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EFFECT OF GAMMA RADIATION ON VARIOUS
PETROCHEMICAL REACTIONS

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TABLE OF CONTENTS

	Page
LIST OF TABLES	iii
LIST OF FIGURES	iv
ABSTRACT	vi
OBJECTIVE	vii
I. INTRODUCTION	1
II. RADIATION FACILITIES	1
III. EXPERIMENTAL	4
A. Batch Experiments at Room Temperature	4
1. Equipment and Procedure	4
2. Reactions Studied and Results	7
B. Batch Experiments at Elevated Temperature	10
1. Equipment and Procedure	10
2. Polymerization of Pentene-1	13
3. Constant-Volume Cracking of Cetane	15
4. Cracking of Cetane at Total Reflux	15
C. Continuous Thermal Cracking of Cetane	18
1. Equipment and Procedure	18
2. Results	20
3. Thermocouple Calibration	24
D. Catalytic Cracking of Cetane	26
1. Equipment and Procedure	26
2. Results	27
IV. INTERPRETATION OF RESULTS AND CONCLUSIONS	29
A. Gamma-Radiation Effects at Room Temperature	29
B. Batch Experiments at Elevated Temperature	29
C. Continuous Thermal Cracking of Cetane	32
D. Catalytic Cracking of Cetane	33
APPENDIX	34
REFERENCES	39

LIST OF TABLES

No.		Page
I.	Irradiation of Methyl-Cyclopentane--Butylene Mixtures	8
II.	Irradiation of 2-Methyl-Pentane--Pentene-1 Mixtures	8
III.	Irradiation of n-Heptane--Pentene-1 Mixtures	9
IV.	Irradiation of 2-Methyl-Pentane--Pentene-1 Mixtures	11
V.	Polymerization of Pentene-1	13
VI.	Cracking of Cetane--Summary of Results	16
VII.	Continuous Pyrolytic Cracking of Cetane--Summary of Results	21
VIII.	Thermal Cracking of Cetane Gas Analysis	22
IX.	Thermal-Cracking Temperature Corrections	25
X.	Catalytic Cracking of Cetane	28

LIST OF FIGURES

No.	Page
1. Cobalt rod for 10-kilocurie source.	2
2. The 10-kilocurie cobalt-60 gamma-ray source.	2
3. Cutaway view of 10-kilocurie gamma-irradiation facility.	3
4. Dose rates on planes normal to source.	5
5. Glass vials.	5
6. Filling apparatus for vials.	6
7. Photo of reactor.	12
8. Constant-pressure reactor.	12
9. Constant-volume reactor.	13
10. Pentene-1, pressure vs temperature, Run No. 158683.	14
11. Pentene-1, heating cycle, Run No. 158683.	14
12. Pressure vs time for cracking of cetane, Run No. 158756.	17
13. Pressure vs time for cracking of cetane, Run No. 158775.	17
14. Continuous flow reactor.	19
15. Cetane present in product vs temperature.	23
16. Liquid-product distribution vs temperature.	23
17. Gaseous-product distribution vs temperature.	24
18. Error in temperature measurement.	25
19. Catalytic cracking unit flow diagram.	26

LIST OF FIGURES
(Concluded)

No.	Page
20. Catalyst arrangement in reactor with spacer.	27
21. Catalyst arrangement in reactor without spacer.	27
22. Slope of linear pressure increase vs reciprocal temperature for cracking of cetane.	30
23. End point of linear increase in pressure vs reciprocal temperature for cracking of cetane.	31
24. Total pressure after one hour at reaction temperature vs reciprocal temperature for cracking of cetane.	31
25. Thermal cracking, approximately 1-hr contact time, moles of gas per mole of feed vs temperature, °C.	33
26. Integration for radiation intensity.	34
27. Vapor pressure vs temperature for compounds studied. A.P.I. Project 44.	37
28. Specific gravity of cetane vs temperature, °C. A.P.I. Project 41.	38

ABSTRACT

Gamma radiation emitted from a nominal ten-kilocurie cobalt-60 source has been used to investigate its effect in initiating some petrochemical reactions.

Approximately a half percent or less conversion was observed for the following mixtures sealed in glass vials and with total doses from 5 to 30 megarads:

methyl-cyclopentane, butylene
2-methyl-pentane, pentene-1
heptane, pentene-1
pentene-1, methanol

Batch experiments at temperatures from 150° to 300°C on pentene-1 showed that a certain degree of polymerization occurred with and without radiation. The extent of the possible effect of radiation was not determined.

Batch experiments on the thermal cracking of cetane at temperatures varying from 287° to 547°C indicated that gamma radiation inhibits gas and coke formation. Reflux experiments gave further evidence that gamma radiation inhibits gas formation. Additional work in which cetane was thermally cracked in a continuous system did not show as much difference between irradiated and non-irradiated runs as in the batch and reflux work; however, it appears that consistently more gas was made in the nonirradiated runs.

Catalytic cracking studies of cetane are in progress. Preliminary results based on the moles of gas formed indicate that the nonirradiated runs produced more moles of gas per mole of feed than the irradiated runs. A more complete analysis of this work will have to await the completion of the chemical analysis of the products as well as additional experimental work now in progress.

OBJECTIVE

The aim of this work is to explore the effects of gamma radiation on a number of chemical reactions which may be of interest to the petroleum and petrochemical industries. It is believed that these exploratory studies will lead to a better understanding of the mechanism of radiation-induced reactions. Also, such studies should permit generalizations of radiation effects on many different chemical reactions.

I. INTRODUCTION

A study of the effect of gamma radiation on various chemical reactions was undertaken for the Standard Oil Company (Indiana) under Project No. 2420 in the Engineering Research Institute of The University of Michigan. The present report embodies the work from August, 1955, to July, 1956, inclusive.

The research program consisted of two distinct phases. In the first, various reactions were screened in batch experiments to obtain qualitative information on the effect of gamma radiation. The systems investigated were:

- a) Methyl-cyclopentane, butylene
- b) 2-Methyl-pentane, pentene-1
- c) Heptane, pentene-1
- d) Pentene-1, methanol
- e) Pentene-1 (up to 200°C)
- f) Cetane (up to 485°C)

The second phase of the work, representing the major part of the research effort, consisted of a more detailed study of the thermal and catalytic cracking of cetane.

II. RADIATION FACILITIES

A cobalt-60 source nominally rated at 10 kilocuries was used in the radiation experiments. It consists of 100 cobalt rods enclosed in aluminum sheaths as shown in Fig. 1. The rods are arranged in two concentric rows at the periphery of a cylindrical rack as shown in Fig. 2. Details on the construction and activation of the cobalt-60 source are to be found in Fission Products Laboratory Progress Report No. 4 (COO-124),¹ for the Atomic Energy Commission.

The source is housed in a radiation cave adjacent to the Fission Products Laboratory, a cutaway view of which is presented in Fig. 3. The sixteen-foot well shown there is filled with water in which the radiation source is submerged in order to allow access to the cave. The source in the raised position is protected by a wire-mesh cage of approximately the same dimensions

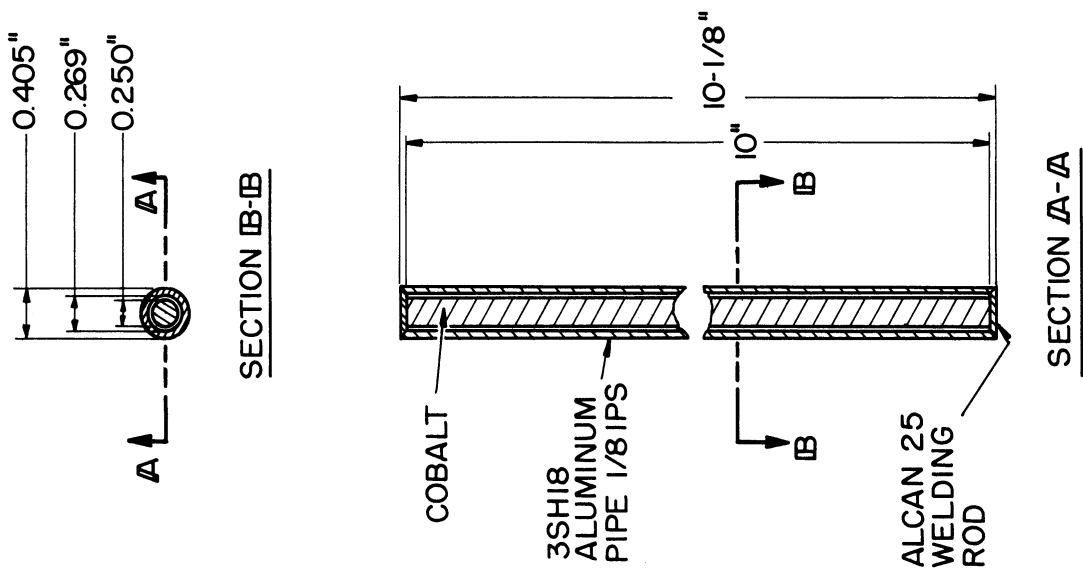


Fig. 1. Cobalt rod for 10-kilocurie source.

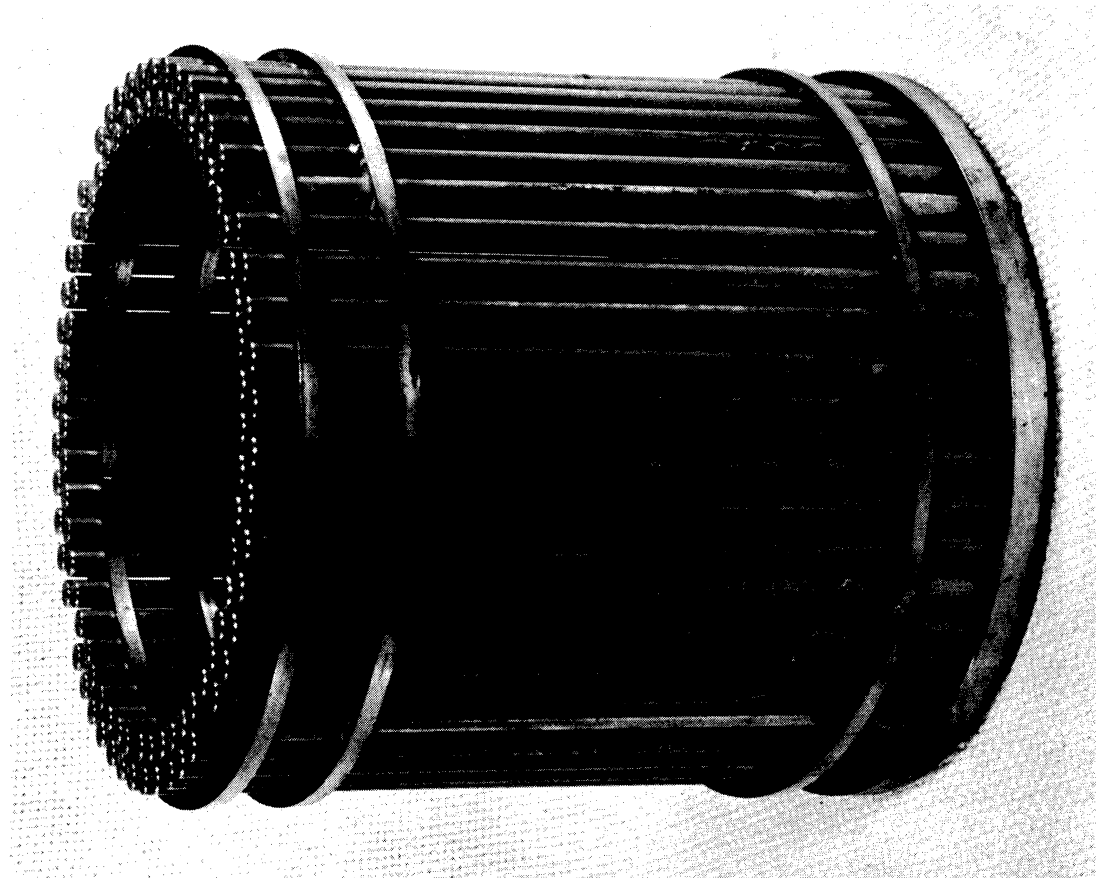


Fig. 2. The 10-kilocurie cobalt-60 gamma-ray source.

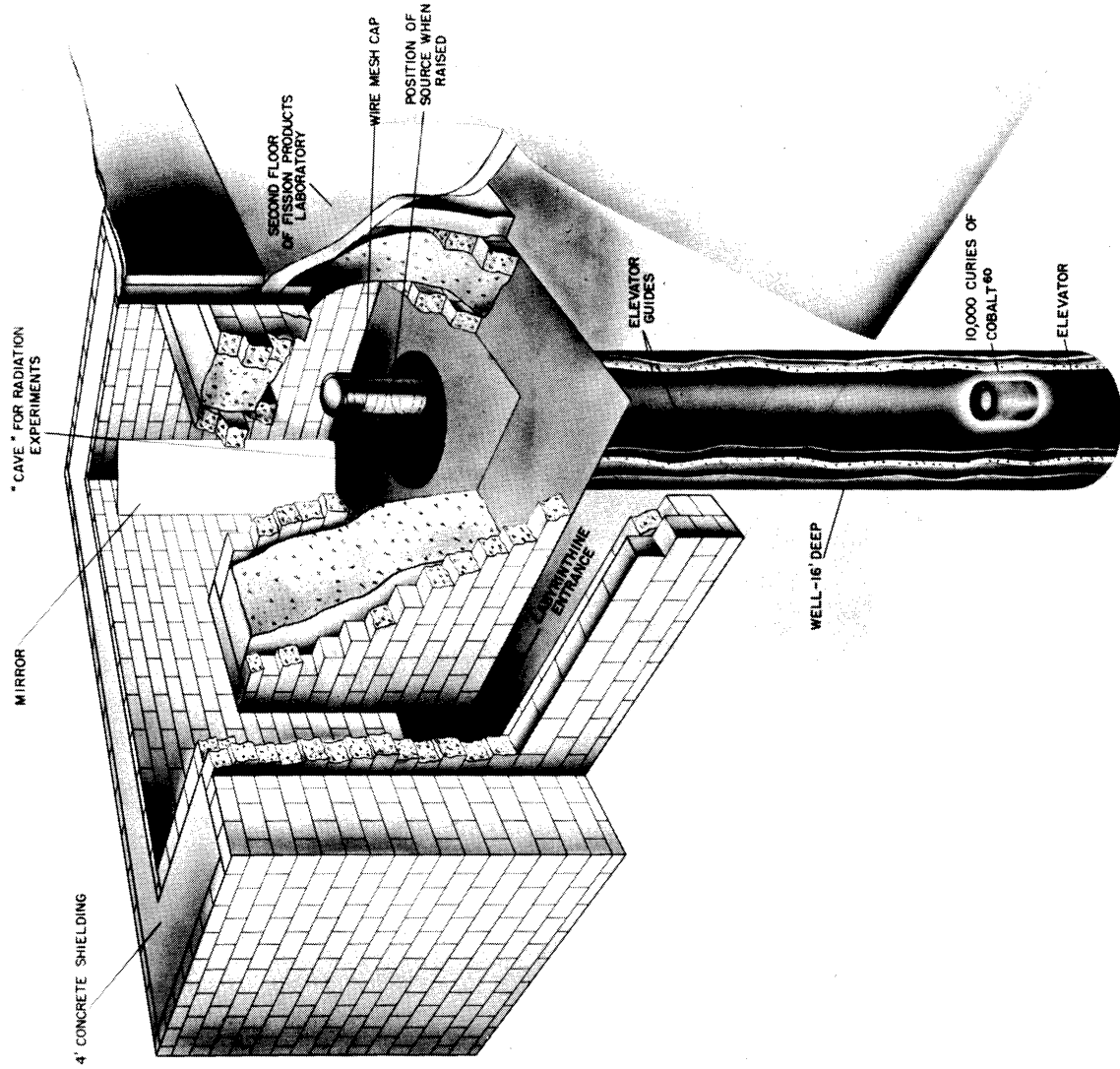


Fig. 3. Cutaway view of 10-kilocurie gamma-irradiation facility

as the cylindrical rack. For the maintenance and routine operation of the source cave, reference is made to Fission Products Laboratory Progress Reports No. 5 (COO-196)² and No. 6 (COO-198)³ for the AEC.

