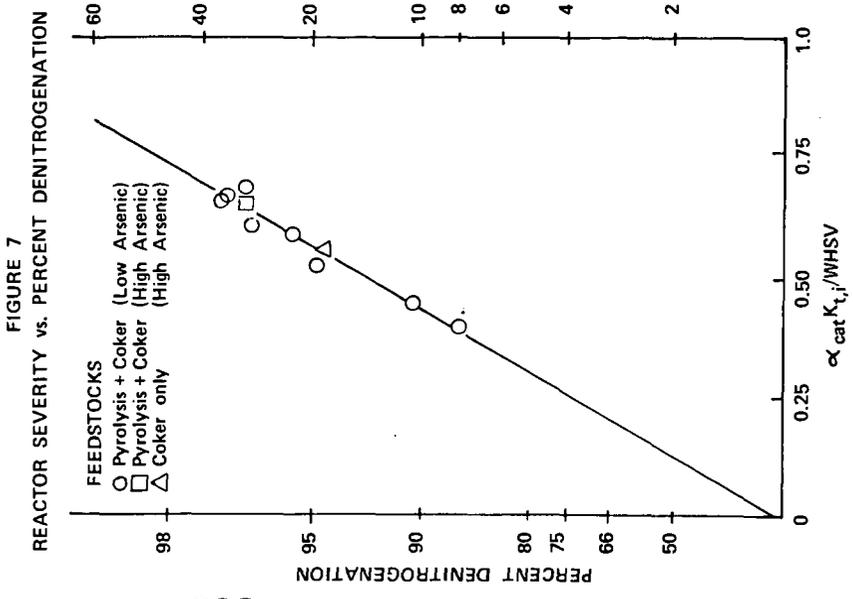
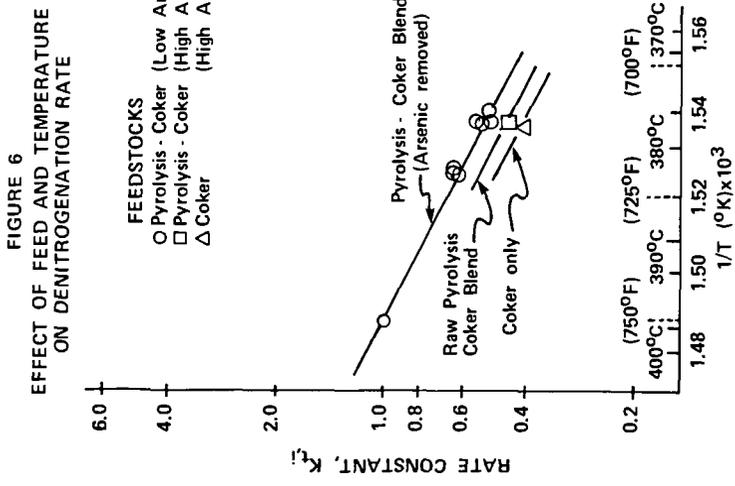


FIGURE 8

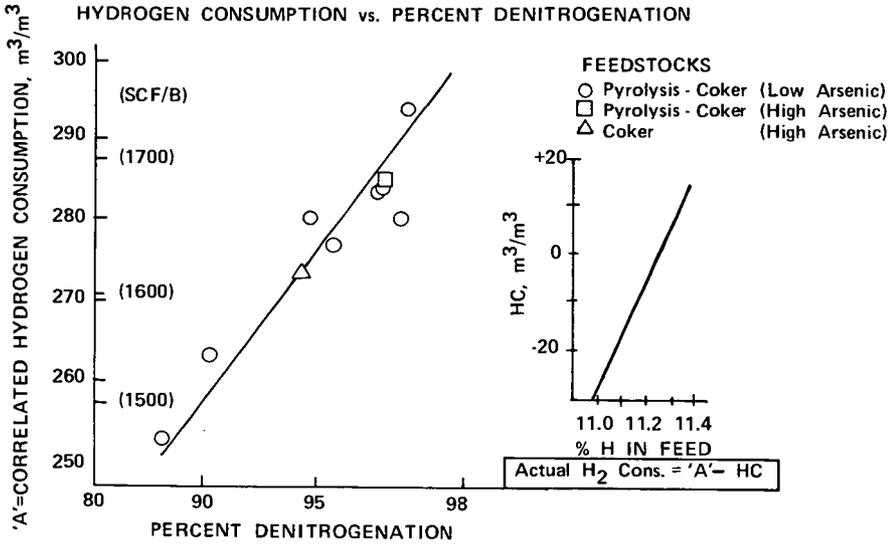


FIGURE 9
CATALYST AGING STUDY

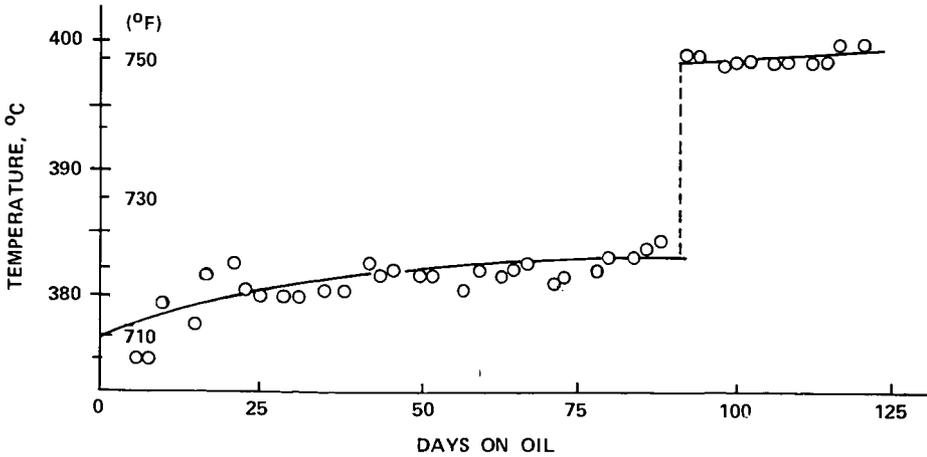


FIGURE 10
SHALE OIL UPGRADING

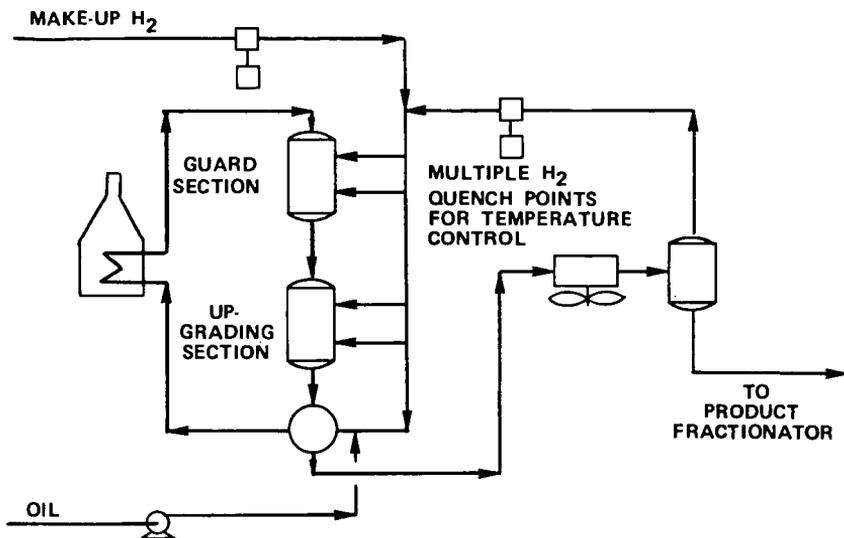
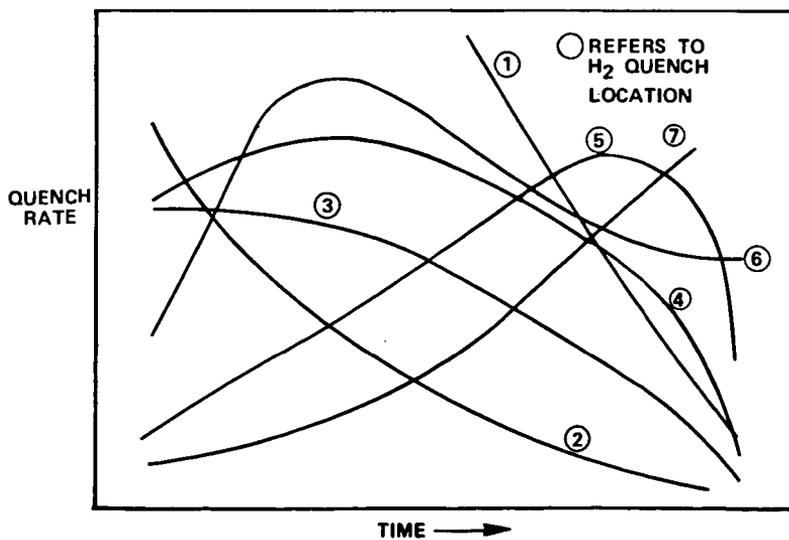


FIGURE 11
QUENCH RATE VARIABILITY



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

Philip L. Cottingham, Frederic A. Birkholz, and Leo G. Nickerson

Department of Energy, Laramie Energy Research Center
P. O. Box 3395, University Station
Laramie, WY 82071

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	40:1	+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		Oil Phase ^{1/} Wt. % of Raw Oil
			Additive, Wt. % of Oil	Water Used, Wt. % of 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

36

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 $\frac{1}{2}$ 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 $\frac{1}{2}$ 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.

EFFECT OF RETORTING ON WAX CRYSTALLIZATION IN UTAH SHALE OILS

P. F. Lovell

Sunoco Energy Development Co.
12700 Park Central Place, Suite 1500
Dallas, Texas 75251

and

W. H. Seitzer

Suntech, Inc.
P. O. Box 1135
Marcus Hook, Pennsylvania 19061

Introduction

The White River Shale Project (WRSP) was formed in June, 1974, by Phillips Petroleum Company, Sunoco Energy Development Co., and Sohio Petroleum Company. The purpose of the project was to develop jointly the oil shale resource on the federal lease Tracts Ua and Ub in northeastern Utah. Tract Ua is jointly owned by Phillips and Sunoco Energy Development, while Sohio holds title to Ub. This combined resource has an estimated 1.06 billion barrels of oil in place, averaging 28 gallons per ton (1).

To abide by the lease terms WRSP prepared and issued a detailed development plan (DDP) in June, 1976. This DDP included the various phases of development necessary to reach commercial production and, ultimately, abandonment of the leases. To this end, WRSP has continued evaluating the technological progress of the various retorting processes. In February, 1976, the WRSP mined several hundred tons of Uinta Basin, Utah, oil shale from an outcrop formation on patented lands about 3 miles east of the Ua-Ub federal leases in a 26 square mile area known as Hells Hole Canyon. This is shown in Figure 1.

The sample was collected in two parts: the first from an approximate 12 foot interval above the Mahogany marker, and a second sample from an approximate 20 foot interval located immediately below the Mahogany marker. The ore body was not pre-assayed at Hells Hole Canyon. Therefore, the grades of the samples were unknown until they were received and Fischer assayed by the respective toll processors, Paraho Development Corporation, Anvil Points, Colorado, and Union Oil Co., Brea, California.

Retorting

A. Paraho Direct Heated (DH) - Approximately 100 tons of 19 gpt Utah shale, sized 1/2" x 2", were processed in the 2 1/2 ft. I.D. pilot plant using the Paraho DH mode at a nominal rate of 1 ton per hour. In the DH mode the retorting heat is supplied by combustion, directly in the retort, of residual carbon by the oxygen in the gas-air mixture. Retort temperatures are controlled by adjusting the composition of the recycle gas return. Figure 2 gives a simple illustration of the process (2).

The oil yield for the Utah shale was 92.8 vol % of Fischer Assay, very similar to what has been reported for the Paraho DH mode on Colorado shale (3). The yield of product gas was about 8000 SCF/T of 66 Btu/Ft³ gross heating value material. The overall weight balance was 98.6%. Some properties of the raw and retorted shale are shown in Table I.

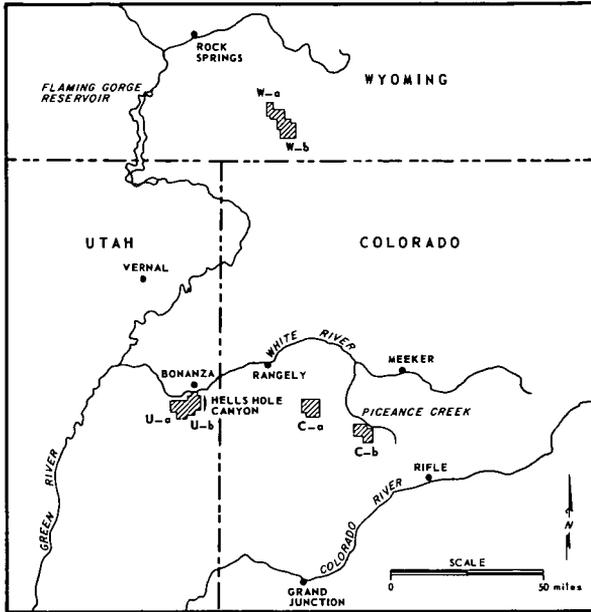


FIGURE 1. LOCATION OF U_a-U_b & HELLS HOLE CANYON

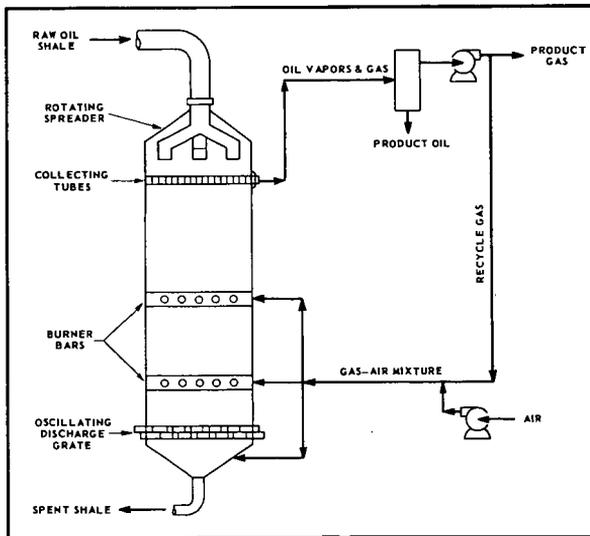


FIGURE 2. PARAHO OIL SHALE KILN

Table I
Utah Shale Properties

	Paraho DH		Union "B"	
	Raw Shale	Spent Shale	Raw Shale	Spent Shale
Fischer Assay				
Oil, gal/ton	18.61	0.69	32.20	-
Oil, Wt %	7.11	0.26	12.21	0.0
Water, gal/ton	5.85	-	2.90	2.10
Water, Wt %	2.44	0.23	1.23	0.86
Mineral CO ₂ , Wt %	19.83	13.39	18.96	21.93
Organic C, Wt %	-	1.93	13.68	2.83
Elemental Analysis				
C, Wt %	15.28	5.58	18.85	8.81
H "	1.46	0.11	2.05	0.35
N "	0.44	0.15	0.46	0.31
S "	0.35	0.31	0.53	0.41

B. Union "B" - The 100-ton sample of 32 gpt Utah shale was reduced to a consist of 1/4" x 1" and retorted in the Union "B" mode in their nominal 6 T/D pilot retort. Raw shale rate for these runs was around 3 T/D. The Union "B" process is an indirect heated mode where the retorting heat is supplied by externally heated recycle gas as opposed to direct combustion of shale inside the retort vessel. A unique aspect of the Union process is the upflow of raw shale using a reciprocating "rock pump" rather than gravity downfeed of the raw shale. A simplified diagram of the Union "B" process is illustrated in Figure 3 (4).

Oil yield was about 97 vol % of Fischer Assay (~101 vol % on a C₄+ basis) for the Union "B" processing. This yield is also similar to results on Union's Colorado shale (5,6). Retort product off-gas yield was about 725 SCF/T. This material had a calorific value of about 900 Btu/Ft³. The material balance for the Utah shale runs averaged 99+ Wt %. Properties of the Utah shale processed by Union are also given in Table I.

Analytical Results

Practically all previously reported data from these two processes have been on Colorado Piceance Basin shales. This present effort was an attempt to obtain data on Utah oil shale and determine if Utah shale oils were any different. No major differences between Utah and Colorado shale oils were found (7). Table II presents comprehensive analytical examinations of both the Paraho and Union produced whole, raw Utah shale oils. Despite the wide variation in shale grades (19 gpt vs. 32 gpt) and the known differences between both retorting processes, the raw shale oil products appeared to be quite similar both physically and chemically.

The only major difference in the two oils was in their respective pour points, 30°F for Union "B" and 75°F for Paraho DH. Known differences between the pour points of the oils produced by these processes from Colorado shale have been reported (4). The 30°F pour point for the Union "B" shale oil was lower than expected.

Transportability of raw shale oils via pipeline is a viable option for eventual marketability. Although pour point isn't the only factor determining the pumpability of oils, it is an important variable. A naturally occurring lower pour point oil could have economic advantages when compared to oils requiring additions of available, chemical pour depressants. Therefore, this observed low pour point

of 30°F for the Union "B" Utah oil is certainly an interesting and serendipitous phenomenon. On closer examination, however, it was observed that the wax in the two oils crystallized differently.

Table II
Physical and Chemical Properties of Raw Utah Shale Oils

Properties		Union "B"	Paraho DH
Gravity	°API	20.2	19.6
Carbon	Wt %	84.27	84.21
Hydrogen	"	11.68	11.82
Oxygen	"	1.23	1.89
Sulfur	"	0.55	0.50
Nitrogen Total	"	1.93	2.09
Nitrogen Basic	"	1.26	1.19
Ash	"	0.3	0.05
Conradson Carbon	"	4.3	3.1
Pour Point	°F	30	75
Viscosity @ 100°F	CS	35.3	60.9
Viscosity @ 210°F	"	4.83	5.95
Arsenic	W ppm	49	19
Chloride	"	15	6
Chemical Structure by ASTM D-2007			
Paraffins	Wt %	9	7
Naphthenes	"	10	10
Olefins	"	7	5
Aromatics	"	45	44
Polar Aromatics	"	24	29
Pentane Insols.	"	5	5
Distillation ASTM D-1160			
IBP		152	220
10		345	503
30		633	690
50		799	827
70		919	952
90		1078	-
EP		1100	1100
% Recovery		92	87

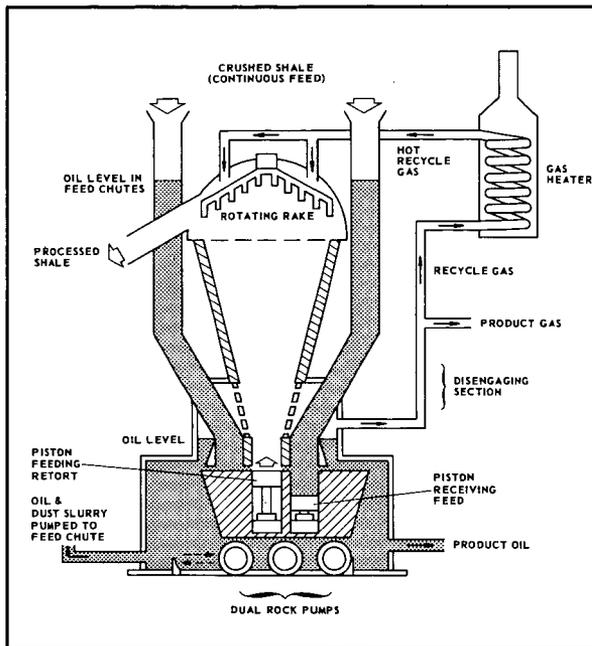


FIGURE 3. UNION "B" OIL SHALE RETORT

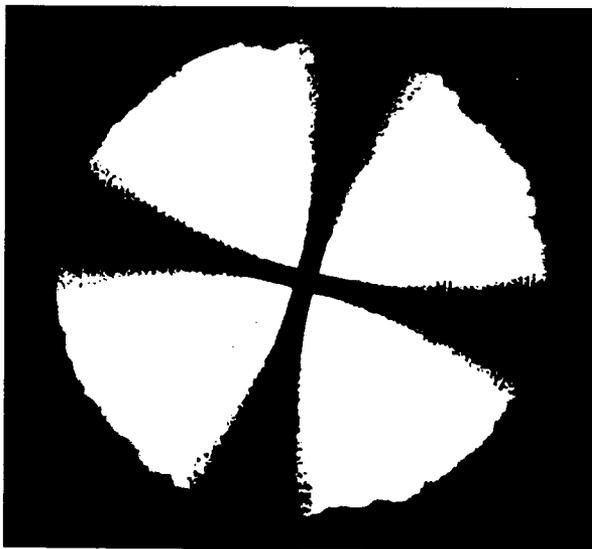


FIGURE 4. SPERRILITE OF ANISOTROPIC CRYSTALS BETWEEN CROSSED POLARS

Wax Spherulites

In the polarizing microscope at room temperature, the wax crystals in the Paraho oil appear as the expected needles and plates, but the morphology of the crystals in the Union oil is quite different. While needles are also present, most of the crystals exhibit properties characteristic (8) of spherulites of anisotropic materials. The particles are round and, between crossed polars in parallel light, display a black maltese cross which remains stationary on rotation of the stage. This is shown schematically in Figure 4 and in photomicrographs in Figure 5. X-ray examination of the oil gives only the pattern for paraffinic wax. Although pure spherulites have not yet been isolated and examined, they are believed to be formed by wax needles arranged radially. Analogous structures are seen commonly in polymers including polyethylene but, to our knowledge, this is the first time spherulites of wax have been observed.

Two questions immediately occur. Why do the spherulites form in the Union oil, and is there a connection between their formation and the lower pour point?

Cause of Spherulite Formation

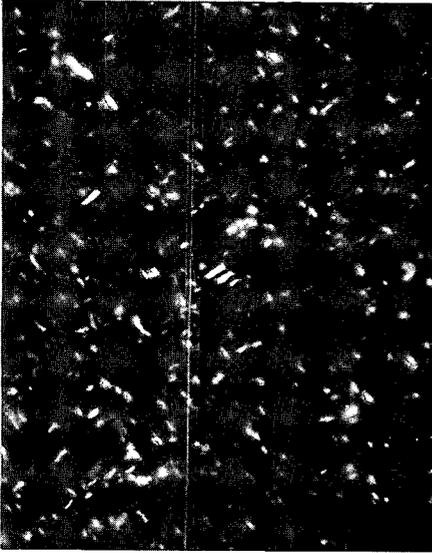
Three aspects of the two oils were examined -- the wax, the mineral, and the effect of various fractions.

A. Wax - These were isolated by removing the pentane-insolubles from the 650°+ fractions, precipitating the crude waxes in methylethylketone-toluene, and deoiling these waxes in ethylene dichloride. The yields, based on total oils, were 5.0% and 4.7% from the Paraho and Union oils, respectively. Although the melting points were different (109 and 140°F), the fingerprints by gas chromatography were quite similar, so that the primary factor in formation of spherulites is not wax composition. This conclusion is further supported by the blending data reported in section C below.

