STEAM PYROLYSIS OF SHALE AND PETROLEUM GAS OIL MIXTURES

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ABSTRACT

Light gas oil and heavy gas oil from Paraho shale oil and their mixtures with a petroleum light gas oil were pyrolyzed in the presence of steam at 880-900°C and contact times between 60 and 90 milliseconds in a nonisothermal bench scale pyrolysis reactor. Blending of petroleum LGO into the shale oil feeds provided product yields that were the weighted linear combination of the yields of the individual components of the blends. Partial denitrogenation and a pronounced decrease in the rate of coke deposition on the reactor walls was observed when petroleum gas oil was blended with the shale gas oils.

INTRODUCTION

Steam pyrolysis of hydrocarbons in tubular reactors is the key process for production of gaseous olefins that serve as major raw materials for the petrochemical industry. While the recent concern regarding cost, supply and availability of petroleum derived feedstocks for petrochemicals production has subsided, at least temporarily, the long term outlook remains sufficiently clouded that the present breathing spell affords an opportunity to examine potential alternative feed sources. These concerns have lead to several investigations[11,12,13] of shale oil as feed for olefins production. Indeed, the M. W. Kellogg Company have recently completed a study[4] to evaluate shale oil fractions and hydrotreated shale oil fractions as feed for olefins production in conventional pyrolysis. The authors concluded from this study that shale oil distillates produce ethylene, propylene and benzene yields similar to those from petroleum, however coking rates were unacceptably high for all except the lightest fraction. Mild hydrotreating improved the tube wall fouling rate of the shale oil naphtha and light gas oil fractions to the range typical of petroleum light gas oil (LGOP); that for the heavy gas oil (HGOS) was improved but still unacceptable. In another study[5], more extensive prerefining by hydrotreating reduced the heteroatom concentration and provided yields of olefins comparable with or exceeding those from petroleum fractions. Substantially lower ethylene yield was obtained from severely hydrotreated TOSCO II distillate due to steam reforming during pyrolysis. Coking rates and liquid products yields were not reported.[5]

While it is clear that shale oil has the potential to eventually be a major source of hydrocarbon for both fuel and chemical production, the near term prospects call for limited production from subsidized programs. Since dedicated refineries and petrochemical plants cannot be justified to utilize this material, it will be necessary either to upgrade the shale oil to its petroleum equivalent or to improve its processability by blending it with conventional petroleum. Indeed, even when shale oil production begins to expand as petroleum declines, the blending of these to produce feedstocks will presage the smooth evolution of shale oil specific processing technology.

The literature on steam pyrolysis of shale oil distillates is limited but adequate to indicate its potential as feedstock, particularly after some prerefining. The literature on steam pyrolysis of petroleum distillates is extensive. However, no literature exists in the cocracking of shale and petroleum distillates. Cocracking of petroleum derived feedstocks has been shown to provide expected product yields, that is, yields which are the linear combination of yields of the individual components of the blend. However, coking behavior of such feedstock mixtures showed[7] remarkable effects where the coking rate of a suitably blended feedstock mimicked the rate of the less coking feed component.

The present study was undertaken to determine the cracking and coking behavior of shale oil distillates under conditions of millisecond pyrolysis and the effects of admixture of petroleum LGO on these properties. Particular interest was paid to liquid products.

EXPERIMENTAL:

Apparatus:

The bench scale pyrolysis furnace and flow system have been described previously in detail.[8,9,10]

The experimental arrangement for pyrolysis comprised a feed system, vaporizer preheater, an electrically heated furnace and product recovery system. Liquid feedstocks were fed from Ruska metering pumps into the vaporizer where they were mixed with superheated steam before passing through the preheater and into the reactor. The reaction zone was an annulus between a reactor tube and a coaxial thermowell, both of 310 stainless steel. Temperature profiles were measured with a calibrated chrome-alumel thermocouple manually driven along the length of the reactor. On leaving the reaction zone, the process stream was rapidly cooled by admixture with a recycled stream of cooled product gas.[6] The quenched products were further cooled against chilled water in an indirect heat exchanger and water condensate plus liquid products were separated by means of a small cyclone separator which was an integral part of the product gas recycle quench system.