The reaction vessels to be irradiated were placed as close as feasible around the protective cage in order to take advantage of the highest possible radiation rates. The position of the reactor with respect to the source was carefully determined during each experiment. Wherever possible, the centerline of the reactor was adjusted so that the midplane of the reactor contents coincided with the centerplane of the source rods. For the 15-cc glass vials used in this work it was possible to obtain large radiation rates by utilizing the center core of the source.

Prolonged irradiations of batch experiments in glass vials were conducted intermittently because of the need for allowing periodic access to the cave. The net irradiation time of such experiments was computed with the aid of a running log book kept at the cave entrance. In general, all experiments at higher temperature than ambient were conducted by maintaining the source in its raised position for the whole duration of the run.

The actual strength of the source is only approximately 30 percent of its 10-kilocurie rating. A thorough description of the radiation field of the source and the procedure used in its determination was made by Lewis and Martin⁴ in March, 1953. Figure 4 gives dose-rate curves in kilorep/hr versus distance from centerline of source along planes normal to the source. The values presented there were calculated from the data of Lewis and Martin, allowing for the decay of cobalt-60 up to March 31, 1956, the half life being 5.3 years. The dose rate in each experiment was calculated with the aid of this graph. A sample calculation for dose rates in a heated metal reactor is given in the Appendix.

It should be noted that the dose rate calculated in this manner for the metal reactor agrees with a ferrous sulfate dosimetric determination recently performed within the limits of error reported by J. Weiss.⁵

III. EXPERIMENTAL

A. BATCH EXPERIMENTS AT ROOM TEMPERATURE

1. Equipment and Procedure.—Glass vials of 15- and 100-cc capacity made from standard heavy-wall pyrex tubing were used in the screening experiments at room temperature. A diagram of these vials with their dimensions is given in Fig. 5.

Considerable precaution was taken in filling the vials to be irradiated

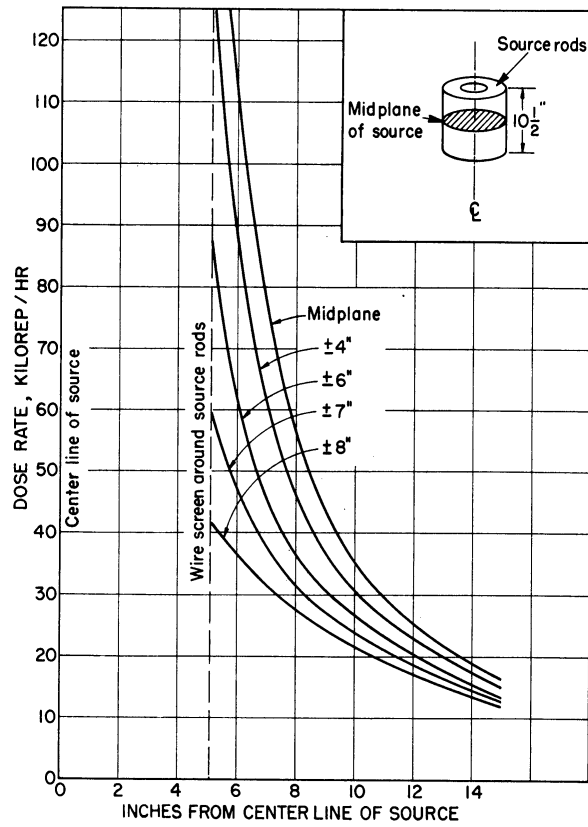


Fig. 4. Dose rates on planes normal to source.

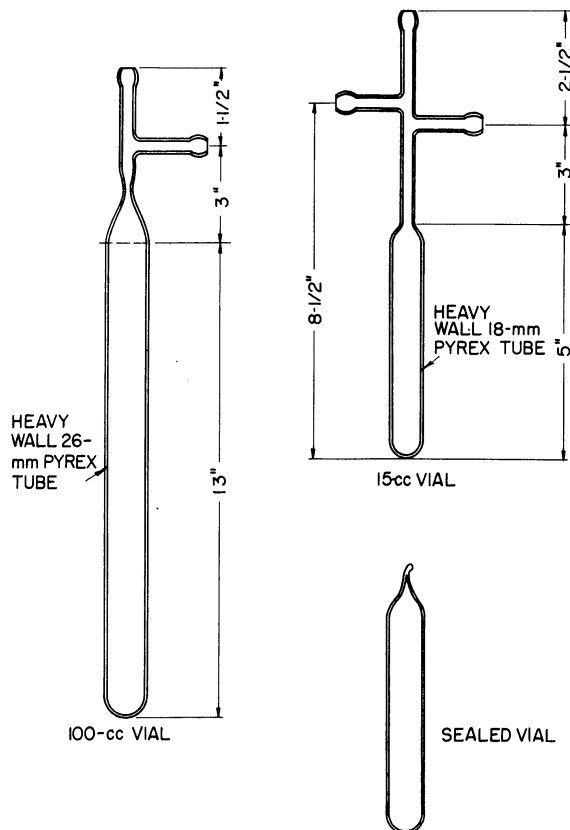


Fig. 5. Glass vials.

diated in order to avoid oxygen contamination. The equipment used is shown schematically in Fig. 6. It consisted of a vacuum manifold, a gas-measuring apparatus, and a vacuum pump.

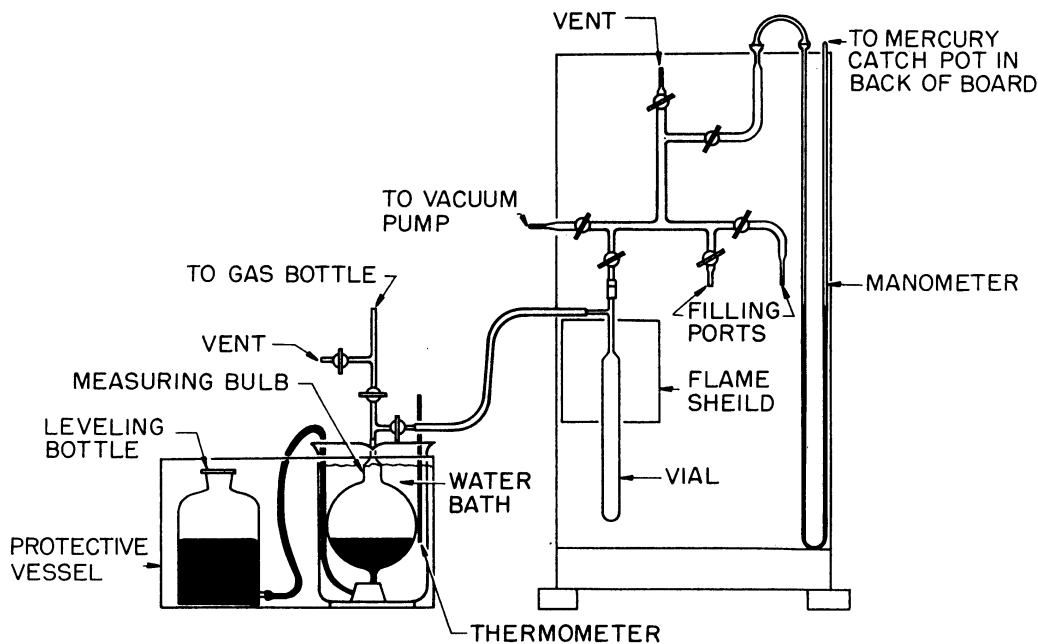


Fig. 6. Filling apparatus for vials.

The vacuum manifold, made of pyrex glass, provided the connection between the vacuum pump and the vial to be evacuated. It was equipped with an open mercury manometer, two gas filling ports, and a vent.

The vacuum pump was a Duo-seal, Welch Pump mounted on a portable stand and equipped with a closed mercury manometer, a McLeod gauge, and a cold trap. The pump was connected to the vacuum manifold by means of rubber tubing.

The gas-filling apparatus consisted of a one-liter calibrated spherical flask immersed in a water bath. The flask was connected to a leveling bottle which permitted the filling of the flask at atmospheric pressure and the discharge of a measured volume of gas in the vial.

The filling operation was made by connecting a vial as shown in Fig. 6 and evacuating it to a pressure of 100 microns or less. A heater was placed around the vial to bring the temperature of the vial up to about 200°C. The vial was then repeatedly purged with nitrogen introduced from one of the left-hand-side filling ports. After the system had been flushed with nitrogen at least three times, the heater was removed and the vial allowed to cool to room temperature. It was further cooled by immersing it in a chloroform-carbon-tetrachloride--dry-ice mixture. The gas to be charged was introduced into the measuring bulb and, when the temperature of the vial reached equilibrium, the gas was introduced into the vial. Condensation occurred very rapidly if the

gas was the first reagent charged to the system. This gas-filling operation was repeated as many times as necessary in order to transfer the desired weight of gas to the vial.

The gas-measuring apparatus was then disconnected and replaced with a graduated burette to deliver the desired amount of liquid reagent in the vial. The vial was sealed with an oxygen flame below the tee connection, making certain that the vial was still under vacuum. All connections were made with neoprene tubing to minimize gas permeability.

The filling of components which were both liquids at room temperature was more conveniently accomplished by introducing the liquids into the vials by means of a syringe piercing through a standard serum bottle stopper inserted into the side arm.

2. Reactions Studied and Results.—

a. Methyl-Cyclopentane, Butylene.

Five glass vials were filled and irradiated. The reactants, furnished by the Standard Oil Company (Indiana), were especially purified in their laboratories to reduce impurities to a minimum. Conditions of the experiments, proportion of reactants, and radiation dosage are summarized in Table I. No visible change in the appearance of the reactants after irradiation was noted.

b. 2-Methyl-Pentane, Pentene-1.

A total of eleven 15-cc vials were charged with varying proportions of 2-methyl-pentane and of pentene-1. The pentene-1 was Phillips, 99 mol percent pure grade, and was purified by passing through a column packed with Davison Silica gel. The column used was $3/4$ inch in diameter and 5 feet long. The purified pentene-1 was stored under nitrogen atmospheres and always handled in the presence of nitrogen. The 2-methyl-pentane was furnished already purified by the Standard Oil Company (Indiana). The experimental conditions are summarized in Table II. No visible change in the appearance of the reactants was noted.

c. Heptane, Pentene-1.

A summary of the conditions for the seven experiments made for the system heptane, pentene-1 is given in Table III. Heptane was furnished by the Standard Oil Company (Indiana) and was used without further treatment. Pentene-1 received a purification treatment as described in (b). Here also no visible change in the appearance of the reactants was noted.

TABLE I
IRRADIATION OF METHYL-CYCLOPENTANE--BUTYLENE MIXTURES

Run No.	Date	Bath Temp. °F	Room Temp. °F	Butylene cc Atm. Press.	MCP cc	Mol. Ratio* Butylene/MCP	Ht. of Liquid in Vial (in.)	Distance of Vial from Source (in.)	Time of Exposure hr	Approx. Radiation Rate krep/hr	Total Dose mrep	Comments
1-158653	11/4	67	72	3220	13.8	1.1	4	4	112.4	41.6	4.7	100-cc vial.
2-158656	11/10	63	74	3220	13.8	1.1	4	4	327.5	41.6	13.7	100-cc vial.
3-158657	11/11	64	74	3220	13.8	1.1	3.5	4	670.8	41.5	28.1	100-cc vial. Some difficulty in handling may have caused some O ₂ contamination.
4-158657	11/15	66	72	3220	7.8	2.0	3.5	4	579	41.5	24.1	100-cc vial. Volume of MCP only approximate.
17-158668	12/9	--	--	--	5	--	1.75		87.8	180	15.8	15-cc vial. Height of liquid above center well, 1.5 in.

*Mol. ratio computed on basis of compressibility factor for butylene of 0.97.

Sp. Gr. of methyl cyclopentane .744.

