

THERMAL CRACKING OF SHALE GAS OIL UNDER A HYDROGEN ATMOSPHERE

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INTRODUCTION

Reserves of shale oil in the Green River Formation of Colorado, Utah, and Wyoming in deposits 10 or more feet thick that average 10 or more gallons of shale oil per ton are estimated to be in excess of two trillion barrels.¹ This oil represents a vast, untapped source of energy. Although there is no commercial shale-oil industry in the United States today, it is generally felt that shale oil will be a valuable supplement to petroleum reserves in the future. Shale oil is produced from the solid organic matter occurring in oil shale by heating the shale to about 900° F or higher in a retort.² Crude shale oils prepared from the Green River shale by many retorting methods are heavy, hydrogen-deficient oils and contain very little material boiling in a gasoline range.³ Therefore, some sort of cracking process is necessary to convert the higher boiling portions of crude shale oil to gasoline.

An investigation of the thermal cracking of shale gas oil under a hydrogen atmosphere has been undertaken in a batch reactor as part of a program designed to study the effect of reaction variables on high pressure hydrogenation of shale oil. Kinetic parameters obtained in this investigation suggest that the initial phases of the cracking reaction involve the more reactive, straight-chain structures, whereas later stages involve aromatic structures. There also appears to be a change in the reaction mechanism as the reaction proceeds.

Other reaction parameters--including hydrogen consumption, hydrocarbon gas and naphtha yields, and nitrogen and sulfur concentration in the unconverted gas oil--have been correlated as functions of cracking conversion.

EQUIPMENT AND EXPERIMENTAL PROCEDURES

The experimental thermal cracking studies of shale gas oil have been carried out in a 2.7-liter Aminco rocking reactor. Details of the experimental equipment and procedure have been reported.⁴

The first step in the experimental procedure was to add 500 grams of shale gas oil to the reactor. Hydrogen was added to the reactor until all air had been flushed from the reactor and the pressure in the system reached 1,000 psi. The reactor was then heated by an electric heating mantle to the desired run temperature and held at this temperature for a predetermined period. At the end of this period the reactor was allowed to cool to room temperature.

The gases produced during a run were analyzed using an Orsat apparatus and a Beckman GC-2A gas chromatograph, and their molecular weights were measured using glass density balloons. The

liquid product was removed from the reactor and water washed to remove low-boiling nitrogen, oxygen, and sulfur compounds. The oil was diluted with toluene and distilled in a Dean-Stark apparatus using the procedure outlined in ASTM D 95-62 in order to eliminate any water remaining in the sample after the water wash.⁵ The toluene added to the liquid shale-oil product during the Dean-Stark distillation and the naphtha boiling below 410° F were removed from the mixture by atmospheric distillation. That portion of the shale-oil product that boiled below 555° F was then separated from the unconverted shale gas oil by a vacuum distillation. The nitrogen concentration in the unconverted gas oil was determined using a Kjeldahl nitrogen analysis procedure, and the sulfur concentration was determined using the procedure outlined in ASTM D 129-58.^{5,6}

RAW MATERIALS

The shale gas oils used in this study were derived from a Green River (Colorado) shale in a gas combustion retort at Rifle, Colorado. Properties of the shale gas oils are presented in table 1.

TABLE 1. - Properties of shale gas oil feed stocks

Property	Feed stock No.	
	1	2
Gravity, °API	23.0	23.0
Nitrogen, wt pct	1.78	1.83
Sulfur, wt pct	.62	.70
Distillation, I.B.P., °F	420	405
10 vol pct, °F	567	580
50 vol pct, °F	700	720
95 vol pct, °F ^a	800	800
Boiling above 555° F, wt pct	91.7	95.2

^a Estimated from simulated distillation by GLC.

EXPERIMENTAL RESULTS AND CALCULATIONS

The extent to which shale gas oil was thermally cracked under a hydrogen atmosphere has been correlated with time and temperature using a parameter called cracking conversion, X_c . Cracking conversion is defined by the relationship:

$$X_c = \frac{W_F - W_P}{W_F} \quad (1)$$

where W_F = grams of shale gas oil that boil above 555° F in the gas oil charged to the reactor, and W_P = grams of shale gas oil that boil above 555° F in the reactor product.

If it is assumed that the cracking reaction is first order with respect to the unconverted gas oil ($1 - X_c$), the integrated rate expression takes the form:

$$\ln(1 - X_c) = -kt, \quad (2)$$

where $(1 - X_c)$ = the unreacted gas oil boiling above 555° F,
 k = reaction rate coefficient, and
 t = reaction time.