To avoid formation of carbon oxides due to steam reforming reactions, as was observed in other studies with hydrotreated shale oil distillate,[5] the walls of the stainless steel reactor were maintained in a catalytically inactive form by sulfiding and the pyrolysis experiments were performed in the presence of 50 ppm sulfur which was introduced to the system as ethyl mercaptan contained in the process feed water.

At the completion of a pyrolysis run the amount of coke deposited on the reactor tube wall during the run was determined by burning out with a steam-air mixture.[10] To accomplish this, the pyrolysis system is modified by replacement of the quenching system with a CO_2 collection system. Air and water rates are controlled by rotameters and needle valves. Contaminant CO_2 is removed from both the water and bottled air used in the burn-off. After the combustion gases leave the reactor, the bulk of the unreacted water is removed with a room temperature trap, and residual water vapor is removed with a drying agent. The dry gases then enter a CuO bed maintained at high temperature to convert any CO to CO_2 and is then passed through another drying agent prior

to being absorbed in a preweighed ascarite/magnesium perchlorate tube. Total carbon deposited in the reactor is calculated from the weight of CO_2 collected. A gas chromatograph in the system periodically measures the CO_2 level in the combustion gas stream to determine when a burnout is completed.

After a pyrolysis run/burnout cycle is completed, the reactor tube is conditioned for the next run by reducing and sulfiding the reactor walls with a flow of hydrogen and hydrogen sulfide.

Product Analysis:

Two gas samples, for duplicate analysis by mass spectrometry, were taken in the first third and final third of the run period. Results of duplicate mass spectrometric determinations fell within the established limits for this analytical method, and the averaged values were then used.

Liquid product, after separation from process steam condensate, is assayed into gasoline (36-218°C), light fuel oil (218-343°C) and heavy fuel oil (343°C$^+$) by gas chromatographic simulated distillation (GCSD) as defined in ASTM method D-2887. Yields of individual C_6-C_8 aromatics (BTX) were obtained by G.C.

Total organic nitrogen present in the C_5^+ liquid products from selected runs was determined by the Kjeldahl method. Boiling range distribution of nitrogen was determined using a gas chromatographic simulated distillation method modified by use of a detector specific for organic nitrogen. The method involves injecting a sample into a chromatographic column equipped with effluent splitter leading to a Thermionic Specific Detector (TSD) for nitrogen and a Flame Ionization Detector (FID) for carbon. The area from the TSD for each time interval is recorded on magnetic tape while the area from the FID over the entire chromatogram is recorded separately. From these data and previously determined calibration factors, nitrogen concentration and boiling range distributions may be determined using the conventional GCSD temperature vs time plot. A Varian 3700 G.C. equipped with TSD and FID was employed for this work.

Feedstocks

Shale light gas oil (LGOS) and heavy gas oil (HGOS), prepared by distillation from Paraho shale oil, were samples of the same materials used in an earlier steam pyrolysis study (4). An Arabian light gas oil comprised the petroleum derived light gas oil (LGOP) used in this study. Blends of shale gas oils and the petroleum gas oil were prepared to contain 20, 40, 60 and 80 wt% petroleum gas oils. Thus a total of ten feedstocks were examined. Inspection data for these feedstocks and blends are summarized in Table I.

DATA AND DISCUSSION

Runs were carried out at maximum temperatures (Tm) of a parabolic temperature profile (9) between 744°C and 899°C with steam dilution corresponding to steam/hydrocarbon weight ratios between 0.5 and 1.0. All runs were isobaric at

a total pressure of 13-15 psig (90-105 kPa). Most of the runs were carried out under millisecond contact times (less than 0.1 seconds); however, one run on each of the neat shale gas oils (LGOS and HGOS) was carried out at conventional contact time (about 0.3 seconds) to determine the effect of this variable on product yields. With the exception of those runs where excessive reactor coking (Runs 11,12 & 13) forced early run termination, material balances fell between 95% and 100%.

Tables II and III summarize the individual run conditions and the observed yields and conversions for all runs with light and heavy shale gas oils (LGOS and HGOS), respectively. Runs No. 1 and 10 were carried out under conventional contact time conditions similar to those used in an earlier study.[4] Results for both the neat LGOS and HGOS are in excellent agreement with the earlier data.[4]

Comparison of runs 1 and 2 show the effect of conventional vs millisecond conditions on pyrolysis of neat LGOS. These data show an enhancement in selectivity to ethylene as described previously[3] for operations at increased temperature and decreased contact time. A similar comparison (Runs 10 & 11) for pyrolysis of heavy shale gas oil (HGOS) was precluded by the rapid coking of the reactor.