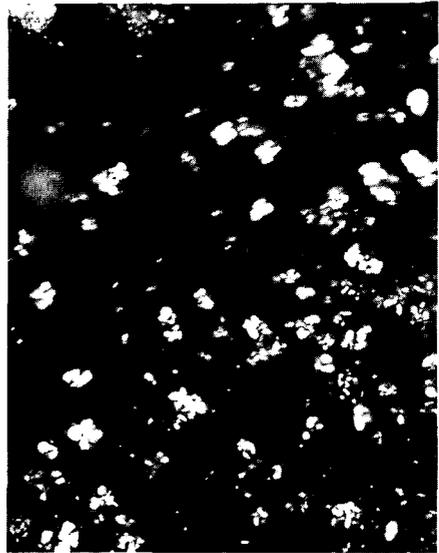
B. Mineral - As could be anticipated from the larger ash content reported in Table II, many mineral particles are observed in the Union oil. These were removed by running the hot oil through a 1.5 micron filter. Removal of the mineral appeared to have no major effect on the spherulites. Heating up the mineral-containing oil on the microscope hot stage causes the spherulites to melt, leaving the mineral. Upon cooling, the wax does recrystallize around the mineral. After filtration the mineral is not present, but the recrystallization of the wax into spherulites does not seem to be appreciably slower. Thus, mineral is not the controlling factor in spherulite formation.

C. Effect of Fractions - Both oils were distilled into I-425-650-850-1050 and 1050°F+ fractions. These fractions were blended in many different ways and the blends observed with the microscope at 77°F to see if spherulites were present. It was found that:

- Paraho Oil
 1. Adding or substituting Union 1050°F+ bottoms gives spherulites as shown in Figure 5D. Also, adding or substituting the pentane-insolubles from the Union bottoms yields spherulites, although perhaps not as well-formed.
 2. No other blends show spherulites.
- Union Oil
 1. Spherulites are formed if the 650-1050°F or 850-1050°F fractions from Paraho oil are substituted. Also, spherulites are present after removing the pentane-soluble bottoms.



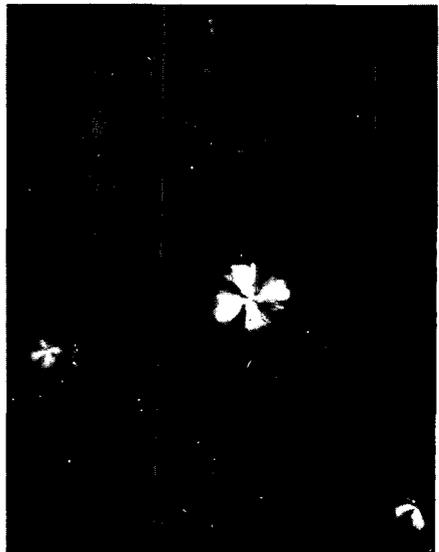
A. PARAHO SHALE OIL



B. UNION SHALE OIL



C. UNION SHALE OIL



D. PARAHO SHALE OIL SUBSTITUTE UNION
1050° F+ FRACTION

SCALE: 30μ

FIGURE 5. PHOTOMICROGRAPHS OF WAX CRYSTALS

2. Only needles are observed if either the 850-1050°F fraction or pentane-insoluble residuum is removed. Also spherulites are absent if Paraho pentane-insoluble, pentane-soluble, or whole 1050°F+ bottoms are substituted for the Union bottoms.

These facts lead to the conclusion that something in the Union 1050°F bottoms, probably in the asphaltenes, causes spherulites to form. The 850-1050°F fraction is necessary but is not unique for the Union oil.

Pour Points

Data measured on the Mectron Autopour are listed below in Table III.

Table III
Pour Points

<u>Oil</u>	<u>Crystal</u>	<u>Pour Pt., °F</u>
Whole Union	Spherulite	27
Whole Paraho	Needle	77
Union, Substitute Paraho 1050+	Needle	58
Paraho, Substitute Union 1050+	Spherulite	21
Union + 9% I-425	Spherulite	36

Substituting Paraho 1050°F+ bottoms into Union oil changes the spherulites to needles and increases the pour point from 27 to 58°F. On the other hand, changing the needles in Paraho oil to spherulites by substituting Union 1050°F+ bottoms lowers the pour point from 77°F to 21°F. Doubling the I-425°F fraction in Union oil, which should lower the viscosity, seems to increase the pour point. While a viscosity study, soon to be made, is needed for confirmation, these data indicate strongly that there is a correlation between spherulite formation and pourability of these oils. It appears in the microscope that the wax changes from a three-dimensional, irregular network of needles to spheres which have less particle-to-particle interaction. Work is continuing in an effort to achieve better understanding and control of the phenomenon.

Acknowledgements

The authors wish to thank Sunoco Energy Development Co. for supporting this work and authorizing this publication. Special credit should be given Ms. Dorothy O'Reilly, who first recognized the spherulites and who has made all of the microscopic observations; also to Suntech Analytical Department for all other analyses.

References

- (1) White River Shale Project, Detailed Development Plan, Vol. 1, June, 1976.
- (2) Jones, J. B., "Technical Evaluation of the Paraho Process," 11th Israel Conference of Mechanical Eng., Haifa, Israel, July 11, 1977.
- (3) Sladek, T. A., "Recent Trends in Oil Shale - Part 2: Mining and Shale Oil Extraction Processes," Mineral Ind. Bull., V. 18, #1, 20 p., January, 1975.
- (4) Atwood, M. T., "Above-Ground Oil Shale Retorting: The Status of Available Technology," Eng. & Mining J., V. 178, #9, Sept., 1977, pp. 148-154, 363.
- (5) Hopkins, J. M., et al, "Development of Union Oil Company Upflow Retorting Technology," 81st National Meeting, AIChE, Kansas City, MO, April 11-14, 1976.
- (6) Duir, J. H., et al, "Continuous Upflow Retort Improves Shale Processing," Hydrocarbon Processing, V. 56, #5, May, 1977, pp. 147-150.
- (7) Lovell, P. F., "Production of Utah Shale Oils by the Paraho DH and Union "B" Retorting Processes," 11th Oil Shale Symposium, Golden, CO, April 12-14, 1978.
- (8) Hartshorne, N. H. and Stuart, A., "Crystals and the Polarizing Microscope," American Elsevier Publishing Co., New York, NY, 4th Edition, 1970, p. 318.

A MARKETING PROSPECTUS FOR SHALE OIL

G. E. Ogden and R. D. Ridley

Occidental Oil Shale, Inc.
5000 Stockdale Highway
Bakersfield CA 93309

Technical developments in shale oil production achieved in the past few years signal the potential beginning of a new liquid hydrocarbon industry. Construction work has begun on commercial scale projects and coupled with the growing sense of national urgency, there is good optimism that significant shale oil production will be forthcoming. These events have generated a need to take a closer look at definition of shale oil markets.

In contrast to past efforts which have dealt hypothetically with this subject, our marketing development efforts are directed at an established objective; that is, to define the specific markets which will return an optimum price for a commercial quantity of shale oil in the mid-1980's. Consuming sectors of the petroleum market have been evaluated and compared. The transportation element has been costed for various geographic regions of interest and combined with quality differentials to identify economic alternates.

Before delving into the distribution logic, some commentary about the nature of the product is warranted. While most of the shale oil technology developed to date is derived from a variety of above ground retorting tests, oil shale projects currently underway indicate that the early production will come from a modified in situ process with later production possibly being a blend of oils from several recovery processes. Many of the early plans called for a prerefining step at the production facility to improve the oil's transportation characteristics and marketability. Strong demand projected for hydrocarbon liquids in the mid-1980's has tempered the concern over marketability of as-produced shale oil and consequently has moderated the need to upgrade at the production site. The capital intensive production operation tends to make developers favorably consider minimizing the initial investment, which can be accomplished by eliminating the oil upgrading step. Concerns over water availability and general high industrial profile in Western Colorado are also factors which will increase the probability that any processing of the oil will be accomplished downstream in existing industrial complexes. Consequently, the commodity of interest in this discussion is the as-produced shale oil from modified in situ retorting.

While shale oil will not be completely interchangeable with crude oil, its properties are sufficiently similar that it will act as a substitute in several applications. The major quality difference between shale oil and conventional crude oil is nitrogen content. Shale oil contains approximately 1.5 weight percent nitrogen compared to 0.1% for typical crude oils produced in the Rocky Mountains. Since nitrogen is an undesirable contaminant in catalytic refining processes, facilities will have to be constructed specifically for its removal. Refining technology is fully developed for this processing step and, in fact, California crudes ranging up to 0.7% nitrogen are routinely refined on the West Coast. The impact of the nitrogen can also be lessened by blending with crude oil in an existing refinery. To verify

this, a successful refinery test run was conducted on as-produced, in situ shale oil at the Chevron refinery in Salt Lake City in November, 1977.

There are also significant differences from crude in fractionation yields. These differences are explained in some detail in the refining quality discussion. A very important shale oil property is its relatively low sulfur content, 0.5-0.7 weight percent. The low sulfur content may allow the oil to be burned directly in boiler applications in its as-produced state. This factor also influences planning against incorporating an upgrading step with the production operation.

Because of its similarity to petroleum, it is expected that shale oil will compete in the same markets with crude oil or products derived from crude. The supply of crude oil to meet incremental U.S. demand is widely accepted to be foreign sourced in the 1980's and reference is made throughout the discussion to economics relative to cost of foreign crude oil.

With that overview in mind we can turn to examination of the logistic factors, the potential consuming industries, and the business and governmental influences.

Geographical orientation of the existing markets will have a strong influence on shale oil disposition, particularly in the early years. As production of shale oil expands we can expect industrial consumers to react to the supply source by locating new facilities to take advantage of logistics. However, at the outset, the processing plants that will absorb the shale oil are essentially in place. Figure 1 shows in general the concentration of the refining industry, the primary petrochemical plants and the utilities running on oil.

The refining industry is the most widespread and while large concentrations are shown in California, the Gulf Coast, the Great Lakes, and the Philadelphia area, a sufficient capacity to absorb 100-200 MB/D of shale oil exists in the Rocky Mountain/Kansas area. In perspective, the U.S. refining capacity stands at 17.6 million B/D of which 5 million B/D is located in the Rocky Mountain/Midwest area. Demand for refined products, of course, is equally widespread and should continue to grow at a moderate pace. Because of its wide geographic distribution, the refining industry has the most flexibility to modify or locate new facilities to take advantage of the logistic flow of the shale oil.

The primary petrochemical industry does not have this luxury. The great majority of the large volume petrochemical operations are centered near the U.S. Gulf Coast. There they have the necessary economic linkage with plants producing intermediates and finished products along with established outlets for by-products. If a large plant were to be constructed in the Rockies, it would have to achieve sufficient benefit to overcome the transportation penalty associated with hauling nearly all the output to the U.S. Gulf for secondary processing or by-product disposition. As traditional supply sources change, we may see evolution in this direction but it will be very slow and in small steps.

The large market for oil in direct burning applications is the utility boiler market. There is some question as to how long this outlet will

exist in light of Government policy trending against using liquids for power generation. As shown on Figure 1, oil use today is centered in three regions: California, the Great Lakes, and the Northeast. There may be a growing use in the Gulf Coast area if economics permit gas fired applications to be converted to oil, but for the very long term oil based generation is likely to be a shrinking market. As new nuclear and coal plants come onstream, they will be put in base load service and existing oil generation will be subordinated first to peak shaving and ultimately retired. With the exception of areas where very tight emission standards are required and/or nuclear and coal plants are faced with very long delays, new oil fired generation capacity is unlikely.

With the qualitative overview in mind, we can now turn to the quantitative impact of the geographical element. The table below attempts to ascribe a transportation premium or penalty for shale oil with respect to common foreign crude oil in the regions of interest. The East Coast was not included in the table since it would represent an extreme physical distribution problem for Rocky Mountain oil. The transportation costs are estimated average values for 200 MB/D and 1,000 MB/D. The estimates assume pipeline transportation to a typical destination within the area. Where existing pipelines are in place, actual tariffs are presumed. Tariffs are approximated for new pipelines using \$.20/bbl per 100 miles for 200 MB/D, and \$.10/bbl per 100 miles for 1,000 MB/D.

RELATIVE TRANSPORTATION ECONOMICS
SHALE OIL VS. FOREIGN CRUDE OIL, \$/BBL

	Shale Oil		Crude Oil	(Penalty)/Premium	
	200 MB/D	1000 MB/D		200 MB/D	1000 MB/D
Los Angeles	1.80	.90	-0-	(1.80)	(.90)
Rocky Mtn.	.60	.30	.80	.20	.50
Chicago	1.20	1.20	1.20	-0-	-0-
U.S. Gulf	2.40	1.20	-0-	(2.40)	(1.20)

The table shows the quantitative effect of transportation in 1977 dollars on a value relationship with crude oil. Location impact may result in a \$.20-\$.50/bbl premium for shale oil routed to a Rocky Mountain destination to a \$.90-\$2.40/bbl penalty for a West Coast or Gulf Coast market. The obvious conclusion is that there is a sizeable transportation advantage for shale oil if a market can be created in the Rocky Mountain/Upper Midwest area instead of a Coastal location.

Definition of quality differentials is much more difficult to accomplish with any degree of certainty. In the long term context, where the liquid demand exceeds supply, today's quality relationships are apt to be distorted. For the purpose of this discussion, however, it is assumed that foreign crude can still be purchased for incremental liquid input.

Refining value of shale oil has probably been investigated in greater detail than the other potential applications. Most of the efforts to prescribe a refining cost for shale oil, however, have viewed the problem in a very hypothetical context. Most of the data is developed for complete new facilities turning out a product slate that may or

may not relate to the actual market conditions in the environment where the oil is likely to be consumed. For the reasons discussed earlier, there is good probability that the shale oil will not be upgraded at the production facility, but rather will be integrated into existing refineries in its as-produced state.

Also, there has been no reported extensive testing on in situ shale oil which is likely to represent the quality of the majority of the early production, based on projects presently underway. Consequently, there is some divergence of opinion on the relative value of shale oil to conventional crude oil.

In our efforts to date at defining this value, we have attempted to cost the effect of integrating as-produced, in situ shale oil into typical Rocky Mountain/Upper Midwest refineries as a substitute for the crude mixes run at those locations. Figure 2 shows the various geographical areas that were analyzed in this fashion. The dollar figures superimposed are the additional refining costs resulting from substituting shale oil. While the numbers range from \$2.05 to \$3.00 per barrel in 1977 dollars, an additional refining cost of \$2.50 probably reflects a good estimate of the average additional cost. It should be noted that these cost figures include a reasonable rate of return on invested capital.

This additional refining cost appears lower than many of the recently published figures but it can be qualitatively reconciled when put in the context of the market environment in the mid-1980's. First, the existing U.S. and worldwide supplies of light crude oil are declining at a significant rate. The refining supply barrel is getting heavier, and more importantly contains a higher volume yield of residual boiling range material. We can see the impact of this phenomenon already in the U.S. noting the very depressed prices for high sulfur residual fuel which is in long supply. In situ shale oil has only 4%, 1000°F. + boiling range material compared to 20% for North Slope crude and 18% for Arabian light crude. These crudes are by no means the worst and are actually significantly better than Kuwait, Arabian Heavy and others which represent a good proportion of the unused worldwide production capacity. Upgrading crude residual material to clean transportation fuels is probably more costly than starting with shale oil.

Another factor that has historically been represented as a negative for shale oil is the very low gasoline yield. Nearly all the refining studies on shale oil have discounted its value because of the need to convert a greater proportion of the distillate to gasoline. However, the strong trend today indicates tapering gasoline growth. The major forecasters are nearly unanimous in projecting a peak in U.S. gasoline demand between 1980 and 1985. The conclusion is that the great majority of facilities to manufacture gasoline will be in place when shale oil comes on the market and the demand growth will take place in the distillate range. If this trend proves to be true, a refiner in 1985 will place a premium value on high distillate yield as opposed to high gasoline yield. The potential yield premium will act to offset the additional refining cost.

While the shale oil yields were very unbalanced with the refinery product mix outlook in 1970, those same yields will be highly attractive in 1985.

The market price for shale oil as a utility boiler fuel can be quantified in a fairly narrow range but is subject to environmental and governmental restrictions. Pricewise, where supply imbalance or regulatory effects do not create distortions in the market, 1% sulfur residual fuel sells for approximately the same price as Arab Light crude. This grade of fuel oil is currently burned in the Great Lakes area for power generation as well as industrial fuel applications. Since shale oil in an untreated form approximates the quality of 1% sulfur residual fuel, we suspect that its value in that application will approach that of Arab Light crude oil. Since we have defined refining costs for processing shale oil to transportation fuels, it is probable that its highest value will result from 1% sulfur boiler fuel.

However, the areas where 1% sulfur fuel oil can be burned are shrinking. Emission restrictions have forced many utilities to use 0.5% and lower fuels and the trend is continuing. Looking forward to the mid-1980's, there may be a market for only a small volume, say 50,000 B/D, for this application.

The potential petrochemical feedstock market has not yet been fully explored. There are some negative aspects of shale oil for petrochemicals. The existing petrochemical plants (olefins, aromatics) are tailored to the light fractions of petroleum such as LPG and naphtha. Shale oil's low yield of light hydrocarbon places it at a disadvantage with respect to crude oil. No attempt has been made to quantify a penalty for this application.

On the other hand, there is good reason for some optimism. Shale oil's very respectable hydrogen content (12%) suggests that new petrochemical technology could be tailored to this input economically. In a very forward thinking manner, members of the petrochemical industry have expressed interest in exploring new applications. However, the competing uses will likely comprise the total early market for a shale oil industry and it will only be in the long term that a petrochemical market will come into play.

The other factors that will have an influence on shale oil distribution will not be directly economic. Government policy may leverage through incentives a particular use for the long term benefit even though it may not be the most economic short term application. As an example, there may be legislation penalizing burning oil in a stationary boiler. National policy seems to be aligned in the direction of converting power plants from oil and gas to coal. For these reasons we suspect that the fuel oil application will not provide a long term market for a shale oil industry; nevertheless this outlet will be of real value for the early stages of an oil shale industry since it can utilize raw shale oil without major capital expenditure.

General business factors should be taken into account in this assessment particularly for the first 200,000 barrels per day of production. There is almost no disagreement that early production of shale oil will be a high risk, capital intensive venture. The production venturers will be inclined to limit their capital exposure to the production and look for a manufacturer to risk the upgrading capital. In this context, the fuel oil market has a strong advantage. Very little capital will need to be exposed to consume the shale oil, very little lead time

will be required and there will be a minimum risk of non-success in the application. Refining on the other hand will require substantial capital modifications, a three year minimum lead time and some risk, in the first cases.

Viewing the industry sectors in summary, a petrochemical market is the most remote. The transportation cost to reach it is high and the upgrading technology for shale oil has not yet been developed. Because it represents one of the more beneficial uses of petroleum, however, we expect that ultimately a market will develop in this sector.

Industrial and utility boiler fuel represent an attractive market for shale oil. Because of the low investment required and a geographically economic location, the first use of shale oil may be for this application in the Great Lakes area. The disadvantages of this market are its susceptibility to environmental and regulatory prohibitions and limited volume demand.

The large market for shale oil is expected to be as refinery input. Refined product growth is expected to continue and sufficient plants to absorb sizeable volumes of shale oil exist in economic proximity to the production area. Conversion of shale oil to transportation fuels is consistent with government policy on use of liquid hydrocarbons. The only deterrent to this application is the substantial capital investment for upgrading facilities. In graphical form, Figure 3 presents our projection of the time related consumption of shale oil.

FIGURE 1
POTENTIAL SHALE OIL MARKETS

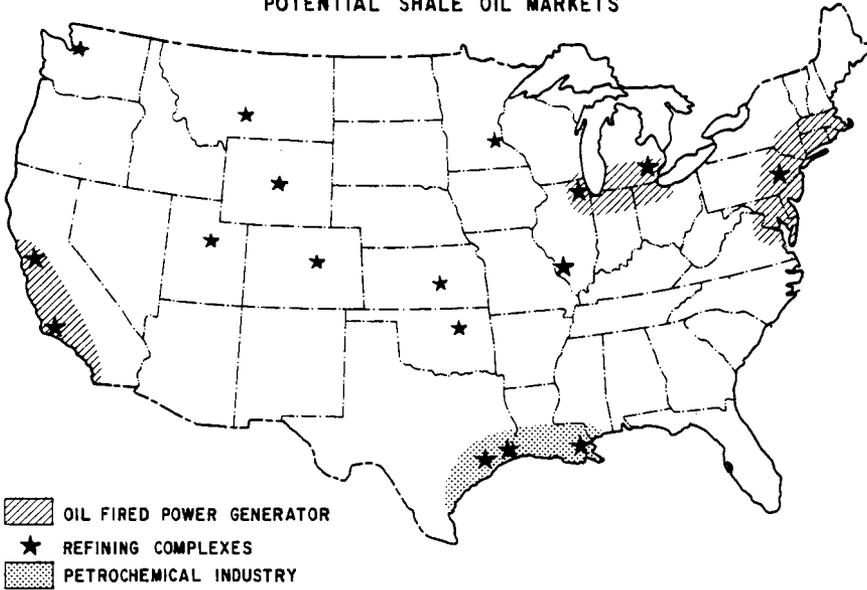
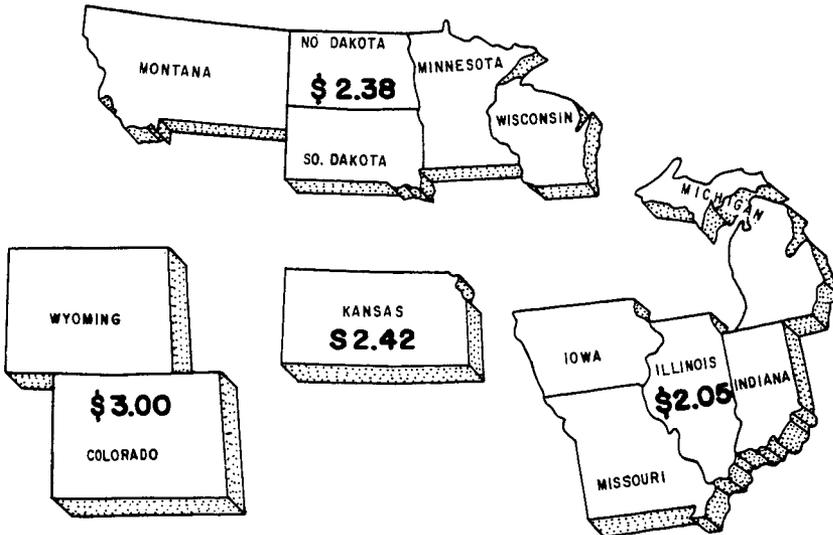
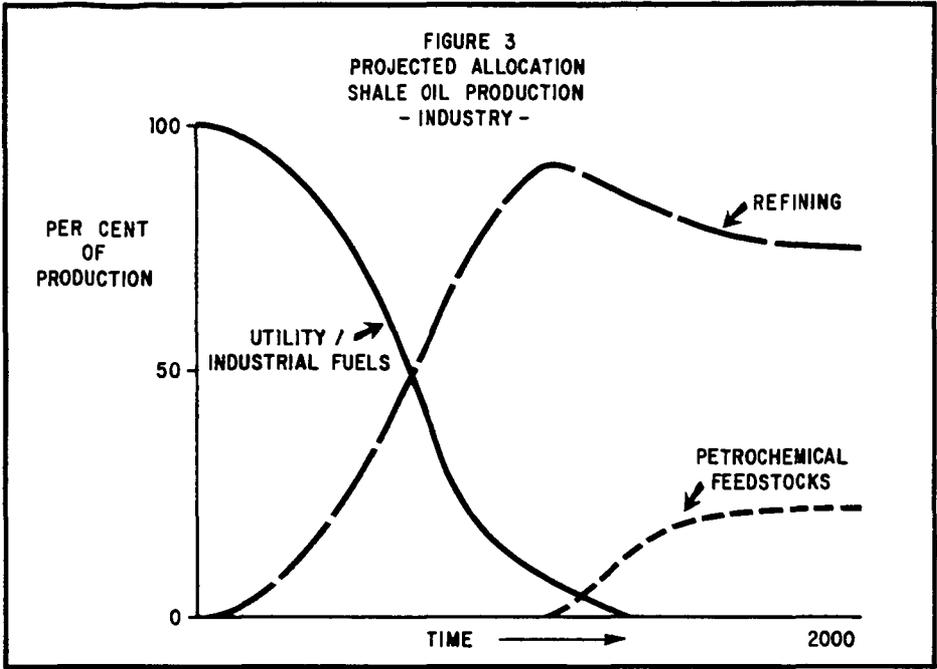


FIGURE 2
SHALE OIL REFINING - ADDITIONAL COST





BATCH EXTRACTION UNIT FOR TAR SAND PROCESSING STUDIES

E.C. Sanford and F.A. Seyer

Syncrude Canada Ltd., Research Department, P.O. Box 5790
Edmonton, Alberta, Canada T6C 4G3

INTRODUCTION

In his early studies on the hot water method of separating bitumen from Athabasca tar sand, Clark (1-4) identified two components of tar sand, the fine solids content and bivalent ion concentration, as being important variables affecting the degree of separation. He also showed that the addition of inorganic bases was generally beneficial and that the amount of mechanical energy imparted to the tar sand slurry during processing was important.