The experimental data obtained in this study have been plotted in the form suggested by equation 2 in figure 1 for reaction temperatures from 600° to 825° F. The times shown in figure 1 are uncorrected for heat-up and cool-down times. The curvature shown in these plots was expected because others have reported this same effect in studies of the cracking of petroleum gas oils. Weekman,⁷ for example, suggests that a similar curvature, which he obtained in a plot of catalytic-cracking results, may be due to the multiplicity of reactant molecular types in the original petroleum charge as well as to catalyst deactivation.

The variation of the reaction rate coefficient (k) with temperature (T) can be described by the Arrhenius equation:

$$k = A \exp(-E_a/Rt). \quad (3)$$

However, this equation does not account for the observed effect of cracking conversion on the reaction rate coefficients. In order to introduce this effect, it has been necessary to compare reaction rate coefficients at the same cracking conversion level but at different reaction temperatures. The results of these comparisons at selected conversion levels have been used to calculate Arrhenius activation energies (E_a) and Arrhenius frequency factors (A) as functions of shale-gas-oil cracking conversion. The relationship that provided the best, least-squares fit between the experimental activation energy and conversion was

$$E_a(\text{kcal/mole}) = 29.4 + 135.5 X_c. \quad (4)$$

Thus the Arrhenius activation energy increases linearly from 29.4 kcal/mole at the onset of cracking to 124.3 kcal/mole at a conversion of 0.70 for X_c , a fourfold increase. This increase in activation energy could indicate that the cracking reaction changes from one involving straight-chain structures to one involving aromatic structures as conversion increases.

The relationship that provided the best fit between the experimental frequency factor and conversion was

$$A(\text{min}^{-1}) = \exp(16.71 + 91.45 X_c). \quad (5)$$

Figure 2 shows the dependency of the 750° F reaction rate coefficient, calculated using equations 3, 4, and 5 upon conversion values. Thus we see a decrease of three orders of magnitude in the coefficient as conversion increases from zero to 0.70. The calculated values at these two conversion levels are $4.9 \times 10^{-3} \text{ min}^{-1}$ at zero conversion and $4.5 \times 10^{-6} \text{ min}^{-1}$ at a conversion of 0.70.

The agreement between the conversions predicted by using the Arrhenius equation, modified to account for the effect of conversion, and the experimentally measured conversion is shown in table 2. The corrected times listed in this table take into account the fact that the cracking reaction proceeds to a certain extent during the time that the reactor is being heated to and cooled from the nominal reaction temperature.

Although the literature on thermal cracking of petroleum does not report data relating the dependency of E_a and of A upon conversion, Nelson⁸ has reported their values at conversions between 0.20 and 0.25 for a petroleum gas oil. He reported an activation energy of about 55 kcal/mole and the value for shale gas oil as calculated by equation 4 is 56.5 kcal/mole. Table 3 compares the specific rate coefficients as reported by Nelson for a petroleum gas oil with those calculated using equations 3, 4, and 5 for shale gas oil. These results suggest that at a conversion of 0.20 shale gas oil may be somewhat more refractory than petroleum gas oil. However, at zero conversion, distillation data suggest that petroleum gas oil is more refractory than shale gas oil. For

TABLE 2. - Comparison of experimental and calculated conversions

Run temperature, °F	Corrected time, ^a hours	Conversion, X _c	
		Experimental	Calculated
600	0.90	0.031	0.011
	3.32	.011	.031
	6.29	.037	.045
	8.35	.029	.053
700	.42	.004	.036
	.81	.009	.059
	3.32	.089	.126
	6.37	.131	.164
	8.29	.123	.179
750	.38	.032	.074
	.92	.210	.128
	3.32	.264	.226
	6.34	.308	.279
	8.29	.315	.302
	8.51	.369	.305
825	.1.20	.508	.394
	3.39	.642	.563
	6.41	.707	.665
	8.41	.699	.706
	8.55	.706	.709

^a Corrected for the amount of reaction taking place during the time the reactor is being heated to and cooled from nominal reaction temperature.