TABLE II
IRRADIATION OF 2-METHYL-PENTANE--PENTENE-1 MIXTURES

Run No.	Date	Vol. Charged	Vol. Ratio 2-Methyl Pentene-1	Mol. Ratio	Ht. of Liquid in Vial (in.)	Ht. of Bottom of Liquid Above Center Well Floor	Time of Exposure hr	Approx. Radiation Rate krep/hr	Total Dose mrep	Comments
1-158658	11/19	15	4.0	3.3	4.0	1.0	39.5	180	7.1	Loaded with burette instead of syringe.
2-158659	11/25	5.0	4.0	3.3	1.75	1.0	118.6	180	21.3	Contaminated with stopcock grease. Bubbles appeared.
3-158659	11/25	5.0	4.0	3.3	1.75	1.0	118.6	180	21.3	
4-158660	11/25	5.0	4.0	3.3	1.75	1.0	87.6	180	15.8	
5-158662	11/26	5.0	9.0	7.5	1.75	1.0	87.6	180	15.8	
6-158662	11/26	5.0	9.0	7.5	1.75	1.0	63.8	180	11.5	
7-158663	11/26	5.0	9.0	7.5	1.75	1.0	63.8	180	11.5	
8-158663	11/26	5.0	4.0	3.3	1.75	1.0	28.6	180	5.1	
9-158664	11/28	5.0	4.0	3.3	1.75	1.0	28.6	180	5.1	
18-158668	12/9	5.0	100% Pentene-1		1.75	1.1	87.8	180	15.8	
19-158670	12/10	5.0	100% 2-Methyl Pentene		1.75	1.1	87.8	180	15.8	

TABLE III
IRRADIATION OF n-HEPTANE-PENTENE-1 MIXTURES

Run No.	Date	Vol. Charged cc	Vol. Ratio Heptane Pentene-1	Mol. Ratio	Ht. of Liquid in Vial (in.)	Ht. of Bottom of Liquid Above Center Well Flr.	Time of Exposure hr	Approximate Radiation Rate, krep/hr	Total Dose mrep
10-158664	12/5	5.0	4.0	3.0	1.75	1.5	99.5	180	17.9
11-158665	12/5	5.0	4.0	3.0	1.75	1.5	60.75	180	10.9
12-158665	12/5	5.0	9.0	6.75	1.75	1.1	29.37	180	5.25
13-158665	12/7	5.0	9.0	6.75	1.75	1.1	60.75	180	10.9
14-158666	12/7	5.0	9.0	6.75	1.75	1.2	99.5	180	17.9
15-158667	12/7	5.0	9.0	6.75	1.75	1.0	29.37	180	5.25
16-158667	12/7	5.0	100% n-heptane		1.75	1.5	87.8	180	15.8

d. Pentene-1, Methanol.

Nine vials were prepared with different concentrations of pentene-1, which was in general maintained in excess to suppress a possible methanol-methanol reaction. To verify such a possibility, one vial with pure methanol was also irradiated. The run conditions for each experiment are summarized in Table IV. Pentene-1 was silica gel purified while the methanol was purified over calcium hydride and filtered in an atmosphere of nitrogen.

e. Cetane.

Two 15-cc vials filled with 5 ml of cetane each were also irradiated (Exp. Nos. 20-158670 and 21-158671). Both were exposed to gamma radiation for a total of 77.2 hours, corresponding to an approximate dose of 14.8 megarep. No apparent change in the appearance of the cetane was noted. The cetane used was supplied by the Standard Oil Company (Indiana).

B. BATCH EXPERIMENTS AT ELEVATED TEMPERATURE

1. Equipment and Procedure.—Stainless-steel reactors of standard design made from a 13-inch-long piece of 1-inch stainless-steel heavy pipe were used for all the experiments that follow. Six such reactors were supplied by the Standard Oil Company (Indiana). The construction is as shown in Fig. 7.

In order to find a simple reliable procedure to obtain preliminary data, two different types of experiments were designed and tested. One type was operated with a constant-pressure system and the other with a constant-volume system.

The constant-pressure experiments were carried out with the equipment shown in Fig. 8. Here a given amount of reactant was heated to a given temperature. The back-pressure regulator was preset to a pressure slightly above the vapor pressure of cetane at that temperature. The noncondensable gases formed in the reaction increased the pressure of the system and escaped through the valve to be collected in the gas bottle. The rate of gas production could be measured by the amount of water displaced in a given time. Although the constant-pressure experiments presented fewer problems in the control of the reaction temperature, they were found to be more complicated and certainly more difficult to run in the source room and were abandoned in favor of the constant-volume experiments.

The constant-volume experiments were conducted in the apparatus shown in Fig. 9. This consisted of a pressure vessel described before, equipped with a pressure gauge, surrounded by an electric heater. The vessel was charged by evacuating it and then injecting a given amount of reactant through the bottom part of the vessel by means of a syringe. The reactor was heated to a given temperature, and the rate of increase in pressure with time was recorded.

TABLE IV

IRRADIATION OF 2-METHYL-PENTANE -- PENTENE-1 MIXTURES

Run No.	Vol. Charged cc	Vol. Ratio Pentene-1 to Methanol	Mol. Ratio	Ht. of Liquid in Vial	Ht. of Bottom of Liquid Above Center Well Flr.	Time of Exposure hr	Approximate Radiation Rate, krep/hr	Total Dose mrep
22-158677	5.0	100% Methanol		1.75	1.1	81.9	180	14.8
23-158677	5.0	1	0.47	1.75	1.1	81.9	180	14.8
26-158679	5.0	3	1.41	1.75	1.1	81.9	180	14.8
29-158680	5.0	19	8.95	1.75	1.1	81.9	180	14.8
24-158678	5.0	1	0.47	1.75	1.1	53.55	180	9.6
25-158678	5.0	1	0.47	1.75	1.1	27.85	180	5.0
27-158679	5.0	3	1.41	1.75	1.1	53.55	180	9.6
28-158680	5.0	3	1.41	1.75	1.1	27.85	180	5.0
30-158681	5.0	19	8.95	1.75	1.1	53.55	180	9.6
31-158681	5.0	19	8.95	1.75	1.1	27.85	180	5.0



Fig. 7. Photo of reactor.

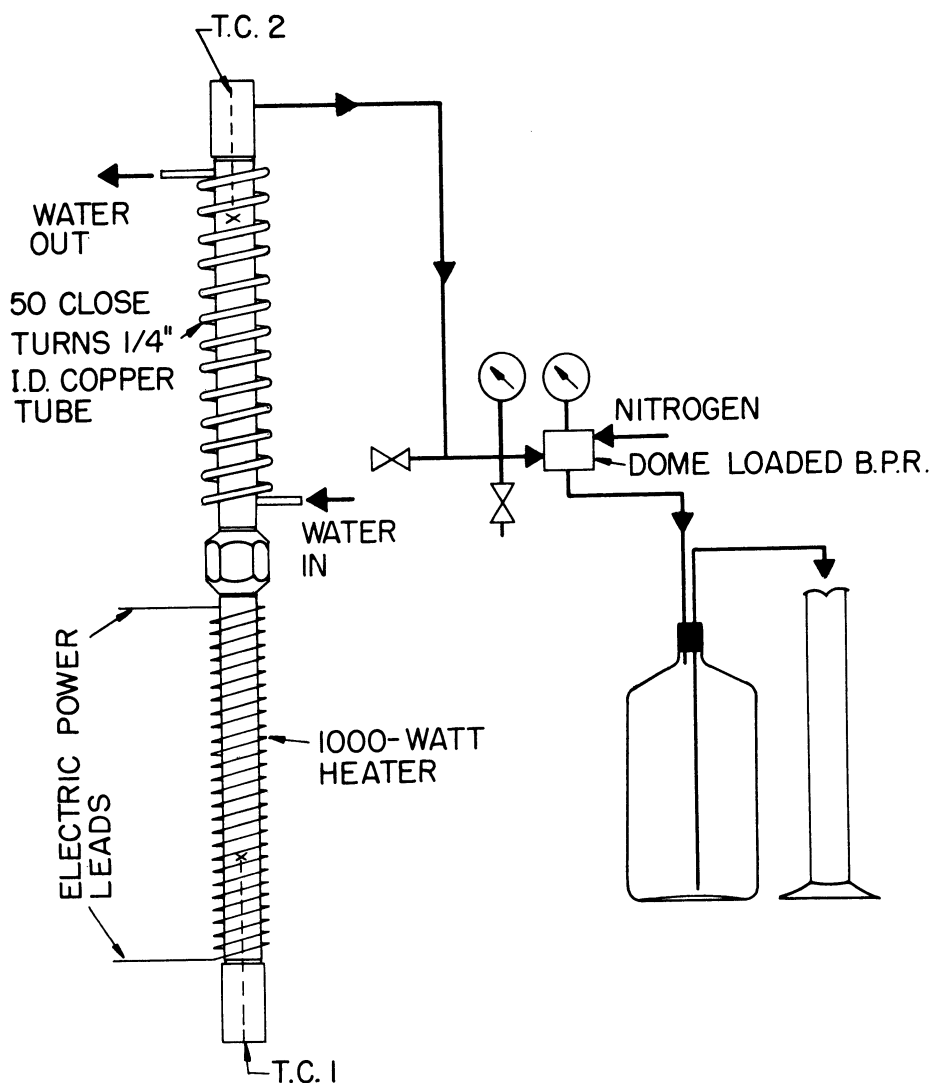


Fig. 8. Constant-pressure reactor.

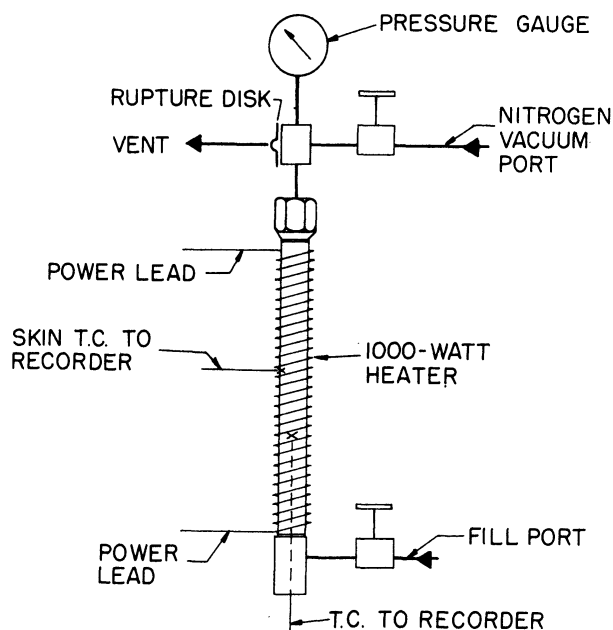


Fig. 9. Constant-volume reactor.

2. Polymerization of Pentene-1.—Some preliminary work at constant volume was done by treating pentene-1 at temperatures varying from 150° to 300°C. The results of six experiments are reported in Table V. The pressure-temperature curve and heating cycle for a typical run are shown in Fig. 10 and Fig. 11, respectively. The total final pressure observed in these runs is considerably below the vapor pressure of pentene-1 at corresponding temperatures, indicating probable polymerization.

TABLE V

POLYMERIZATION OF PENTENE-1

Run No.	Date	Temp. °C	Total Heating Period min	Final Pressure psig	Dose Rate krep/hr	Refractive Index N_D^{25}	Color Product
158683	1/19	150	95	277	--	1.3701	colorless
158752	1/30	200	65	405	--	1.3759	yellow
158753	2/1	300	45	750	--	1.3783	light brown
158758	2/3	200	75	380	--	1.3790	brown
158762	2/7	200	118	360	--	1.3762	light yellow
158765	2/8	200	60	290	42	1.3720	colorless

Note: Refractive index of pentene-1 N_D^{25} 1.3699 - 1.3709 - the variation is due to the poor refractometer used.

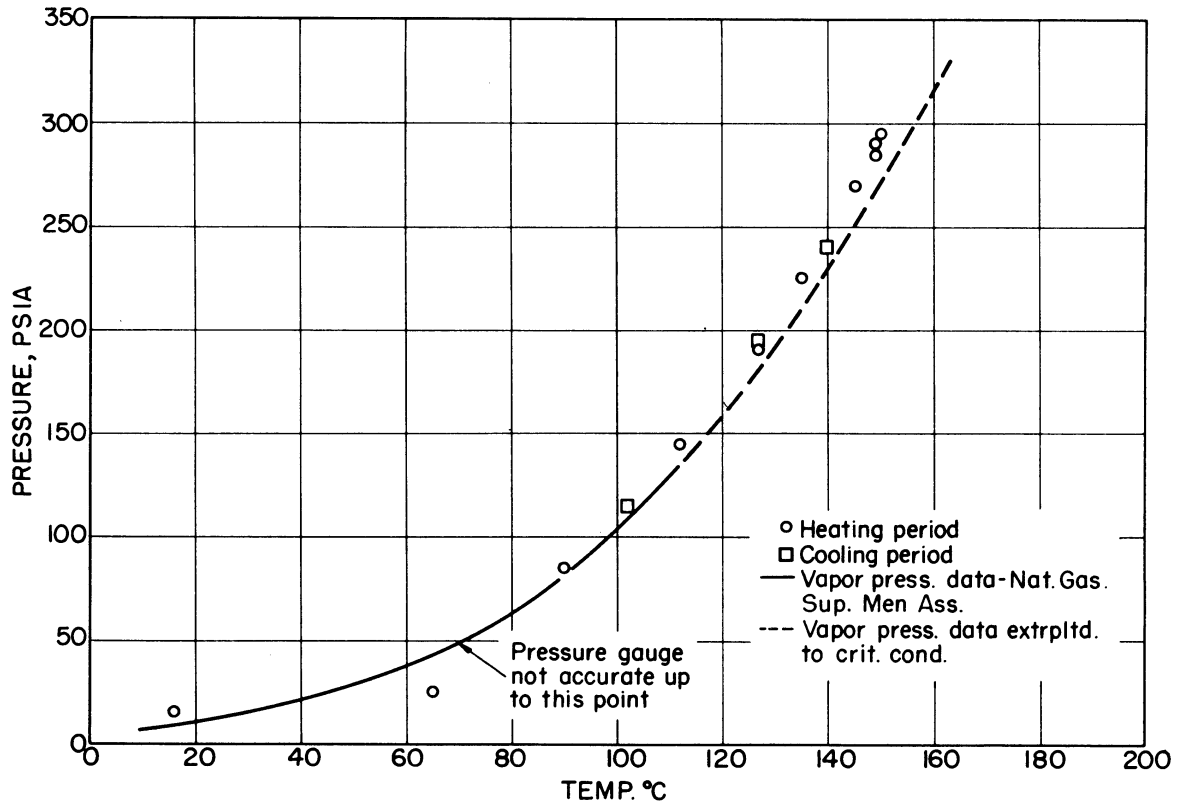


Fig. 10. Pentene-1, pressure vs temperature, Run No. 158683.