Clark's studies were carried out in a laboratory scale separation plant which took a charge of approximately 8 kg of tar sand (1). Beaker extractions, which consisted essentially of stirring 0.2 kg tar sand with hot water in a beaker, were used for demonstration purposes(5).

In a later study, Seitzer (6) described a stirred reactor (capacity 0.2 kg of tar sand) which utilized a broad U-shaped paddle for slurring and which with proper manipulation of variables could be made to simulate pilot plant extractions (7). Malmberg (8,9) used this reactor to further study the variables identified by Clark as well as others. Sepulveda utilized a commercial high shear stirred reactor for slurring and a commercial flotation cell for the separation (10). One of the main objectives of these different groups was to find a parameter or parameters which would explain differences in bitumen yield from different tar sand samples under standard conditions, in short, the factors affecting tar sand processibility. Although much useful information was generated, this objective was not fulfilled.

This paper provides details of the design and operation of a convenient laboratory batch extraction unit, which was designed specifically for studying the chemical and physical properties of tar sand as they affect processibility. The unit was used to demonstrate the importance of surfactants in the hot water extraction process and to show the interrelationship between inorganic bases used as process aids and surfactants.

Description of the Unit

The objective was to design a unit that would a) give reproducible yield data; b) be sensitive to changes so that additives could readily be evaluated; c) be versatile, so that temperature, stirring rate, etc. could easily be changed; and d) establish trends that would parallel trends in larger continuous units.

One of the problems in dealing with tar sand is the natural variability of the deposit (7). It is therefore necessary to be able to homogenize a relatively large batch and use portions of this for comparative experiments yet the sample size must not be too small, otherwise loss of bitumen on the walls, etc. of the extraction apparatus will become significant. Based on these criteria, a sample size of 0.5 kg per experiment was chosen.

Details of the unit itself are given in Figures 1 to 3. The extraction cell is jacketed to provide for constant temperature during operation; the height is sufficient to provide a quiescent zone; and the cell is square to facilitate slurring and subsequent agitation without the need for baffles. Air is added through the impeller shaft which allows good control even at low addition rates and avoids problems of plugging by fine solids experienced with other methods of addition, such as a porous plate. The air-introduction feature permits aeration of the slurry during mixing and allows one to simulate the secondary recovery step subsequent to primary recovery, practised in commercial units. After extraction is complete, tailings can easily be removed through a valve on the bottom of the cell. The valve also permits easy cleaning of the cell. The impeller speed is controlled by a variable speed fractional horsepower motor and is measured by a tachometer mounted on the impeller drive shaft. The impeller itself is easily removed so that different sizes and shapes can be used if desired.

The bitumen yield in the primary extraction step was known to be a function of stirring time and impeller speed for some types of tar sand (3,6,8). Experience with the unit has shown that for the times and speeds given in the procedure, the yield is relatively insensitive to these effects and errors resulting from small deviations are insignificant. When using a standard procedure the unit is ideally suited for studying processibility differences due to tar sand composition, the amount and type of process aid and other chemical additives.

Although a secondary recovery step similar to that practised in commercial units can readily be carried out, normally only primary bitumen recovery is used in processibility studies. The secondary recovery step is more efficient than commercial units and gives higher recoveries.

EXPERIMENTAL

Procedure I

Lab Scale Simulation of the Hot Water Extraction Process

Apparatus, Reagents, Materials:

1. Batch Extraction Unit and related components. The assembly is described in Figures 1, 2, and 3.
2. Constant Temperature Water Bath, maintained at 180°F (82°C). A pump allows water to be circulated from the bath to a jacket surrounding the stainless steel pot.
3. Timing Device, hot plate and distilled water.

Procedure:

1. Assure all air and water connections are sealed. Allow water from the bath to circulate through the surrounding jacket of the unit.
2. Heat approximately 1500 ml distilled water to 195°F (90.5°C) on a hot plate. Homogenize a quantity of the tar sand under test as outlined in Procedure II and submit three representative samples for bitumen/water/solids analysis (Procedure III). Collect 500 g of the remaining sample and weigh to the nearest 0.1 g.

3. Transfer 150 ml of the hot water to the stainless steel pot. Lower the motor and impeller assembly to its lowest possible position on the shaft rod and turn on. Allow the remaining water on the hot plate to cool to 180°F (82°C). (Impeller - ¼" from the bottom).
4. Add the 500 g tar sand sample to the pot. Within as little time as possible:
 - a) Raise and lower the motor assembly to break up tar sand lumps present and leave the assembly two notches above the lowest one. (Impeller ¾" above the bottom of the vessel).
 - b) Adjust mixer to 600 rpm.
 - c) Turn on air flow and adjust to approximately 465 cc/min on the flowmeter.
 - d) Initiate timer.Mix in this manner for 10 minutes.
5. When complete, turn the air supply off and flood the mixture with approximately 1000 ml of 180°F (82°C) water, thus bringing the froth level to the top of the pot. Mix for an additional 10 minutes at 600 rpm. (No air).
6. Cease mixing and skim as much primary froth as possible from the top of the pot with the specially designed spatula. Collect the froth in a 4 oz sample bottle and submit for bitumen/water/solids analysis. (Procedure III).
7. For recovery of secondary froth mix the remaining material for 5 minutes at 800 rpm while aerating at approximately 232 cc/min. Collect secondary froth in the same manner and submit for analysis. (Procedure III).
8. Drain the residual material from the bottom valve and wash the pot and impeller with toluene. When shut down, insure that the circulating water pump and air flow are turned off.

Comments

1. Residual material held in the stainless steel pot after recovery of the secondary froth may be differentiated as either secondary tailings or primary tailings in the following manner: Allow the mixture to settle one minute from the time mixing and aeration ceases. Decant the aqueous phase and denote as secondary tailings. The remaining heavier particles are termed primary tailings. Oil losses to the primary and secondary tailings may be obtained from bitumen/water/solids analyses of the samples.

Procedure II

Subdivision of Bulk Tar Sand Samples for Subsequent Analysis

Apparatus, Reagents, Materials:

1. Polyethylene sheet, approximately 3 feet square (1 m²).
2. Spatula, with 12 inch (30.5 cm) stainless steel blade. A handle welded in place to the center of cutting edge facilitates use.

Procedure:

1. Empty bulk sample (ideal weight = 3000 g) onto the polyethylene sheet. Remove stones greater than $\frac{1}{4}$ inch (6.5 mm) in any dimension.
2. Chop the tar sand for a period of time ensuring all particles to be less than $\frac{1}{4}$ inch (6.5 mm) diameter. Pile and quarter the mixture.
3. Combine two opposite corners.
4. Repeat the chopping, quartering, and combining procedure as outlined, twice again. Resultant particles should not exceed $\frac{1}{8}$ inch (3 mm) in any dimension.
5. Transfer approximately 50 g tar sand from the latter pile to a 4 oz sample jar and submit for analysis. Store the remaining tar sand in a tightly capped bottle at 40°F.

Procedure III

Determination of Bitumen/Water/Solids Content of Tar Sand, Froth, Middlings and Tailings Samples

Procedure:

The sample is separated into bitumen, water, and solids, by refluxing with toluene in a solids extraction apparatus (10). Condensed solvent and co-distilled water are continuously separated in a trap, the water being retained in the graduated section. The solvent recycles through the extraction thimble to further dissolve the bitumen. The bitumen/solvent and non-filterable solids fractions are subsequently separated by centrifuging. An aliquot of the resultant bitumen extract is evaporated to remove the solvent. The weight of bitumen water and solids is determined gravimetrically.

NaOH as a Process Aid

It was recognized very early in studies on the hot water extraction process that the acidity or alkalinity of the tar sand had an important effect on the efficiency of the separation (1). Strong inorganic bases, when added in small quantities, generally improved the separation efficiency. Separation efficiency was also thought to be dependent upon the concentration of certain substances which were present in the tar sand and dissolved or became suspended in the water phase during slurring (2,3). Bowman (11) isolated some of the dissolved organics by foam fractionation technique and showed that the materials were surface active. Bitumen/water, air/water and air/bitumen interfacial tensions were measured and a thorough discussion of the theoretical implications of changes in interfacial transformations was presented. A similar discussion, from a thermodynamic approach was given by Leja and Bowman (12). The batch extraction unit described here was used to study the relationship between inorganic bases and surfactants in process streams.

A typical plot (8) showing the relationship between added NaOH and bitumen recovered in the primary separation step is shown in Figure 4. As expected, there is a corresponding increase in the pH of the aqueous tailings. Less obviously, as the amount of NaOH used increases, there is also a steady decrease in the surface tension of the secondary tailings and a corresponding increase in the organic carbon content of

the samples (Figure 5). This establishes a connection between surfactants in the water and NaOH used during hot water extraction of bitumen from tar sand. Further confirmation was obtained on titrating samples of tailings. Titration curves are given in Figure 6. All tailings samples exhibited an end point characteristic of sodium oleate soap. Only at 0.056 wt% NaOH is there an end point which might be due to NaOH.

These data show that NaOH neutralizes organic bitumen acids, to give salts which are surface active in the aqueous phase. They further show that NaOH results in increasing bitumen yield. To establish that the important agent responsible for improved recovery is the surfactants produced by caustic addition, tailings samples were centrifuged to remove solids and concentrated by evaporation. The concentrate was then added to the next experiment such that the organics in total aqueous tailings from one run would be present in the slurry water of a second run. The data is given in Table I. The surfactants recovered from tailings are as effective as NaOH in improving recovery, showing that surfactants are indeed the active process aid. With repetitive recycle the effectiveness of concentrated tailings decreases, probably due to losses in handling and through the formation of salts with bi- and trivalent metals present in tailings streams. Table I also shows that commercial surfactants can be used as well although these are not economically competitive with NaOH at this time for commercial use.

TABLE I
Effect of Surfactants on Bitumen Recoveries in
the Hot Water Extraction Process

Conditions	Bitumen Recoveries Primary Froth (%)
No Additive	61
NaOH: 0.04 wt% of T.S.	88
Concentrated, centrifuged tailings	87
No Additive	71
NaOH 0.008 wt% of T.S.	81
0.024 wt% of T.S.	91
Tide 0.020 wt% of T.S.	82
0.100 wt% of T.S.	89
Na Oleate 0.020 wt% of T.S.	70
0.100 wt% of T.S.	83
Lignosulfonate nil	35
HGX 0.020 wt% of T.S.	58
0.100 wt% of T.S.	74

Conclusions

Details of the design and an operating procedure for a laboratory scale batch extraction unit have been described. Utilizing this unit, it has been shown that NaOH, when used as a process aid for tar sand processing, reacts with components of bitumen to form surfactants and that these surfactants are the primary agent responsible for improved bitumen recovery.

Acknowledgements

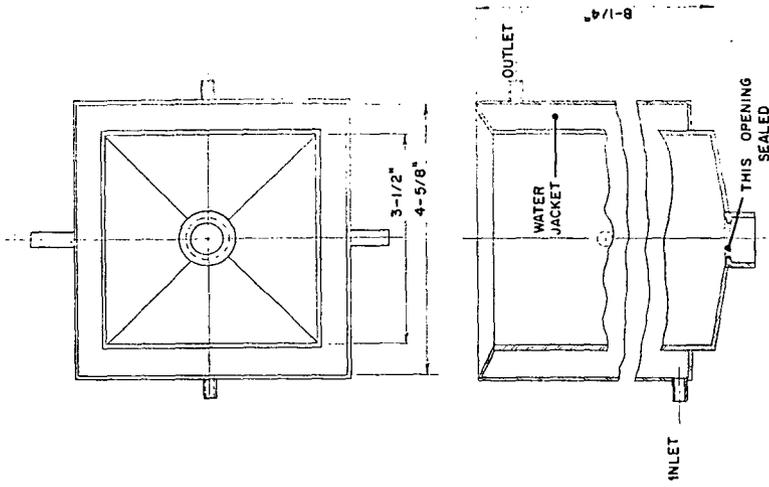
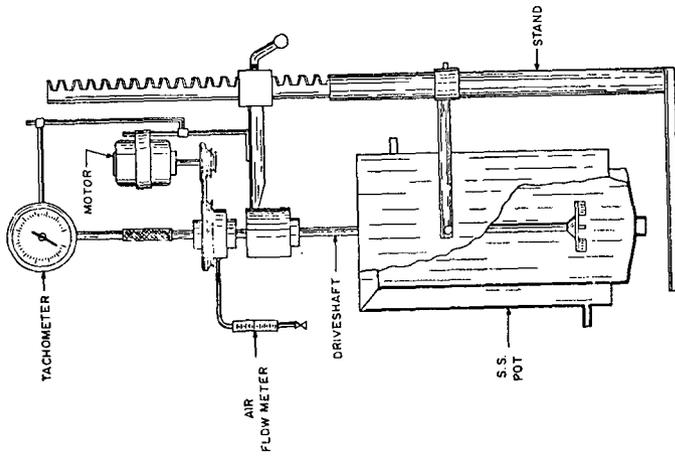
The authors wish to acknowledge the contributions of J.A. Bichard, C.W. Bowman, L.M.O. Cymbalisky, C. Guarnaschelli, and E. Nagy who, while members of or associated with Syncrude Canada Ltd. Research Department, were involved in the initial design, modification and testing of the batch extraction unit. The experiments described in this paper were carried out by M. Dmytriw and D. Famulak. The authors are grateful to Syncrude Canada Ltd. for permission to publish this paper.

References

- (1) Clark, K.A., and Pasternack, D.S., Ind. and Eng. Chem. 24(12) 1410(1932).
- (2) Clark, K.A., The Can. Inst. of Mining and Metallurgy, Transactions, XLVII 257(1944).
- (3) Clark, K.A., and Pasternack, D.S., Research Council of Alberta, Report No. 53, University of Alberta, Edmonton, Alberta (March, 1949).
- (4) Clark, K.A. Can. Oil and Gas Industries, 3(6), 46(1950).
- (5) Pasternack, D.S. Hodgson, G.W., and Clark, K.A. Proc. Ath. Oil Sands Conf. 200(1951).
- (6) Seitzer, W.H., ACS San Francisco Meeting, April 2-5, 1968, p. F19.
- (7) Innes, E.D., and Fear, J.V.D., Seventh World Petroleum Congress, Mexico City. Proceedings 3 633 (1967).
- (8) Malmberg, E., and Bean, R.M., ACS San Francisco Meeting, April 2-5, 1968, p. F25.
- (9) Malmberg, E.W., and Robinson, W.M., Ibid. p. F38.
- (10) Sepulveda, J.E., Miller, J.D., and Oblad, A.G. PREPRINTS, Div. of Petrol. Chem. ACS 21 No. 6 110 (1976).
- (11) Bowman, C.W., Proceedings of the Seventh World Petroleum Congress, 3 583 (1967).
- (12) Leja, J., and Bowman, C., Can. J. Chem. Eng., 46(12) 479(1968).

FIGURE 1

SYNCRUDE BATCH EXTRACTION UNIT



STAINLESS STEEL POT

FIGURE 2.

BICHARD, BOWMAN, CYMBALISTY, GUARNASCHELLI, NAGY

FIGURE 4 The Effect of NaOH on Bitumen Recovery in the Primary Froth and pH of Secondary Tailings

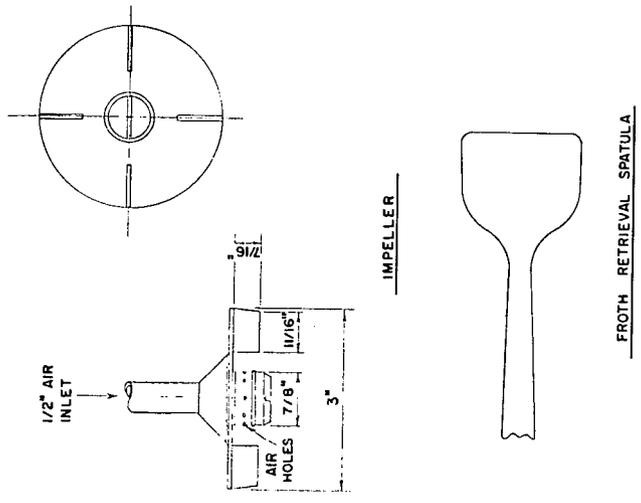
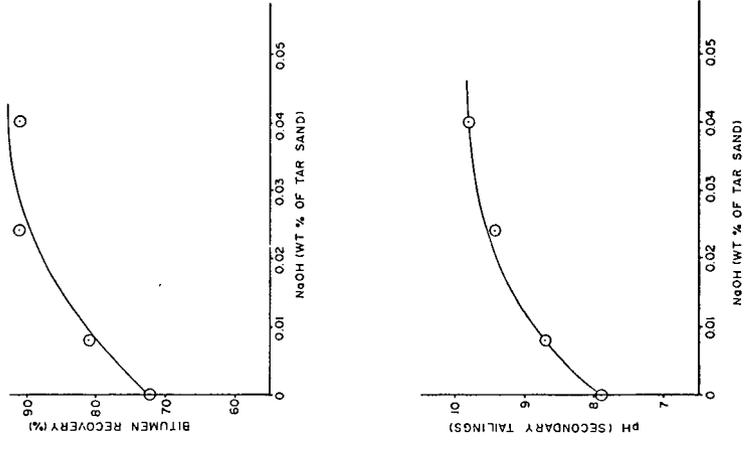


FIGURE 3.

FIGURE 5 The Effect of NaOH on Surface Tension and Total Organic Carbon Concentration of Secondary Tailings

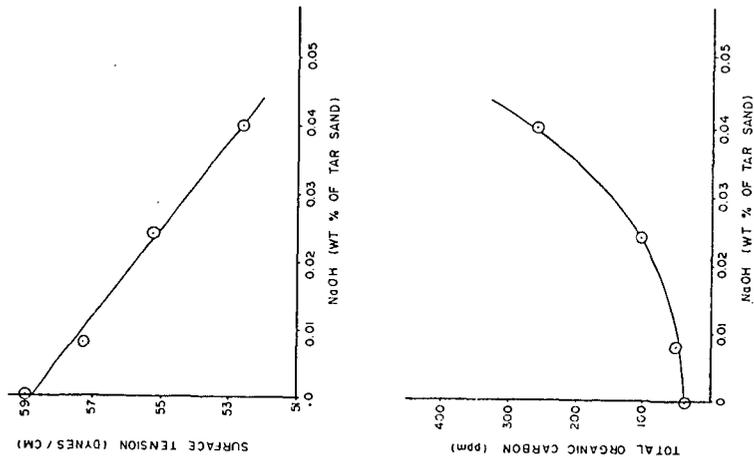
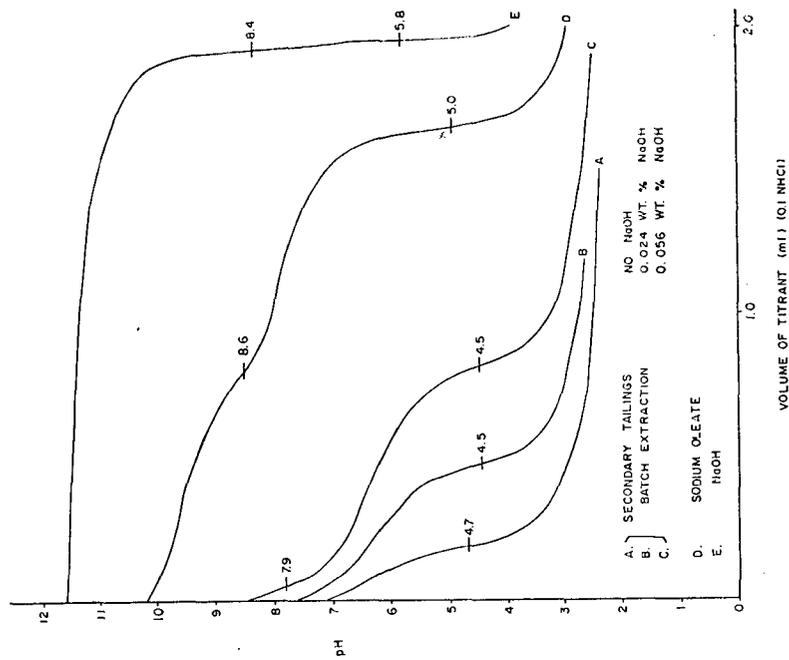


FIGURE 6 Titration Curves for NaOH, Na Oleate and Aqueous Tailings



THERMAL HYDROCRACKING OF ATHABASCA BITUMEN:
COMPARISON OF COMPUTER-SIMULATED FEED AND
PRODUCT VAPORIZATION VALUES WITH PILOT PLANT DATA

D.J. Patmore and B.B. Pruden

Energy Research Laboratories
Canada Centre for Mineral and Energy Technology
Department of Energy, Mines and Resources
555 Booth Street, Ottawa, Ontario, Canada, K1A 0G1

INTRODUCTION

The Energy Research Laboratories of the Canada Centre for Mineral and Energy Technology (CANMET) are engaged in a continuing upgrading project involving the hydrocracking of Canadian oil sand bitumen and heavy oil. Such upgrading is necessary to remove sulphur and to reduce the viscosity of the bitumen to facilitate transport by pipeline to the refinery. Currently upgrading is accomplished on a commercial scale by Great Canadian Oil Sands Limited using a coking process which converts up to 20% of the bitumen to char. One aim of the CANMET work is to develop an economical process which would convert all of the bitumen to usable products, and thus reduce the waste of a valuable resource. For this purpose a one-barrel-per-day pilot plant was built and has been operated successfully with a variety of feedstocks. This work has concentrated on both plant operability, in particular the prevention of reactor coking (1), and on the effect of operating conditions on yields and product qualities (2).