TABLE 3. - Comparison of reaction rate coefficients at a conversion of 0.20 for shale gas oil and petroleum gas oil

Temperature, °F	Reaction rate coefficient, min ⁻¹	
	Shale gas oil	Petroleum gas oil ^a
700	1.1 × 10 ⁻⁴	1.8 × 10 ⁻⁴
750	6.8 × 10 ⁻⁴	1.0 × 10 ⁻³
825	8.0 × 10 ⁻³	1.5 × 10 ⁻²

^a See reference 8.

example, in the Bureau of Mines routine distillation⁹ used in crude petroleum analysis, the atmospheric distillation is carried to a temperature of 527° F; whereas, to avoid cracking in the analysis of crude shale oil, the atmospheric distillation is carried to a temperature of only 392° F. One is led to conclude, then, that shale oil contains materials that crack very readily as well as materials that crack with extreme difficulty.

The exponential relationship best relating conversion to frequency factor (equation 5) is suggestive of the exponential relationship between the theoretical frequency factor from the theory of the activated complex and the entropy of activation.¹⁰ Because of this similarity, entropies of activation were calculated for the shale-gas-oil cracking reaction at 825° F. These entropies of activation ranged from a -32 e.u. at low conversion to +89 e.u. at high conversion. This range in entropies of activation may be compared with values obtained by Wiser,¹¹ who observed values ranging from -63 e.u. at low conversion to -12 e.u. at high conversion during coal pyrolysis. Entropy of activation values of about -30 e.u. have been reported for polymerization reactions.¹² Condensation reactions might also be taking place. Thus the assumed polymerization and condensation products of the early part of the reaction would add to the multiplicity of the aromatic structures in the original charge oil. These proposed, additional aromatics would have their influence in the latter stages of the cracking reaction.

Other reaction parameters obtained in this study have been correlated as functions of cracking conversion. The amount of hydrogen consumed in the reaction is correlated as a function of cracking conversion in figure 3. Figure 4 shows the weight percent of the charge that was converted to gasoline and to hydrocarbon gases. The results in figure 3 suggest that there was a net production of hydrogen below a conversion of about 0.2, and that only above this conversion was the rate of consumption of hydrogen greater than the rate of production. This consumption of hydrogen at higher conversion levels undoubtedly resulted from the hydrogenation of low-molecular-weight fragments to form the quantities of hydrocarbon gas and gasoline shown in figure 4. For example, at a conversion of 0.70, the combined quantities of hydrocarbon gases and gasoline amount to 70 weight-percent of the original oil.

The weight-percents of nitrogen and sulfur in the unreacted gas oils are shown in figures 5 and 6 as functions of conversion. Because the nitrogen in shale gas oil is primarily in heterocyclic aromatic structures,¹³ the increase in nitrogen in the unreacted gas oil can be explained by postulating that the nitrogen heterocyclics do not react to form lower boiling materials as rapidly as does the nonaromatic portion of the gas oil. This lack of any thermal denitrification of shale gas oil under hydrogen pressure was also observed by Koros.¹⁴

On the other hand it appears from the results shown in figure 6 that up to conversion levels of 0.30, the sulfur-containing molecules are more easily cracked to lower boiling compounds than are the nonsulfur compounds. It also appears that at conversion levels greater than 0.30, the sulfur-containing compounds crack at about the same rate as does the bulk of the remaining shale gas oil.

SUMMARY

The results obtained in this work show that the rate at which shale gas oil cracks at constant temperature under hydrogen pressure decreases as the extent of cracking conversion increases. The values for the reaction rate coefficient for the 750° F cracking reaction decrease from $4.9 \times 10^{-3} \text{ min}^{-1}$ at zero conversion to $4.5 \times 10^{-6} \text{ min}^{-1}$ at a conversion of 0.70. Calculated Arrhenius activation energies range from 29.4 kcal/mole at the onset of conversion to 124.3 kcal/mole at a conversion of 0.70. These variations could indicate a change in reacting species as the reaction proceeds. For example, initial phases of the shale-gas-oil cracking reaction could involve

long, straight-chain structures, whereas later phases of the reaction involve aromatic structures. Entropies of activation, calculated for the reaction at 825° F, ranged from -32 e.u. at low conversions to +89 e.u. at high conversions. The results could indicate a shift in reaction mechanism from polymerization reactions at low conversions to decomposition reactions at high conversions. Hydrogen-consumption data, product-yield data, and the rates of denitrification and desulfurization also suggest changes in the reacting species as well as in the reaction mechanism.