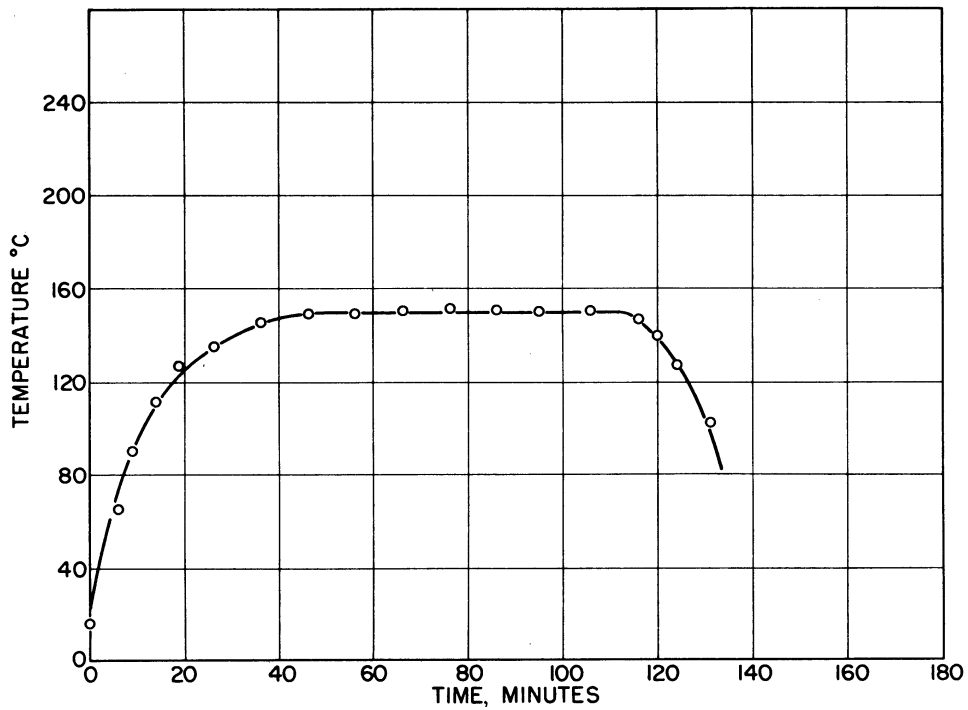


Fig. 11. Pentene-1, heating cycle, Run No. 158683.

The results obtained in a single run (158765) under gamma radiation are not considered sufficient to warrant any conclusion. No gas was made in any of the experiments and the inspection of the products was limited to refractive index measurements which revealed little reproducibility in runs conducted under the same conditions.

3. Constant-Volume Cracking of Cetane.—A total of 17 runs were made in order to determine the effect of gamma radiation on the thermal cracking of cetane at temperatures ranging from 400° to 475°C. Run conditions and results are summarized in Table VI.

The first seven runs were made by evacuating the constant-volume reactor shown in Fig. 9 and charging 25 cc of cetane by means of a 30-cc syringe connected with rubber tubing to the bottom inlet of the reactor. The reactor was then rapidly heated to a given temperature which was maintained constant by manual control for approximately one hour. Pressure readings were taken at frequent intervals throughout the experiment. A typical pressure-time curve for Run No. 158756 is shown in Fig. 12.

Considerable difficulty was encountered in trying to approach the reaction temperature in a uniform and reproducible manner, especially for comparable runs outside and inside the gamma-source room, due to the appreciable differences in ambient temperature of the two sites.

Recourse was made to automatic control of the temperature by using an especially prepared double-wound heater. The inner winding of the heater was controlled automatically, the outer being kept at a constant current input by manual adjustments. In addition, the experimental technique was modified by heating the reactor to the desired constant temperature, then evacuating it and introducing 25 cc of cetane. The temperature, after a sharp fall, would increase rapidly, becoming constant after about 15 minutes from the time of injection of the cetane.

The length of each experiment was carefully timed from the start of the injection for the duration of exactly 60 minutes. The last nine experiments presented in Table VI were carried out in this manner. A typical pressure-time curve for Run No. 158775 is presented in Fig. 13. The pressure-time curves for both types of experiments are quite similar in that a linear increase in pressure with time is observed in the early part of the experiments and then gradually slopes off toward the end of the run. The slope of the linear pressure increase and the point where the pressure increase begins to depart from linearity are included in Table VI.

4. Cracking of Cetane at Total Reflux.—The large number of variables made control and reproducibility difficult in the present apparatus preventing an accurate comparison between irradiated and nonirradiated runs. Therefore, a simple fouling point experiment was made.

TABLE VI
CRACKING OF CETANE--SUMMARY OF RESULTS

Run No.	Date, 1956	Reaction Temp., °C	Heating Period, min	Constant Temp. Period, min	Final Pressure, psia	Dose Rate, krep/hr	Amount Recovered, gm	Color Product	Appearance of Product at 32°F	Slope of Linear Increase in Pressure, psi/min	End Point of Linear Increase in Pressure, psia	Comments
158755	2/3	470	70	65	1085	0	13.0	brown	solid	6	970	New bomb used.
158757	2/3	475	75	64	1500	42	13.6	dark brown	liquid	13.9	1222	
158760	2/4	477	52	62	1640	42	12.3	dark brown	liquid	26.9	1322	
158764	2/7	400	117	47	175	0	17.0	dark yellow	solid	1.7	--	
158766	2/8	400	50	61	90	42	17.0	white	solid	2.1	--	
158767	2/9	435	55	60	540	42	15.4	yellow	solid	8.6	375	
158768	2/9	485	52	10	1875	0	10.2	dark brown	little liquid	47.5	1750	Run interrupted, pressure increase too rapid.
158771	2/10	435	--	60	300	0	8.9	yellow	solid	4.0	250	New bomb used.
158772	2/11	436	--	60	380	0	12.6	dark yellow	solid	6.0	267	
158773	2/13	435	--	60	350	0	10.0	dark yellow	solid	6.0	285	
158775	2/15	437	--	60	420	42	11.6	light brown	solid	7.5	280	
158776	2/15	470	--	60	1815	0	11.6	dark brown	solid	58.0	965	
158777	2/18	470	--	19	1230	42	14.2	brown	solid	--	915	Run interrupted, short circuit occurred.
158778	2/18	435	--	60	338	42	15.6	yellow	solid	7.4	215	
158779	2/20	470	--	60	1415	42	13.0	dark brown	partly liquid	42.0	765	
158781	2/22	470	--	60	1923	0	10.8	dark brown	solid	94.0	1000	

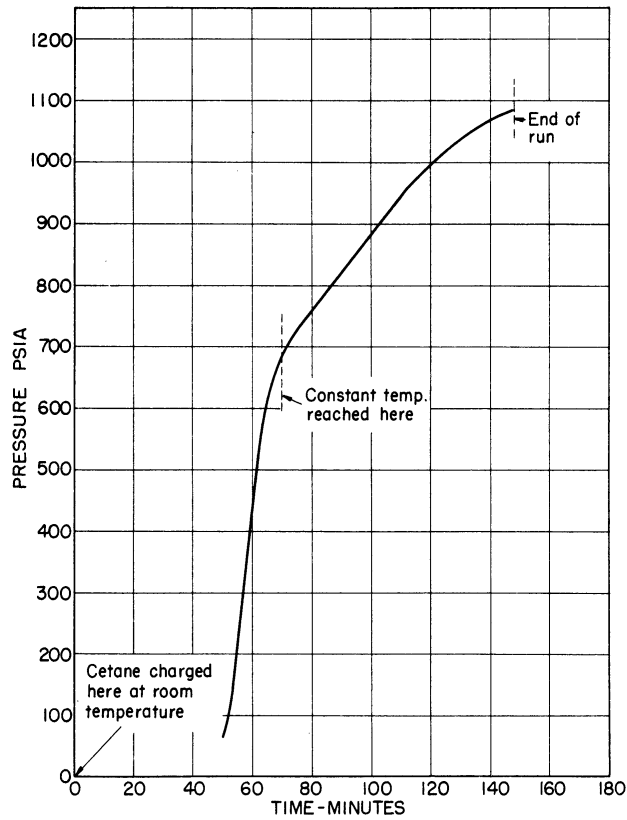


Fig. 12. Pressure vs time for cracking of cetane, Run No. 158756.

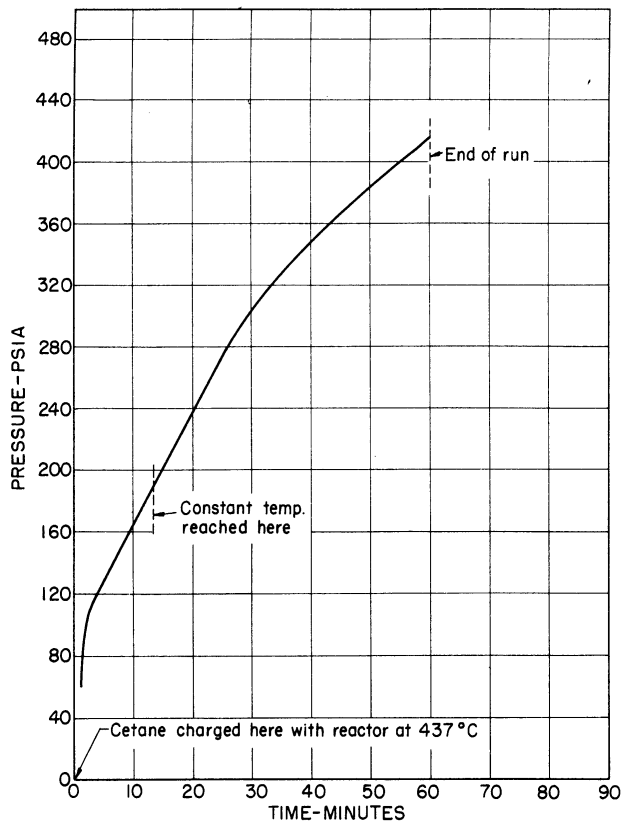


Fig. 13. Pressure vs time for cracking of cetane, Run No. 158775.

One-hundred cc of cetane were charged to a 200-cc three-neck, round-bottom flask equipped with reflux condenser and a thermocouple immersed in the liquid. The reflux condenser was connected to a gas bottle and all joints were sealed with DeKhotinsky cement to avoid leakage. The cetane was then heated to boiling (287°C) and refluxed for one hour. Fifty cc of gas were liberated in this experiment when no radiation was used. The same experiment was conducted simultaneously under an approximate radiation rate of 80 krep per hour; no gas was liberated here. Both liquid samples were very slightly discolored. These results were closely reproduced by repeating a set of comparison runs on three different days. The collected gas from the nonirradiated reflux reaction was analyzed with a Burrell gas analyzer and found to have the following composition:

Hydrogen	63.5 mole percent
Paraffins computed as:	
Methane	14.1 mole percent
Ethane	22.4 mole percent

No olefins, carbon monoxide, or carbon dioxide were detected. Because of the presence of air over the cetane at the time of charging, the hydrogen and paraffins constituted only about 4 percent of the total gas sample.

On the basis of the above result it appears that simple thermal cracking of cetane tends to split off hydrogen or one or two carbon atoms and their associated hydrogen. If one assumes that one mole of gas is formed per mole of cetane decomposed, the corresponding conversion or degree of cracking is less than one-tenth of a percent during one hour of refluxing at 287°C. In the radiation cracking runs it appears that the cetane molecule is broken near the center of the chain of carbon atoms, which would account for no light gases being liberated.

It may be noted at this point that the temperature in the reflux experiments should have been strictly the same for both irradiated and nonirradiated runs because the experiments were conducted at the boiling point of cetane under practically the same atmospheric pressure on any given day. An inspection of the records shows, however, that while the temperature of the simple thermal runs was 287°C (boiling point of cetane), the temperature of the irradiated runs was at all times slightly higher. At the time no importance was given to such an anomaly in the temperature recording which was to influence later experiments as discussed in the following pages.

C. CONTINUOUS THERMAL CRACKING OF CETANE

1. Equipment and Procedure.—The various components of the flow system used were supplied by the Standard Oil Company (Indiana). The equipment consisted of a feed tank connected to a "Ruska" positive displacement pump cap-

able of delivering a minimum of 0.016 cc/min to a maximum of 3 cc/min. The transfer line from the pump led to the reactor, which is the standard-type vessel used in all other high-temperature experiments (refer to Fig. 7). The reactor volume was reduced to 25 cc by use of properly designed cores.

The vessel was equipped with a rupture disk, pressure gauge, and internal thermocouple. A 2000-watt double-wound heater surrounded the reactor. The inner winding of the heater was controlled automatically by means of a "Guardman" temperature controller. The outer winding was kept at a constant current input by manual adjustment. The outlet of the reactor was connected to two receivers installed in parallel to permit separate collection of the product obtained during steady state. Gases formed during cracking were released from the receiver by means of a back-pressure regulator. The gas was collected by displacement with water and measured, depending on its volume, either by a wet test meter or by the amount of water displaced. Transfer lines from the pump to the radiation cave and from there to the receiver permitted the installation of the reactor in the source. These transfer lines were 1/4"-OD, 1/16"-ID stainless-steel high-pressure tubing and were 51 feet long. They were wrapped on the outside with properly insulated No. 20 nichrome wire to avoid freezing of cetane in the lines. A flow diagram of the system is shown in Fig. 14.

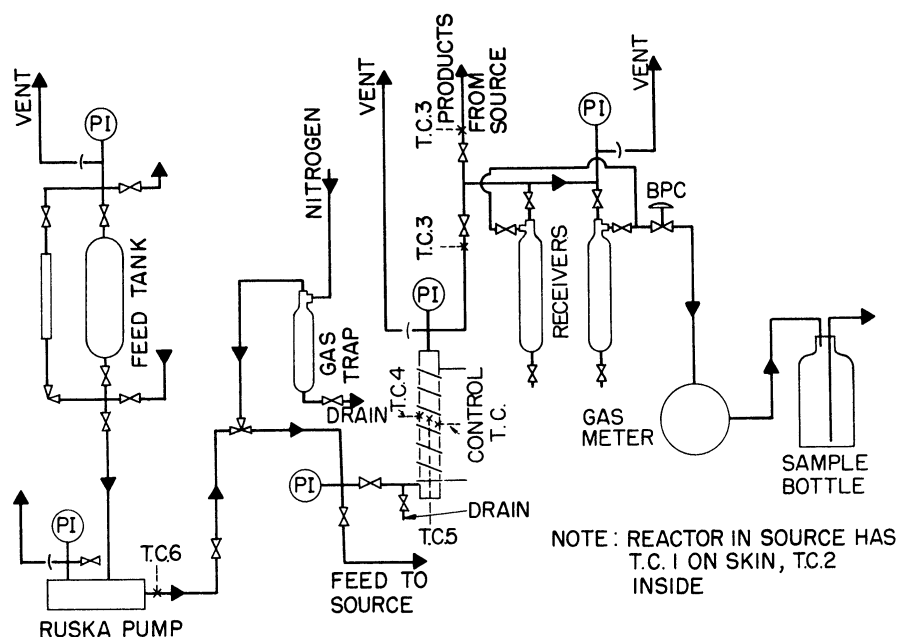


Fig. 14. Continuous flow reactor.