Pyrolysis of Shale-Petroleum Gas Oil Blends:

Gaseous Product:

In runs No. 3,4,5,6 and 7, blends of an Arabian light gas oil (LGOP) and shale light gas oil (LGOS) were pyrolyzed under closely identical operating conditions. Conversion and product yields changed monotonically in the mixtures between those for neat LGOS and for neat LGOP. Figure 1 illustrates the changes in conversion and yields of major gaseous products for the LGOS/LGOP feedstock blends. Yields of major products for these blends are the arithmetic weighted average of the yields for the individual feedstocks in the blends. Accordingly, full yield benefits normally attainable from separate steam pyrolysis of shale LGO may be realized by cocracking the shale feed with petroleum gas oil in an existing gas oil pyrolysis furnace. Since the shale oil feed, in this case, is intrinsically poorer in terms of ethylene yield, a proportional penalty in furnace ethylene capacity will obtain. To some extent, this penalty can be compensated by increasing severity or decreasing hydrocarbon partial pressure, e.g. runs no. 2 vs 3.

Due to the higher coking rates attendant to the pyrolysis of the shale heavy gas oil (HGOS), fewer data are available for this feedstock. Figure II summarizes the conversion and yields of major gaseous products for cocracking HGOS/LGOP blends. While these data are limited to blends at the low end of the HGOS content, extrapolation to 100% HGOS provides an estimate yield that might be realized from high severity pyrolysis of neat HGOS. The extrapolated results appear reasonable in view of those obtained from HGOS under milder conditions (Run 10).

Liquid Products:

Gasoline and fuel oil become major products of olefins production processes when liquid hydrocarbon feedstocks are used in steam pyrolysis. These, so-called, co-products comprise from 35-55 wt% of the feed depending on feed properties and pyrolysis conditions. Consequently, these liquid co-products exert a large effect on the economics of naphtha and gas oil pyrolysis for both petroleum or shale oil derived feedstocks.

With the exception of a related study (4) which reports the gasoline and fuel oil yields from pyrolysis of shale oil distillates, no literature exists on the effects of operating conditions on yields or on the quality of these liquid products. In the present work both of these topics were investigated.

Yields of boiling range fractions of the pyrolysis liquids as determined by gas chromatographic simulated distillation (GCSD) (ASTM method D-2887) are summarized in tables II and III. Gasoline yield from LGOS appears to be somewhat greater than that for the petroleum gas oil studied. This result may not be unique, however, since gasoline yield is known to depend on characteristics of various petroleum gas oils. It is of greater interest that the yield of potential motor gasoline appears to change little with either pyrolysis severity or with composition of the blended feedstocks. Since gasoline yields for LGOS are comparable to those of petroleum feedstock, it is of interest to determine the quality of this for use as motor fuel. A special gas chromatographic method was used to provide data needed for calculation of Research Octane Number (RON) of the gasoline fraction in the pyrolysis liquid from Run #9 (60% LGOS/40% LGOP). According to this method, a cutting column is used to separate the gasoline from the higher boiling materials which are discarded in a back flush. The gasoline cut is fed to a capillary column for quantitative analysis and identification of the components in the gasoline. The Research Octane Number calculated from this G.C. analysis using the method of Anderson et al (1) was found to be 99.4.

Light and heavy fuel oil yields are greater for the shale oil feedstocks and these vary linearly with composition for the blended feedstocks.

Nitrogen Distribution:

Shale oil as well as its distillate fractions have a high content of organic nitrogen, typically between 1 and 2 wt percent. Since nitrogen is a catalyst poison for current refinery operations and a detriment to liquid fuel products, most schemes for utilization of shale oil require upgrading by severe hydrotreating. While steam cracking (a non catalytic process) is not inhibited by organic nitrogen, the quality and hence the value of liquid products are adversely affected. Typically in steam pyrolysis of liquid feedstocks approximately one half of the feed is converted to gaseous products which contain no organic nitrogen. It becomes very interesting then to determine to what extent, if any, this gasification involves net denitrogenation of feedstock and also to determine the distribution of remaining nitrogen among the liquid products.