Efficient and economical scale-up of this process to a commercial-size plant requires quantitative knowledge of both the degree of vaporization of feed and product and the fraction of the reactor occupied by gas under reactor conditions. The latter, usually referred to as voidage, has already been investigated in detail (3). Such knowledge is needed to calculate hydrogen partial pressures and true liquid and vapour residence times. These in turn are necessary to accurately estimate the size of various plant components as well as to formulate a kinetic model for the thermal hydrocracking reaction.

Because it is not feasible to measure liquid and vapour compositions in the reactor directly, recourse must be made to computational methods. These involve estimating the equilibrium vaporization constant, K , for various components of the system using known or estimated values of their thermodynamic properties.

Computations for the present study were carried out using the Grayson-Streed modification of the Chao-Seader correlation employing the principle of corresponding states (4,5). A package program was employed.

Vapour-liquid equilibrium data were obtained from measurements in a hot separator downstream of the pilot plant reactor. This well-mixed separator, which was temperature controlled, was assumed to behave as a single stage contactor, and measurements of liquid and vapour flows and concentrations were taken at steady state conditions.

EXPERIMENTAL

The pilot plant is shown schematically in Fig. 1. Bitumen and hydrogen are fed at the bottom of a long unpacked heated tubular column (3.81 cm diam. x 3.95 m long). The hydrocracked products are led from the top of the reactor to a hot separator kept at a temperature below that of the reactor. The heavy oil product is withdrawn and the vapour passed into a cold receiver and condensed. The light oil product is again withdrawn and collected. The hot separator was well mixed as the reactor products entered below the liquid level, and there was a high ratio of gas to liquid. It follows that the fraction of liquid vaporized, f , was the weight of light oil product divided by the total liquid product. The hot separator was temperature controlled so that the above ratio could be obtained as a function of temperature. The gas flow was metered using the orifice, and the gas composition at the reactor inlet controlled by scrubbing. Accordingly the actual gas composition and flow in the hot separator could be computed by using these data along with dissolved gas flows and compositions, reaction hydrogen requirements and hydrocarbon gas make.

Athabasca bitumen containing 51% pitch (material boiling above 524°C equivalent atmospheric boiling temperature) was fed in all cases. Products are identified by the amount of pitch conversion based on feed. Further details are given in Reference 6.

The computer simulation was carried out for CANMET by Saturn Engineering, Calgary, Alberta, using the DISTILL program licensed by the Chem Share Corporation, Houston, Texas. Simulations were carried out for Athabasca bitumen and four typical hydrocracked products covering the range 49 to 93% pitch conversion. Input to the program consisted of liquid and gas rates, compositions and properties. The composition and properties of liquid feed and product were approximated by ten fractions with mean average boiling points ranging from 65.5°C (150°F) to 648.9°C (1200°F). These fractions were derived from Hempel distillations and gravities of each cut, using standard correlation procedures for petroleum fractions.

For each specified temperature and pressure combination the program calculated f , the weight fraction of liquid that vaporizes under the specified conditions, as a function of specified values of G/L, the ratio of gas rate at STP (in g mol/h) to liquid rate at STP (in kg/h). Gas composition was also entered and treated as a parameter.

RESULTS AND DISCUSSION

Calculated values of the degree of vaporization were plotted as functions of G/L and temperature (Figs. 2 to 5). From these graphs interpolations can be made to obtain f values at conditions other than those specified. Figures 2 and 3 illustrate the effect of G/L on f for different pressures and temperatures for bitumen and for a hydrocracked product with 93% pitch conversion. The trend is an initial rapid increase in f followed by a general flattening out of the curve, a trend which becomes more pronounced at higher temperatures and pressures. This reflects the presence of a very high boiling fraction (pitch) which is vaporized to only a small extent. A similar trend is seen when f is plotted against temperature as shown in Figs. 4 and 5 for bitumen and 3 hydrocracked products (49, 76 and 93% pitch conversion) at 10.44 MPa and various G/L values. The degree of vaporization in the high conversion case reached very high values.

The effect of pressure on f is also illustrated in Figs. 2 and 3. For typical conditions of 450°C and G/L = 40 g mol/kg, increasing pressure from 10.44 to 17.34 MPa decreases f by 50% from 0.37 to 0.185 for Athabasca bitumen, and by 20%,

from 0.86 to 0.69 for product hydrocracked to 93% conversion; while for G/L = 10, f is decreased by 54% and 44% respectively.

Another factor which influences the degree of vaporization is the gas composition; increasing the concentration of hydrogen causes a decrease in f. This is illustrated in Fig. 6 for 350°C and 13.89 MPa for a product hydrocracked to 83% conversion. In the range 50 to 90 mol % H₂, f is linearly proportional to hydrogen concentration. For all hydrocracked products, f was calculated for both 60 and 80 mol %; for most cases studied an increase of 33% from 60 to 80 mol % H₂ caused an approximate 10% decrease in f.

Average liquid residence times (t) can be calculated from these vaporization figures by taking average values for bitumen and hydrocracked product, after making allowance for the fraction of reactor volume occupied by gas (voidage), as follows:

$$t = \frac{[(\text{reactor vol}) \times (1 - \text{voidage})]}{(\text{vol of liquid fed per h}) \times (1 - \text{ave. fraction vaporized})}$$

Such calculations were carried out for a series of pilot plant runs as shown in Fig. 7, where the product of average residence time and liquid hourly space velocity (LHSV) were plotted against the temperature at which each hydrocracked product was obtained. The average fraction vaporized was taken as the average of f for bitumen and for product. As each product represented a different pitch conversion, and as the computer simulation gave vaporization values only for a limited number of products at fixed conversions, a linear interpolation was used to calculate values for these intermediate conversions. A similar interpolation was also used to correct for different hydrogen concentrations. Figure 7 shows that the calculated residence times are very sensitive to reaction temperature, and become increasingly higher than the nominal space time as temperature and space velocity increase.

Although experimental vaporization data for the reactor were not available, it was possible to test the computer simulation by comparing the calculated values of f with experimental data obtained at lower temperatures for the hot separator where vapour/liquid ratios are routinely measured. Again the f values calculated by computer were interpolated to correct for pitch conversion and hydrogen concentration for each run considered. To test the data for bitumen itself a series of runs were carried out with both reactor and hot separator at 350°C and 370°C at which temperatures hydrocracking reactions occur to only a limited extent (≈ 3% pitch conversion at 370°C). Calculated values were plotted against experimental data (Fig. 8). The best line fitted the equation:

$$F_E = (3.3 \pm 0.9) + (0.85 \pm 0.07)F_C$$

where F_E and F_C are experimental and calculated values of the per cent of liquid vaporized. The agreement is reasonable considering all the possible sources of experimental error, and in fact F_E and F_C are in close agreement above about 15%.

The results for hydrocracked products are shown in Fig. 9, in which 75 data from pilot plant runs carried out under a variety of conditions are compared with calculated values. Pressure ranged from 10.44 to 17.34 MPa, and temperature from 300 to 430°C. Although there is considerable spread in the data, the best line lies close to the diagonal and is given by the equation:

$$F_E = (1.8 \pm 1.2) + (0.95 \pm 0.04)F_C$$

It is believed that much of the spread is caused by experimental error, particularly in measurements of gas rate and composition where errors of ± 5% or

more can occur. Errors can also occur in weighing and in temperature determinations. The following Table illustrates the sensitivity of f to variations in G/L and temperature for typical values of these variables.

Sensitivity of f to Variations in G/L and Temperature

	G/L = 20 g mol/kg					G/L = 40 g mol/kg				
	400°C	δ , % ^a	450°C	δ , % ^a	Δ , % ^b	400°C	δ , % ^a	450°C	δ , % ^a	Δ , % ^b
Bitumen	0.1175	8.5	0.241	8.3	105.1	0.205	10.0	0.378	4.2	84.4
93% Prod.	0.505	4.6	0.712	3.2	29.1	0.672	4.2	0.860	1.7	28.0

^a Percentage increase in f for a 12.5% increase in T.

^b Percentage increase in f for a 12.5% increase in T.

It is seen that for a 12.5% increase, temperature has a greater effect than G/L. However, as the accuracy of temperature measurements is much greater than those of G/L determinations, the errors are probably of similar magnitude.

Errors can also be introduced by the approximations used in the interpolations for pitch conversion and hydrogen concentrations, as well from discrepancies between simulated and actual liquid and gas properties.

CONCLUSIONS

Comparison of calculated values of liquid vaporization using a computer simulation with experimental data indicated that such computational methods will give reasonably accurate values for the degree of vaporization, considering the approximation and experimental errors involved, for a very heavy oil such as tar sand bitumen and its hydrocracked products.

REFERENCES

1. Merrill, W.H., Logie, R.B. and Denis, J.M. "A pilot scale investigation of thermal hydrocracking of Athabasca bitumen"; CANMET (Canada Centre for Mineral and Energy Technology, formerly Mines Branch, Department of Energy, Mines and Resources) Research Report R-281; Dec. 1973.
2. Pruden, B.B., Logie, R.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen: Reduction of reactor fouling"; CANMET Report 76-33; Aug. 1976.
3. Shah, A.M., Pruden, B.B. and Denis, J.M. "Thermal hydrocracking of Athabasca bitumen: Correlation of reactor voidage in vertical two-phase flow"; CANMET Report 77-48; Dec. 1976.
4. Chao, K.C. and Seader, J.D. "A general correlation of vapour-liquid equilibria in hydrocarbon mixtures"; Am. Inst. Chem. Eng. Journ.; v. 7, no. 4, p 598; Dec. 1961.
5. Grayson, H.G. and Streed, C.W. "Vapour liquid equilibria for high temperature, high pressure hydrogen-hydrocarbon systems"; Proc. Vith World Petrol. Congr., Frankfurt/Main; Sect. VII, paper 20, P07, p 233; June 1963.
6. Pruden, B.B. and Denis, J.M. "Heat of reaction and vaporization of feed and product in the thermal hydrocracking of Athabasca bitumen"; CANMET Report 76-30; Apr. 1976.

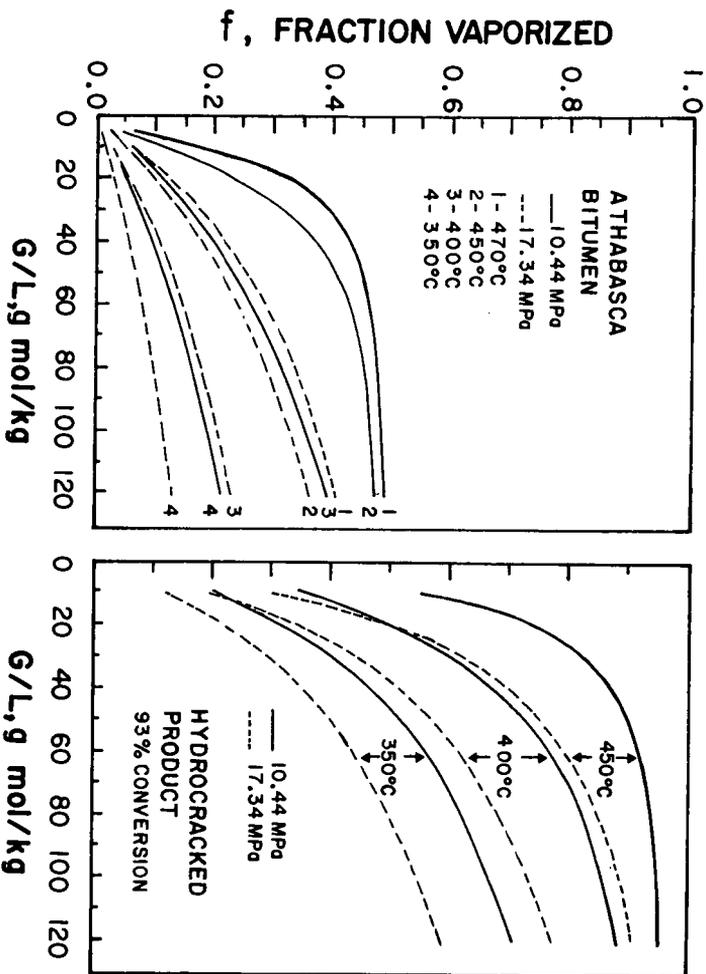


FIGURE 2 - Fraction of Liquid Vaporized, f , as a Function of Gas to Liquid Feed Rate Ratio, G/L g mol/kg, for Bitumen at 10.44 to 17.34 MPa and 350 to 470°C

FIGURE 3 - Fraction of Liquid Vaporized, f , as a Function of Gas to Liquid Feed Rate Ratio, G/L g mol/kg, for 93% hydrocracked product at 10.44 to 17.34 MPa, and 350 to 450°C

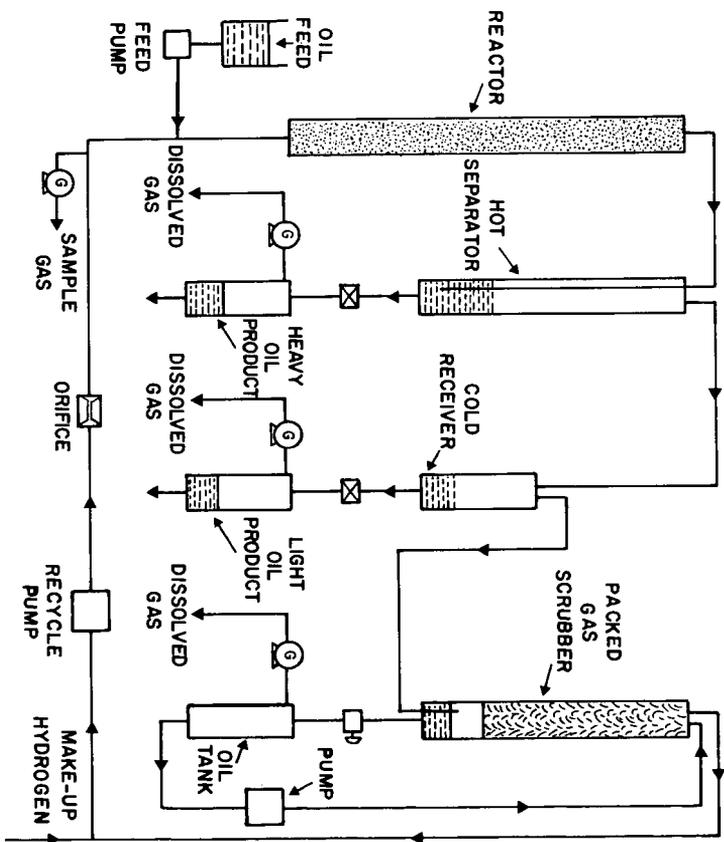


FIGURE 1 - Schematic Diagram of CANMET Hydrocracking Pilot Plant

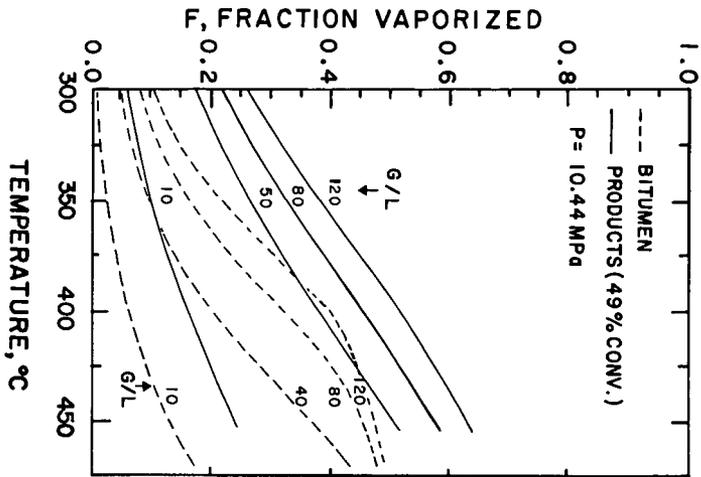


FIGURE 4 - Fraction of Liquid Vaporized, f , as a Function of Temperature for Bitumen and 49% Hydrocracked Product at 10.44 MPa and G/L Values of 10 to 120 g mol/kg

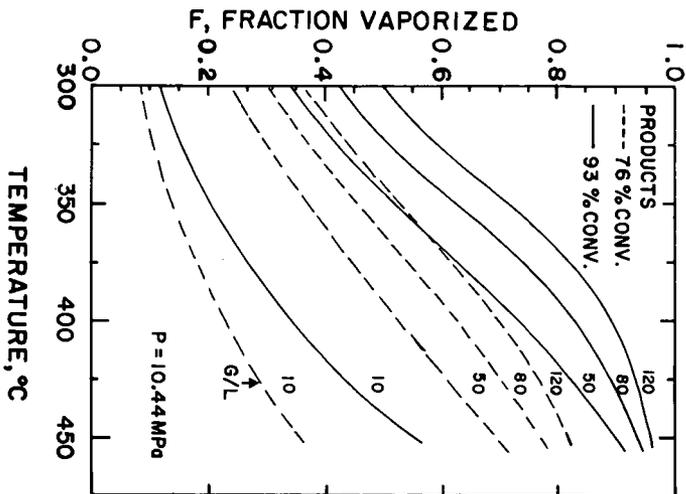


FIGURE 5 - Fraction of Liquid Vaporized, f , as a Function of Temperature for 76 and 93% Hydrocracked Products at 10.44 MPa and G/L Values of 10 to 120 g mol/kg

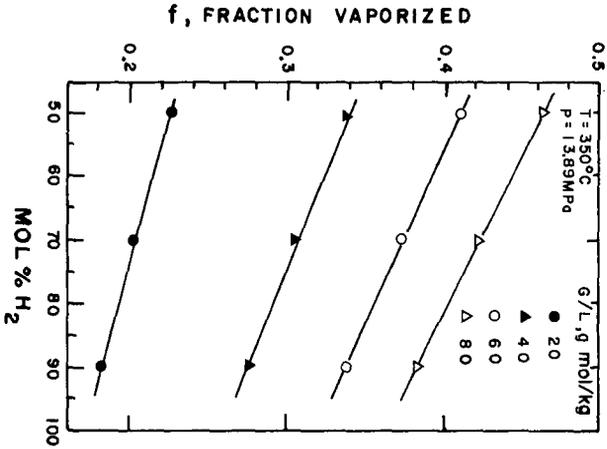


FIGURE 6 - Fraction of Liquid Vaporized, f, vs mol % H₂ for 83% Hydro-cracked product at 350°C, 13.89 MPa and G/L Values of 20 to 80 g mol/kg

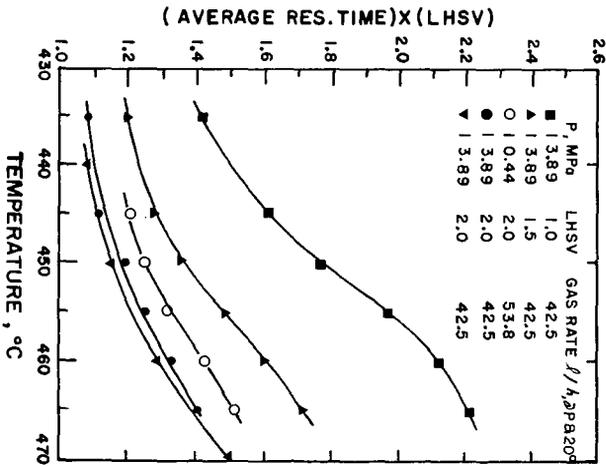


FIGURE 7 - Product of Calculated Average Liquid Residence Time and Liquid Hourly Space Velocity vs Temperature for a Series of Hydrocracked Products Obtained Under the Indicated Conditions

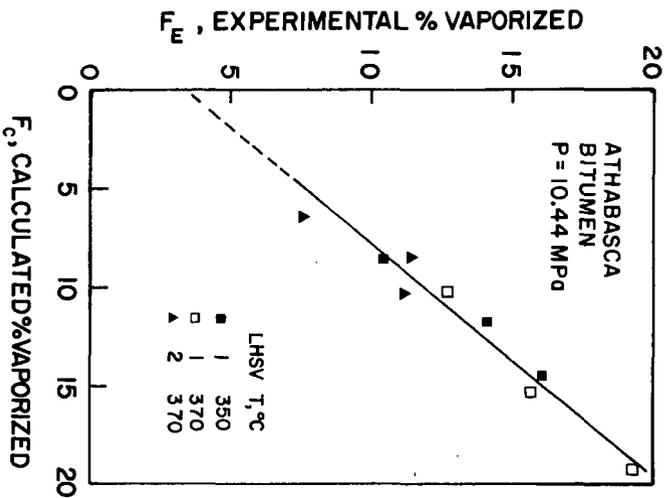


FIGURE 8 - Experimental vs Calculated Per Cent of Liquid Vaporized for Athabasca Bitumen at 10.44 MPa

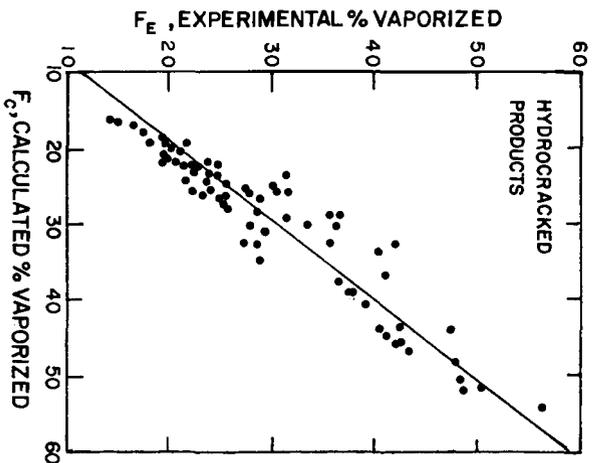


FIGURE 9 - Experimental vs Calculated Per Cent of Liquid Vaporized for 75 Hydro-cracked Products for Pressures of 10.44 to 17.34 MPa and Temperatures of 300 to 430°C.

The Effect of Tin Catalysts on Hydrorefining
of Athabasca Oil Sand Bitumen and on Coal Hydrogenolysis

J.F. Kriz, K. Belinko and B.N. Nandi

Energy Research Laboratories,
Canada Centre for Mineral and Energy Technology,
Department of Energy, Mines and Resources,
Ottawa, Canada

INTRODUCTION

The development of catalysts for up-grading of Canadian oil-sand bitumen and for conversion of coal into liquid products has been of considerable interest at the Energy Research Laboratories. The study reported below was part of an investigation of the suitability of different catalyst systems for hydrocracking heavy oils, and involved the use of tin compounds with bitumen and heavy oil feeds.

Tin compounds have generally been found to be particularly effective in coal hydrogenation processes (1-4). Recent studies have included the use of tin catalysts in hydrorefining of coal-derived feeds such as asphaltenes (3) and solvent refined coal (4). Although much attention has been given to the activity of supported and unsupported tin catalysts, little effort has been made to examine the fate of the tin during the liquefaction process.

Guided by the outcome of previously published work, a series of tin-containing catalysts was tested for bitumen and coal up-grading. Emphasis was placed on studying the changes occurring within the catalysts during these processes. Results obtained in preliminary tests stimulated further development such as the use of different methods of catalyst preparation.

EXPERIMENTAL

Feedstocks and Equipment

Athabasca bitumen was obtained from Great Canadian Oil Sands, Fort McMurray, Alberta, Canada, and some of its properties are given in Table I. Asphaltene feedstock from bitumen was obtained by precipitating the asphaltenes by addition of pentane to bitumen according to the ASTM method (7). High volatile Devco 26 coal was obtained from Cape Breton Development Corporation, Nova Scotia, Canada. The properties of this coal are given in Table II.

