NOTATION

c = specific heat of new phase

$F_o(t) = -\left.\frac{dT}{dx}\right|_{x=0}$

k = thermal conductivity of new phase

$L = \Lambda/cT_s$

$p = \delta^2$

$\dot{p} = d\delta^2/d\tau$

t = time

T = absolute temperature of new phase

T_w = wall temperature

T_s = fusion temperature

$U = T/T_s$

$U_w = T_w/T_s$

x = distance from plate

Greek Letters

α = thermal diffusivity, $k/\rho c$

$\delta(t)$ = distance from plate to phase boundary

$\delta^*(\eta) = \delta/\sqrt{\tau}$ dimensionless melt (or frost) thickness

$\eta = \frac{C F_o \sqrt{\tau}}{\Lambda}$, dimensionless thermal boundary layer thickness

$\lambda = x/\delta$, dimensionless distance coordinate

Λ = latent heat of fusion

ρ = density of material in contact with plate

$\tau = \alpha t$

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Nuclear Radiation-Induced Cracking of *n*-Hexadecane

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A representative paraffin hydrocarbon in the gas oil range, *n*-hexadecane, has been irradiated in the Industrial Reactor Laboratories' 5 mw. nuclear research reactor. In the vapor phase radiation-induced cracking proceeded efficiently, and G values* for radiation conversion of *n*-hexadecane were 200 to 1,200 at temperatures near 750°F. Total conversions of *n*-hexadecane were less than 3 wt. % and were due only in part to the radiation effect. The distributions of products which were obtained were similar to those which result from thermal cracking of *n*-hexadecane. There were however significant increases in the yields of hydrogen, reductions in the yields of very light hydrocarbons and small yields of high molecular weight products. At temperatures above 850°F. extensive thermal cracking obscured the effects of radiation.

In liquid phase radiation-induced cracking at 750°F. conversions of *n*-hexadecane up to 15 wt. % have been obtained at liquid spaces velocities near 4 v./hr./v. In many exposures nearly one-half of this conversion was attributed to the direct utilization of radiation. The corresponding G values were 30 to 60. The products obtained have been accounted for by adding together the products which would be expected from a radiation-induced reaction producing primarily dimer, from radiation-initiated chain propagated cracking, and thermally initiated chain cracking. The product distribution from these reactions can be changed by variation of the cracking temperature and/or radiation dose.

Nuclear reactors built to produce electric power are now competitive in high fuel-cost areas of the United States. Nuclear reactor technology, under continuing development, may in the near future be applied to the design of reactors which will be used for chemical or petroleum processing. In addition kilocurie sources of Co-60 and Cs-137 are available, and techniques for their application are being developed.

Radiation processing will become of commercial interest when nuclear radiation energy can be employed more economically than other energy forms to sustain established processes. In addition radiation processing may be of commercial interest if unique and valuable products can be produced. Growth in nuclear radiation processing thus depends strongly upon the basic information obtained in research in radiation chemistry and upon development of the ability to use large nuclear radiation sources.

The radiation chemistry of hydrocarbons, studied extensively at ambient temperatures (*1, 2, 3, 4, 5*), has more recently been studied at elevated temperatures (*6, 7, 8*). Radiation-induced cracking in the vapor phase was emphasized at elevated temperatures, since it was anticipated that the radiation might effectively be utilized by initiating free-radical chain types of reactions. High radiation yields were reported at intermediate (*6*) and high temperatures (*8*). Although these high yields have been reported, thermal cracking tended to mask radiation effects at high temperatures, while at intermediate temperatures and short residence times conversions were low. It gen-

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* Molecules *n* hexadecane converted per 100 ev. of energy absorbed.

erally has been concluded that high G values are obtainable in vapor phase radiation-induced cracking, and product distributions are nearly identical to those obtained in thermal cracking. It was noted that large radiation doses were less effectively utilized than small doses.

In the present study several exposures were made to investigate the vapor phase cracking of *n*-hexadecane at intermediate and high temperatures. Radiation doses were much higher than those used in other investigations. In addition many liquid phase exposures were made. Thermal conversions were minimized in these liquid phase exposures, even for long residence times where radiation doses were high. Under these conditions radiation conversions were significant when total conversions reached 15 wt. %, and considerable control over product distribution was possible.