A typical continuous run was performed in the following manner. The reactor was brought up to temperature and controlled at the temperature indicated by the internal thermocouple (T.C.-5 or T.C.-2), which was placed in the thermowell at the center of the reaction zone. The system was pressurized to 400 psig with N₂ and, when all temperatures were lined out, the feed pump was

started. Pressure, temperature, feed-rate, and gas-meter readings were taken at regular fifteen-minute intervals. The liquid product was collected in the discard receiver. When process conditions had reached steady state, as evidenced by the constant rate of gas production, the liquid product was diverted to the second receiver for collection of the official period product.

The period required to attain steady state in blank runs was of the order of two hours. A longer period, generally three to four hours, was required to obtain steady state in irradiated runs, due to the increased volume of the longer transfer lines. The steady-state period averaged six hours, except where pronounced coking made impossible the continuation of the runs. The same reactor, heater, and thermocouples were employed for all runs. Temperature profiles of the reaction zone were taken during each run to establish the temperature distribution in the reactor.

At the end of each run the liquid sample was collected in a 250-ml flask cooled in dry-ice--acetone mixture. The flask was then fitted with a reflux condenser, the outlet of which was connected to a gas bottle. The low-pressure gas was thus allowed to escape overnight from the solution standing at room temperature. The unit was completely drained and all liquids were weighed to obtain an overall material balance. Gas samples for the run gas, blow-down gas, and weathered gas obtained in depressurizing the unit were collected.

2. Results.—The results of 13 runs performed in the manner described above are presented in Table VII. Here the average temperature is given as an integrated average of the temperature profile. Values of temperature along the reaction zone are also tabulated.

The contact time is defined as

$$\frac{\text{volume of reactor}}{\text{volume of liquid feed/hr}},$$

where the volume of the reactor was taken as 25 ml. This volume was calculated from the actual dimensions of the reaction zone, which was 3-1/8 inches long. When the reactor was filled with water, the total volume was found to be 32.5 ml. The difference in volume was due to the void volume of the fitting and to dead space between the cores, the thermowell, and the walls of the vessel. It can be thought of as a preheater volume since the temperature of the feed through it was sensibly lower than the reaction temperature.

The radiation dose was computed from Fig. 4, allowing a 58.6-percent absorption due to the reactor and heater surrounding it, as shown in calculations presented in the Appendix. Lower dose values reported in the monthly summaries of April and May, 1956, are due to erroneous calculations.

TABLE VII
CONTINUOUS PYROLYTIC CRACKING OF CETANE
SUMMARY OF RESULTS

	3	4	6γ	7γ	8	9γ	10γ	11	12	13γ	14	15γ	16
	Run No.												
Exp. Book Page No.	158786	158788	158791	158795	158793	158700	158702	158704	158706	158708	158710	158711	158712
Date	4/2	4/3	4/6	4/11	4/14	4/16	4/18	4/21	4/23	4/25	4/28	4/30	5/5
Avg. React. Temp., °C	503	452	452	449	427	425	510	474	510	473	547	547	547
Temp. Along Reactor Zone, °C													
0 in. (inlet)(1)													
1/2 in.	495	451	455	443	428	421	505	474	--	466	536	536	536
1-1/2 in. (center)(1)	500	455	455	449	430	425	509	475	--	470	543	543	543
2-1/2 in.	505	450	450	451	425	425	512	475	--	475	551	551	551
3 in. (outlet)(1)	508	450	449	449	423	425	510	473	--	474	549	549	549
Corr. Avg. React. Temp., °C(2)	507	448	449	449	422	425	507	471	--	474	544	544	544
Avg. React. Press., psig	503	452	449	445	427	421	506	474	510	468	547	543	547
Approx. Rad. Dose, krep/hr(3)	400	403	404	405	401	400	406	401	408	402	403	402	402
Feed Rate, cc/min	--	--	42	42	--	42	42	--	--	31	--	42	--
Contact Time, Reciprocal Hours	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380	0.380
Duration of Run, min	1.098	1.098	1.098	1.098	1.098	1.098	1.098	1.098	1.098	1.098	1.098	1.098	1.098
Total Feed During Steady State, cc	270	375	375	390	360	360	345	360	195	345	135	255	165
Total Feed During Steady State, gm	102.2	142.8	143.3	149.3	137.2	137.0	130.0	136.4	74.1	131.2	51.1	97.1	62.9
Total Feed During Steady State, mole	0.346	0.484	0.485	0.485	0.467	0.464	0.442	0.459	0.249	0.448	0.173	0.331	0.214
Liquid Product, gm	53.7	102.7	98.4	97.6	100.9	101.4	78.2	92.9	40.4	92.5	15.0	14.0	12.2
Liquid Lighter than Cetane, wt % (4)	94	--	25	27	16	9.0	72	59	74	50	87	93	96
Liquid Lighter than Cetane, gm	50.5	--	24.6	26.4	16.1	9.1	56.3	54.8	29.9	46.3	13.05	13.0	11.7
Off Gas, S.C.F.	0.269	0.156	0.140	0.152	0.137	0.130	0.262	0.176	0.198	0.163	0.276	0.367	0.330
Off Gas, gm	8.8	5.2	4.6	5.0	4.5	4.3	8.7	5.8	6.6	5.4	9.1	12.1	10.9
Weather Gas, S.C.F.	0.165	0.014	0.003	0.003	0.003	0.003	0.122	0.047	0.164	0.019	0.065	0.074	0.079
Weather Gas, gm	7.8	0.5	0.1	0.1	0.1	0.1	5.7	2.2	7.7	0.9	3.0	1.5	3.7
Moles of Total Gas/Mole of Feed	1.50	0.421	0.353	0.382	0.358	0.343	1.04	0.595	1.74	0.487	2.36	1.45	2.28
Material Balance, wt %	90	99	94	93.6	99.5	100	92.6	96.6	98.4	97.3	69	38.2	54.9
Total Product Lighter than Cetane, gm	67.1	--	29.3	31.5	20.7	13.5	70.7	62.8	44.2	52.6	27.1	26.6	26.8
Cetane Converted, wt %, output basis	95.5	--	28.4	30.7	19.6	12.8	76.4	62.4	80.8	53.2	92.8	96.4	98.1
Liquid Product, wt %, output basis	72.0	--	23.8	25.8	15.3	8.6	60.8	54.5	54.6	46.8	48.2	47.1	43.6
Gaseous Product, wt %, output basis	23.5	--	4.6	4.9	4.3	4.2	15.6	7.9	26.2	6.4	44.6	49.3	54.5

(1) Interpolated values.
(2) This correction is made on the basis of Table VIII.

(3) These values were reported incorrectly in the April report.
(4) Gas chromatography determination from Standard Oil Company (Indiana).

The product inspections were carried out by the Standard Oil laboratories and they consisted of mass-spectrographic analysis of the gases and of fractional distillation and gas chromatography of the liquid products. The product distributions in the gas samples were nearly the same in all cases. A typical analysis of the gas is reported in Table VIII. The molecular weight obtained from them was used to calculate the weight of the gas produced. Fractional distillation of the liquid products was not very conclusive and did not give a satisfactory comparison of the liquid products of irradiated and non-irradiated runs. Gas chromatographic determinations gave the percent unconverted cetane in the liquid and are reported in Table VII. These values, along with the gas-analysis data, were used to calculate the material balance and the product distributions in the manner indicated in the Appendix. The unconverted cetane, liquid, and gas distributions are shown in Figs. 15, 16, and 17, respectively.

TABLE VIII

THERMAL CRACKING OF CETANE GAS ANALYSIS

Typical Composition of Off Gases Collected During Run

<u>Components</u>	<u>Volume %</u>
Hydrogen	6
Methane	35
Ethane	25
Ethylene	7
Propane	13
Propylene	8
Butane	3
Butylene	<u>3</u>
Total	100

Avg. MW = 27.7

Typical Composition of Gas Obtained by Weathering at 25°C

<u>Components</u>	<u>Volume %</u>
Methane	3
Ethane	17
Ethylene	4
Propane	38
Propylene	18
Butane	11
Butylene	<u>9</u>
Total	100

Avg. MW = 39.2

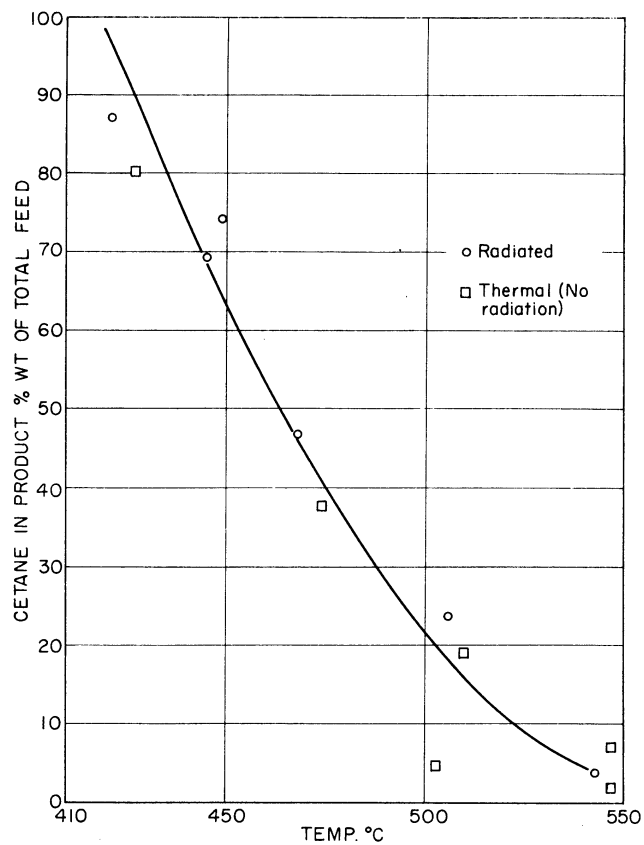


Fig. 15. Cetane present in product vs temperature.

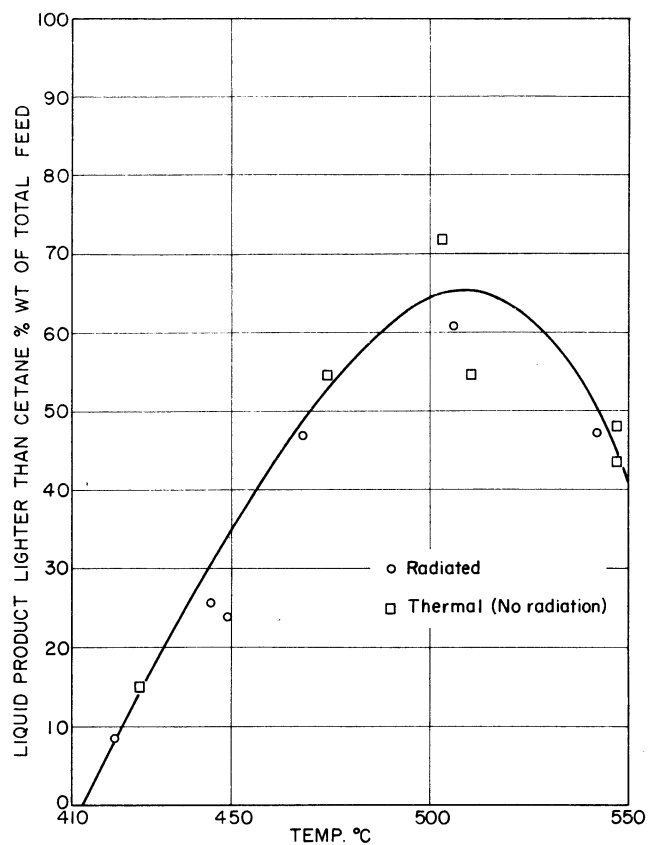


Fig. 16. Liquid-product distribution vs temperature.

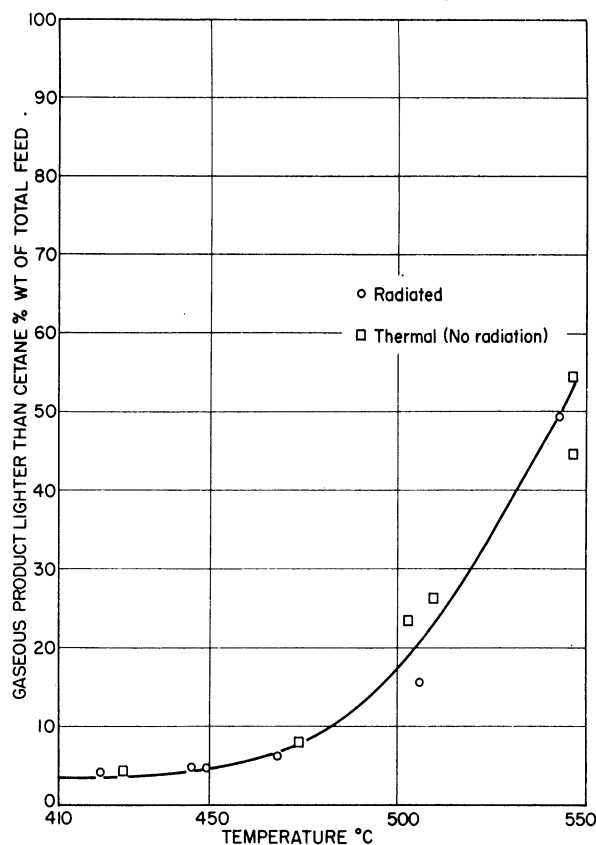


Fig. 17. Gaseous-product distribution vs temperature.