Boiling range distribution of organic nitrogen in the LGOS feedstock and in the pyrolysis liquid products from runs with neat LGOS (Run #8) and with LGOS/LGOP blend (Run #9) were determined by gas chromatography. Results are illustrated in Figure III and summarized in Table IV.

TABLE IV

Nitrogen Distribution in Pyrolysis Liquid Fractions

Run No.	8		9	
	Wt% of Feed	Wt% N	Wt% of Feed	Wt% N
Liquid Fraction				
C_5-218°C (Liquid only)	17.0	2.34	17.9	0.26
C_5-218°C Total gasoline[a]	21.7	1.83	21.6	0.22
218-354°C Fuel Oil	21.1	2.72	20.6	0.71
354°C + Hy Fuel Oil	11.9	4.08	10.7	4.23
Whole Liquid Product	50.0	2.92	49.2	1.39
% Nitrogen Balance[b]	98.6		72.5	
Apparent Denitrogenation %	1.4		27.5	

(a) Includes C_5,C_6 gasoline components contained in the gas samples.

(b) Total Nitrogen in Liquid Products/N in Feed.

In Figure III, the results of gas chromatographic determination of cumulative nitrogen content as a function of boiling point (retention time) is plotted against the analogous data for cumulative carbon (GCSD) in the liquid samples. In this way, the retention time is eliminated from the plot and a distribution curve relating the nitrogen content with the carbon content is obtained in which the slope of the curve at any point is the concentration of nitrogen in the fraction of the sample boiling below that point. Thus a straight line with unit slope (45°) indicates uniform nitrogen concentration in all fractions of the total liquid.

Nitrogen in the LGOS feedstock is fairly uniformly distributed over the entire boiling range (Figure III-a). The liquid produced from pyrolysis of neat LGOS contains almost all of the organic nitrogen from the feed and this nitrogen is also broadly distributed over the boiling range of this product (Figure II-b). In this case, there is a small trend toward increasing nitrogen concentration with increasing boiling range.

A pronounced change in nitrogen distribution (Figure III-c) is found in the liquid product from cracking a blend of LGOS and LGOP. In this case, the nitrogen concentration is strongly shifted into the heavier portion of the pyrolysate and a significant part of the feed nitrogen appears to have been removed. Partial denitrogenation by steam pyrolysis provides a clear economic benefit from cocracking shale oil/petroleum blends. Additional benefits may be derived from the reduced nitrogen content of the gasoline and light fuel oil products which, although they still require upgrading, can be denitrogenated with less severe hydrotreating than would be required for denitrogenation of the entire feedstock or the products from separate cracking of LGOS. Disposition of the heavy fuel is an equivalent problem in either case. In any event, cocracking of shale oil and petroleum feedstocks offers an interesting alternative to severe hydrotreating of shale oil.

Reactor Tube Wall Fouling:

The high fouling rate exhibited by heavier shale oil fractions has been identified (4) as being the major hurdle that must be overcome in its utilization as feedstock for olefins production. Partial hydrotreatment of the pyrolysis feed resulted in reducing the fouling rate (4) but not to an acceptable level, especially for the heavy gas oil (HGOS). Severe hydrotreatment, on the other hand, reduced fouling adequately (5) but at considerable expense due to high hydrogen consumption and the high pressures required (2).

Inhibition of tube wall coking in pyrolysis furnace tubes by cocracking in the presence of a low coking hydrocarbon has recently been described (7). It has now been found that an analogous phenomenon occurs in the cocracking of shale gas oils in admixture with a low coking petroleum gas oil. Figure IV illustrates this effect for both the HGOS/LGOP and LGOS/LGOP feed blends. With the addition of less than 40% LGOP to LGOS, the fouling rate of the feedstock combination is substantially reduced and closely approaches the rate characteristic of the petroleum gas oil itself. Substantially more LGOP must be added to suppress the fouling rate of HGOS. This is in accord with the intrinsically higher coking propensity of the heavier shale feedstock.