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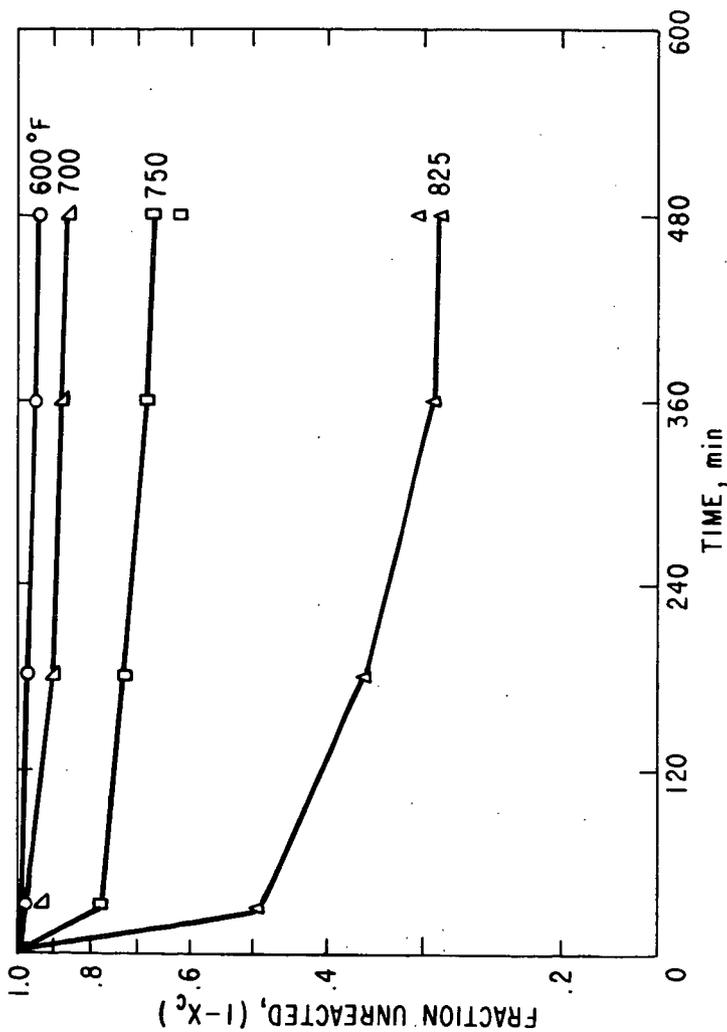


FIGURE 1.-First-Order Plot for Shale Gas Oil Cracking.

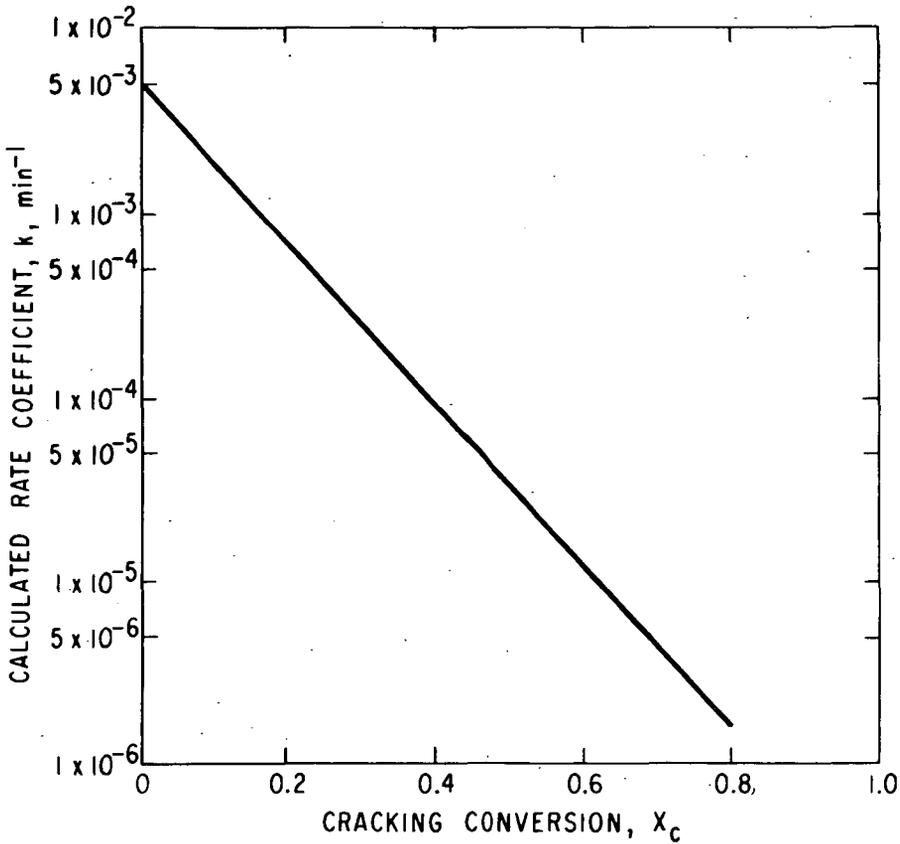


FIGURE 2.—Effect of Conversion on Shale Gas Oil Cracking Reaction Rate Coefficients at 750° F Cracking Temperature.