3. Thermocouple Calibration.—On several occasions during the course of this research, questions arose about the accuracy of temperature measurements, especially since two entirely different sets of ambient conditions were being used; namely, the laboratory for runs without radiation and the source cave for radiation runs. During the colder months the temperature in the source cave was appreciably lower than in the laboratory.

Repeatedly the temperature recorder was checked by immersing the thermocouples in boiling water. Also, all leads were checked by feeding to the recorder an emf generated by a portable potentiometer. No anomaly was noted in these tests, at least within the accuracy of the recorder scale (0.1-0.2 percent of full scale).

Later a considerable amount of time was spent to check more closely the whole temperature-measuring system, since it appeared that a temperature difference occurred when the thermocouple connections to the extension wires in the source cave were held at temperatures lower than the corresponding connections at the recorder which was installed in the laboratory. Such conditions prevailed throughout the period in which continuous thermal-cracking runs were conducted.

In order to determine the extent of the error incurred, chromel-alumel

thermocouples were immersed in molten fixed-point substances. The temperature of the thermocouple-extension-wire connections was varied by immersing the connections in water maintained at constant temperature below the ambient temperature. The observed positive error is plotted in Fig. 18 vs the temperature difference between recorder-extension-wire connection and thermocouple-extension-wire connection for lead, antimony, and potassium hydroxide. Table IX gives approximate average temperatures for the laboratory and source cave for those runs carried out under the influence of gamma radiations. It can be observed that this correction is never more than 5°C. The corrected temperatures are also reported in Table VII.

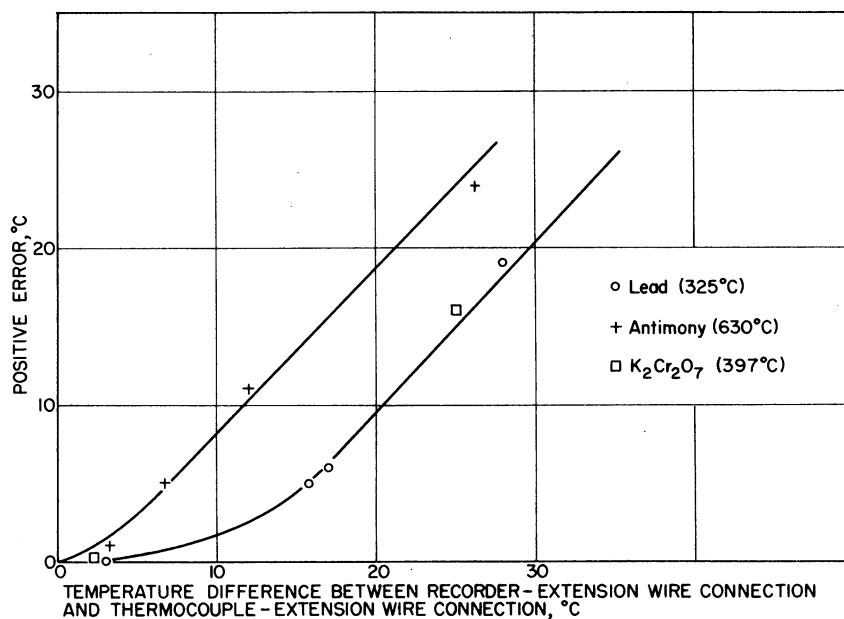


Fig. 18. Error in temperature measurement.

TABLE IX

THERMAL-CRACKING TEMPERATURE CORRECTIONS

	Run No.					
	6y	7y	9y	10y	13y	15y
Recorded Avg. React. Temp., °C	452	449	525	510	473	547
Avg. Source Temp., °C	20	15	16	12	14	16
Avg. Room Temp., °C	26	24	25	20	24	23
Temp. Diff. Between Junctions	6	9	9	8	10	7
Negative Temp. Error	3	4	4	4	5	4
Corrected Avg. React. Temp., °C	449	445	421	506	468	543

D. CATALYTIC CRACKING OF CETANE

1. Equipment and Procedure.—The equipment used for the catalytic-cracking study is shown diagrammatically in Fig. 19. The reactor consisted of the standard stainless-steel reactor described in Fig. 7. The top of the reactor was connected to the "Ruska" positive displacement pump and to a nitrogen cylinder so that downflow of cetane and purge gas is obtained. The outlet of the reactor was connected to a 500-cc round-bottom flask which served as a product receiver. The receiver was immersed in an ice bath. The uncondensed vapors escaping from the receiver were further cooled by a salt-ice condenser. The vapors were then measured and collected in a gas bottle. The reactor was heated in an analogous manner as for the thermal-cracking experiments without catalyst.

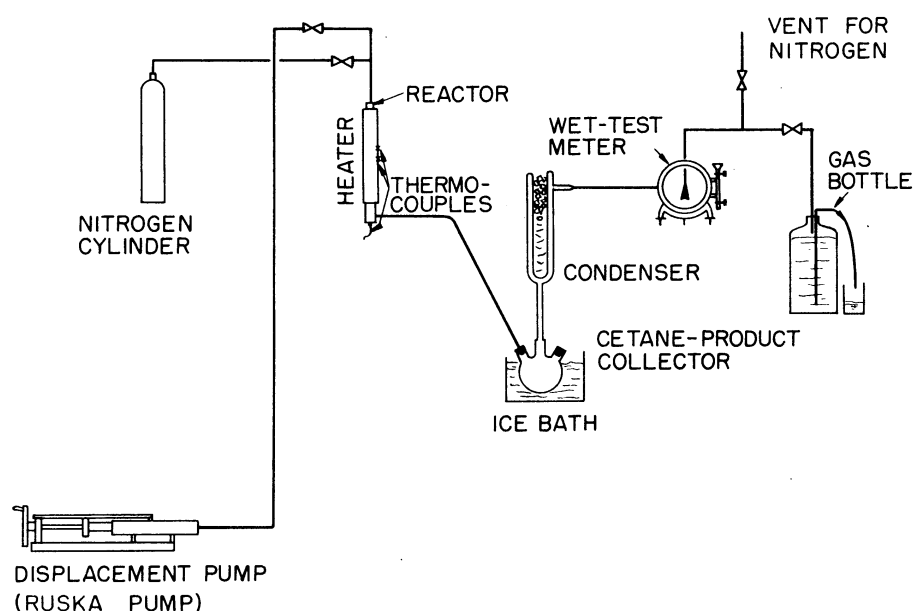


Fig. 19. Catalytic cracking unit flow diagram.

The catalyst was charged to the reactor in such a way as to form a bed at approximately the centerline of the reactor in order to obtain the most uniform temperature profile in the reaction zone. Two typical arrangements used in charging the catalyst are shown in Figs. 20 and 21. Before closing the reactor a glass-wool plug was introduced at the top in order to facilitate the vaporization of cetane.

The reactor was then heated to a temperature of from 20° to 30°C above the desired reaction temperature, while nitrogen at a rate of from 5 to 6 cubic feet per hour was passed through the reactor in order to dry out the catalyst. A charge of 250 cc of cetane was placed in the "Ruska" pump and the transfer line from the pump was filled with cetane up to the reactor. The run was started by turning on the pump and opening the valve at the upper extremity

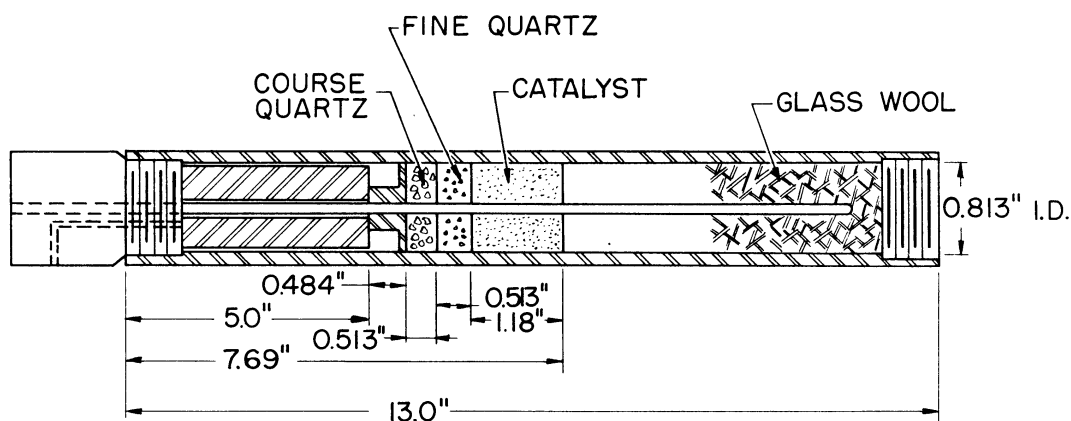


Fig. 20. Catalyst arrangement in reactor with spacer.

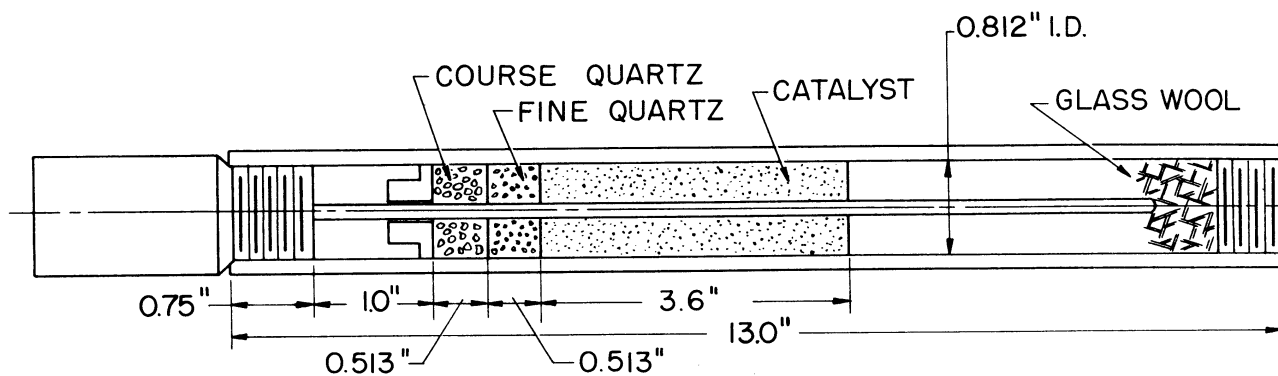


Fig. 21. Catalyst arrangement in reactor without spacer.

of the reactor simultaneously. Feed rate, temperature, and gas make were recorded at five-minute intervals. The run was continued until enough product was collected, usually one or two hours, depending on the feed rate used. At the end of the run, the catalyst was stripped with 2000 cc of nitrogen slowly introduced into the reactor. The liquid product was weathered at 65°C for three hours.

2. Results.—A summary of the runs so far undertaken is presented in Table X. The overall average temperature was taken as the integral average of the temperature profile across the catalyst bed. No significant pressure drop was observed in any of the runs reported. The radiation dose was calculated as shown in the Appendix. The space velocity is defined as

$$\frac{\text{weight of feed/hr}}{\text{weight of catalyst}}$$

Some data are lacking for Runs 1c through 8c because these runs were made in order to gain familiarity with the equipment and to set up a rigid run

TABLE X
CATALYTIC CRACKING OF CETANE

	Run No.																		
	1c	2c	3cy	4c	5c	6cy	7c	8cy	9c	10c	11cy	12c	13cy	14cy	15cy	16c	17cy	18c	
Date	5/24	5/25	5/28	5/29	5/31	6/2	6/4	6/6	6/11	6/12	6/12	7/8	7/9	7/12	7/13	7/16	7/19	7/19	
Depth of Bed, in.	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Average Temp., °C	495	495	500	534	542	544	542	541	475	482	488	525	522	529	526	527	520	525	532.5
Middle of Bed Temp., °C	500	500	505	539	547	549	547	543	475	495	492	532	527	534	531	531	525	531	532.5
Bottom of Bed Temp., °C		499					547	538	485	471	487	515	527	534	531	506	525	531	532.5
Top of Bed Temp., °C		477					536	533	440	487	487	523	527	534	531	506	525	531	532.5
Pressure Drop, psig	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Approx. Rad. Dose, krep/hr	--	--	42	--	--	42	--	42	--	--	38	--	42	42	42	--	42	42	--
Catalyst Charged, gm	7.75	8.27	7.59	8.17	7.96	7.82	8.01	8.11	25.02	24.56	25.13	25.20	25.54	25.20	25.20	25.20	25.20	25.20	25.20
Feed Rate, cc/hr	120	120	120	120	120	120	120	120	120	120	120	120	122.4	122.2	122.1	122.6	121.3	121.3	121.3
Total Run Time, hr	1.0	1.0	0.834	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total Feed, cc	120	120	120	120	120	120	120	120	120	120	120	120	122.4	122.2	122.1	122.6	121.3	121.3	121.3
Total Feed, gm	92.5	92.5	77.0	92.5	92.5	92.5	92.5	92.5	92.5	92.5	92.5	92.6	94.4	94.1	93.9	94.0	93.5	94.0	93.5
Total Feed, mole	0.409	0.409	0.340	0.409	0.409	0.409	0.409	0.409	0.409	0.409	0.409	0.409	0.416	0.415	0.414	0.415	0.413	0.415	0.413
Space Velocity, w/hr/w	11.92	11.20	12.20	11.31	11.61	11.81	11.51	11.40	3.70	3.77	3.68	3.68	3.70	3.74	3.72	3.73	3.71	3.71	3.71
Liquid Product, gm	--	93.5	57.4	92.0	--	--	--	--	--	79.2	81.3	72.0	50.7*	81.4	62.15	68.25	67.27	67.27	67.27
Off Gas, S.C.F.	0.0188	0.0249	0.00	0.0560	0.0938	0.00	0.0758	0.0802	0.1460	0.1345	0.0042	0.399	0.2985	0.279	0.280	0.362	0.295	0.295	0.295
Weathered Gas, S.C.F.	--	--	--	--	--	--	--	0.0111	0.0300	0.0143	0.0229	0.028	0.0121	0.0074	0.0313	0.0285	0.0154	0.0154	0.0154
S.C.F. Total Gas/Gm-Mole Feed	0.046	0.0649	0.00	0.165	0.230	0.00	0.185	0.223	0.431	0.364	0.0663	1.058	0.746	0.690	0.750	0.941	0.752	0.752	0.752
Gm-Mole Gas/Gm-Mole Feed	0.055	0.0729	0.00	0.197	0.274	0.00	0.221	0.266	0.516	0.435	0.0793	1.265	0.894	0.825	0.898	1.125	0.900	0.900	0.900
Mat. Lighter than Cetane, %	7	8	6	9	12	10	12	9											

* Spill

procedure. Considerable difficulties were encountered in maintaining constant-temperature conditions throughout the run due to irregular vaporization of the feed and to the comparatively short life of the catalyst, which does not permit a waiting period to reach steady state before the products are collected. The first problem was corrected by introducing a glass-wool plug at the top of the reactor to obtain a better distribution of the feed; the latter may be controlled by establishing a given temperature profile in the catalyst before each run is started.