While the fouling behaviour of the HGOS and LGOS blends with LGOP is in qualitative agreement with the coke inhibition index (CII) concept,(7) it does not agree quantitatively with the correlation developed for petroleum feedstocks. High organic oxygen and nitrogen contents of the shale liquids exert a positive influence on their coking properties as evidenced by the observed (5) decrease in coking rate upon removal of these heteroatoms.

According to the observed coking behavior of mixtures of shale and petroleum distillates, acceptably low coking rates can be expected from blends containing significant quantities of shale liquid. This provides an interesting alternative to hydrotreating prior to pyrolysis.

CONCLUSIONS:

Shale oil distillates may be a substitute feed for olefins production in high severity pyrolysis. Cocracking in admixture with suitable petroleum derived feedstocks offers a potential alternative to costly hydrotreating by providing partial denitrogenation of the liquid fuel coproducts as well as by largely overcoming the barrier due to the inherent excessive tube wall fouling characteristics of the shale oil liquids.

REFERENCES

1. P. C. Anderson, J. M. Sharkey & R. P. Walsh, J. Inst. Petr. 58 ,84 (1972).

2. R. F. Anderson, et al, D.O.E. Report No. FE-2315-25, (May 1978).

3. B. P. Ennis, H. P. Boyd & R. Orriss, Chem. Technol. 5 ,(11) 693 (1975).

4. H. J. Glidden & C. F. King, Chem. Eng. Prog. 76 ,(12) 47 (1980).

5. C. F. Griswold, A. Ballut, H. R. Kavianian, D. F. Dickson & V. F. Yesavage, Chem. Eng. Prog. 75 ,(9) 78 (1979).

6. J. Happel & L. C. Kramer, Ind. Eng. Chem., 59 ,39 (1967).

7. H. P. Leftin & D. S. Newsome, U.S. 4,176,045, Nov. 27, 1979.

8. H. P. Leftin, D. S. Newsome, T. J. Wolfe & J. C. Yarze, "Industrial and Laboratory Pyrolysis", Am. Chem. Soc. Symposium Series 32 ,373 (1976).

9. H. P. Leftin and A. Cortes, Ind. Eng. Chem. Proc. Des. & Dev. 11 ,613 (1972).

10. D. S. Newsome & H. P. Leftin, Chem. Eng. Prog. 76 ,(5) 76 (1980).

11. C. G. Rudershausen & J. B. Thompson, Prepr. Div. Pet. Chem. Am. Chem. Soc. 23 ,(1) 241 (1978).

12. E. G. Shultz, J. B. Guyer & H. R. Linden, Ind. Eng. Chem. 47 ,2479 (1955).

13. P. D. Smith, P. F. Dickson & U. F. Yesavage, Prepr. Div. of Pet. Chem. Am. Am. Chem. Soc. 23 ,(2) 756 (1978).

TABLE I

FEEDSTOCK INSPECTIONS

TYPE	SHALE	LIGHT GAS OIL BLENDS			PETROLEUM	SHALE	HEAVY GAS OIL BLENDS			
Feed Designation	LGOS	L-1	L-2	L-3	LGOP	HGOS	H-1	H-2	H-3	H-4
Wt% Shale oil	100	80	60	40	0	100	80	60	40	20
Wt% Petroleum LGO	-	20	40	60	100	0	20	40	60	80
ASTM Dist'n (°F)										
IBP	424	-	-	-	335	662	-	-	-	-
10%	458	-	-	-	427	714	-	-	-	-
30%	497	-	-	-	478	756	-	-	-	-
50%	536	-	-	-	512	797	-	-	-	-
70%	572	-	-	-	546	844	-	-	-	-
90%	614	-	-	-	599	889	-	-	-	-
E.P.	637	-	-	-	638	918	-	-	-	-
°API	28.9	31.0	33.1	35.3	39.9	19.7	23.3	27.2	31.2	35.4
Molecular Wt(1)	210	212	213	215	218	371	325	290	261	238
Elemental Analysis (Wt%)										
C	85.16	85.39	85.61	85.84	86.29	85.41	85.59	85.76	85.94	86.15
H	12.36	12.57	12.79	13.00	13.43	11.38	11.79	12.20	12.61	13.02
N	1.49	1.20	0.90	0.60	N.D.	2.14	1.71	1.28	0.86	0.43
S	0.76	0.63	0.49	0.35	0.09	0.64	0.53	0.42	0.31	0.20
O	1.78	1.42	1.07	0.71	N.D.	1.64	1.31	0.98	0.66	0.33
H/C Atom Ratio	1.73	1.75	1.78	1.80	1.85	1.59	1.64	1.69	1.75	1.80