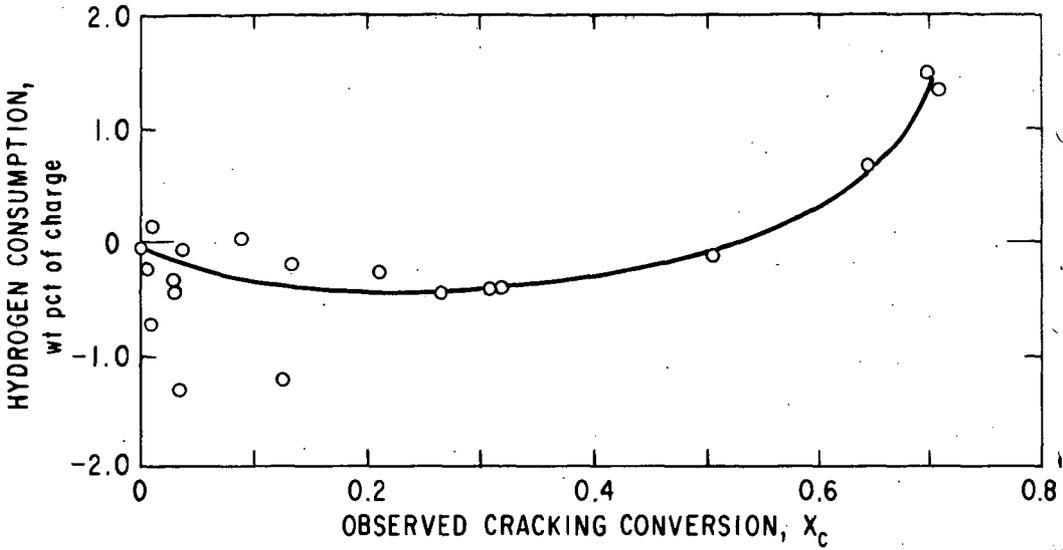


FIGURE 3.-Hydrogen Consumption.

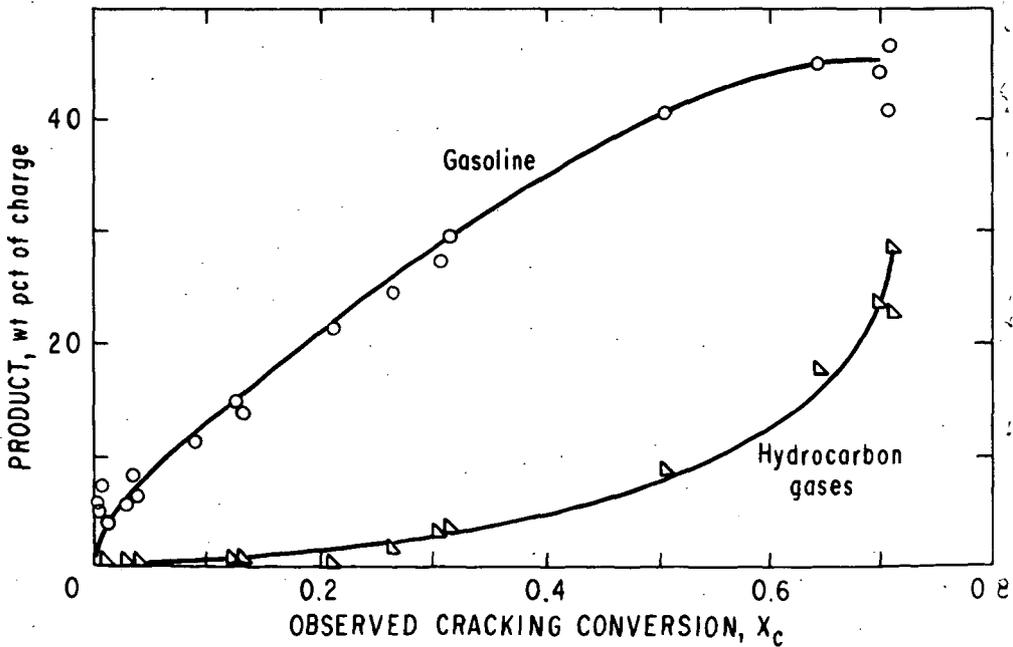


FIGURE 4.-Hydrocarbon Gases and Gasoline Production.

