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Effect of Gamma Radiation Upon the Hydrocracking of a
Heavy Paraffin

Work done at Columbia University, New York City 27, N.Y.

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Introduction

Although a great deal of work dealing with the effect of ionizing radiation on hydrocarbons at low temperatures has been reported, very little has been published regarding the behavior of these systems at elevated temperatures and pressures. It has been well established that at room temperature pure hydrocarbons ultimately cross link and form insoluble gels (1,2). Recent work has shown that at elevated temperatures the reverse process seems to occur; i.e. degradation of the hydrocarbon molecules (3). If the latter findings are correct, radiation may then be regarded as a potential tool for those industries that customarily employ high temperatures, high pressures, and catalysts, to initiate reactions. An obvious application would be in the gasification processes where coal, waxes, and petroleum stocks are hydrocracked to natural gas substitutes. It was with this potential use in mind that the present investigation was undertaken.

Apparatus -

All runs were conducted in a static system. The reactor, was a type 303 stainless steel pressure vessel rated at 15,000 psia when cold and about 8,000 psia when at working temperatures. A lipless pyrex test tube served as a vessel liner and as a container for the wax samples. The capacity of the reactor with liner was 90 ml., and the entire system (reactor, liner, piping, etc.) had a capacity of 108 ml. Temperature in the autoclave was measured with a copper-constantan thermocouple whose junction was located about one third of the distance up the inside of the reactor. A gage was used whose

nominal pressure reading extended to 5,000 psi. Before using the gage it was calibrated with a dead-weight gage over the range of 200 to 3,000 psia, and was set to read true absolute pressure at 1,500 psia. The maximum deviation over the calibrated range was 20 psia. A blowout disc rated at 4,200 psia was incorporated in the system as a safety precaution. A 750 watt hollow cylindrical heater was employed that afforded a 1/4 in. air bath all around the reactor. Temperature within the reactor was maintained within $\pm 10^\circ\text{F}$ of the desired level.

The Co^{60} radioisotope used has a half-life of 5.26 years and emits gamma rays of 1.17 and 1.33 m.e.v. per disintegration. The radiation facility is in the form of a pit, 20 in. x 20 in. square and 40 in. deep below ground level, into which a bundle of four 12 in. x 2 in. x 1/8 in. Co^{60} bars can be lowered. In situ dosimetry was accomplished with the Fricke dosimeter. The dose rate was 46,000 R/hr.

Two analytical systems were used, one for gaseous and one for solid products. The small amount of liquid residue produced in some runs was not analyzed. The gaseous products were analyzed with a Perkin-Elmer Model 154 Vapor Fractometer. A combination of packed columns was used that made possible the quantitative analysis of mixtures of hydrogen, nitrogen, argon, and hydrocarbons from C_1 to C_5 . A Leeds and Northrup Speedomax Recorder was used in combination with the fractometer. The Perkin-Elmer Company claims for its instrument an analytical reproducibility of $\pm 0.25\%$ and an accuracy of $\pm 1-2\%$, both figures being absolute percentages. The actual experimental reproducibility was found to be ± 0.59 .

For those runs where a solid wax residue remained, the wax was examined for evidence of physical change by taking the melting point of the sample. The equipment used was a scaled-down version of the ASTM D87-42 apparatus for the determination of paraffin wax melting points (4). An ASTM 144F paraffin melting point thermometer having a range of 100-180°F and a maximum scale error of 0.2°F was used in the apparatus. In order to check the results obtained by the melting point method, several wax samples were examined for evidence of change by running them, and corresponding control samples, in a standard Beckmann boiling point elevation apparatus. Toluene was chosen as the solvent for these analyses.

Procedure - Experimental

A large quantity of paraffin wax was melted in a 1000 ml. Erlenmeyer flask and while molten, about twenty ml. was poured into each of thirty clean, lipless, pyrex test tubes that had previously been numbered and tared. The samples were then carefully degassed under vacuum. The wax was purchased from the Fisher Scientific Company and had a melting point of 126°F. From a published correlation between melting point and molecular weight (5), it was possible to estimate the molecular weight of this straight chain paraffin to be about 345.

Before charging, the reactor was cleaned thoroughly with a wire brush and then it and all other parts of the system were flushed with acetone. The reactor was then pressure tested, the sample was inserted, and then the system was thoroughly sparged with nitrogen.

To make a run the system was inserted in its heating jacket and the power was turned on. The duration of the initial heating period varied between 30 and 50 minutes, the latter duration being necessary to reach 900°F. The automatic temperature controller then maintained the temperature level to within $\pm 10^\circ\text{F}$ of the desired setting. At the conclusion of a run the final temperature and pressure were recorded and the reactor was withdrawn from the heater and allowed to cool. About three hours were required for the reactor to cool from 900°F to ambient temperature.