Results of the product analysis are incomplete at the present time. Gas chromatographic results reported as percent of material lighter than cetane are included in Table X for Runs 1c through 8c.

IV. INTERPRETATION OF RESULTS AND CONCLUSIONS

A. GAMMA-RADIATION EFFECTS AT ROOM TEMPERATURE

The various experiments in glass vials were intended to serve as exploratory tests at room temperature. As shown from Table I through IV, the vials were exposed to doses from 5 to 30 megarep. The irradiated vials were shipped to the Standard Oil Company (Indiana) for inspection. An analysis of the data revealed that the maximum conversion detectable was of the order of 0.5 percent. In light of these results, the experimental work at room temperature was discontinued.

B. BATCH EXPERIMENTS AT ELEVATED TEMPERATURE

Attention was turned to batch experiments at elevated temperature. Although they required more elaborate equipment than glass vials, it was hoped that they would serve to determine a possible temperature threshold above which appreciable radiation effects could be detected.

Pentene-1 and cetane were selected as the most suitable starting compounds for this study, since the former would tend to polymerize at moderate temperature while cetane would tend to decompose.

After various trials, a constant-volume technique, previously described, was selected as most suited for this work. Experiments with pentene-1 from 150° to 300°C showed that some polymerization was taking place even without irradiation, as revealed by reactor pressures lower than the corresponding vapor pressure; however, the results were difficult to reproduce. The only run conducted under gamma radiation resulted in a lower final pressure as compared to those runs where pentene was only heated. The small number of experiments precludes, however, any further conclusion.

Cetane was exposed to heat and radiation in a similar manner at temperatures from 400° to 475°C. Cracking was evidenced by reactor pressures much higher than the corresponding vapor pressure of cetane. The pressure-time curves observed during a run consisted of an initial straight-line portion and a terminal curvature (see Figs. 12 and 13). No consistent correlation of the slopes of the straight-line portion of the curves was possible because of the seemingly erratic change from experiment to experiment, as shown in Fig. 22, probably due to different rates of total heat input. The end-point pressure at which further increases in pressure depart from a straight line seems to be fairly consistent for all the experiments, as shown in the plot of Fig. 23. In addition, there seems to be no difference between the amount of gas formed in the irradiated and nonirradiated runs when the total pressure after one hour at reaction temperature is plotted vs the reciprocal temperature as shown in Fig. 24.

An inspection of the nature of the products of the reaction shows, principally for those runs at and above 470°C, a greater degradation of cetane, as evidenced by the amount of liquids present in the products stored at 32°C (since cetane is solid at this temperature). On the other hand, the color of the product gives no clue to possible differences of the cracking reaction.

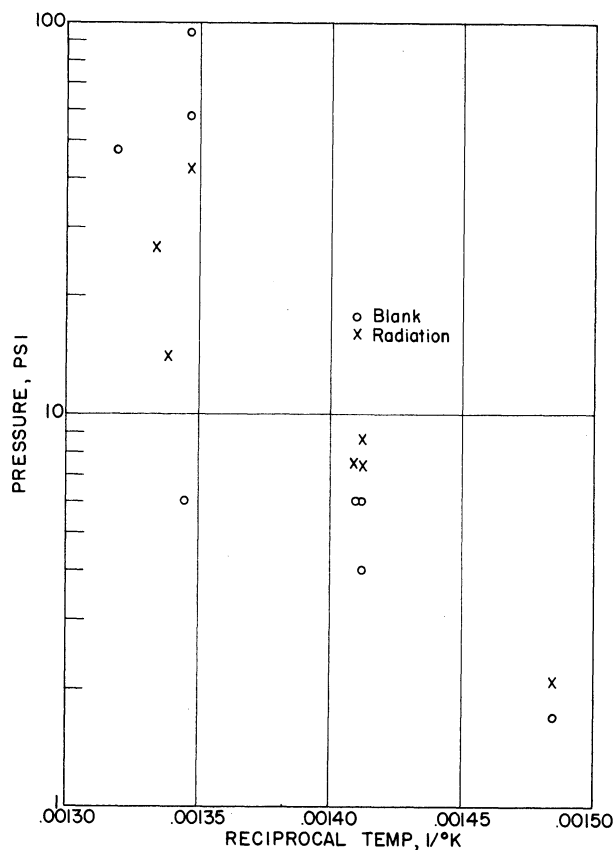


Fig. 22. Slope of linear pressure increase vs reciprocal temperature for cracking of cetane.

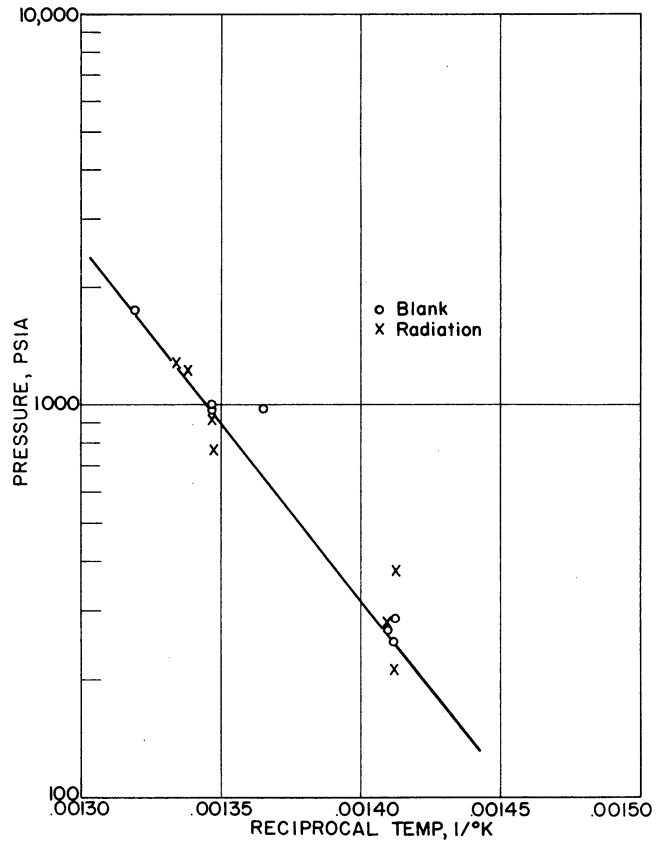


Fig. 23. End point of linear increase in pressure vs reciprocal temperature for cracking of cetane.

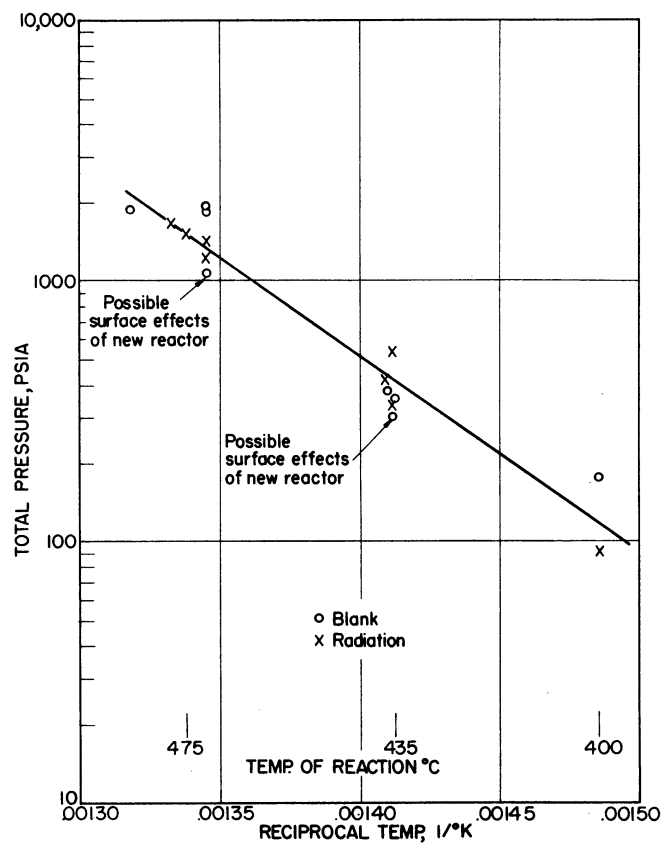


Fig. 24. Total pressure after one hour at reaction temperature vs reciprocal temperature for cracking of cetane.

The failure to obtain more concrete information from pressure-time behavior of the experiments is due to the complexity of the constant-pressure system. The possible factors that produce the various discrepancies are: (1) the possible surface effects due to the degree of oxidation of the metal surface of the reactor; (2) the presence of the liquid and gaseous phase in the reactor, which makes it difficult to differentiate between pressure effects due to vaporization and those due to reaction; (3) changes of rate of heat transfer from the walls of the reactor to the body of the fluid, which were seemingly affected even by slight changes in room temperature; (4) complexity of the reaction, so that increases in pressures due to the reaction cannot be directly translated into degree of conversion; (5) undetectable leaks; and (6) varying heating and cooling cycles.

No information from chemical analysis of the products could be obtained since their quantity was too small.

The experiments under reflux conditions described earlier gave more definite evidence in favor of the inhibition of gas formation by gamma radiation. The simplicity and excellent reproducibility of these experiments make their results hard to confute and completes the picture partially gathered in the batch-cracking experiments.

C. CONTINUOUS THERMAL CRACKING OF CETANE

The favorable results obtained in the batch experiments justified further study of cetane cracking. The failure of improving the reproducibility of the batch runs was judged to be mainly attributable to the impossibility of preheating the feed rapidly and uniformly and suddenly quenching the reaction products. This shortcoming could be effectively eliminated only with the use of the available continuous reactor.

All the continuous runs were conducted at the same space velocity; the only variable changed was temperature. The radiation dose was also kept constant, except that radiation runs were compared directly with blank runs, i.e., runs conducted outside the source. The results of the 13 experiments are somewhat ambiguous, mainly because a temperature error was discovered, as discussed earlier. This error, however small, unfortunately casts some doubts on the results, especially in the face of only minor differences caused by gamma radiation.

Figures 15, 16, and 17 give the complete summary of the continuous work. The points shown are corrected for temperature, yet a consistently lower gas conversion is noted for the radiation runs. This is better illustrated in Fig. 25, where moles of gas per mole of feed are plotted vs temperature. The result is in agreement with the evidence obtained in the batch work.

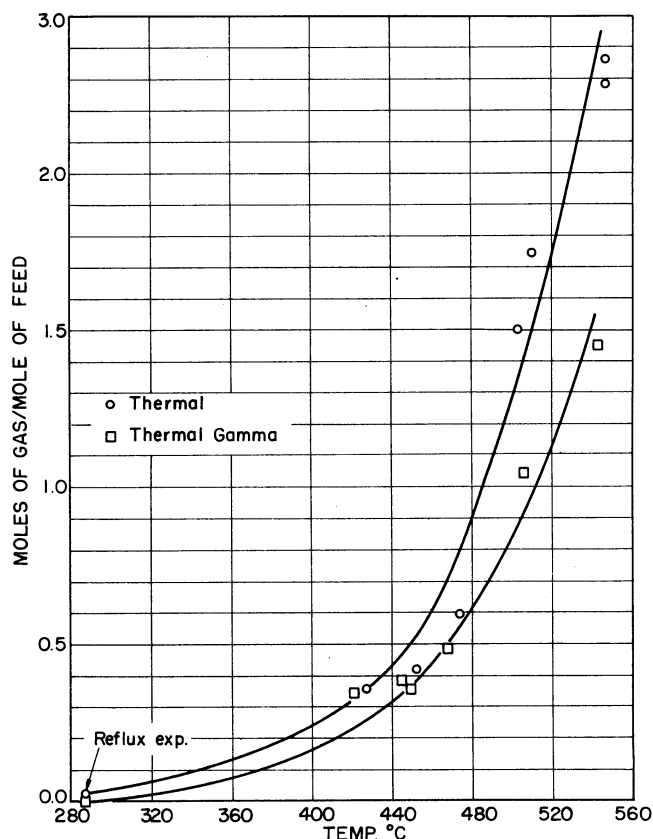


Fig. 25. Thermal cracking, approximately 1-hr contact time, moles of gas per mole of feed vs temperature, °C.

No further significant comment can be made for the following reasons:

1. The product analysis was not very complete for the liquid products. In two cases the Podbielniack fractionation of the liquid was not very satisfactory, especially when condensation products heavier than cetane are considered.
2. A rather limited amount of data which includes only experiments at the same contact time cannot be easily generalized.

D. CATALYTIC CRACKING OF CETANE

The data so far collected in the catalytic-cracking work are not sufficient to be analyzed in detail. The preliminary results indicate that for runs at approximately the same temperature, the nonirradiated runs produce more moles of gas per mole of feed than the irradiated runs. It is anticipated that the results can be interpreted better when the chemical analyses of the gas, liquid, and catalyst are received.

APPENDIX

A. SAMPLE CALCULATIONS FOR DOSE RATE

Unshielded Radiation Intensity = I_0

Centerline of reactor from centerline of source: 7 inches

Height of reaction zone: 3.5 inches symmetrical to the centerplane of the source

The intensity at various planes parallel to the centerplane of the source from Fig. 4 is plotted as a function of the distance from the midplane x on Fig. 26.