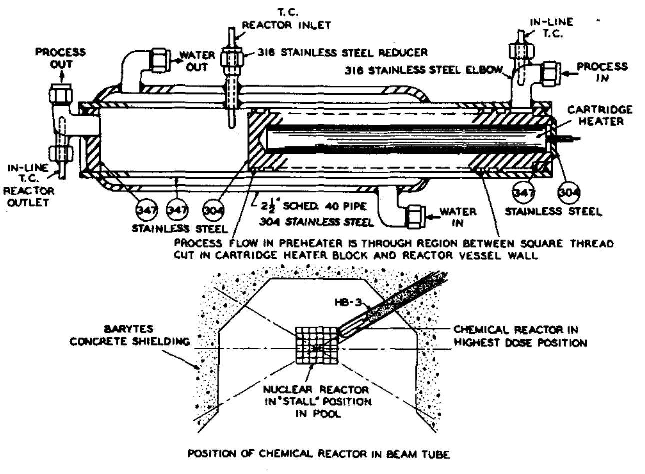
EXPERIMENTAL

Equipment

The equipment used in this study was a continuous flow chemical processing unit, the reactor of which was placed within a 6-in. diameter beam tube at the Industrial Reactor Laboratories 5-mw. pool type of nuclear research reactor. Three in-line thermocouples provided information concerning temperatures in the process stream. Their positions are shown in Figure 1. One of the couples measured the temperature of the process stream as it entered the preheater. The other two couples measured the temperature of the process stream upon its entrance to the reaction vessel and just after it leaves the reaction vessel.

Figure 1 shows the chemical reactor in its highest dose position in the beam tube and details of its design. It was used in conjunction with portable consoles which housed process and instrument portions of the processing unit and which were positioned on the reactor room floor adjacent to the beam tube. The chemical reactor was a cylindrical stainless steel pressure vessel housed within and at the end of an aluminum cylinder which was selected to fit the beam tube. Lead and concrete, sufficient to provide the required biological shielding, were also placed in this tube behind the reaction vessel. Process flow lines, water cooling lines, electrical leads, and thermocouple leads passed through this shielding. Process lines were routed and sized in a manner to reduce reaction outside the reaction vessel.

During liquid phase exposures liquid filled the reaction vessel to an overflow point. Overflow was through the exit process tube which was attached off-center to the end of the reaction vessel. The liquid volume which was to be held up could be changed by rotating the aluminum cylinder and the contained reactor. Thus the dose received by the process stream could be varied at constant nuclear reactor power and constant unit throughput.



POSITION OF CHEMICAL REACTOR IN BEAM TUBE

Fig. 1. Details of chemical reactor and its position in nuclear reactor beam tube.

With this method of operation two phases existed in the reaction vessel during what have been designated as liquid phase exposures. Liquid occupied from 21 to 79% of the vessel volume. Greater than 98% of the radiation energy was absorbed in the liquid.

The aluminum cylinder containing the reaction vessel could be withdrawn from the nuclear reactor core face for a distance of up to 46 cm. This movement provided a method by which the dose rates could be varied without changing the nuclear reactor power level. The method was particularly useful for vapor phase exposures. Withdrawal or insertion was accomplished by use of a positioning mechanism mounted at the operations end of the beam tube assembly.

The unit was capable of processing 1 liter of liquid charge per hour at temperatures up to 1,000°F. and at pressures up to 1,000 lb./sq.in. gauge.

N-hexadecane, Humphrey-Wilkinson technical grade, was charged to the unit through a gear pump fed from calibrated burettes. Products were recovered in a system consisting of a condenser, a high pressure liquid-gas separator, a low pressure liquid-gas separator, a back pressure regulator, liquid level control valve, liquid product receiver, gas meter, and gas holder.

To protect the experimental equipment and the adjacent nuclear reactor, temperatures, pressures, and temperature recorder power were monitored. It was arranged that signals arising under particular conditions of temperature or pressure would shut down the processing unit. Signals arising from other preselected conditions were relayed to the nuclear reactor control console through a special signal panel. These signals indicated an alarm condition or scrammed the nuclear reactor. Each of the several signals was simulated prior to start of the nuclear reactor each week and its action verified. No unanticipated scram of the nuclear reactor occurred at any time during operation of the experimental equipment.

Analyses

For each *n*-hexadecane exposure separate gas and liquid product analyses were combined to obtain a complete product spectrum. Gas samples were analyzed with a two-column, two-detector chromatograph. The first column, 50 ft. of *n*-propyl sulfone dimethyl sulfolane, was used to separate noncondensable gases from product hydrocarbons and the hydrocarbons (up to five carbon atoms per molecule) from one another. The second shorter column separated oxygen, nitrogen, methane, and ethane. Liquid samples were analyzed with a temperature programed chromatograph. The column was 12 ft. of glass microbeads coated with 0.5% silicone grease. Hydrocarbon products ranging from three carbon atoms per molecule to thirty-two carbon atoms (*n*-hexadecane dimer) were measured.

Direct measurements were made of the *n*-hexadecane remaining in the liquid products, and from these measurements *n*-hexadecane conversions were calculated. It was necessary to reduce the *n*-hexadecane response by diluting the liquid samples with benzene. The diluted samples were then examined with the chromatograph, and the peak heights were compared with those obtained from samples of known *n*-hexadecane concentration run consecutively. These measurements of *n*-hexadecane conversion were inherently difficult, since the conversions generally were small (1 to 20%) and the values for this conversion were based upon the difference of two large chromatographic responses. The error in the conversion value was minimized by averaging the responses obtained in a number of repetitive traces.