The gas analysis was complicated by the fact that due to a small amount of liquid present after each run, there existed an equilibrium between the gaseous and the liquid products, hence the composition of the gas is a function of the number of samples taken. Figure 1 shows the variation of product composition with reactor sampling pressure. This difficulty was circumvented in most of the analyses by obtaining, with a syringe, a 50 ml gas sample at a reactor pressure of 500 ± 5 psia and another at 200 ± 5 psia. In this way several analyses of a gas sample could be made in order to determine the reproducibility of the analysis, and it would also be possible to compare the product composition of different runs, provided that they were compared for the same sampling pressure. Toward the end of this investigation a small gas cylinder of 857 ml. capacity became available, and by using it as a reservoir into which all of the reactor gas was bled, it

was possible to isolate virtually all of the product gas from the liquid residue in the reactor, and thus arrive at a composition for the total amount of gas produced.

Discussion of Results

Figure 2 shows a plot of reactor temperature vs. pressure as suggested by Shultz and Linden (6). The graph clearly shows that until about 860°F is reached, nothing happens other than heating of the gas in the reactor. At 860°F cracking begins, and because of the additional gas formed, the pressure begins to rise rapidly. The maximum duration of a cracking run was only 5 hours which was not sufficient to attain equilibrium. Figure 2 shows a typical plot of pressure vs. time for a run in progress. Because of the nearly constant rate for run times exceeding 3 hours, no attempt was made to obtain data for very long durations. Instead, runs of 2, 3, 5, and 5 hour duration were made, with the greatest number of duplicate runs at 2 hours. Figure 3 shows typical product spectra for the cracking runs. It is readily seen that the products are almost identical for radiation and for non-radiation runs. This tends to indicate that the same type reaction prevails for both processes, and that if radiation has any influence, it serves merely as an accelerator.

From the experimental data a value of S , designated as the moles of gas formed per gram of wax initially present, was computed for each run. In computing S it was necessary to know n , the number of moles formed during the reaction. Accordingly, a correction factor z was introduced so that at 900°F, the expression $PV = z(nRT)$ would be valid. The factor was computed as the ratio of the actual system pressure at 900°F, (determined by heating a gas with no wax in the reactor) to the perfect gas pressure at 900°F for a comparable quantity of gas. The value of the factor was taken to be 0.78. Figure 4 shows a plot of S vs. run time wherein all the calculated S values for 2 hour radiation runs were averaged to give a point, and the same procedure was followed to obtain the other points shown. The points shown represent the averages of over thirty runs. The initial hydrogen pressure in each run was about 1000 psi.

It is of interest to determine the value of G , which is the number of gas molecules formed per 100 ev. of incident radiation. Figure 5, shows a plot of G vs. run duration. The G values are in the range of 60,000 to 80,000, and are seen to decrease with increasing run duration. The experimental G values are low when compared with the results obtained by Lucchesi, et al. (10) who report a value of about 560,000 for the same conditions. However, the latter value was determined for a short radiation exposure administered during the first minute of cracking. It has been shown in these experiments that the cracking rate is very rapid at first and therefore the G value would necessarily be quite high for shorter duration runs. Figure 5 shows that the G value curve is asymptotic with the ordinate axis and it can be seen that for a run duration of about one minute, the value of G would be appreciably higher than 80,000.

Since the points considered until now have indicated that radiation served to accelerate the cracking reaction, it is important to determine if this conclusion can also be reached by a statistical analysis of the data. The value chosen for comparison between runs was S , the moles of gas formed per gram of wax charged. Since the number of paired sets of radiation and non-radiation runs was small, it was necessary to employ a non-parametric test (7). A suitable one is the Wilcoxon Signed Rank Test (8). By means of it one is able to show that at the 0.025 level of significance radiation has served to increase cracking yields. Or, put in different words, there is a possible error of 2 1/2 percent when one concludes that radiation increases cracking yields.