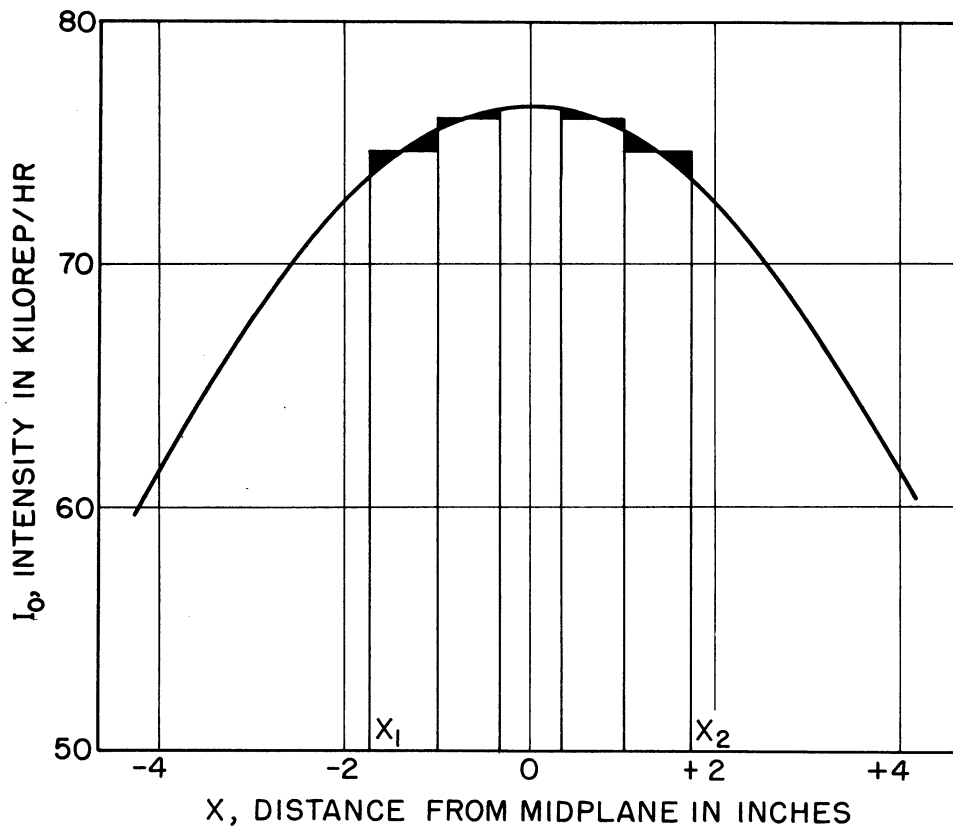


Fig. 26. Integration for radiation intensity.

The intensity $I_0(x)$ is integrated graphically between the limits x_1 and x_2 which represent the extremities of the reaction zone. This gives the average intensity as

$$I_{0\text{avg.}} = \frac{1}{x_2 - x_1} \int_{x_1}^{x_2} I_0(x) dx = \frac{75 \text{ kilorep}}{\text{hour}}$$

B. SHIELDING CALCULATION

The heater consists of a mixture of ceramic materials and aluminum. Since the densities and shielding properties of ceramics are similar to those of aluminum, the heater is considered to be all aluminum for shielding calculations.⁶ The simple exponential absorption law is assumed as

$$I = I_0 e^{-\frac{\mu x \rho}{\rho}}$$

where

I = intensity after shielding,
 I_0 = intensity before shielding,
 μ/ρ = mass absorption coefficient,
 x = thickness, and
 ρ = density.

Shielding due to heater:

$$\begin{aligned} I_0 &= 75 \text{ kilorep/hr} \\ \mu/\rho &= 0.055 \text{ cm}^2/\text{gm} \\ \rho &= 2.7 \text{ gm/cm}^3 \\ x &= 1.85 \text{ cm} \\ I &= 75 e^{0.055 \times 2.7 \times 1.85} = 57 \text{ kilorep/hr} \end{aligned}$$

Shielding due to reactor:

$$\begin{aligned} I_0 &= 57 \\ \mu/\rho &= 0.053 \text{ cm}^2/\text{gm} \\ \rho &= 7.8 \text{ gm/cm}^3 \\ x &= 0.625 \text{ cm} \\ I &= 57 e^{0.053 \times 7.8 \times 0.625} = 44 \text{ kilorep/hr} \end{aligned}$$

The dose determined by ferrous sulfate dosimetry⁵ in the reaction zone was 42 kilorep/hr.

C. SAMPLE CALCULATIONS FOR RUN NO. 12

Average reaction temperature was determined by the integral of the temperature profile, i.e., the average temperature throughout the reaction zone.

Off gas = 0.198 S.C.F. (S.C.F. at 60°F and 1 atmosphere)

$$\text{Off-gas weight} = 0.198 \text{ S.C.F.} \times 1.197 \frac{\text{gm moles}}{\text{S.C.F.}} \times 27.7 \frac{\text{gm}}{\text{gm moles}} = 6.6 \text{ gm}$$

Weathered gas = 0.164 S.C.F.

Weathered-gas molecular weight = 39.2, from gas analysis

$$\begin{aligned} \text{Weathered-gas weight} &= 0.164 \text{ S.C.F.} \times 1.197 \frac{\text{gm moles}}{\text{S.C.F.}} \times 39.2 \frac{\text{gm}}{\text{gm moles}} \\ &= 7.7 \text{ gm} \end{aligned}$$

$$\text{Liquid-product weight} = \frac{40.4 \text{ gm}}{54.7 \text{ gm}}$$

Total product weight = 54.7 gm

Total feed weight = 56.5 gm

$$\text{Material balance} = 54.7/56.5 \times 100 = 98.4 \text{ percent}$$

Liquid lighter than cetane, wt percent = 74 from liquid analysis

$$\text{Liquid product lighter than cetane} = 40.4 \times .74 = 29.9 \text{ gm}$$

Total product lighter than cetane = 29.9 + 6.6 + 7.7 = 44.2 gm

Product distribution output basis:

$$\text{Cetane unconverted} = 54.7 - 44.2 / 54.7 \times 100 = 19.2 \text{ percent}$$

$$\text{Liquid product} = 29.9/54.7 \times 100 = 54.6 \text{ percent}$$

$$\text{Gaseous product} = (6.6 + 7.7)/54.7 \times 100 = 26.2 \text{ percent}$$

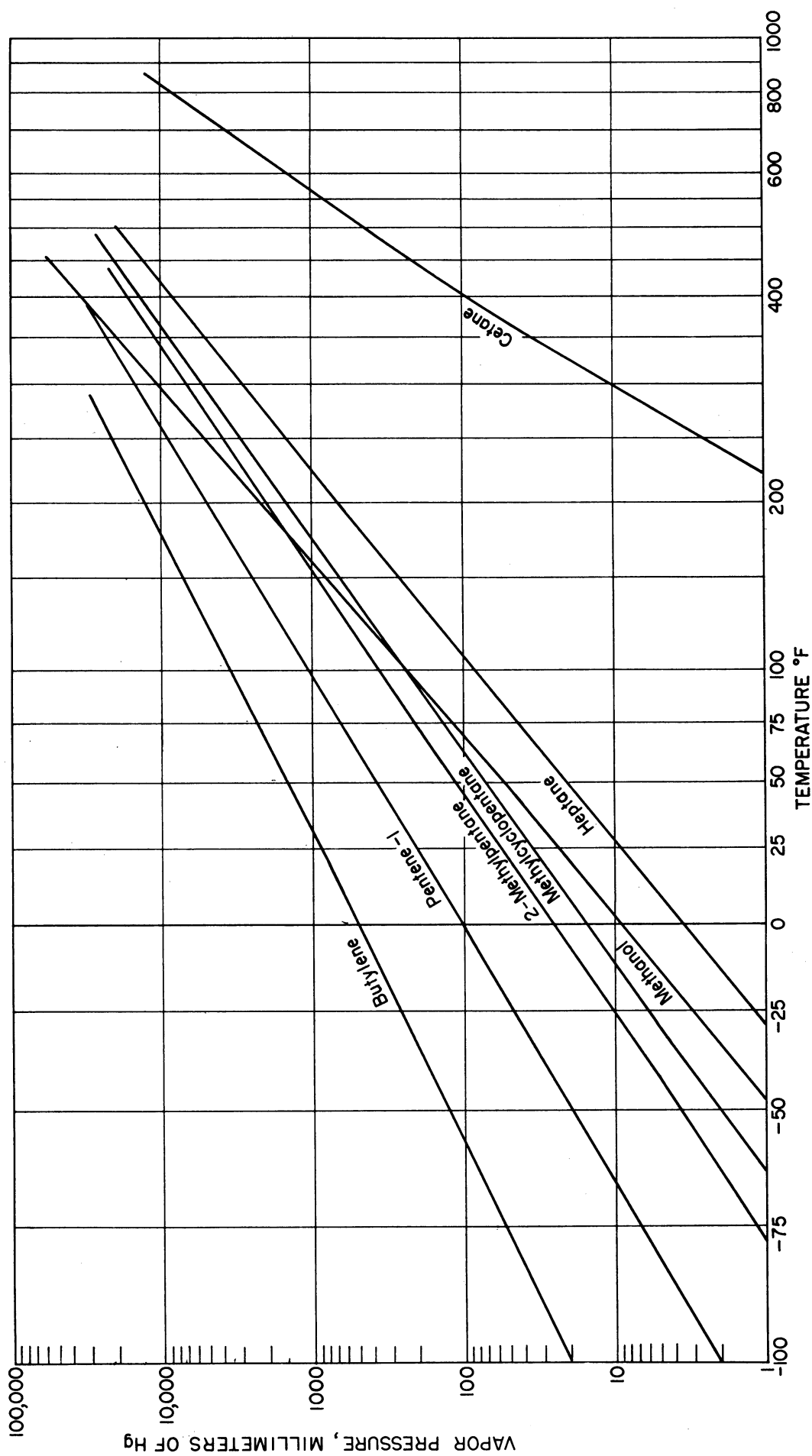


Fig. 27. Vapor pressure vs temperature for compounds studied. A.P.I. Project 44.

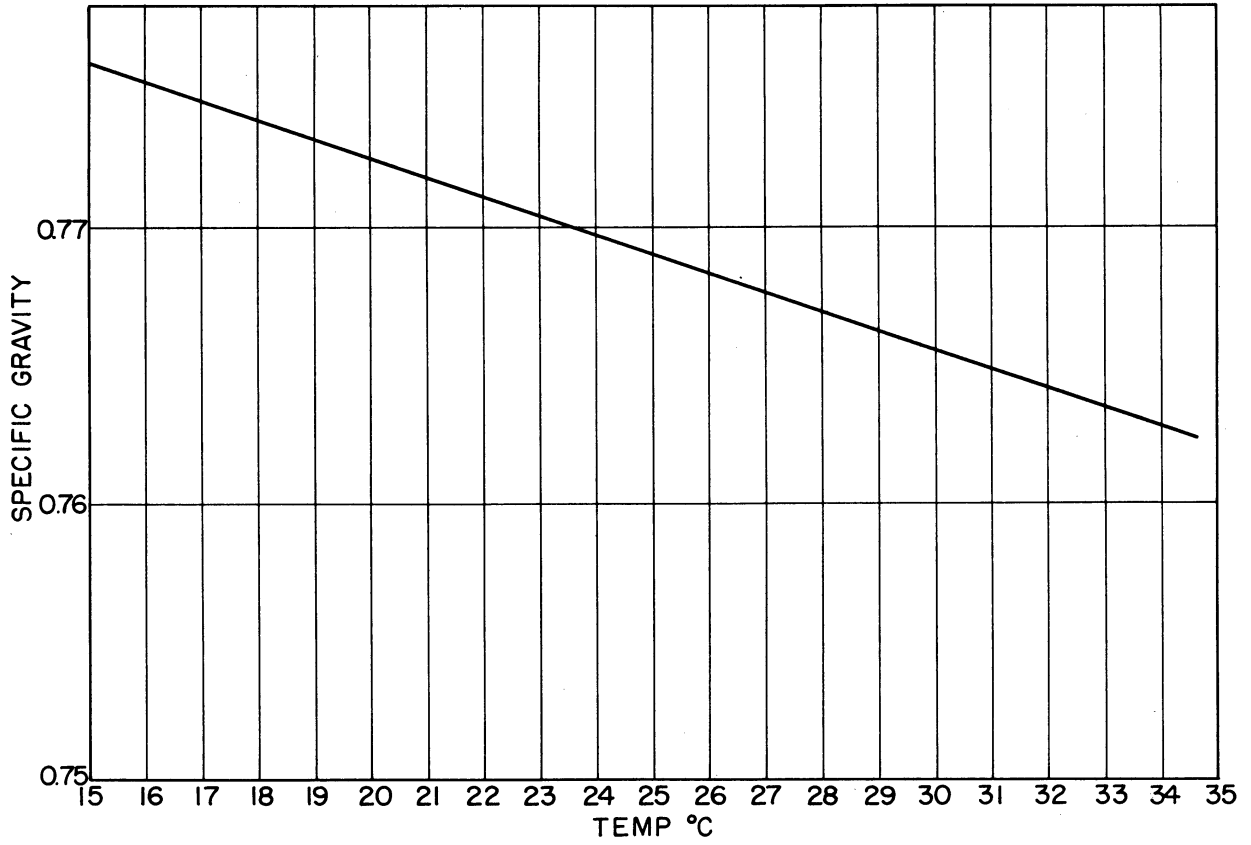


Fig. 28. Specific gravity of cetane vs temperature, °C. A.P.I. Project 41.

REFERENCES

1. Martin, J. J., Anderson, L. C., and associates, "Utilization of Gross Fission Products," Progress Report 4 (COO-124), Univ. of Mich., Ann Arbor, Eng. Res. Inst. Project M943, March, 1953.
2. Martin, J. J., Anderson, L. C., and associates, "Utilization of Gross Fission Products," Progress Report 5 (COO-196), Univ. of Mich., Ann Arbor, Eng. Res. Inst. Project M943, September, 1953.
3. Martin, J. J., Anderson, L. C., and associates, "Utilization of Gross Fission Products," Progress Report 6 (COO-198), Univ. of Mich., Ann Arbor, Eng. Res. Inst. Project M943, April, 1954.
4. Lewis, J. G., and Martin, J. J., "Promotion of Some Chemical Reactions by Gamma Radiation," Univ. of Mich., Ann Arbor, Eng. Res. Inst. Project M943-4, January, 1954.
5. Weiss, J., "Chemical Dosimetry Using Ferrous and Ceric Sulfates," Nucleonics 10, No. 7, pp. 28-31, 1952.
6. National Bureau of Standards Bulletin 54, "Protection Against Radiations from Cobalt-60 and Cesium-147," Washington, D. C., 1954.