Yields of products were determined with smaller errors. The concentration of products in the liquid samples generally were close to 100 millimoles/liter, and the error in measurement of these concentrations was near 3%. At the limit of detectability in these samples, 1 millimole/liter, the error was greater than 20%. Hydrocarbon products in the gas samples were detectable down to a concentration of 0.05%.

The carbon atoms contained in the *n*-hexadecane that was converted were compared with those contained in the indicated yields of products. Carbon accounted for in the prod-

Table 1. Batch Exposures at North Face of Reactor Core

Reactor grid position 56, core configuration 44S + 7A + 7B

Material exposed	Length of exposure, min.	Dose, Megarads	Dose rate Megarads/hr. (5-mw. reactor power)
Sodium formate solution	5	20.8	250
ASTM grade *n*-hexadecane	35	146	250
Technical grade *n*-hexadecane	37	154	250

ucts was usually 70 to 100% of that determined from *n*-hexadecane conversions. This variation and failure to fully account for carbon atoms is related primarily to errors in *n*-hexadecane conversion measurements, to a lesser extent to a failure to observe all products of the conversion.

Dosimetry

Primary measurements of dose rates, against which later comparisons were made, were done in the nuclear reactor pool at the face of the reactor core. These measurements involved the exposure of a solution of sodium formate and titration of the resulting sodium oxalate with acid permanganate (*9*). The sodium formate dosimeter was chosen since it can be used in metal systems, the radiation products are stable, and because doses up to 200 megarads can be measured. Most importantly aqueous sodium formate is very much like *n*-hexadecane in radiation stopping power. Results of the sodium formate exposure and exposures of several samples of *n*-hexadecane are shown in Tables 1 and 2. Dose rates determined from the sodium formate exposure were shown to be reliable by using them in calculations of the G values for hydrogen production from *n*-hexadecane, for exposures made in the same reactor pool position. The G value for hydrogen production was found to be in good agreement with that reported from exposures of straight chain saturated hydrocarbons (*1, 10*) with a variety of different radiation sources. The radiation at the nuclear reactor core face and in the beam tube, contributing to energy absorbed in the process materials, was primarily gamma radiation and fast neutrons. The sodium formate dosimeter is responsive to both of these. In addition a thermal neutron flux near 10^{13} neutrons/sq.cm./sec. (at 5-mw. reactor operation) was present.

Dose rates at several positions of the chemical reactor within the beam tube, comprising a dose rate profile, were measured with a technique involving the exposure of the *n*-hexadecane. *N*-hexadecane was pumped through the chemical reactor. Gamma heat deposited in chemical reactor materials was removed by cooling water which flowed through the chemical reactor jacket. At low dose rates this cooling effectively maintained reactant temperatures near 100°F., and no question concerning the temperature effect on the dosimetry measurements arose. However at high dose rates gamma heating was large, and the process-out temperature rose to nearly 500°F.

To estimate the dose rate at each position in the beam tube yields of hydrogen, light hydrocarbons, and dimer were measured and compared with yields obtained from batch exposures of *n*-hexadecane. These batch exposures were made at 100°F. at the core face (where the primary measurements of dose rate had previously been made). It was assumed that for the range of doses measured the yield of products was linear with dose. Residence times, also required to make these estimates, were calculated from the chemical reactor volume and *n*-hexadecane pumping rates.

Figure 2 shows the dose rates estimated from each of the product yields. Although there was general agreement concerning the manner in which dose rate decreased with distance, there was considerable spread in the dose rate values obtained at any single chemical reactor position. The dose rates estimated from n-hexadecane conversion and light hydrocarbon yield were consistently higher than those estimated from hydrogen and dimer yields. This suggested that some conversion other than that occurring through dimer production at low temperature (100°F.) had occurred. This is understandable since, as noted above, gamma heating forced process exit temperatures to nearly 500°F. in several dosimetry exposures made when the chemical reactor was closest to the nuclear reactor core. The dose rate curve drawn in Figure 2 assumes that hydrogen and dimer yields are most indicative of the radiation dose rates. It represents the dose rate profile which existed when the exposures reported upon in this study were made and for the corresponding nuclear reactor core configuration.

RESULTS AND DISCUSSION

Vapor Phase Exposures

In vapor phase exposures the very high radiation yields which were reported by Lucchesi (*8*) were not observed. At temperatures above 850°F., where thermal cracking was large, radiation-induced cracking did not contribute sufficiently to the *n*-hexadecane conversion to be distinguished against a somewhat uncertain thermal cracking background. This was true even for doses up to 300,000 rads*, in contrast to significant conversions reported by

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* Rad = quantity of energy absorbed equal to 100 erg./g.