TABLE I

Properties of Athabasca Bitumen

Specific gravity	1.009 (15/15°C)	Benzene insolubles	0.72 wt%
Sulphur	4.48 wt%	Carbon	86.36 wt%
Ash	0.59 wt%	Hydrogen	10.52 wt%
Conradson carbon residue	13.3 wt%	Nitrogen	0.45 wt%
Pentane insolubles	15.5 wt%	Pitch (524°C+)	51.5 wt%

TABLE II

Properties of Devco 26 Coal
(High Volatile Bituminous A)

Proximate Analysis wt%		Ultimate Analysis wt%		Petrographic Analysis vol%	
Moisture	1.13	Carbon	83.97	Vitrinite	77.8
Ash	2.18	Hydrogen	5.36	Exinite	6.6
Volatile matter	31.35	Sulphur	0.62	Micrinite	3.6
Fixed carbon	65.34	Nitrogen	1.80	Semi-fusinite	8.8
		Oxygen (by dif)	4.94	Fusinite	2.6
				Pyrite	0.6

Bitumen tests were carried out in a bench-scale fixed bed reactor having a volume of 155 cm³, a length to diameter ratio of 12 and a continuous up-flow arrangement (5). Experiments were performed at a pressure of 13.9 MPa, a liquid volumetric space velocity of 0.278 ks⁻¹ (1.0 h⁻¹) based on the reactor volume and a hydrogen (electrolytic) flow rate of 37.5 cm³s⁻¹ at STP (5000 cu ft/bbl). The temperature range was 420^o-460^oC. 2000 P51
?

A batch shaker autoclave, into which about 25 g of coal was charged, was used for experiments involving coal hydrogenolysis. The runs were carried out without a vehicle oil, at an initial (cold) hydrogen pressure of 6.5 MPa and a temperature of 350^oC for 2 hours.

Optical microscopic examinations of the catalysts were made before and after use and were complemented by electron microprobe analysis.

Catalyst Description and Preparation

The catalysts tested with bitumen were alumina-supported and were prepared as described below.

Catalyst A:

Alpha alumina monohydrate (obtained from the Continental Oil Company, Peterboro, New Jersey) was gelled with slightly acidified water and made into 3.2 mm (1/8 in) extrudates. These were then dried at 110^oC for 6 hours and calcined at 500^oC for 6 hours. The calcined extrudates were impregnated with a solution of SnCl₂ in methanol, the volume of which was about one-half that of the extrudates. Methanol was subsequently purged out of the extrudates in a nitrogen flow at 150^oC. The final concentration of Sn was ca. 7 wt%.

Catalyst B:

Extrudates of Catalyst A were sulfided in a flow of a mixture of H₂S and H₂ (1:3 by vol.) at 150^oC for 5 hours at atmospheric pressure.

Catalyst C:

An aqueous solution of SnCl₂ was added to the alpha alumina monohydrate and milled in a mix-muller. The resulting paste was extruded, dried and calcined as in the case of Catalyst A. The final concentration of Sn was ca. 7 wt%.

Catalyst D:

A solution of aluminum isopropoxide and SnCl_2 in isopropanol was co-precipitated by hydrolysis using diluted ammonium hydroxide. The precipitate was extruded, dried and calcined as in the case of Catalyst A. The final concentration of Sn was ca. 15 wt%.

Separate experiments with bitumen involved testing alumina extrudates used for preparation of Catalyst A and B, and also testing a series of catalysts containing both Mo and Sn in different concentrations. The latter series was prepared by adding, successively, an aqueous solution of ammonium paramolybdate $(\text{NH}_4)_6 \text{Mo}_7 \text{O}_{24} \cdot 4\text{H}_2\text{O}$ and an aqueous solution of stannic chloride $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ to alumina monohydrate in the mix-muller. Atomic ratios of molybdenum and tin added were, respectively, either 1:1 or 1:0. The resulting paste was extruded, dried and calcined as described above.

For experiments involving hydrogenolysis of coal and bitumen-derived asphaltenes, an aqueous slurry of pulverized feed and tin catalyst was prepared and subsequently dried under vacuum at 80°C . The catalysts tested included stannous chloride, stannous oxalate and stannous sulfide. The concentration of tin in the feed was approximately 5 wt%.

RESULTS AND DISCUSSION

Compared with pure alumina, tin compounds supported on alumina were generally found to exhibit only marginal improvements in liquid product quality in bitumen hydrotreating. The usual properties of the liquid product, such as specific gravity, sulfur and nitrogen content and percent pitch conversion, were not significantly changed when, for instance, in one series of tests the tin concentration was varied. The results are shown in Figure 1, which compares Mo/ Al_2O_3 -type catalysts both with and without a tin additive. It was found that the extent of decrease in the specific gravity of the liquid product caused by an increasing molybdenum concentration was not significantly affected by a simultaneous increase in tin loading.

The influence of the conversion of bitumen-derived asphaltenes into pentane-soluble products was also investigated. The influence of SnS on asphaltene conversion was much less apparent than on coal. The conversion of bitumen-derived asphaltenes increased from 69% with no catalyst to about 75% in the presence of SnS.

The conversion of coal into benzene-soluble products was found to increase substantially in the presence of the various tin catalysts tested. The conversion increased from 12.4% with no catalyst to an average of approximately 51% for all three tin catalysts investigated. The effectiveness of tin compared favourably with other catalysts tested, as shown in Table III.

TABLE III
Effect of Catalysts on Conversion of Coal
into Benzene-Soluble Products (350°C)

Catalyst	None	SnCl_2	SnS	$\text{Sn}(\text{COO})_2$	FeSO_4	FeCl_2	ZnCl_2
Conversion (% daf)	12.4	53.2	52.0	47.5	23.2	19.3	51.5

These results agree well with those obtained previously by Kawa *et al* (2,3) showing high activity of tin compounds for coal hydrogenolysis. Asphaltene production is probably the first step in coal liquefaction and more severe conditions are needed to increase the yield of pentane-soluble products. The conversion of asphaltenes produced from coal was not determined in the present work. However, the effect of stannous chloride on bitumen-derived asphaltenes appeared smaller than would be expected if asphaltenes produced from coal were used (2). In this respect the work with asphaltenes from solvent refined coal (4) produced more comparable results. The reason for the differences in reactivity between asphaltenes from coal and asphaltenes from bitumen feedstocks are not known and one can only speculate that they result from variations in chemical structures. A detailed analysis of bitumen-derived asphaltenes was presented by Strausz (6), and the sulfur content (about 8 wt%) is higher and oxygen content (about 1 wt%) is lower than those in asphaltenes produced from coal (2,3,4). The high sulfur content suggests that Mo/Al₂O₃ based catalysts may be the most efficient catalysts for hydrogenolysis since they seem to be the best hydrodesulfurizing agents.

Notable changes resulting from different catalyst preparation methods were observed. Table IV presents some results of analyses of liquid products from bitumen experiments for different tin-containing catalysts.

TABLE IV
Effect of Catalysts on Liquid Products from Bitumen***

Catalyst	Specific Gravity	%S Removed	%N Removed	% Pitch Converted
Al ₂ O ₃	0.951	33.3	26	62
A	0.932*	41.1*	52*	77*
	0.952**	31.0**	32**	66**
B	0.947	30.1	28	67
C	0.928	34.2	-	87
D	0.903	41.6	40.0	97

* Initial run
** Second run
*** Run at 440°C

It is noteworthy that there was a drop in the activity of Catalyst A from the initial run to the second. Presumably, the impregnated SnCl₂ initially present was not completely transferred into SnS before the first run commenced and exhibited a greater activity at that stage. Two separate batches of SnCl₂ impregnated on alumina showed such deactivation. The deactivation was not observed when pre-sulfided batches were used (Catalyst B). Liquid products of improved quality, namely lower specific gravity, were obtained when Catalysts C and D were used. A different procedure was applied to prepare these catalysts and their properties are discussed below.

The supported tin catalysts of the type A and B tested with bitumen were found to exhibit little increased activity when compared with alumina alone. Microscopic examinations of the used extrudates revealed extensive sintering of the tin component within the cracks in the alumina, (Figure 2). Identical results were obtained regardless of whether the starting material was SnCl₂ (Catalyst A) or SnS (Catalyst B). These observations suggested that very little of the tin catalyst was actually exposed to the bitumen during the process. The optical reflectance of the streaks seen in Figure 2 compared well with that of pure SnS.

In addition, electron microprobe analysis of the spent catalyst confirmed that the high reflectance streaks were composed of tin and sulfur in atomic ratios of approximately 1:1. No streaks were observed in the unused extrudates, indicating even dispersion of the tin compounds on the surface of alumina. This was confirmed by electron microprobe analysis. Microscopic examination of the benzene-insoluble residue from coal liquefaction experiments revealed a sintering effect similar to that noted with bitumen runs, irrespective of whether SnCl_2 , $\text{Sn}(\text{COO})_2$ or SnS was used as the catalyst, (Figure 3). The high reflectance streaks were again found to be composed of tin and sulfur in atomic ratios of about 1:1.

The formation of SnS from SnCl_2 is feasible under typical hydrogenation or hydrotreating conditions provided sufficient sulfur is present in the feed material. It has been suggested (1) that SnS becomes the most stable form of tin and would be formed from SnCl_2 , for example, according to:



At reaction temperatures, SnCl_2 could conceivably flow into pores and cracks of the support or coal, and subsequently be converted to the sulfide form. On the other hand, SnS melts at 880°C , which is considerably higher than the reaction temperature used. Nonetheless, sintering had occurred to the same extent when SnS was used. The migration mechanism may therefore involve an intermediate species having a low melting point, such as elemental tin. This species could then migrate into void areas of the support before being converted back to SnS . In a separate experiment the fresh SnS - and SnCl_2 -containing catalysts were subjected to reaction conditions in the absence of the feed. Spots of high reflectance indicated the possible formation of metallic tin in extrudates subjected to this type of reducing condition.

In view of the extensive sintering effect the original dispersion of the tin compound was reduced considerably and consequently the effectiveness of both high- and low-surface area supports was expected to be comparable, as reported by Kawa *et al* (3). Figures 4 and 5 show sintering of SnS in the extrudates of Catalysts C and D (Table IV). Comparison with Figure 2 indicates that a more even dispersion of tin sulfide was established in the extrudates of Catalysts C and D. The sintering still occurred but the SnS appeared to assume a larger surface area. The higher dispersion correlated well with the activity observed with bitumen tests using these catalysts. One additional observation relates to Catalyst D in Figure 5. It appears that concentration of the tin component is greater in the regions between the particles of alumina than inside the particles. One could speculate that these regions may have been more accessible to the reactant fluids than the regions within the alumina particles. This would be in agreement with the enhanced activity of Catalyst D.

In conclusion, the present findings may be summarized as follows:

Tin compounds were found relatively less effective for bitumen hydro-refining than for hydrogenolysis of high volatile bituminous coals, possibly because of the different structure of bitumen-derived asphaltenes. The original dispersion of the catalyst on the support was significantly reduced. The extent of sintering of tin catalysts under reaction conditions correlated with their activity. It may be that an improved catalytic system would require a stronger bond between the tin compound and the support to hinder surface migration.

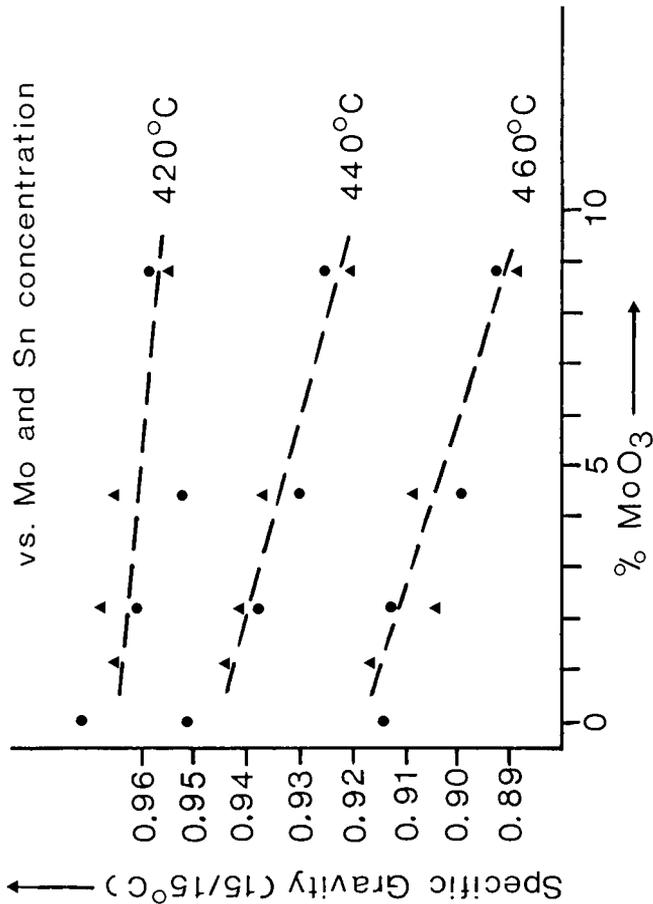
ACKNOWLEDGEMENT

The authors gratefully acknowledge the contribution of L.E. Galbraith and B.M. Moffat for their technical assistance. Thanks are also due to Dr. R.H. Packwood for carrying out the electron microprobe analyses.

REFERENCES

1. Weller, Sol and Michail G. Pelipetz. Catalysis in Liquid-Phase Coal Hydrogenation. Proc. 3rd World Petrol. Cong., Sect. IV, Subsect 1, 91 (1951).
2. Kawa, Walter, H.F. Feldmann and R.W. Hiteshue. Hydrogenation of Asphaltene from Coal Using Halide Catalysts. Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1970, 14 (4) (Pt. 1), 19-26.
3. Kawa, Walter, Sam Friedman, W.R.K. Wu, L.V. Frank and P.M. Javorsky. Evaluation of Catalysts for Hydrodesulfurization and Liquefaction of Coal. Amer. Chem. Soc., Div. Fuel Chem., Prepr. 1974, 19 (1), 192-206.
4. Lovetro, David C. and Sol W. Weller. Stannous Chloride and Cobalt Molybdate-Alumina Catalysts in Hydrogenolysis of Solvent Refined Coal. Ind. Eng. Chem., Prod. Res. Dev., 1977, 16 (4), 297.
5. O'Grady, M.A. and B.I. Parsons. The Hydrogenation of Alberta Bitumen over Cobalt Molybdate Catalysts. Mines Branch Research Report R-194, Department of Energy, Mines and Resources, Ottawa, 1967.
6. Strausz, O.P. Some Aspects of the Chemistry of Alberta Oil Sand Bitumen. Amer. Chem. Soc., Div. Petro. Chem. Prepr. 1976, 21 (3), 456-481.
7. American Society for Testing and Materials, Part 15, D-2042; 1975.

Figure 1: Specific Gravity of Liquid Product



▲ Mo:Sn=1:1

● Mo:Sn=1:0



FIGURE 2: OPTICAL MICROGRAPH OF USED CATALYST A SHOWING HIGH REFLECTANCE STREAKS OF SINTERED TIN COMPONENT

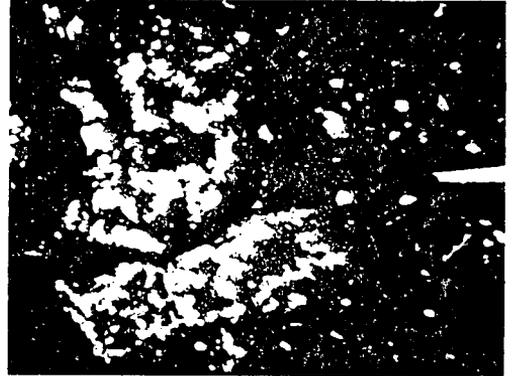


FIGURE 3: MICROGRAPH OF THE BENZENE-INSOLUBLE RESIDUE FROM COAL LIQUEFACTION EXPERIMENTS WITH STANNOUS OXALATE

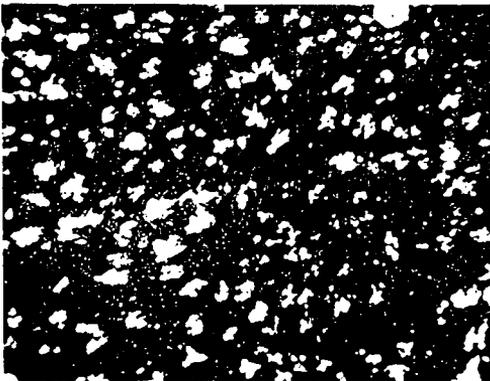


FIGURE 4: OPTICAL MICROGRAPH OF USED CATALYST C

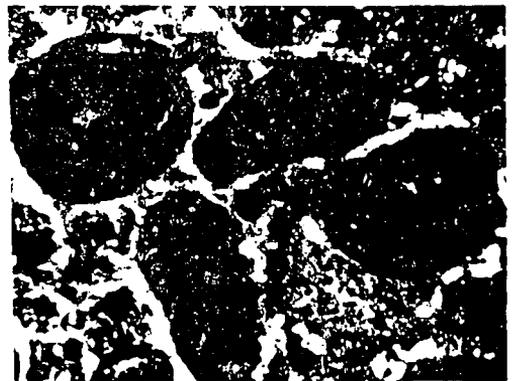


FIGURE 5: OPTICAL MICROGRAPH OF USED CATALYST D

50 μ m

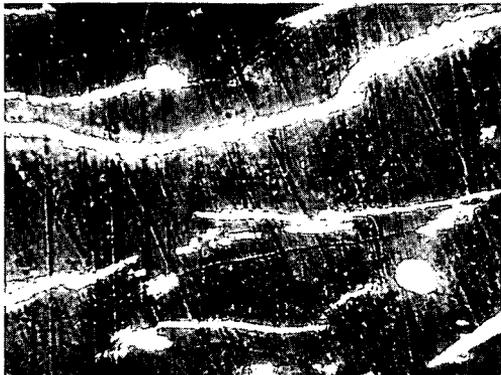


FIGURE 2: OPTICAL MICROGRAPH OF USED CATALYST A SHOWING HIGH REFLECTANCE STREAKS OF SINTERED TIN COMPONENT

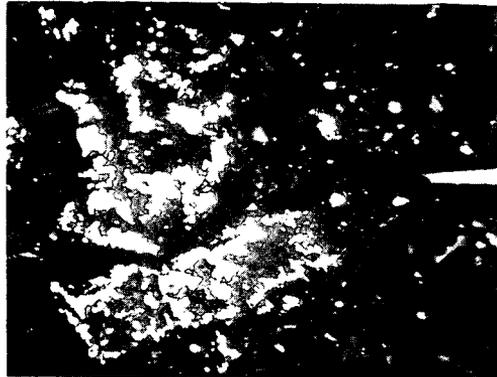


FIGURE 3: MICROGRAPH OF THE BENZENE-INSOLUBLE RESIDUE FROM COAL LIQUEFACTION EXPERIMENTS WITH STANNOUS OXALATE

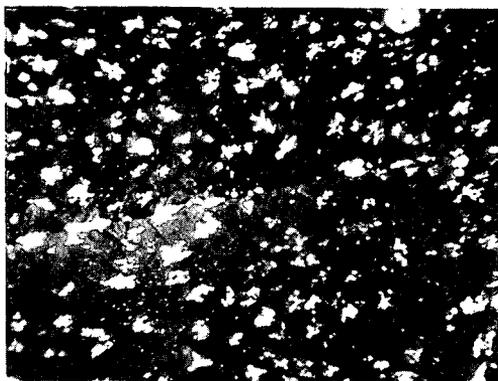


FIGURE 4: OPTICAL MICROGRAPH OF USED CATALYST C

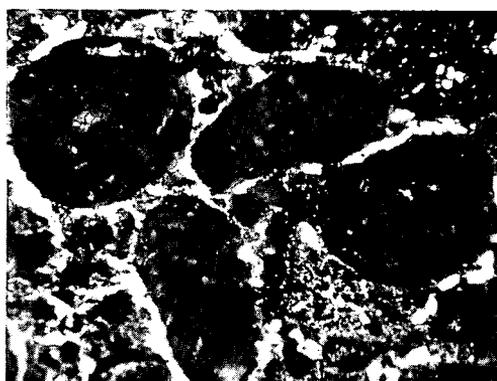


FIGURE 5: OPTICAL MICROGRAPH OF USED CATALYST D

50 μ m

Behavior of Tar Sand Bitumen With Paraffinic Solvents and Its Application to Separations for Athabasca Bitumen

Edward W. Funk
Exxon Research and Engineering, Linden, N.J., 07036

The main purpose of this paper is to present the behavior of tar sand bitumen when contacted with low-molecular-weight paraffins at ambient temperatures. We have found that an understanding of this phenomenon can lead to new separation and upgrading approaches for Athabasca tar sands. Furthermore, the ideas generated by the study of tar sand bitumen may possibly also be applied to other synthetic fuels such as coal liquids and shale oil.

1. Tar Sand Bitumen Dissolution Using the Spinning Disc Method. The dissolution behavior of tar sand bitumen depends primarily on the solvent, contacting conditions, and the temperature. For studying the dissolution mechanism we have chosen the spinning disc technique as a simple, well-understood system. The spinning disc technique for examining mass transfer and dissolution phenomena is well established in electro-chemistry but can be applied to a variety of systems (1,2). The experimental procedure consists of rotating a circular disc immersed in a liquid at a constant speed. Mass transfer from the disc can be experimentally measured as a function of time and rotational speed. The principal advantage of this geometry is that the mass-transfer coefficient is the same at all points on the surface and can be expressed as

$$k = 0.62 D^{2/3} \nu^{-1/6} \omega^{1/2} \quad 1)$$

where D is the binary diffusion coefficient, ν is the kinematic viscosity and ω is the rotational speed of the disc. The dependence of k on the rotational speed allows separation of mass transfer resistances between phases from resistances within the bulk phase.

For our study, a glass disc 2.54 cm. in diameter was coated with 0.10 grams of tar sand bitumen. The concentration of bitumen in solution was measured using a Beckman DB-G spectrophotometer operating at 530 nm. Details of this analytical technique are given by Funk and Gomez (3).

Figure 1 presents the experimental data for *n*-pentane as the solvent at 25°C. The data were obtained at rotational speeds of 0, 7 and 17 RPM. Figure 1 shows that, over the range of speeds studied, the rate of bitumen dissolution is independent of the rotational speeds. Equation 1 then indicates that the principal resistance to dissolution resides in the bitumen layer and not in transport across the solvent-bitumen interface. This resistance within the bitumen layer is large enough to require several minutes (≈ 10 minutes) for all the deasphalted oil to diffuse out of the bitumen layer.

For a variety of paraffinic solvents, dissolution data were obtained at 25°C and the discs were removed and the remaining asphaltene crust was examined by microscopy. Figure 2 presents SEM photomicrographs for pentane and decane asphaltenes at a magnification of 500. The results show that the asphaltenes form a porous network similar to an alloy which has had one component leached out. For the pentane asphaltenes, the pore size is $\approx 1 \mu$; for decane-precipitated asphaltenes the pores are considerably smaller. Examination of asphaltenes from dissolution using other paraffins showed that the pore size became smaller the higher the carbon number of the paraffinic solvent.