(1) Calculated

TABLE II

STEAM PYROLYSIS OF SHALE LIGHT GAS OIL
AND MIXTURES WITH PETROLEUM LIGHT GAS OIL

Run #	1	2	3	4	5	6	7	8	9
Feed Composition:									
Wt% LGOS	100	100	100	80	60	40	0	100	60
Wt% LGOP	0	0	0	20	40	60	100	0	40
Temp. max (°C)	766	899	899	899	899	899	899	882	879
Log Mean O (Sec)[a]	0.32	0.073	0.086	0.086	0.088	0.093	0.091	0.090	0.094
H_2O/Oil (g/g)	1.00	1.02	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Outlet Pressure (Psig)	13	13	15	15	15	15	15	15	15
Conversion (1-C_5+)	49.8	48.0	46.1	46.4	51.6	53.1	61.6	44.4	46.9
Yields (Wt%)(Basis Output)									
H_2	0.44	0.73	0.72	0.68	0.72	0.73	0.84	0.55	0.59
CH_4	8.70	10.9	10.7	9.87	10.6	10.8	11.5	9.08	8.21
C_2H_2	0.06	0.88	0.82	0.76	0.74	1.05	0.90	0.29	0.32
C_2H_4	15.6	20.4	18.1	18.7	21.9	22.7	27.5	16.3	19.0
C_2H_6	3.63	2.01	2.37	2.32	2.49	2.39	2.59	2.70	2.13
C_3H_4	1.14	0.65	0.64	0.60	0.56	0.63	0.82	0.38	0.31
C_3H_6	11.6	7.56	7.63	7.93	8.79	8.94	10.2	8.90	9.36
C_3H_8	0.60	0.18	0.08	0.11	0.15	0.30	0.12	0.31	0.40
C_4H_6	3.28	3.23	3.26	3.37	3.84	3.59	4.78	3.15	3.05
C_4H_8	4.71	1.49	1.67	1.93	1.93	1.89	2.20	3.24	3.45
C_4H_{10}	0.10	0.01	0.15	0.13	0.02	0.01	0.17	0.06	0.09
C_5+ (liq)	49.0	51.3	53.2	52.9	48.1	46.6	38.2	54.7	52.9
Coke	1.24	0.72	0.70	0.66	0.31	0.28	0.21	0.35	0.21
Gasoline (C_5-218°C)	20.6	20.2	21.3	19.3	21.2	21.2	18.7	21.7	21.6
Fuel Oil (218°-343°C)	20.4	19.0	20.0	20.3	17.1	17.3	13.0	21.1	20.6
Fuel Oil (343°-454°C)	6.43	7.49	7.89	8.26	6.27	5.34	4.45	8.48	8.71
Pyrolysis Tar (454°C+)	1.57	4.61	4.01	5.08	3.52	2.76	2.05	3.43	1.98
BTX[b]	4.3	4.4	5.8	6.2	7.4	7.5	7.0		5.1
Tube Wall Fouling:									
Run Length (Min.)	237	89	111	69	120	120	120	131	135
Wt of Coke Product (gm)	1.03	0.85	1.59	0.96	0.79	0.71	0.54	1.41	0.83
Coking Rate (mg/min)	4.53	9.60	14.3	13.8	6.59	5.91	4.51	10.8	6.15
Nitrogen Wt%									
Gasoline	-	-	-	-	-	-	-	1.83	0.22
Fuel Oil	-	-	-	-	-	-	-	2.72	0.71
Fuel Oil + Tar	-	-	-	-	-	-	-	4.08	4.23
Nitrogen Balance Prod/Feed (%)	-	-	-	-	-	-	-	98.6	72.5
RON (C_5-218°C)									99.4

(a) Temperatures between 600°C and Tmax.
(b) Benzene, Toluene, O,M & P Xylene, Ethylbenzene and Styrene.