Table 2. G Values from Batch Exposures of *n*-Hexadecane. Comparison with Values from the Literature

Hydrocarbon irradiated	ASTM grade *n*-hexadecane	Technical grade *n*-hexadecane	*n*-hexadecane (1)	*n*-tetradecane (10)	*n*-dodecane (1)	*n*-decane (10)
Dose, Megarads (See Table 1)	146	154				
Grams hydrocarbon irradiated	39.0	39.0				
Total energy absorbed, ev.	3.54×10^{23}	3.75×10^{23}				
Hydrogen production						
vol. % in collected gas	94.3	94.4				
yield, mmoles	25.28	25.31				
*G value	4.32	4.06	4.8	3.9	4.9	4.0
Methane production						
vol. % in collected gas	0.7	0.6				
yield, mmoles	0.19	0.16				
*G value	0.032	0.026	0.04	0.07	0.05	0.11
Hydrocarbon conversion						
mmoles	40.25	38.6				
*G value	6.84	6.23				

* Molecules/100 ev. of energy absorbed.

Lucchesi (8) for doses 300 times smaller, and 100 to 1,000 fold increases in radiation conversion reported in Russian exposures on *n*-heptane (7). On the other hand at temperatures near 750°F. increases in *n*-hexadecane conversion due to radiation were observed, and G values of 200 to 1,200, decreasing with increasing dose, were estimated. These observations result from a series of exposures made over a temperature range from 700° to 900°F. and at reactor residence times near 15 sec. Pressures were varied over a range of 10 to 30 lb./sq. in. gauge for the purpose of adjusting residence times. Radiation doses were varied from 0 to 300,000 rads.

Determination of a reactor temperature, which properly represents its behavior, is extremely important in the estimation of vapor phase radiation yields. Thermal cracking proceeds rapidly at temperatures of interest. Small errors in temperatures, taken to estimate thermal cracking yields, introduce large errors in the conversion which is attributed to radiation. This radiation conversion occurs in excess of that expected thermally. Investigators have sought to circumvent this problem by making paired exposures in which identical conditions are maintained except that a radiation field is added for one of the exposures. Identical conditions are not generally achievable however in high radiation fields where gamma heating is significant. In this investigation appreciable differences in the chemical reactor temperature profiles were observed. For example in thermal cracking exposures in the absence of radiation temperatures dropped as much as 215°F. from reactor inlet to outlet. In radiation exposures on the other hand temperatures fell in low dose rate exposures as much as 231°F. and rose as much as 218°F. in high dose rate exposures. It was necessary therefore, in order to compare total conversion in the presence of radiation with that expected thermally, to determine a representative average chemical reactor temperature for each exposure. In Figure 3 the average temperature for each exposure was taken as that temperature at which thermal cracking would proceed isothermally at the same rate as it would by averaging the rates over the temperature profile in the reactor (if a constant temperature gradient along the length of the reactor and no temperature change radially in the reactor are assumed). *N*-hexadecane conversion is expressed as the millimoles of *n*-hexadecane which would be converted during 1 hr. of operation. Only for the exposures made at temperatures near 750°F. was an increase in conversion

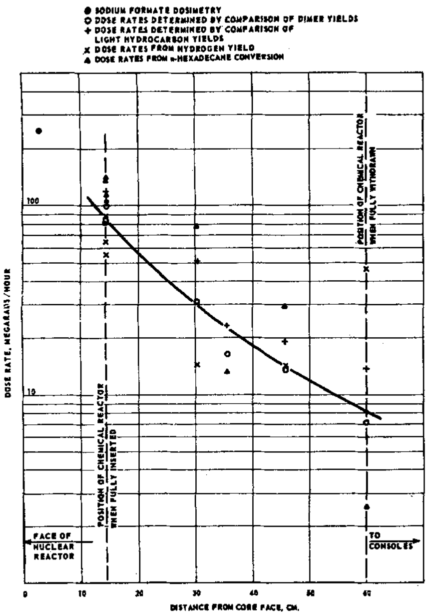

Fig. 2. Dose rates in chemical reactor in beam tube (reactor power = 5 mw.).

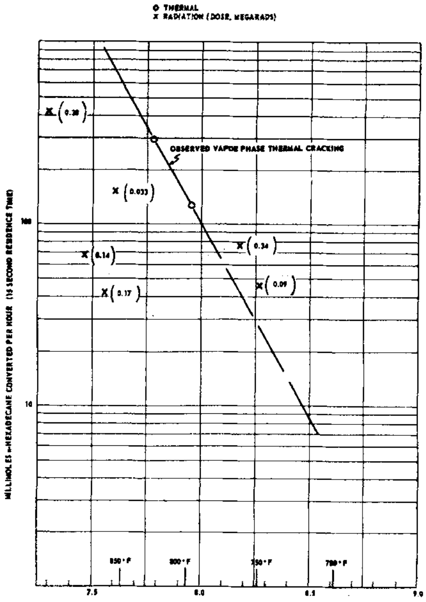

Fig. 3. Vapor phase-*n*-hexadecane conversion as function of weighted average temperature and dose.