The experimental data can be modeled using Fick's second law which is expressed as

$$\frac{\partial c}{\partial t} = D_{AB} \frac{\partial^2 c}{\partial x^2} \quad 2)$$

To describe the unsteady-state diffusion in the spinning-disc experiments, we use the boundary conditions of $c=c_0$ for $t < 0$ and $c = 0$ in the solvent for all t . Crank (4) gives the solution to Equation 2; the expression for D_{AB} , the binary diffusion coefficient expressing mutual diffusion of solvent and deasphalted oil, is particularly simple at time where one-half of the deasphalted oil has been leached out

$$D_{AB} = \frac{0.049}{(t/L^2)} \quad 3)$$

where L is the thickness of the bitumen layer on the disc. Experimental data consistent with the above model usually show a linear plot of M_t/M_∞ (the fraction of deasphalted oil leached out) versus t^2 over a considerable time range. Figure 3 presents M_t/M_∞ as a function of t^2 for dissolution using pentane, heptane and decane. Equation 3 was used to calculate effective diffusion coefficients from the experimental data. For the pentane system, D_{AB} is 1.41×10^{-7} cm²/sec at 25°C. The results with heptane give a value of D_{AB} of 1.21×10^{-7} cm²/sec and the value for the decane system is 6.50×10^{-9} cm²/sec.

2. Particle Size Analysis of Asphaltene Aggregates. To determine the particle-size distribution of asphaltene aggregates which would be breaking away from the crust, tar sand bitumen was deasphalted using pentane, hexane and heptane at room temperature. The bitumen was contacted with ten times its weight of solvent and the asphaltenes were precipitated using a laboratory centrifuge operating at 2000 RPM. The asphaltenes were washed until they were free of deasphalted oil.

The HIAC model PC-230 was used to measure the particle-size distribution. This instrument uses a light-sensitive diode to determine light attenuation due to particles flowing past the sensor. Figure 4 shows the particle-size distributions for pentane, hexane and heptane precipitated asphaltenes. The results indicate that the pentane asphaltenes are somewhat larger than the hexane asphaltenes; this trend was found consistent through heptane.

3. Structure of Athabasca Tar Sands. For the tar sand system, the bitumen is associated with the sand and water as shown schematically in Figure 5. Typically the Athabasca tar sands contain 12% bitumen, 5% water and 83% sand and other minerals. Details of characterization of tar sands are summarized by Camp(5).

4. Fluid-Bed Studies. A liquid-fluidized bed is a convenient and conventional technique for contacting solids and liquids and we have applied this technique to contact tar sands with paraffinic solvents. Experimental data on the size of asphaltene aggregates for the tar sand system were obtained by using paraffinic solvents to elutriate the asphaltenes from a well-mixed fluidized bed of tar sands. Figure 6 gives a schematic diagram of the equipment used for the elutriation studies. The tar sands were placed in the 2" I.D. glass extraction column and a set of turbine mixers operating at 200 RPM was used to assure good solids-solvent contact. For each run, solvent was passed up through the tar sand bed at a known flowrate and collected at the top of the extraction

column. The extract was then analyzed for the percentage of asphaltenes. Figure 7 presents the results of the elutriation studies at 25°C. The percentage of asphaltenes entrained is expressed relative to the total asphaltenes in the bitumen for the particular paraffinic solvent used. As an example, we expect the extract with pentane to be 20% asphaltenes if all are small enough to be entrained; if the extract is 10% asphaltenes we calculate that only 50% of the asphaltenes were entrained. We see from Figure 7 that liquid flowrates in the range of 1 cm/sec are required to entrain all the asphaltenes with the extracted oil. Consistent with the results shown in Figure 4, the pentane asphaltenes behave as larger particles than the hexane asphaltenes and this trend continues through octane. Figure 8 presents similar data as a function of temperature for heptane as the solvent. As the temperature increases, higher liquid flowrates are required to entrain the asphaltene aggregates and this indicates that the size of the aggregates is increasing. The change in solvent density and viscosity is much too small to account for the higher liquid flowrates.

Use of Stokes' law and the elutriation data shown in Figure 7 were used to calculate effective maximum diameters for the asphaltene aggregates. For heptane, the maximum aggregate diameter is 100 μ and for pentane 150 μ ; these values are somewhat higher than those found using the HIAC particle-size analysis. The difference may be due to the estimated asphaltene density used in the Stokes' law calculation.

5. Novel Approach to Bitumen Separation from Athabasca Tar Sands. We have examined the use of paraffinic solvents for separation of bitumen from tar sands in a fluid bed since this type of contacting equipment has reasonable potential to be scaled up to the very large sizes required for tar sands.

Fluidization data were measured using the equipment shown schematically in Figure 6. For the sample of tar sands used, the particle-size distribution of the inorganics is shown in Figure 9. Figure 10 presents a plot of $\ln U$ versus $\ln \epsilon$ for the tar sand system; these data are for heptane as the solvent and at ambient temperature. The bed shows some expansion at liquid velocities substantially below the minimum fluidization velocity; this is not the case for a bed of equal-sized particles; it probably occurs in the tar sand system due to some segregation of different sized particles to give a fixed-bed region and a fluidized region. The curves A and B for dry tar sands (water removed by evaporation) give an approximate minimum fluidization velocity of the inorganics equal to 1 cm/sec. Curve B simulates the bottom of a hypothetical extractor where the solvent is nearly pure heptane; curve A simulates the other end of the extractor where the solvent has a relatively high bitumen concentration (in this case, heptane/bitumen = 4). The fluidization behavior is very different for fresh water-wet tar sands. These data are shown in Figure 10 by the solid dots. The minimum fluidization velocity is much higher than for dry tar sands. This great difference can be explained by agglomeration of the inorganics in the tar sand bed. Spherical agglomerates are formed in the fluid bed because the water-wet inorganics associate to minimize surface area between water and the hydrocarbon. Details of spherical agglomeration and its application to other systems are given by Smith and Puddington (6).

The results of Figure 10 show that the tar sand inorganics behave like large particles in a fluid bed if care is taken to maintain them as

water-wet. From Figure 7, we know that the asphaltenes behave as relatively small particles. Combining the results of Figures 7 and 10 suggests the conceptual separation approach shown in Figure 11. Figure 11 shows that for a paraffinic solvents there is a range of liquid flowrates which gives carryover of asphaltenes from a fluidized-bed type contactor but does not entrain the inorganics. For example, operating at 1.0 cm/sec to entrain the asphaltenes would entrain an important fraction of the unagglomerated inorganics. Then, a further separation of bitumen from inorganics would be required. The separation shown in Figure 11 is for essentially ambient temperatures.

The results shown in Figure 11 only suggest a conceptual approach for bitumen separation from tar sands. Use of this separation approach on a commercial scale requires considerable process development to generate an integrated system including tar sands preparation, solid-liquid contacting equipment, solids handling, and economic solvent recovery from the extracted tar sands.

6. References

- (1) Levich, V. G., "Physicochemical Hydrodynamics," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.
- (2) Chan, A. F., Evans, D. F., and Cussler, E. L., "Explaining Solubilization Kinetics," AIChE Journal 22,1006 (1976).
- (3) Funk, E.W., and Gomez, E., "Determination of Vanadium in Athabasca Bitumen and Other Heavy Hydrocarbons by Visible Spectrometry," Anal. Chem. 49,972 (1977).
- (4) Crank, J., "The Mathematics of Diffusion," Oxford University Press, Second Edition, 1975.
- (5) Camp, F. W., "The Tar Sands of Alberta, Canada," Cameron Engineers, Denver, Colorado, 1969.
- (6) Smith, H. M. and Puddington, I. E., "Spherical Agglomeration of Barium Sulfate," Can. J. Chem., 38, 1911 (1960).

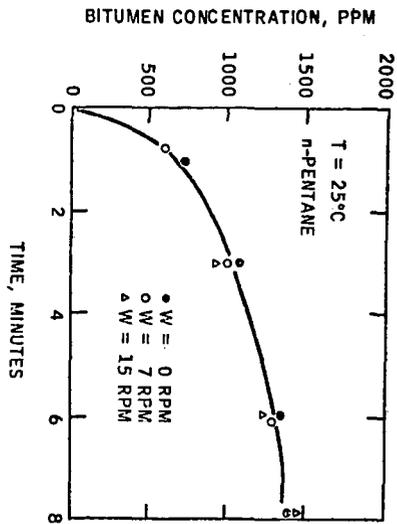
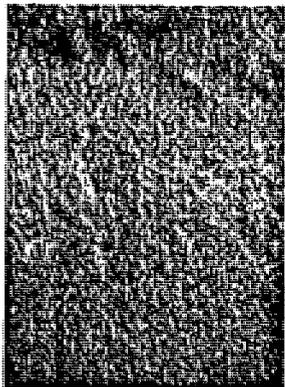


Figure 1 - Spinning Disc Experiments for Tar Sand Bitumen Dissolution in Pentane



Pentane Asphaltenes



Decane Asphaltenes

Figure 2 - Photomicrographs at 500x of Pentane and Decane Asphaltenes

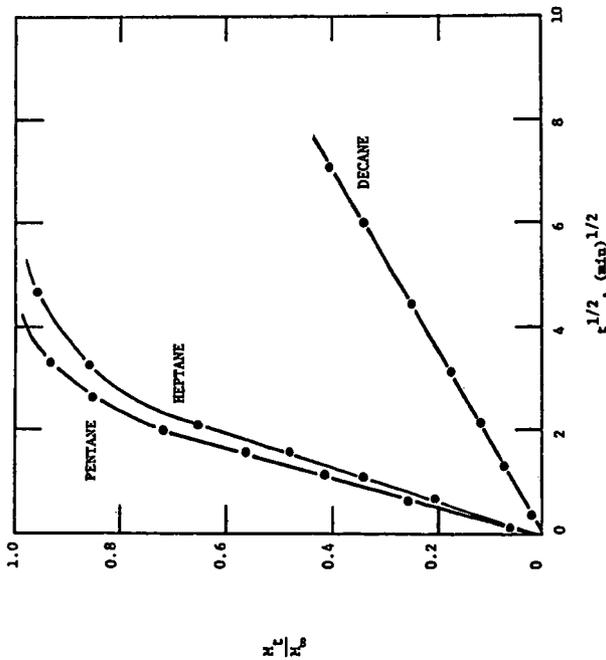


Figure 3 - Bitumen Dissolution in Normal Paraffins

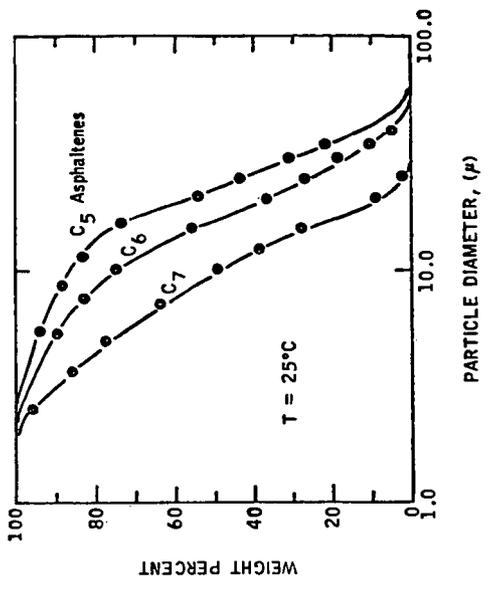


Figure 4 - Particle-Size Distribution of Asphaltene Aggregates

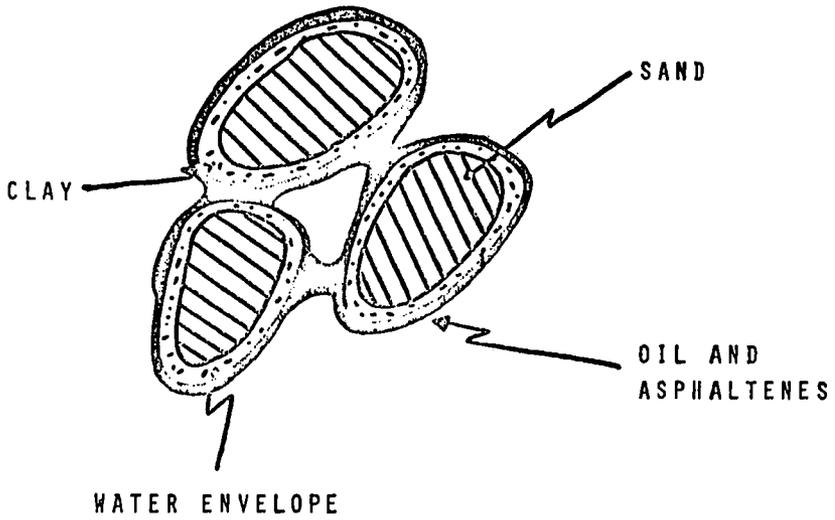


Figure 5 - Basic Model of Athabasca Tar Sands

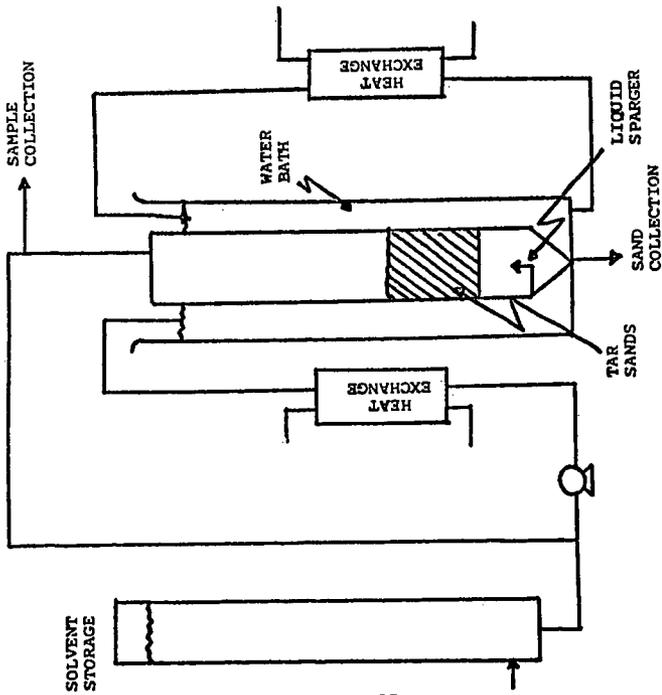


Figure 6 - Schematic Diagram of Fluid-Bed Contactor for Tar Sands

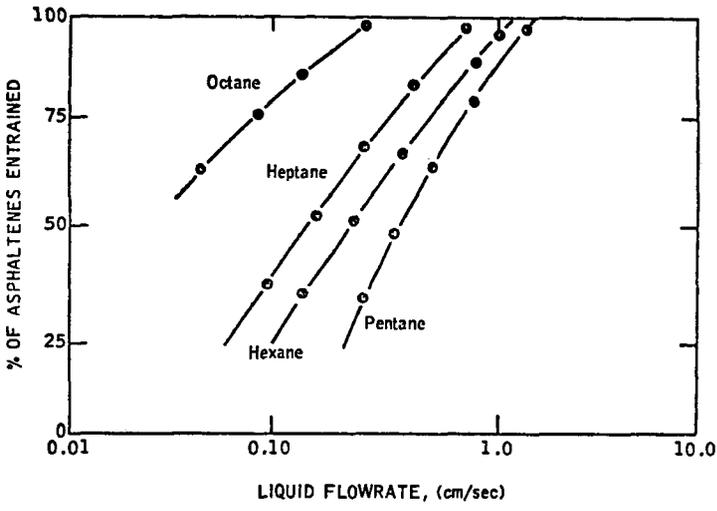


Figure 7 - Entrainment of Asphaltenes from a Tar Sand Bed as a Function of Liquid Velocity

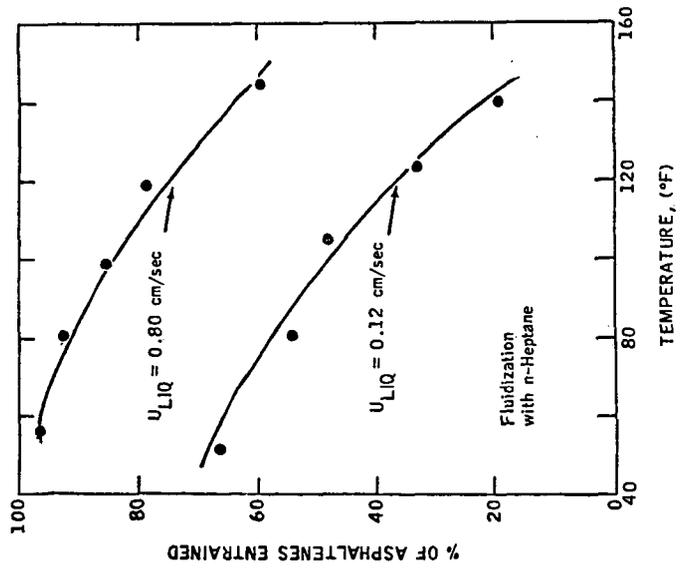


Figure 8 - Effect of Temperature on Entrainment of Asphaltenes from a Fluidized Tar Sand Bed

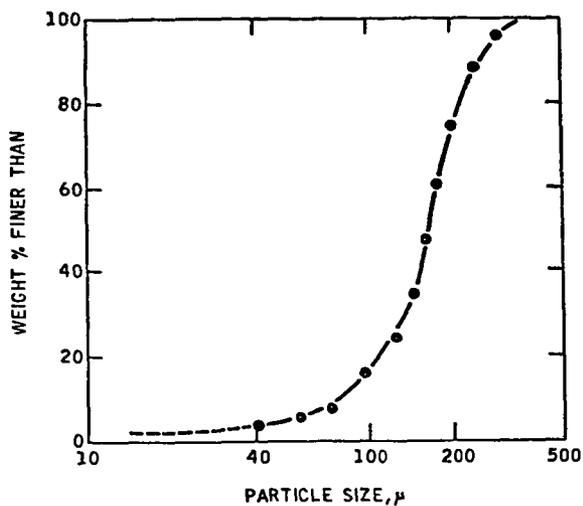


Figure 9 - Typical Particle-Size Distribution of Athabasca Tar Sand Inorganics

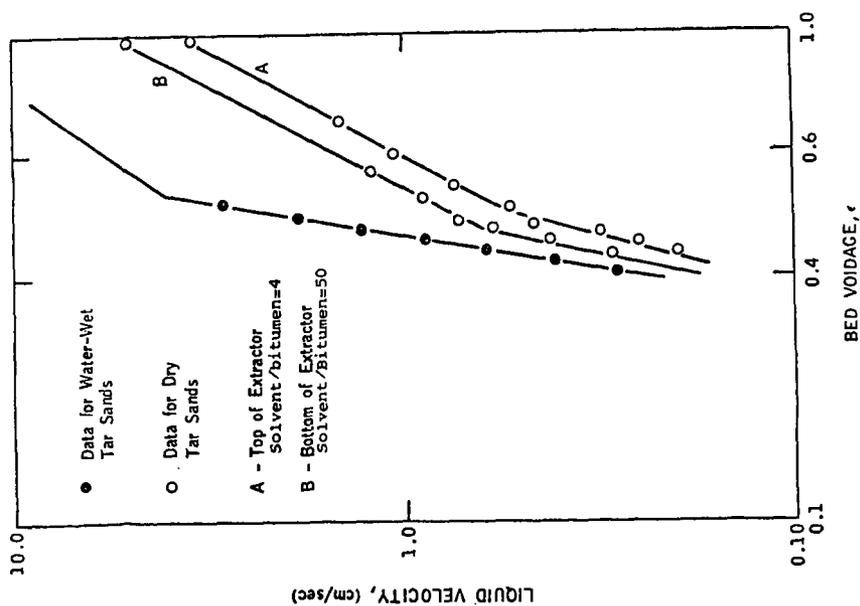


Figure 10 - Fluidization Data for Athabasca Tar Sands with n-Heptane

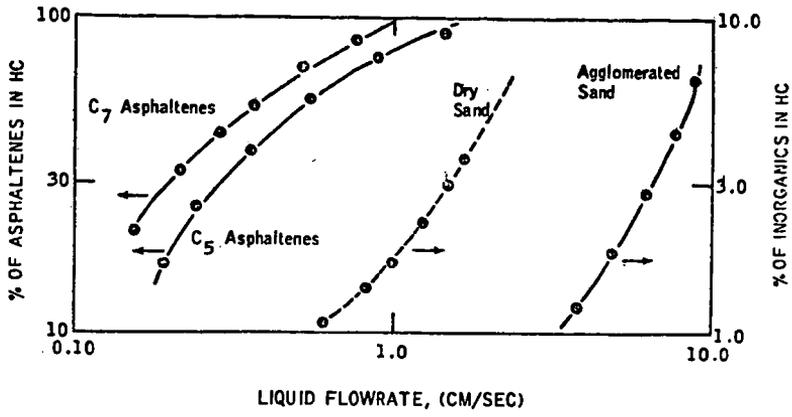


Figure 11 - Conceptual Process for Bitumen Separation from Athabasca Tar Sands

OXIDATION OF THE ATHABASCA OIL SAND AND ITS FRACTIONS

K.N. Jha, P.M. Rao and O.P. Strausz

Hydrocarbon Research Centre
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada, T6G 2G2

INTRODUCTION

The Athabasca oil sand and its fractions are known to be thermally unstable and sensitive to air (1-2). They react with molecular oxygen even at low temperatures. It has been reported that oxidation of bitumen generates high molecular weight material (3). The high susceptibility of the oil sand to aerobic oxidation could have practical relevance with regard to the surface strip mining and processability of the oil sand. Apart from its influence on the quality of the product, the phenomenon is also relevant to the origin, history, thermal and microbial maturation of the deposits and also to the *in situ* fire-flooding recovery technology of the oil sand.

Results of laboratory and field experiments on the production of crude oil by *in situ* forward and reverse combustion have been reported (4-7). However, quantitative studies of the parameters related to the chemical aspects of these processes, such as oxidation kinetics, have not been performed.

The chemical transformations in the oil sand due to oxidation reactions at low temperatures are difficult to detect by analysis of the bulk composition but they can be easily monitored by measuring the gaseous and highly volatile materials which are produced therefrom.

The present study was undertaken in order to gain an insight into the oxidation and weathering processes taking place in the Alberta oil sand.

EXPERIMENTAL

The high vacuum apparatus employed in this study was similar to that used previously (1-2). The experimental details for the collection and analysis of gases and the volatile materials have also been described (1-2). About 130 g Athabasca oil sand was placed in a 500 cm³ Pyrex vessel fitted with a breakseal and several 1 cm³ ampoules. The vessel was attached to the vacuum apparatus and degassed at room temperature for one hour. Oxygen was then introduced into the vessel at about 150 torr, the vessel was sealed off and heated to the desired temperature in a silicone oil bath. The vessel was shaken intermittently and the ampoules were sealed at desired time intervals and analyzed for oxygen on a 2.4 m molecular sieve column. The samples heated at 130°C in the absence and presence of oxygen were analyzed for both non-condensable and condensable materials at -196°C. Standard extraction procedures for bitumen and for the separation of asphaltene and maltene from the oil sand samples were followed (8). Elemental analyses for C, H, N, O and S were performed in the Microanalytical Laboratory of the Chemistry Department.