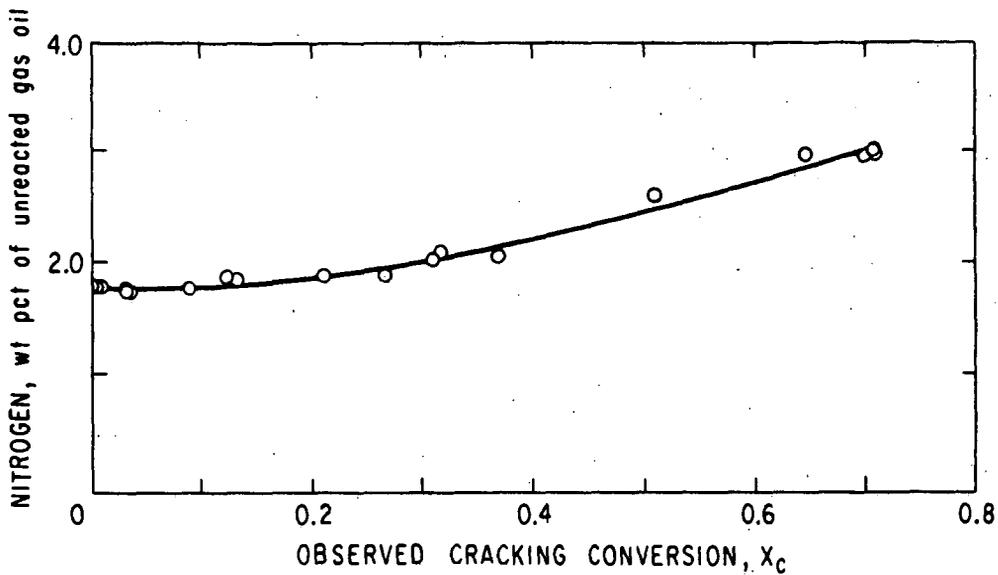


FIGURE 5.—Nitrogen Concentration in Unreacted Shale Gas Oil.

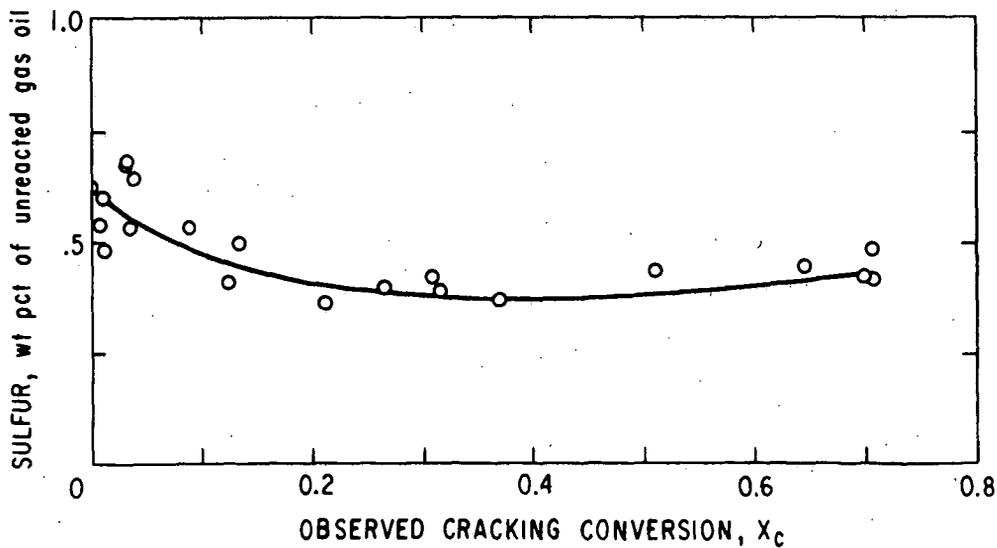


FIGURE 6.—Sulfur Concentration in Unreacted Shale Gas Oil.