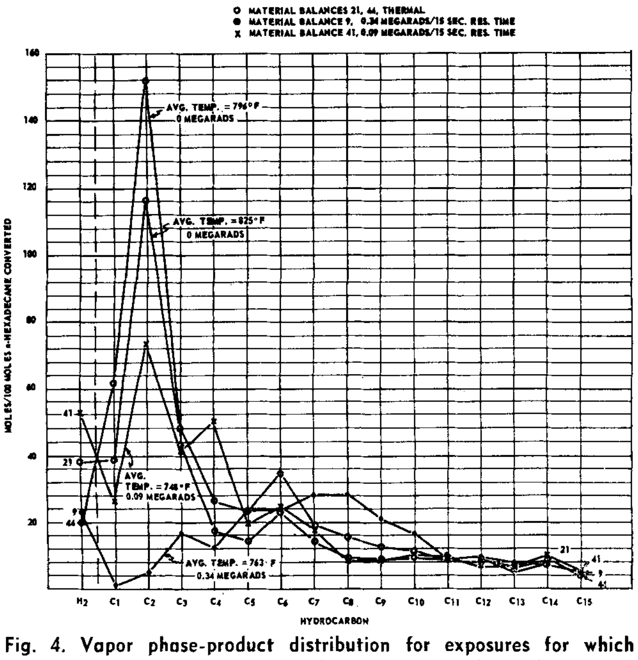

Fig. 4. Vapor phase-product distribution for exposures for which increase in conversion with radiation was observed.

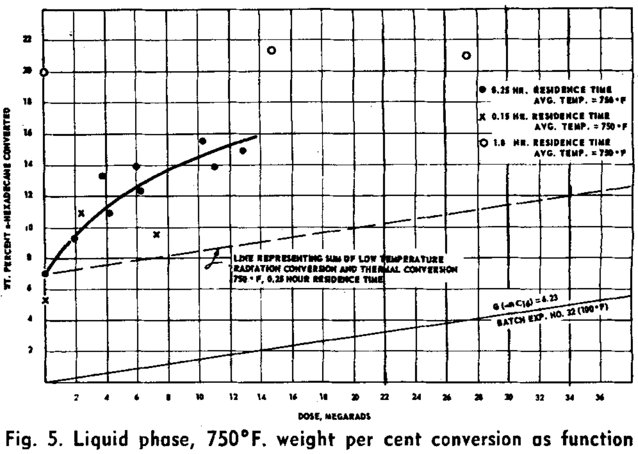

Fig. 5. Liquid phase, 750°F. weight per cent conversion as function of dose.

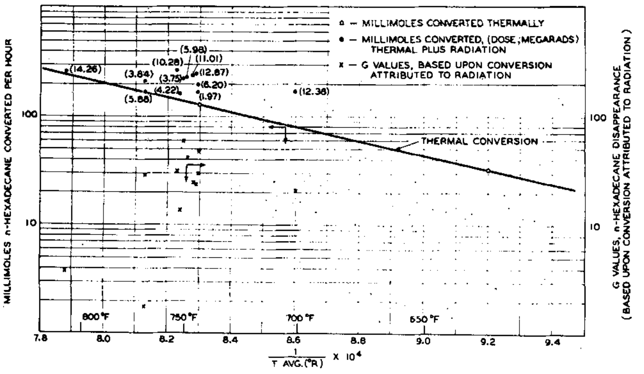

Fig. 6. Liquid phase-*n*-hexadecane conversion as function of average temperature and dose, 0.25 hr. residence time.

observed in the presence of radiation. In contrast if the reactor inlet temperatures were chosen to characterize the thermal conversion, the total conversions usually revealed significant radiation contributions.

In this investigation the outlet thermocouple was at all times closer to the nuclear reactor core than the inlet thermocouple. Particularly in the vapor phase exposures, there was some concern whether the thermocouples in a high radiation field would read correct fluid temperatures because of the very strong gamma heating effects. In an attempt to provide some clarification a pair of vapor phase material balances was made. The first of these material balances was made in the absence of a radiation field. The second material balance was made with the nuclear reactor operating and a radiation field existing. The preheater and trace heater thermostat settings were the same in this second material balance as in the first. Under these conditions the temperatures existing in the chemical reactor were observed to be higher when the radiation field was applied. For this pair of material balances no increase in *n*-hexadecane conversion was observed. This observation is reported not to contradict the conclusion that radiation increases *n*-hexadecane conversion; rather it is reported to indicate the difficulties inherent in this particular type of investigation.