Between 5 and 10 g bitumen, asphaltene or maltene was introduced into a 250 cm³ Pyrex vessel. The vessel was joined to a Hoke valve fitted with a standard taper joint on the other end through which it was attached to another Hoke valve fixed to the vacuum apparatus. The volume enclosed between the two Hoke valves was used as a sampler. All samples were evacuated uniformly at ambient temperature before introduction of 250 torr oxygen. The oxygen concentration was determined by transferring it from the sampler into the gas burette and injecting it into the *gc*. The silicone oil bath was used to heat samples at 137°C. For higher temperatures, an electric furnace equipped with a 2-mode API Instrument Co. temperature controller and a Hewlett-Packard 3420 A d.c. differential voltmeter was employed. The consumption of oxygen was followed by expanding oxygen from the vessel into the sampler at desired time intervals and measuring the concentration as described above.

RESULTS AND DISCUSSION

The presence of oxygen has an enhancing effect on the rate of the low temperature thermolysis of the Athabasca oil sand, bitumen, asphaltene and maltene. The product yields obtained from heating oil sands at 130°C for 24 hours in the absence and presence of oxygen are presented in Table I. The products include C₁-C₇ hydrocarbons including neopentane, CH₃CHO, CO, CO₂, COS and H₂S. In the presence of oxygen, CH₃COCH₃ and SO₂ are produced in addition to these compounds. Unfortunately, the acetone peak masked the C₅ hydrocarbon peaks and consequently the latter could not be determined accurately. It is evident that in the presence of oxygen, the rates of production of hydrocarbons are increased by factors ranging from 2 to 70, those of the apparent oxidation products by up to 500, and H₂S is probably converted to SO₂.

The thermolysis products obtained from heating bitumen at 137°, 172° and 207°C are given in Table II. The product distribution is similar to that from the whole oil sand (Table I), but the ratios of the product yields in the presence and absence of oxygen at 207° are higher than those at 137°C. The rates of production of hydrocarbons at 207°C in the presence of oxygen are increased by factors up to 100 and those of the apparent oxidation products, by up to 170. Oxidation of asphaltene and maltene at 172°C produced similar results.

Although many details of the complex reaction network involved in the oxidation of hydrocarbons by molecular oxygen have not yet been elucidated, it is commonly accepted that a chain mechanism is operative and that one of the first products formed is a hydroperoxide which may be oxidized further or decompose thermally, thereby initiating new chains (9,10). At 100° and 130°C Kovalev and Denisov (11) reported that peroxides, alcohols and carbonyl compounds are intermediate products whose time profile concentrations pass through a maximum (11). It is also known that these intermediates are responsible for the enhanced yields of hydrocarbons and oxygenated compounds in the thermolysis of hydrocarbons in the presence of oxygen (9-11). The enthalpy changes of the oxidation and combustion reactions leading to the observed end products range between 80 and 105 kcal per mol of oxygen (7).

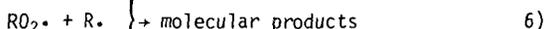
The efficiency of oxygen in the low temperature thermolysis of the oil sand, bitumen, asphaltene and maltene could also be explained by such a general mechanism, where the initial reaction between the organic free radicals formed by thermolysis and molecular oxygen to form a hydroperoxy radical



is followed by the chain propagating steps



Typical chain terminating steps could be



The combustion type reactions in our system will produce additional amounts of hydrocarbons, carbon monoxide, carbon dioxide and water.

A simple mechanism for the oxidation of hydrogen sulfide to sulfur dioxide could be expressed as follows:



The overall heat of oxidation is exothermic by about 124 kcal per mol.

The rates of consumption of oxygen by the oil sand were studied at various temperatures between 24° and 130°C. The data obtained are plotted in Figure 1. The semi-logarithmic plots of the concentration of oxygen in the gas phase as a function of time at each temperature follow first order reaction kinetics. The half-lives, i.e., time required for one-half of oxygen to be used up, vary between 111 days at 24° and 0.6 hours at 130°C. The rate constants, k, were estimated from the slopes of these plots and Equation 10 was used for the Arrhenius plot of $\ln k$ versus $1/T$:

$$\ln k = \ln A - E_a/RT \quad (10)$$

where k is the rate constant, A the preexponential factor, E_a the activation energy, R the gas constant and T is the temperature in °K.

The Arrhenius parameters estimated from the plot are temperature dependent (Table III). Around room temperature, the rate of depletion of oxygen features a lower activation energy and preexponential factor than at the higher temperatures. The temperature dependence of the rate parameters is indicative of changes in the reaction mechanism and suggests a largely surface-catalyzed, i.e., heterogeneous reaction network at the lower temperature, changing over to non-catalytic gas phase reactions at the higher temperatures. It is to be noted that an increase in temperature from 24° to 130°C brings about a 4000-fold rate increase in oxygen uptake. The last column of Table III lists the time required to deplete 99 percent of oxygen added at each temperature and is equivalent to 7 half-lives.

Bousaid and Ramey determined the rates of oxygen disappearance in the 13.9° API Athabasca crude at 23°, 38° and 52°C and found them to follow first order reaction kinetics (5). In this temperature range, they estimated an activation energy of 12.7 kcal per mol which is in agreement with our value of 13 kcal per mol. However, the rate constants and preexponential factor estimated from their data are larger than ours by about two orders of magnitude. We have also estimated the activation energies for the oxidation of hexadecane by molecular oxygen in the temperature ranges 100°-120° and 120°-150°C from the rate data of Kovalev and Denisov to be 17 kcal and 40 kcal per mol, respectively (11). These results show trends similar to ours.

The rates of disappearance of oxygen in bitumen at 137°, 172° and 207°C and in asphaltene and maltene at 137° and 172°C obey first order kinetics (Figure 2). The rate constants estimated from these plots are listed in Table IV. It is apparent that the trend in reactivity is oil sand, asphaltene, bitumen and maltene in decreasing order. It should be pointed out that the rate of oxygen uptake is a measure of the oxidizability of the fractions, which in turn is a function of the chemical composition of the sample.

In the oil sand experiment at 130°C, the 6 mmol oxygen added was completely consumed: 9.3% appeared in the volatile oxygen-containing products and 45% in the bitumen as determined by the elemental analysis (Table V). The rest was presumably converted to water and other oxygenated compounds which were lost during the bitumen extraction. Table V shows that the bitumen contents of non-oxygenated and oxygenated oil sand samples are the same, 13.3%. However, the maltene and asphaltene contents of the former were 83.2 and 16.8 while those of the latter were 76.1 and 23.9%, respectively. It should be noted that in these experiments the oxygen was completely consumed and that the alteration effect of oxygen would have been much larger if the oxygen concentration had been maintained throughout the course of the experiment.

The substantial increase in the asphaltene content of the oxygenated sample, at the expense of maltene, demonstrates that exposure of the oil sand to air has an adverse effect on the quality of the bitumen. The increase in asphaltene content would likely lead to an increase in the yield of coke formation and a lowering in the yield of synthetic crude in the upgrading process. The possibility of aerobic oxidation should therefore be taken into consideration in the storage of the mined oil sands, especially during the summer months when sand temperatures could significantly exceed ambient air temperature. It could also be a factor in affecting bitumen quality during storage of liquid bitumen and in the initial stages of the *in situ* recovery processes of the bitumen.

ACKNOWLEDGEMENTS

The authors thank the Alberta Oil Sands Technology and Research Authority and the Department of Energy, Mines and Resources for financial support, and Dr. P. Neudorfl for helpful suggestions.

REFERENCES

1. Strausz, O.P., Jha, K.N., and Montgomery, D.S., *Fuel*, (1977) 56, 114.
2. Jha, K.N., Montgomery, D.S., and Strausz, O.P., In: "Oil Sand and Oil Shale Chemistry, Eds. O.P. Strausz and E.M. Lown, Verlag Chemie International, New York, 1978, in press.
3. Moschopedis, S.E., and Speight, J.G., *Fuel*, (1975) 54, 210 and references therein.
4. Reed, R.L., and Reed, D.W., *Petro. Trans., AIME*, (1960) 219, 99.
5. Bousaid, I.S., and Ramey, Jr., H.J., *Soc. Petrol. Engg. Jour.*, (1968) 137.
6. Tadema, H.J. and Weijdema, J., *Oil and Gas Jour.*, (1970) 77.
7. Burger, J.G., and Sahuquet, B.C., *Soc. Petrol. Engg. Jour.*, (1972) 410.
8. Selucky, M.L., Chu, Y., Ruo, T., and Strausz, O.P., *Fuel*, (1977) 56, 359.
9. Sieg, L., "Low Temperature Oxidation", ed. Jost, W., Gordon and Breach Science Publishers, New York (1965) 191.
10. Allara, D.L., Mill, T., Hendry, D.G., and Mayo, F.R., "Oxidation of Organic Compounds, Vol. II", *Adv. Chem. Series*, 76, (1968) 40.
11. Kovalev, G.I., and Denisov, Y.T., *Neftekhimiya* (1976) 16, 457.

Table I. Composition of Gases from the Oxidation of the Athabasca Oil Sand at 130°C^a

Product	10 ⁻⁸ mol hr ⁻¹ kg ⁻¹ oil sand				
	Nil		6 mmol		O ₂
	Nil	6 mmol	Nil	6 mmol	
Methane	4.97	81.8	C ₅	34.8	37.0
Ethylene	0.82	57.0	C ₆	2.74	148.0
Ethane	1.14	21.6	C ₇	3.68	11.5
Propylene	1.95	67.9	CH ₃ CHO	5.50	1,640
Propane	0.73	20.1	(CH ₃) ₂ CO	n.o. ^c	459
<i>i</i> -Butane	0.20	1.74	CO	11.1	5,920
<i>i</i> -Butene	0.72	25.7	CO ₂	2,830	56,400
Butane	14.5	29.5	COS	0.41	42.2
Butenes	0.35	7.70 ^b	H ₂ S	35.7	n.o.
<i>Neo</i> -pentane	20.0	n.d. ^b	SO ₂	n.o.	23.4

^aThe oxygen pressure was 150 torr and the sample was heated for 24 hours.

^bNot determined, due to the large interfering peak of acetone.

^cNot observed.

Table II. Composition of Gases from the Oxidation of the Athabasca Bitumen as a Function of Temperature^a

Product	10 ⁻⁸ mol hr ⁻¹ per 100 g bitumen				
	137°C		172°C	207°C	
	Nil	3.3 mmol	3.6 mmol O ₂	Nil	3.9 mmol
		O ₂		O ₂	
Methane	2.6	11.0	36.4	114	1,000
Ethylene	1.2	3.4	52.1	21	171
Ethane	n.o. ^b	2.5	68.5	14	234
Propylene	1.8	6.4	59.0	2.0	209
Propane	n.o.	4.5	49.0	17	202
<i>i</i> -Butane	0.6	3.4	41.8	13	41.0
<i>i</i> -Butene	n.o.	2.1	23.4	n.o.	36.0
<i>n</i> -Butane + Butenes	3.5	4.5	476	20	440
Acetaldehyde	2.4	108	494	18	2,920
Acetone	n.o.	2,760	2,830	n.o.	51,100
Carbon monoxide	44.0	392	421	213	12,400
Carbon dioxide	330	1,320	11,700	2,880	33,800
Carbonyl sulfide	1.0	7.7	129	39.0	556
Sulfur dioxide	n.o.	1.8	314	n.o.	28
Hydrogen sulfide	n.o.	n.o.	n.o.	1,270	270

^aThe samples had 250 torr pressure of oxygen.

^bNot observed.

Table III. Arrhenius Parameters for the Uptake of Oxygen by Athabasca Oil Sand

Temp. °C	k hr ⁻¹ kg ⁻¹ oil sand	E_a kcal/mol	A hr ⁻¹ kg ⁻¹ oil sand	Time required to deplete 99% of O ₂ added
24	2.6×10^{-4}	13	1×10^6	2.0 years
60	2.6×10^{-3}			0.2 year
85	1.1×10^{-2}			17 days
105	9.8×10^{-2}	29	6×10^{15}	47 hours
130	1.1			4.1 hours

Table IV. Rate Constants for Oxygen Depletion

t°C	Oil Sand	Asphaltene	Bitumen	Maltene
	hr ⁻¹ kg ⁻¹ oil sand	hr ⁻¹ per 100 g		
130	1.1	-	-	-
137	-	0.22	0.076	0.055
172	-	0.22	0.20	0.102
207	-	-	0.36	-

Table V. Elemental Composition of Athabasca Oil Sand^a

Fraction	[O ₂] ^b	C	H	N	O	S
		%				
Bitumen						
13.3%	none	82.58	10.26	0.39	1.36	5.22
13.3%	6 mmol	82.21	10.09	0.40	1.99	4.95
Asphaltene						
16.8%	none	79.35	8.14	1.06	1.58	7.39
23.9%	6 mmol	76.68	7.95	0.97	3.30	7.97
Maltene						
83.2%	none	83.74	10.90	0.20	1.03	3.78
76.1%	6 mmol	83.05	11.09	0.09	0.99	3.87

^a130 g of the Athabasca oil sand was heated at 130°C for 24 hours.

^bAn oxygen pressure of 150 torr was used.

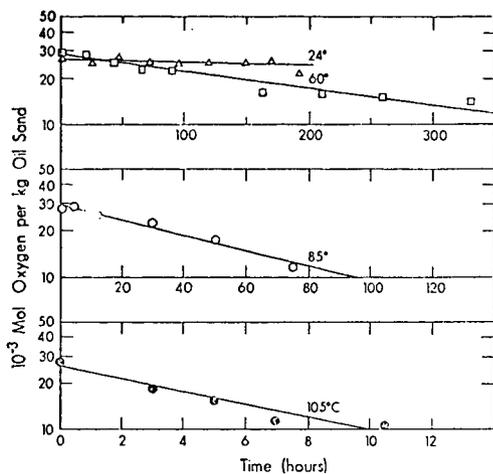


Figure 1. Depletion of oxygen concentration as a function of time in the Athabasca oil sand: Δ , 24°C; \square , 60°C; \circ , 85°C; \bullet , 105°C.

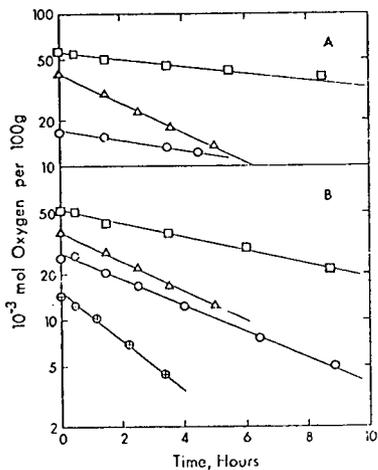


Figure 2. Depletion of oxygen concentration as a function of time in the Athabasca bitumen (\circ), asphaltene (Δ) and maltene (\square): A, 137°C; B, 172°C and Θ , bitumen at 207°C, abscissa reduced to half.

INFLUENCE OF CHEMICAL FACTORS ON
PRIMARY PROCESSING OF UTAH TAR SAND BITUMEN

James W. Bunger, Donald E. Cogswell and Alex G. Oblad
Department of Mining and Fuels Engineering
University of Utah
Salt Lake City, Utah 84112

INTRODUCTION

Research of recovery and processing technology applicable to Utah tar sands is currently in progress. Development of this hydrocarbon resource has not yet occurred, principally because of high costs associated with present recovery methods. The processing of bitumens is also expected to be relatively more expensive than conventional petroleum processing because of the heavy nature and high heteroatom content of the bitumen. In processing of bitumen the primary conversion appears to be the most important step because of the possible high cost of hydrogen processing or loss in yields attendant with reducing the high molecular weight bitumen to synthetic crude. Methods and conditions of primary processing have a major effect on the composition of the products subsequently used as feedstocks for secondary processing. Secondary processing for production of fuels and other hydrocarbon products will probably utilize adaptation of processes developed for conventional petroleum.

The primary process most commonly used for upgrading of heavy oils, petroleum residuum or bitumen is some form of coking such as delayed or fluid coking. For these processes the range of operating variables which can be employed is rather limited and the product distribution and quality (composition) generated is primarily a function of the feedstock composition. Because the coking process is relatively inexpensive, industrial processes are often content with optimizing coking yields and then subsequently optimizing some secondary process more specifically aimed at altering the composition to produce a desired product. Such an approach is presently used with the Athabasca deposit where 15 to 20 weight percent of the feed is converted to a high sulfur coke and the liquid products are subjected to an expensive hydrotreating to obtain a synthetic crude oil amenable to conventional refining.

Recent work on the structure of Utah and Athabasca bitumens (1,2) has shown that Uinta Basin (Utah) bitumens possess a significantly different hydrocarbon and non-hydrocarbon structure than Athabasca bitumen. The higher molecular weight, higher viscosity, and lower volatility points toward a heavier material for the Uinta Basin bitumen, but the higher hydrogen content and API gravity, and the lower asphaltene content and carbon residue points toward a less aromatic bitumen. Interpretation of the structural analysis indicates that the Uinta Basin bitumen is comprised of relatively high molecular weight naphthenic hydrocarbons. The Athabasca bitumen is of lower molecular weight, but higher in aromatics. A comparison of compound type analysis suggests that Athabasca bitumen contains roughly twice the amount of aromatic carbon that Uinta Basin bitumen contains.

The differences apparent in the two groups of bitumens suggested that direct adaptation of process conditions used with Athabasca bitumen may not be the most desirable route for development of processes for Utah bitumens. Therefore, several alternatives for the primary conversion of bitumen have been examined, in addition to coking. Examination of alternate processing steps served two useful purposes. First, results of such a study helped identify processes particularly amenable to this unusual feedstock. Second, by paying particular attention to the structure of the feedstock and products more will be learned about conversion mechanisms and pathways influencing residual material processing.

In this paper results from coking, catalytic cracking, and hydrolysis of virgin Asphalt Ridge bitumen are compared. This study includes the effect of variables on yields and product composition. Product distribution and composition are compared

as a function of process variables and the conversion process employed. Detailed structural analysis is used in the evaluation of the respective processes. Implications of the product structure to thermal and catalytic conversion pathways are discussed.

EXPERIMENTAL

Analytical Methods

Physical properties and elemental analysis were obtained by conventional analytical techniques. All average molecular weights reported are those obtained by VPO in benzene. Average molecular weights determined in this fashion are expected to give values somewhat higher than the true average molecular weight because of solute-solute molecular associations (3). Liquid and gas densities were obtained by an electronic densitometer accurate to better than three significant figures.

Separation of products into compound type classes was accomplished by the dual silica-alumina column chromatographic technique (4) without prior separation of acids, bases, and neutral nitrogen compounds. Simulated distillation was accomplished by previously published procedures (1) utilizing as an internal standard a series of alkyl benzenes.

Coking

Batch coking experiments were conducted in a stainless steel reactor fitted with a Vycor glass liner. The reaction was brought to temperature by a preheated fluidized sand batch heater. Charge to the reactor was approximately 10 g. (See also references 5, 6). Pressure, when applied, was with helium, without sweep.

Catalytic Cracking

Two reactor configurations were used in order to assess various factors influencing catalytic cracking. (See also reference 8). One configuration was a semi-batch downflow reactor patterned after the CAT-A (7) test in which bitumen and catalyst are preheated before mixing. The other configuration was a batch type reactor in which feed and catalyst were intimately mixed prior to heating. This configuration minimized the diffusion limitations but required volatilization of products in a static atmosphere.

Hydropyrolysis

Reactor design for hydropyrolysis has been published by Ramakrishnan *et. al.* (9). The reactor tube was coiled 3/16 x 236 inch stainless steel tube which was held isothermally within $\pm 10^{\circ}\text{C}$ of the desired temperature. The interior surface was pre-sulfided to minimize catalytic effects.

RESULTS AND DISCUSSION

The approach taken in this work was to subject virgin bitumen to various processing steps and to then evaluate the results in terms of product yield and composition. Because the cost of recovery is expected to be high, it is critical that the processing steps maximize both yield and product quality. The ever increasing cost of hydrogen processing places an additional constraint on economics so optimum utilization of hydrogen is also a prime consideration.

The major primary processes which have been preliminarily examined are coking, catalytic cracking, hydropyrolysis, visbreaking and deasphalting. Catalytic hydrocracking and hydrotreating of virgin bitumen have not been examined in enough detail to make comment at this point. Visbreaking or deasphalting may play a role as pretreatment to the primary conversion process.

Characteristics of Asphalt Ridge bitumen are given in Table 1 and have been previously discussed in the literature (2,3,5,6).

Coking

Results of the coking (destructive distillation) of various deposits have been previously reported (5). These results showed that heteroatom content of the liquids followed the trends exhibited in the virgin bitumen. Total yields of liquids and gases were a function of hydrogen content; conversely the higher the aromatic content, the greater the coke yield. A secondary correlation was observed between increasing molecular weight and decreasing liquid and gas yield for a given hydrogen content.

Table 1

	C	H	N	S	O
Elemental Analysis	86.2	11.3	1.1	0.4	0.9
Average molecular weight (VPO-benzene)			713		
Viscosity (Poise @ 77°F, cone-plate, .05 sec ⁻¹)			69,300		
API gravity			12.5		
Heating value (Btu/lb)			19,305		
Asphaltenes (n-pentane)			11.8		
Carbon residue (Rammbottom)			9.1		
% distillable below 535°C			40		

The effect of temperature on process yields is given in Figure 1. The data represent ultimate yields from a series of isothermal runs. Note that near asymptotic values are reached by a temperature of 460°C. Elemental analysis and physical properties of liquids obtained at selected temperatures are given in Table 2.

Table 2

Characteristics of Pyrolysis Condensates
from Isothermal Cracking of Asphalt Ridge Bitumen (6)

Property	Temperature of Pyrolysis		
	380°C	415°C	460°C
Carbon	86.7	86.7	86.7
Hydrogen	12.1	12.3	12.2
Nitrogen	0.25	0.39	0.48
Sulfur	0.33	0.29	0.29
Oxygen	0.50	0.30	0.31
C/H Ratio	0.603	0.591	0.599
Density (20°C) g/cc	0.897	0.893	0.892
API gravity	25.9	26.7	26.9
Refractive index	1.4970	1.5010	1.4998
Molecular weight	261	296	321

The results shown in Table 2 reveal remarkably little difference in the average properties considering that the total condensate yields varied from 11% to 82% of the bitumen between 380°C and 460°C. Some difference is noted in the average molecular weight due to higher temperature of distillation of cracked products. Simulated distillation reveals that about 12% of the virgin bitumen would exhibit a TBP below 380°C; thus, a significant percentage of the 380°C products might be expected to be virgin material. For the 460°C condensate, no more than 27% of the condensate can be attributable to virgin compounds and to the extent that virgin material of this boiling range undergoes cracking the percentage contribution of virgin distillate would be reduced.

Although the properties of the condensates varied little over the temperature range examined, visual inspection of the residue/coke revealed that drastic chemical changes

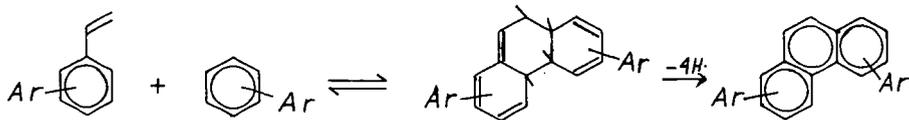
were being affected over the temperature range studied. At lower temperatures the residue was a viscous, soluble fluid, while at higher temperatures the residual material resembled a glassy char or coke. In an attempt to determine the temperature effect on the formation of this coke, presumably condensed aromatic species, the solubility of the residue in pyridine was measured. For this test to be meaningful, it was reasoned that dealkylation, dehydrogenation, or cyclization reactions would not likely result in the production of pyridine insoluble material, but that condensation or polymerization reactions producing higher ring aromatics would. The mechanisms leading to production of higher condensed aromatics are not well understood and will be referred to in this discussion simply as condensation reactions.