TABLE III

STEAM PYROLYSIS OF SHALE HEAVY GAS OIL AND MIXTURES WITH PETROLEUM LIGHT GAS OIL

Run #	10	11	12	13	14	15	16
Feed Composition:							
Wt% HGOS	100	100	80	60	40	20	0
Wt% LGOP	0	0	20	40	60	80	100
Temp. Max (°C)	744	899	899	899	899	899	899
Log Mean O (Sec)[a]	0.33	0.07	0.07	0.07	0.073	0.071	0.063
H_2O/Oil (g/g)	1.00	0.75	0.74	0.76	0.75	0.77	0.79
Outlet Pressure (Psig)	13	15	15	15	15	15	15
Conversion ($1-C_5^+$)	36.5	(b)	(b)	(b)	52.7	59.4	66.6
Yields (Wt%) Basis (output)							
H_2	0.45	-	-	-	0.67	0.79	0.82
CH_4	9.66	-	-	-	9.74	11.0	11.4
C_2H_2	0.05	-	-	-	0.81	1.10	0.81
C_2H_4	10.6	-	-	-	23.2	26.6	28.1
C_2H_6	3.74	-	-	-	2.17	2.36	2.42
C_3H_4	0.42	-	-	-	0.53	0.74	1.01
C_3H_6	7.51	-	-	-	9.06	10.2	12.6
C_3H_8	0.52	-	-	-	0.20	0.25	0.30
C_4H_6	1.45	-	-	-	3.85	4.34	5.57
C_4H_8	2.00	-	-	-	2.26	2.08	3.40
C_4H_{10}	0.08	-	-	-	0.16	0.03	0.01
C_5^+(liq)	49.2	-	-	-	46.9	40.4	33.3
Coke	14.3	-	-	-	0.40	0.20	0.13
Gasoline (C_5-218°C)	-	-	-	-	23.4	19.4	19.9
Fuel Oil (218°-343°C)	-	-	-	-	12.8	12.0	8.77
Fuel Oil (343°-454°C)	-	-	-	-	6.04	5.40	3.35
Pyrolysis Tar (454°C$^+$)	-	-	-	-	4.66	3.60	1.28
BTX[c]	-	-	-	-	5.5	3.6	7.1
Tube Wall Fouling:							
Run Length (min)	77	12	29	47	100	123	120
Wt of Coke Produced (gas)	4.27	0.56	1.06	0.94	0.80	0.49	0.32
Coking Rate (mg/min)	55.5	46.6	36.5	20.0	9.97	3.98	2.65

(a) Temperatures between 600°C and Tmax.
(b) Run terminated due to reactor pressure drop buildup from rapid coking.
(c) Benzene, Toluene, O,M & P Xylene, Ethylbenzene and Styrene.

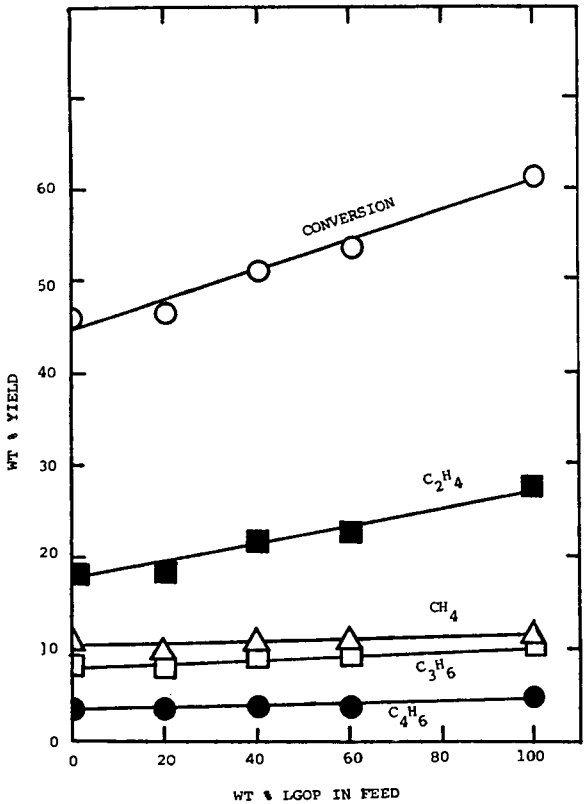

FIGURE 1. PYROLYSIS OF SHALE & PETROLEUM GAS OIL BLENDS (LGOS+LGOP). PRODUCT DISTRIBUTIONS.