Normalized yields of hydrogen and of hydrocarbons, expressed as moles per 100 moles of *n*-hexadecane converted, are shown in Figure 4 for exposures made at average temperatures near 750°F. These yields differed from those obtained in thermal exposures made in the absence of radiation. For the lowest temperature radiation exposure the yields were very different. A product distribution showing some peaking in the C_5 to C_{10} hydrocarbon range was obtained; high yields of C_1, C_2, and C_3, characteristic of thermal cracking, were less evident.

Liquid Phase Exposures

The weight per cent of *n*-hexadecane converted as a function of dose for liquid phase exposures made at an average temperature of 750°F. is shown in Figure 5. The pressure established in the reaction vessel in each of these exposures was a pressure just greater than the vapor pressure of *n*-hexadecane at the highest temperature observed in that exposure. Pressures varied from 70 to 200 lb./sq. in. gauge. For exposures made at a residence time of ¼ hr. conversion increased regularly from a value of 7.0 wt. % at zero dose (a thermal exposure) to near 16 wt. % at 14 megarads. The conversion observed at 750°F. for any dose was greater than the sum of the conversion expected thermally and the conversion which would be brought about by that dose at 100°F. The G value for *n*-hexadecane conversion thus was greater than the value 6.23 which was obtained at 100°F. and varied from 50 at small doses to 25 at 14 megarads.

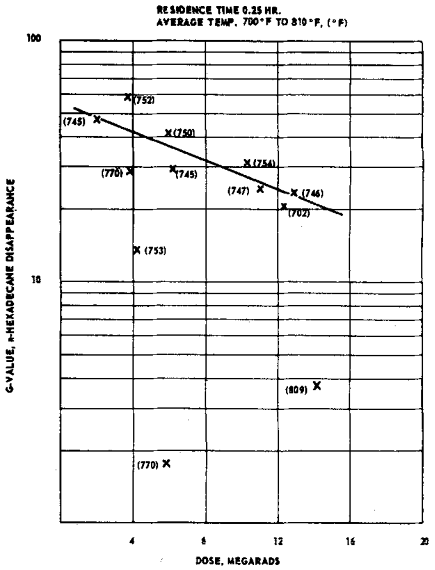

Fig. 7. Liquid phase, G value dependence upon dose.

A few exposures were made at residence times different than 0.25. Results of these are also shown in Figure 5. At 1.0-hr. residence time a greater amount of thermal conversion occurs than at 0.25 hr., conversion through radiation cracking becomes a smaller part of the total conversion, and the amount of unsaturation in the products increases. This change in product unsaturation is illustrated in Table 3. Possible variation in the action of radiation which would be due to dose rate changes (at constant total dose) was hidden by the accompanying changes in residence time and the amount of thermal cracking.

In Figure 6 *n*-hexadecane conversion (expressed as millimoles of *n*-hexadecane converted during an hour's operation) is shown as a function of the average reactor temperature. The solid line represents thermal conversion experimentally determined; each point represents the total conversion obtained in a single exposure. The radiation conversion in each exposure was assumed for purposes

Table 3. Unsaturation in Products of Liquid Phase Material Balances

Material balance	Average temp, °F.	Residence time, hr.	Dose, Megarads	Moles Ci olefin / (Moles Ci olefin + moles Ci paraffin) C_8	C_9	C_{10}	C_{11}	C_{12}
24	744	0.24	0	0.50	0.51	0.51		
30	750	0.27	5.98	0.37	0.35	0.33	0.33	0.35
40	747	0.26	11.01	0.32	0.32	0.31	0.33	
38	634	0.9	0	0.68	0.67	0.74	0.72	0.71
37	749	0.96	14.8	0.67	0.69	0.71	0.72	0.72
33	750	1.23	27.35	0.59	0.60	0.59	0.59	0.57

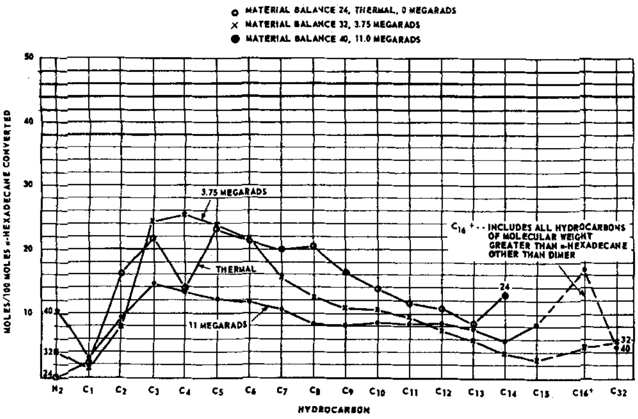

Fig. 8. Liquid phase-product distribution as function of dose-0.25 hr. *residence time, 750°F. average temperature.*