Results of pyridine solubility of residues are shown by the dotted line in Figure 3 and reveal that a dramatic change in pyridine solubility occurs between 425° and 435°C. Also plotted in Figure 3 is the percent yield of residue. This curve exhibits an inflection point some 22°C lower than the inflection point in the pyridine solubility curve. Scales on the vertical axis have been arbitrarily adjusted to allow some visual comparison of the various parameters measured. The data shows that volatiles formation and char formation are not simultaneous events and that the major reactions leading to volatiles and char formation occur at substantially different temperatures. Aromatics condensation apparently does not occur appreciably below 422°C even though over 70% of the bitumen has been produced as cracked products at this temperature. (See Table 8 for maximum possible contribution of virgin distillate).

In order to help confirm that pyridine solubility of the residue was a significant index for measuring aromatics condensation, a second parameter, H/C ratio, was measured. The results of this examination are also plotted in Figure 3 and reveal an inflection point quite near to the inflection point for pyridine solubility. This data showed that a linear correlation between H/C ratio and depth of cracking did not exist but that the reactions giving rise to the reduction in H/C ratio may possibly be the same as those resulting in pyridine insolubility. A correlation of pyridine solubility with H/C ratio reveals a linear relationship between 380° and 423°C, another linear relationship of different slope, between 433° and 460°C, with a non-linear transition region between 423° and 433°C. This correlation is shown in Figure 4 along with the corresponding temperature of cracking. The entire transition region actually occurs over a narrow temperature range of about 10°C.

Based on this information one can speculate about the general mechanism giving rise to the results. From 380° to 423°C primary cracking is limited to rupture of relatively weak σ bonds. The free radicals thus formed can participate in transfer or propagation reactions with aliphatic or naphthenic hydrocarbon systems. The decrease in pyridine solubility of the residue, which is accompanied by a dramatic decrease in H/C ratio, may be attributable to dehydrogenation of naphthenic ring systems, dealkylation reactions and volatilization of saturated hydrocarbons. Naphthenic ring systems may or may not be associated with aromatics but the inductive effects of aromatic rings, as exemplified by the compound tetralin, are known to promote hydrogen transfer.

Above 423°C additional reactions are introduced. These reaction mechanisms are not identified but they are characterized by several features observed in the results presented above. If fractional reduction in H/C ratio is used as a measure of the progress of reaction, an activation energy of about 70 Kcal/mole is calculated for the reaction occurring between 423° and 433°C. The calculations assumed zero order dependence on reactant concentration as assumptions of higher order produced an unreasonably high activation energy. The calculated activation energy is consistent with several possible polymerization and/or condensation reaction mechanisms. One possibility is that aromatic or benzyl hydrogens are abstracted in a free radical propagation step. The resulting phenyl or benzyl free radicals subsequently attack other aromatic rings to form biphenyl or diphenyl methane type linkages. The resulting molecules subsequently undergo further addition or ring closure depending on the alkyl substituents which might be present. An alternative reaction mechanism which might be considered is that of Diels-Alder type condensation of α -olefin aromatics acting as the diene and aromatics as the dienophile:



The reaction involves a partially hydrogenated intermediate which donates hydrogen in the process of volatiles formation.

In the region between 433° and 460°C the reduction in hydrogen content is attributable to several factors. One factor is the loss of aromatic C-H resulting from condensation of aromatics as discussed. Another factor is the significant increase in primary decomposition reactions such as dealkylation of aromatics. Analysis of products produced between 430° and 460°C show a definite trend toward increased paraffinic carbon compared to lower temperature products which were more naphthenic. Whereas transfer and free radical propagation reactions can occur at moderate temperatures, primary decomposition requires higher temperatures. Whichever the dominant mechanism, Figure 4 shows that the loss of hydrogen at higher temperatures has a much greater influence on decreasing the solubility of the residue than occurred at the low temperature end where considerable loss of hydrogen content had little effect on pyridine solubility.

There are several important implications of the proposed gross mechanism to thermal processing of bitumen. First, production of refractory molecules can be inhibited by maintaining temperatures below 425°C. The residue obtained at these conditions should remain amenable to further processing. Second, inhibition of condensed aromatics formation above 425°C can be accomplished only by shortening the residence time (reducing the relative importance of second order reactions) or by dilution of the aromatics such as with hydrogen or hydrogen rich molecules. This interpretation appears to be consistent with the vast body of processing literature which has empirically determined that processes operating below 425°C are significantly different from those operating above this temperature where residence time becomes highly important.

Industrial coking processes typically operate at pressures higher than atmospheric. Correspondingly, the effect of pressure (P) on yields and yield structure was determined, holding the temperature constant at 460°C. Results are given in Figure 2. The results show that the amount of coke formed increases steadily with increasing pressure. These results and those acquired for visbreaking of bitumen at elevated pressures suggest that pressure exerts an influence on chemical reactions over and above the effects pressure has on volatility and diffusion of products.

The products from this set of experiments were evaluated in terms of elemental analysis and physical properties. Results are shown in Table 3. Elemental analysis are not shown because variations from the atmospheric pressure results (Table 2) were minor. The API gravity results show interesting curvature at about 80-100 psig. The yield data in Figure 2 suggested that the liquids curve may not be a smoothly decreasing function of pressure, as drawn. Should these deviations in API gravity and yields as a function of pressure prove to be real, it may have interesting implications regarding the effect of pressure on thermal cracking mechanisms.

Catalytic Cracking

Analysis of Uinta Basin bitumen revealed a material that was high in naphthenic character (2). The results are exemplified by the group type analysis of P. R. Spring saturated hydrocarbons where over 60% of the saturates are comprised of substituted decalins and perhydroanthracenes and perhydrophenanthrenes (1). Only 7% of the saturates which represented 27% of the bitumen contained no alicyclic rings. The

highly naphthenic character of aromatic containing molecules is thought to persist in the remaining 73% of the bitumen.

Table 3
Properties of Condensates Derived at Elevated Pressures

Property	Pressure (psig)				
	0	40	80	120	250
API gravity	26.9	33.4	34.1	37.1	39.2
n_{D}^{20}	1.4998	1.4891	1.4914	1.4830	1.4801
Avg. molecular weight	321		263		265

Naphthenic gas oils are highly responsive to catalytic cracking and give high yields of branched alkanes. Based on this rationale, direct catalytic cracking was attempted. The presence of significant quantities of basic nitrogen, metals, or particulates would be expected to have an appreciable impact on a commercial operation and utilization of catalytic cracking may require some form of feed pretreatment. However, at the present stage of research it is important to assess the chemical responsiveness to catalytic cracking. Preliminary results of this study and a description of catalysts have been previously reported (8).

Gravimetric results for cat cracking under selected conditions are given in Table 4. Results of Bt(1) reveal that significant catalytic activity was present at 412°C; purely thermal cracking (Figure 1) produced only 47% liquids plus gases at this temperature. Results of Bt(2) show that significant cracking occurred with the powdered molecular sieve catalyst. Further, the catalyst exhibited a strong selectivity toward production of liquids rather than gases and the slightly higher API gravity reflects the increased amount of hydrogen retained in the liquids. These trends are expected from molecular sieve catalysts when zeolite catalyzed cracking is operative.

Table 4
Catalytic Cracking Results

Feed (Run)	Catalyst	Mode	Cat/Oil	T°C	Gas	Liquid	Residue (Coke)	API (Liquid)
Bt(1)	S/A	SB	1.3	412	6	67	26	27.9
Bt(2)	M.S.(f)	SB	1.8	412	1	79	20	29.5
Bt(3)	S/A	SB	1.3	470	11	76	13	25.1
Bt(4)	S/A	B	2.0	460	10	74	16	30.8
M(5)	S/A	B	2.0	460	10	78	12	32.0
Bt(6)	M.S.	B	3.0	460	7	80	13	27.1
VB(7)	M.S.	B	3.0	460	4	83	13	28.8

Symbol Designation: Bt (virgin bitumen); M (pentane soluble maltenes from virgin bitumen); VB (visbroken bitumen, 425°C, 150 psig, ~11 min.); S/A (Houdry 159CP silica-alumina catalyst); M.S. (Mobil Durabead-8 molecular sieve catalyst); SB (semi-batch Cat A mode); B (batch mode); f (powdered catalyst).

When temperatures were raised to 460-470°C additional yields were experienced. Results of Bt(3) and Bt(4) show good agreement between the two reactor configurations. The batch operation, requiring volatilization of products, exhibited a tendency to retain heavier materials with the coke. The results of runs Bt(3) and Bt(4) are quite encouraging because they exhibit yield and product quality equal to or better than experienced with thermal cracking.

An attempt was made to remove coke precursors by prior deasphalting. Results of cat cracking of the maltenes, which represented 90% of the virgin bitumen, are given in Run M(5). Removal of 10% asphaltenes resulted in a coke reduction of only 4%. In retrospect, this is not too surprising because the asphaltenes from Uinta Basin bitumen, although consisting of the highest molecular weight species present, also contain significant quantities of hydrogen (H/C = 1.2) and contribute to the volatiles product yield. Conversely, not all of the coke precursor aromatics are precipitated due to the effects that the naphthenic and alkyl substituents have on increasing the solubility of the aromatics. Thus, a one-to-one correlation between molecules comprising the asphaltene fraction and coke precursors does not exist.

Results of run Bt(6) suggested that substantial thermal reactions were taking place. Property data of liquids and gas analysis have strong resemblance to the thermally derived products. The thermal vs. catalytic effects are illustrated in the gas analysis for selected runs in Table 5. Compared to the thermal gases the cat cracking gases, Bt(4), exhibited a strong selectivity for production of C₃ and C₄ and gave very high yields of isobutane. Results for the run Bt(6) show some characteristics of cat cracked products but also show many similarities to the thermal products. The results of Bt(6) are presented to illustrate the difficulty which may be encountered through competitive reactions and is not intended to represent optimum results for this catalyst.

Table 5
C₁ to C₄ Gas Analysis

	<u>Thermal</u> <u>(460°C)</u>	<u>Mol-Sieve</u> <u>Run Bt(6)</u>	<u>Sl/Al</u> <u>Run Bt(4)</u>	<u>Hydropyrolysis</u> <u>(525°C)</u>
Methane	41.0	32.3	18.9	27.5
Ethane	16.5	16.1	10.3	18.3
Ethylene	15.1	5.0	4.2	5.5
Propane	10.0	15.4	12.2	23.4
Propylene	11.6	10.2	15.4	2.8
n-butane	1.3	5.4	3.3	10.6
i-butane	1.4	4.0	18.0	7.3
Butylenes	3.1	11.6	17.7	4.6

When the average molecular weight of the feed was reduced from about 700 to about 500 by visbreaking, significantly greater catalytic activity was observed (Run-VB(7)). These results are consistent with the general observation that catalytic activity was strongly enhanced if some reduction of molecular size preceded the contact with the catalyst.

The results of catalytic cracking have shown that the bitumen is highly responsive to catalytic cracking if the molecular size can be reduced to minimize diffusional limitations. It thus appears that a good catalytic cracking feedstock should be derivable from the Uinta Basin bitumen. It is quite possible, that by a more systematic and thorough search for optimum catalysts, process configurations, and process conditions considerable improvements on the results given in Table 4 can be realized.

Hydropyrolysis

The Asphalt Ridge bitumen was subjected to hydropyrolysis in a tubular flow reactor. Yields and process conditions are given in Table 6. Results show that the virgin bitumen can be converted to liquids and gases with little or no coke formation.

Virtually no change in pressure drop across the reactor was observed over the course of the 15 to 20 minute runs. These yield results suggest that molecular hydrogen has successfully inhibited the condensation reactions discussed in the section on coking.

Table 6
Hydropyrolysis Yields and Process Conditions

Reaction Conditions			Yields		
Temp. °C	Pressure psig	Residence Time (Seconds)	Weight Percent		
			Gas	Liquids	Coke
500	1500	18	17	83	0
525	1500	18	27	73	0

Elemental analysis and physical property data for the liquids are given in Table 7. Results show that little change was affected in the elemental composition and hydrogen to carbon ratio. However, physical property data reveals a dramatic increase in API gravity and a large reduction in molecular weight. The percentage hydrogen added was calculated from a material balance on hydrogen and included the amount added to the gases. The amount of hydrogen added to the system appears to be closely related to the amount of gas produced. On the average, the liquid products are slightly more condensed than the starting bitumen. The gases formed derive largely from the paraffins and alkyl substituents present. Pentane asphaltenes amounted to 3.5% of the liquids, were quite hydrogen deficient ($H/C = 0.97$), and contained a 5% nitrogen concentration.

Table 7
Hydropyrolysis Product Characteristics

	Feed	Temperature of Run	
		500°C	525°C
Carbon	86.2	86.7	86.8
Hydrogen	11.3	11.6	11.4
Nitrogen	1.1	0.8	0.8
Sulfur	0.4	0.3	0.3
Oxygen	0.9	0.3	0.3
C/H ratio	.640	.627	.639
API gravity	12.7	22.1	25.2
Average molecular weight	713	336	321
Refractive index		1.52	1.52
Wt. % H ₂ added to total products		0.8	1.2
SCF H ₂ /bbl feed		600	900

The preliminary results of the hydropyrolysis are particularly interesting because hydropyrolysis promises to be a simple process which can produce a drastic reduction in molecular weight without a high consumption of hydrogen.

Simulated Distillation

Simulated distillation results are given in Table 8 for virgin bitumen and the various liquid products. These results show significant changes in volatility were affected, even in the case of mild visbreaking. The lightest products were those from thermal cracking at 80 psig and catalytic cracking. In both cases, yields were about 74% of the charge material; however, the cat cracking run produced 4% more gases.

The catalytic cracking produced 23% gasoline. This gasoline was found to exhibit a calculated 50% point at 128°C and a calculated research octane of 78. Analytical results showed that the octane number was reduced by the presence of some low octane thermal products in the heavy gasoline range.

Table 8
Simulated Distillation
Cumulative Weight Percent

Corresponding, BMCOA Fraction(1)		Cumulative Weight Percent					
No.	Cut Pt. °C	Bt	TC(0)	TC(80)	CC	HP	VB
1	50			1.2	0.9	1.0	
2	76			2.7	2.4	2.2	0.5
3	100		1.2	5.0	8.3	4.5	1.1
4	125		2.3	7.7	11.2	7.3	1.7
5	150		4.2	11.9	14.9	10.6	2.7
6	175		6.3	16.5	18.9	13.5	4.0
7	200	0.1	8.7	21.6	22.8	17.2	5.5
8	225	0.4	11.0	26.5	27.3	20.9	7.4
9	250	1.1	14.7	33.4	32.5	25.6	10.3
10	275	2.4	19.4	40.9	38.2	30.5	13.9
11	305	5.0	25.2	50.3	46.0	37.6	18.6
12	335	7.4	32.5	60.4	54.9	44.5	24.2
13	365	10.4	40.3	69.7	62.9	51.2	29.7
14	395	13.8	49.5	78.6	71.0	58.0	35.8
15	425	17.3	58.8	86.2	78.6	64.5	41.6
16	455	21.7	68.8	91.9	85.2	71.6	48.0
17	485	27.4	80.4	96.2	92.1	77.7	55.6
18	515	32.7	90.6	98.8	96.6	82.1	62.0
19	538	39.8	96.6	100.0	99.1	84.6	67.1
Residue	>538	100	100		100	100	100
10% Point °C		362	211	146	115	145	247
50% Point °C		>538	397	303	321	359	463
90% Point °C			511	444	449	>538	>538

Symbol Designation: Bt (virgin bitumen); TC (thermally cracked @ 0 psig and 80 psig, respectively); CC (cat cracked Bt(4), Table 4); HP (hydropyrolysis, 525°C liquids); VB (Visbreaking, 475°C, 80 psig, ~8 min.).

The simulated distillation results for the hydropyrolysis liquids reveal a broad boiling point distribution. Although substantial amounts of light material are produced, certain heavier aromatics remain virtually unchanged. These aromatics are present in the hydropyrolysis liquids but went to form coke in the coking and cat cracking conversion processes. The distillation data presented here suggest that the hydro-pyrolysis liquids, with their relatively low olefin content, would make a good feed-stock for refining.

Separation into Compound Types

Separation of total liquid products into saturated, mono-aromatic, di-aromatic, and poly-polar aromatic compound types gives important information regarding the distribution of structural features. Results of the separation are given in Table 9.

Perhaps the most striking feature of these results is the high percentage of purely saturated hydrocarbons. All samples have high concentrations of higher aromatics as well, indicating a very broad distribution of compound types. The

comparatively low percentage of saturates in the hydropyrolysis liquids can be explained on the basis that nearly twice the gases were formed and 12% heavy material is present that was removed with the coke in the other two processes. Elemental analysis revealed that the vast majority of nitrogen and sulfur compounds were retained with the poly-polar aromatics. The high percentage of monoaromatics in the hydro-pyrolysis liquids seems to indicate that some hydrogenation of higher aromatics has occurred.

Table 9
Compound Type Classification of Products

Fraction	Thermal 460°C, 0 psig	Catalytic Bt(4)	Hydropyrolysis 500°C
Saturates	55.1	62.0	48.5
Monoaromatics	11.7	9.1	15.3
Diaromatics	8.4	5.5	5.6
Poly-polar aromatics	24.8	23.4	30.6
	<u>100</u>	<u>100</u>	<u>100</u>
Percent Recovery	89.6	85.3	94.8

CONCLUSIONS

The unusual chemical nature of Uinta Basin bitumen requires that examination of various primary processes and a search for optimum conversion conditions be made. The principal chemical objective in primary processing is to reduce the molecular weight with a minimum cost in light product yields and a minimum requirement for hydrogen. Coking was shown to produce high yields of liquids and gases with a low sulfur coke as a potentially valuable by-product. Temperature was shown to have a significant effect on total yields in coking but had little effect on volatiles composition. Pressure was shown to have a significant effect both on composition and yields. Catalytic cracking produced high yields of liquids and gaseous products. Further research to find optimum conditions and the most appropriate role for catalytic cracking in bitumen processing is indicated. Hydropyrolysis was shown to convert bitumen in virtually 100% yields to gases and medium volatility liquids with low consumptions of hydrogen. This process shows good potential as a viable primary processing step. Analysis revealed that the structure of products can be significantly affected by various processing sequences studied. Analytical results are highly instructive as to what must be accomplished chemically during the conversion of virgin bitumen. The structure of the products also gives important clues as to the gross mechanisms of conversion. The results of this study provide a basis for further evaluation of the most desirable approach to processing of Uinta Basin bitumen.

ACKNOWLEDGEMENTS

Appreciation is extended to Dr. Robert Beishline and students of Weber State College for the distillation of products to produce the gasoline cuts and for the dual silica-alumina column separations of the catalytically and thermally cracked products.

This work was sponsored by the U.S. Department of Energy and the State of Utah.

REFERENCES

- (1) Bunger, J. W., "Shale Oil, Tar Sands and Related Materials", T. F. Yen, ed., Amer. Chem. Soc., Washington, D.C., 121-136 (1976).
- (2) Bunger, J. W., K. P. Thomas and S. M. Dorrence, "Analysis of Compound Types and Properties of Utah and Athabasca Tar Sand Bitumens", Fuel, submitted for publication.
- (3) Bunger, J. W., Preprints, Division of Petroleum Chemistry, Amer. Chem. Soc. 22, 2, 716-727 (1977).
- (4) D. E. Hirsch, et. al., Anal. Chem. 44, 6, 915 (1972).
- (5) Bunger, J. W., S. Mori and A. G. Oblad, Preprints, Division of Fuel Chemistry, Amer. Chem. Soc. 21, 6, 147 (1976).
- (6) Bunger, J. W., D. E. Cogswell and A. G. Oblad, The Oil Sands of Canada-Venezuela, 1977. D. A. Redford and A. G. Winestock, eds., CIM Special Volume 17, 178-182 (1977).
- (7) Alexander, J. and H. G. Shimp, National Petroleum News 36, p. 537 (1944).
- (8) Bunger, J. W., D. E. Cogswell and A. G. Oblad, Preprints, Div. of Petr. Chem., Amer. Chem. Soc. 22, 3, 1008 (1977).
- (9) R. Ramakrishnan, J. Shabtai and A. G. Oblad, Preprints, Div. of Petr. Chem., Amer. Chem. Soc. 23, 1, 159 (1978).
- (10) Eastwood, S. C., C. J. Plank and P. B. Weisz, Proceedings of the 8th World Petroleum Congress, 245 (June, 1971).
- (11) Rim, J. J., "Chemical Characterization of Molecular Sieve Catalysts", Ph.D. Thesis, Department of Fuels Engineering, University of Utah, 113, (1974).

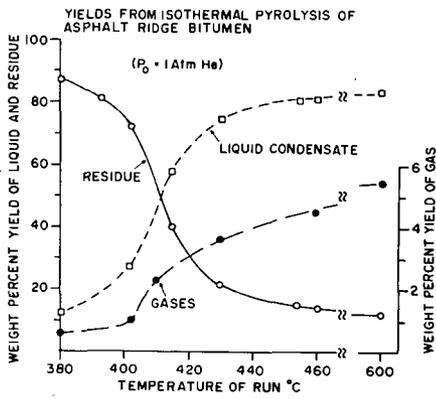


Fig. 1

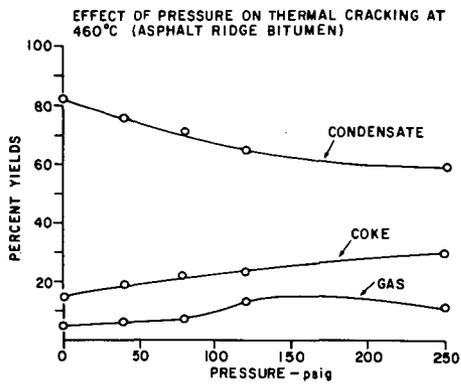


Fig. 2

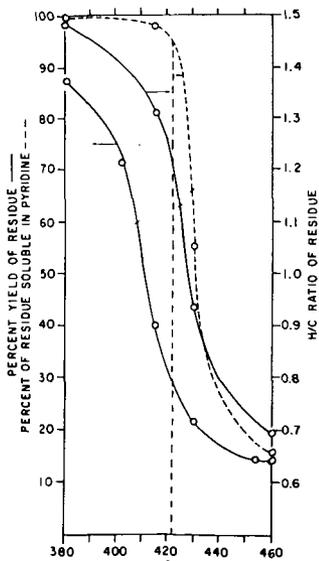


Fig. 3

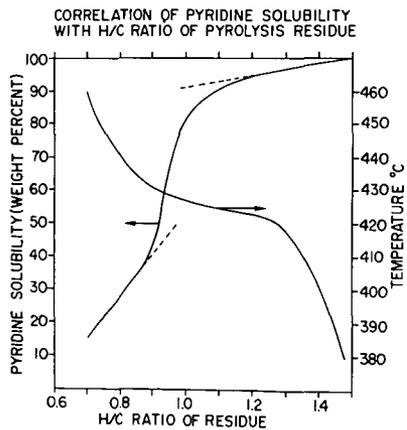


Fig. 4