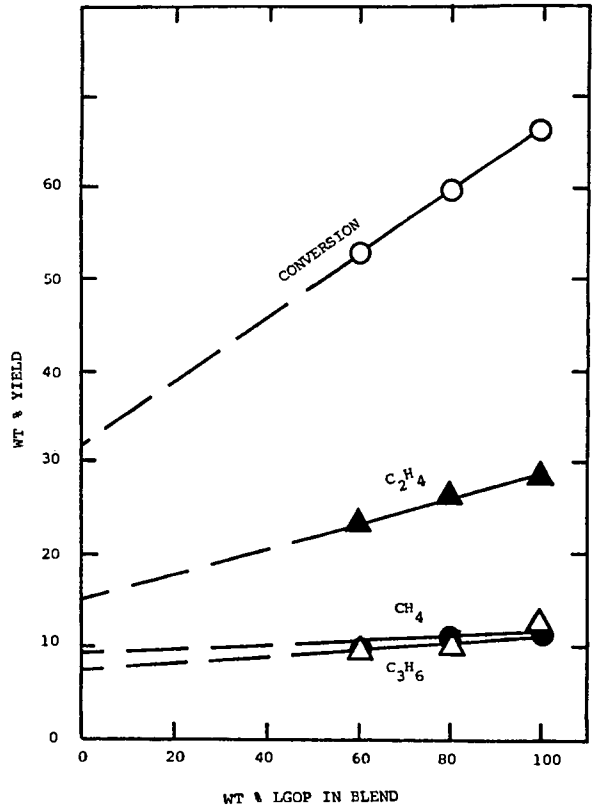

FIGURE 2. PYROLYSIS OF SHALE+PETROLEUM GAS OIL BLENDS (LGOS + LGOP). PRODUCT DISTRIBUTION.

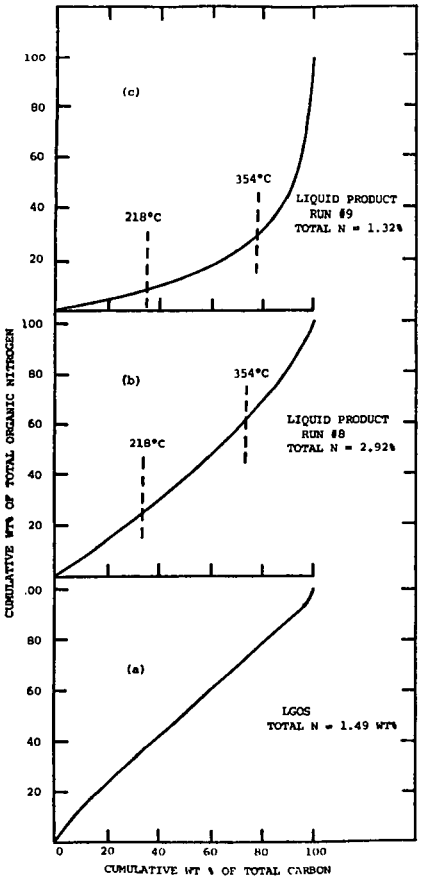

FIGURE 3. ORGANIC NITROGEN DISTRIBUTIONS

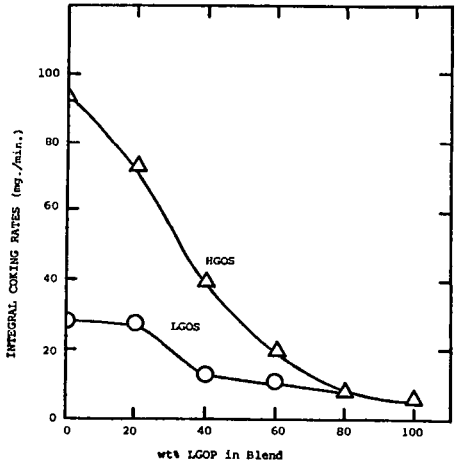

FIGURE 4. REACTOR FOULING RATES
SHALE/PETROLEUM GAS OIL BLENDS