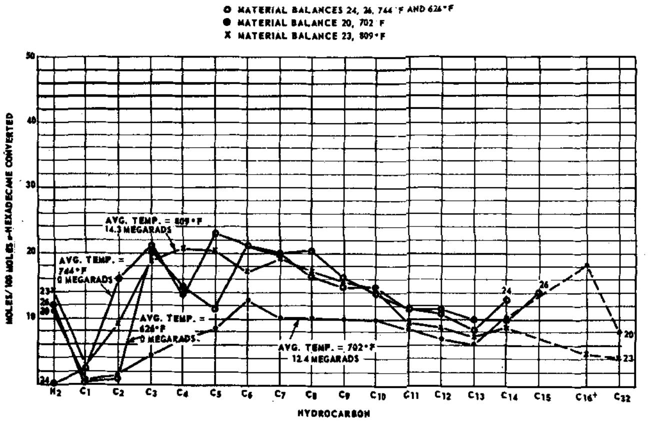

Fig. 10. Liquid phase, product distribution as function of temperature—0.25 hr. *residence time.*

of data representation to be that conversion in excess of that which would occur thermally in the absence of radiation. It was estimated by subtracting the conversion to be expected thermally from the total conversion. Finally a G value for *n*-hexadecane conversion was calculated from the radiation conversion and the measured dose. G values so obtained are shown in Figure 6. They varied between 20 and 60 but decreased sharply at the higher temperatures. This decrease may be related to the error introduced by extrapolation of the thermal cracking yields.

Even though the data scatter, the G values at average temperatures near 750°F. appear to be dependent upon dose as Figure 7 shows; the two most remote points represent the highest temperature exposures.

Figure 8 shows the product distributions which resulted from several exposures made at an average temperature near 750°F. and at different doses. A dose of 11 megarads flattened the distribution and produced relatively large quantities of hydrocarbons heavier than *n*-hexadecane. The low dose distribution produced some peaking at C_3 to C_6. It was found that this peaking could be accentuated at low radiation doses by increasing the reactor inlet and average temperatures. This is shown in Figure 9.

It was also found possible, by varying the average temperature, to change the product distribution resulting from exposures made at constant dose. Figure 10 shows that increasing temperature at constant dose brought about a product distribution more nearly like that obtainable thermally.

In radiation-induced cracking of *n*-hexadecane in the liquid phase, thermal conversions and radiation conversions can occur. At temperatures above 800°F. the thermal conversion of *n*-hexadecane under the conditions of this study predominated. It was extremely difficult to bring about radiation conversion that was significant in comparison with the thermal. Between 400° and 700°F. both radiation conversion and thermal conversion were important. It was possible to change significantly the resulting product distribution by varying the dose. At lower temperatures thermal conversion was not significant.

In Figure 11 the experimental data are brought together in a plausible interpolative representation to provide a convenient means for estimating the *n*-hexadecane conversion to be expected at different temperatures and doses. This method of representing the results is similar to that proposed by Turner (*11*) and discussed by Miley and Martin (*6*). In the present work radiation conversion was observed to increase with temperature. (It is assumed further in Figure 11 that the logarithm of the radiation conversion increases linearly with the reciprocal of the absolute temperatures.) Because of this dependence it was possible to substantially increase *n*-hexadecane conversion at temperatures below those at which significant thermal cracking occurs.

The most efficient radiation utilization would be that in which chain types of reactions were initiated. The behavior shown in Figure 11 may be explained if it is postulated that some portion of the radiation energy in each exposure has been used in this or a related way, while the rest has been used to convert *n*-hexadecane through mechanisms which produce primarily hydrogen and dimer plus other high molecular weight products. These high molecular weight products comprise 90 wt. % of all of the prod-

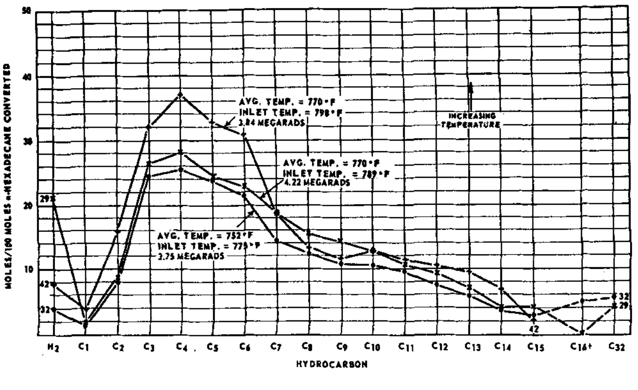

Fig. 9. Liquid phase, effect of temperature upon product distribution at low doses—0.25 hr. residence time.