Acknowledgement

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FIGURE II

HEAT-UP CURVE for RUN #56

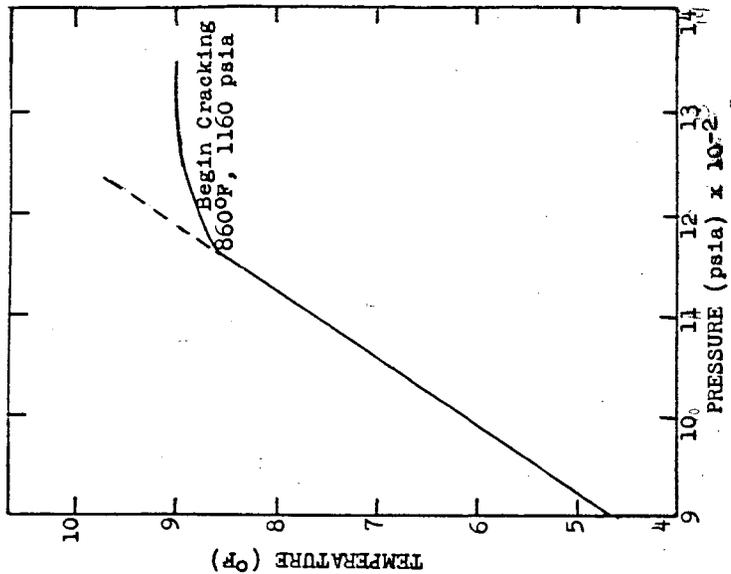


FIGURE I

VARIATION of PRODUCT COMPOSITION
With REACTOR SAMPLING PRESSURE

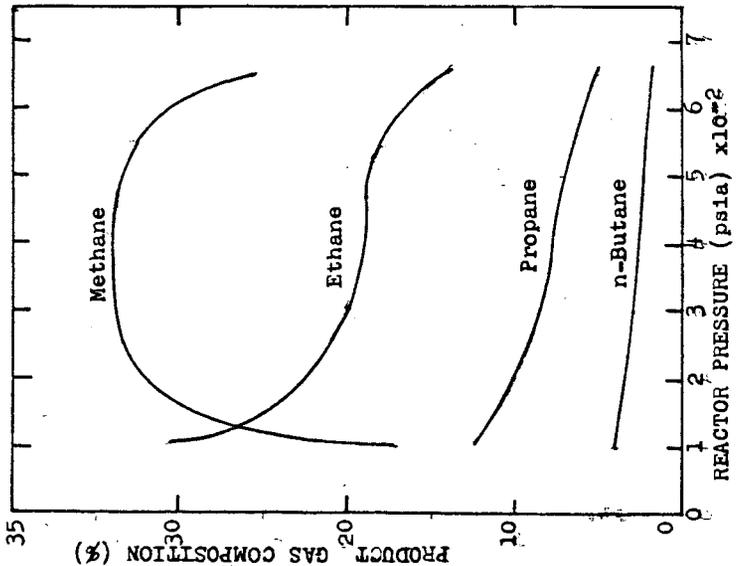


FIGURE IV
VARIATION of S with DURATION
of 900°F HYDROCRACKING RUNS

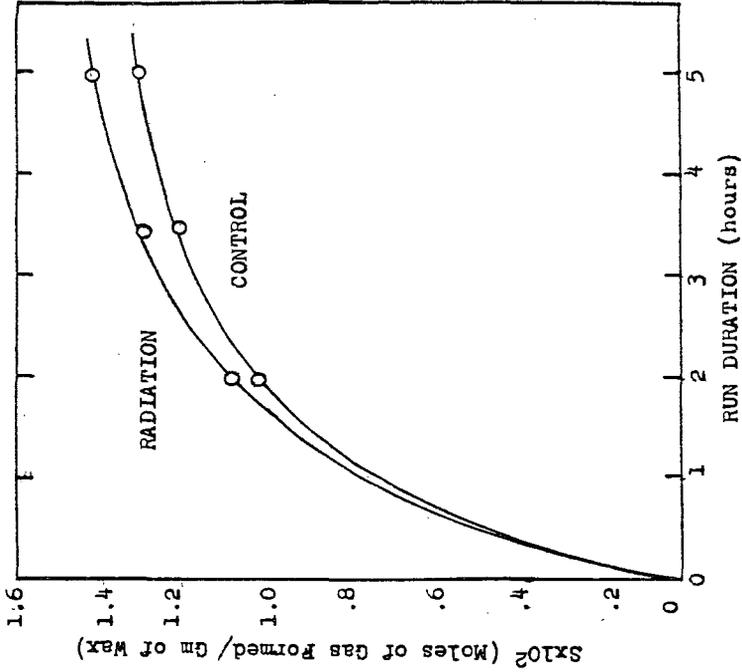


FIGURE III
TYPICAL SPECTRA of PRODUCTS
FORMED by HYDROCRACKING

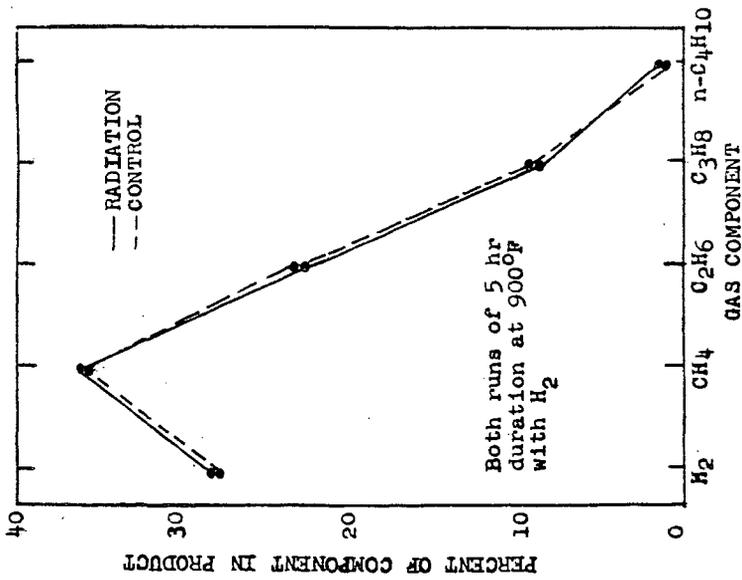


FIGURE V

VARIATION of G with DURATION
of 900°F HYDROCRACKING RUNS