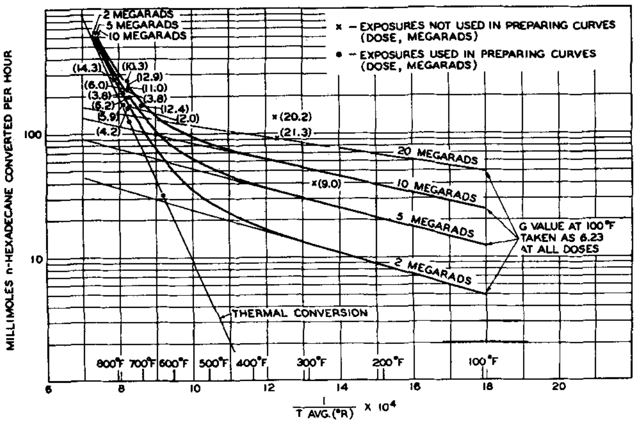

Fig. 11. Liquid phase—empirical data representation showing *n*-hexadecane conversion as function of temperature and dose, 0.25 hr. residence time.

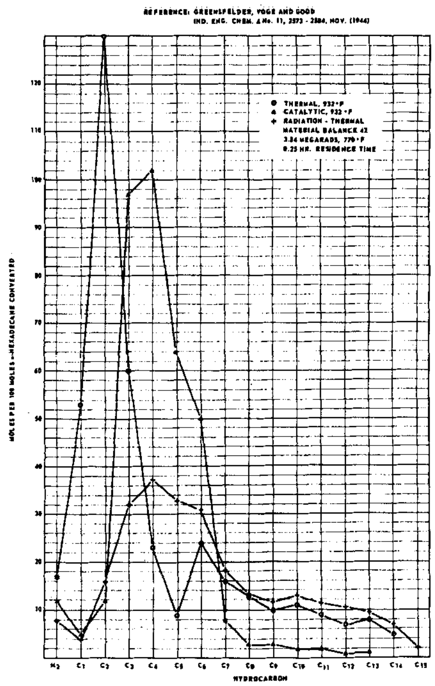

Fig. 12. Product distribution comparison, low dose liquid phase radiation induced cracking with vapor phase catalytic and thermal cracking.

ucts produced by radiation at ambient temperatures. Thermal cracking of *n*-hexadecane however produces few such products, and they are unlikely products of a radiation-induced, chain-propagated cracking mechanism. Conversions attributed to radiation at elevated temperatures in this investigation produced mixtures of products in which hydrogen, dimer, and higher molecular weight products comprised a smaller fraction of the total product than would be produced at room temperature, evidence supporting the postulated division of the conversion into different mechanistic regimes.

An optimum combination of conversion by these two postulated radiation mechanisms and by thermal cracking to produce a desired product distribution may be possible. If gasoline production were to be emphasized, the best product distributions obtained in this study would be those already shown in Figure 9. Material balance 42 was made near the end of the investigation after the results of other balances were known. It was planned as an irradiation in which the production of the gasoline-range products would be emphasized. A degree of predictability and reproducibility in irradiations of this type is thus shown. A comparison of the distribution obtained in material balance 42 with distributions from vapor phase thermal and catalytic cracking of *n*-hexadecane is shown in Figure 12. The distribution obtained with radiation does not reveal the preponderance of very light hydrocarbons characteristic of vapor phase thermal cracking and peaks in the same hydrocarbon range as the distribution from catalytic cracking. The specificity for production of C_3 to C_6 hydrocarbons however is not as great as that for catalytic cracking.

CONCLUSIONS

A considerable degree of control can be exerted over the product distribution from radiation-induced cracking through variation of exposure temperature and radiation dose. In general radiation energy will be divided between that deposited in structural materials (and degraded to heat) and that absorbed directly in reacting hydrocarbons. At dose rates as high as those attainable near the core of a nuclear reactor the product distribution obtained can be related to the quantity of structural material used and the amount of cooling provided. Consider a design in which the metal to process stream volume ratio within the radiation field is high. Under this circumstance, and with cooling provided only by the process stream, gamma heat would raise temperatures to high levels where thermal cracking would predominate. If additional cooling were provided, temperature could be controlled, but clearly the radiation energy would be used inefficiently. A better design would be one in which the metal to process stream volume ratio is low and in which a large fraction of the radiation energy is deposited directly in the process stream. Preheating would be employed when needed.

For most of the exposures in the present investigation *n*-hexadecane was not preheated, nor was cooling employed. Product distributions were obtained which resulted in part from radiation conversion even when thermal conversions were high. Total conversions of *n*-hexadecane up to 15 wt. % were obtained at liquid space velocities near 4v./hr./v. For some exposures up to one-half of this conversion was attributed to the direct utilization of radiation.

The products from vapor phase radiation-induced cracking are very similar to those from ordinary thermal cracking. Products from liquid phase cracking, at elevated temperatures where yields are moderately high, resemble those from catalytic cracking except that there is less specificity for producing C_3 to C_6 hydrocarbons. Ambient temperature liquid phase irradiation converts *n*-hexadecane principally through dimer production rather than cracking, and radiation yields are low.

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