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EFFECT OF GAMMA RADIATION ON VARIOUS PETROCHEMICAL REACTIONS

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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 eventually permit generalizations of radiation effects on many different chemical reactions.

ABSTRACT

Gamma radiation produced no appreciable effects on the catalytic cracking of cetane at a radiation level of 42 kilorep per hour. Small differences could have been masked by experimental and analytical variables.

Para-Xylene inhibits the polymerization of ethylene by gamma radiation at pressures of 500-900 psig and at room temperature. Propylene in the presence of para-xylene does not react when irradiated.

Ethylene reacts with ethyl mercaptan at pressures of 450-1500 psig and room temperature only when irradiated and forms predominately (90-98 %), diethyl sulfide. Only under radiation will propylene react with ethyl mercaptan at temperatures of 20-50°C and pressures of 80-170 psig forming ethyl propyl sulfide (95-100 %). When 1:1 molal ratios of propylene and ethyl mercaptan are present, the reaction is of the first order with respect to total pressure. The reaction rate constant is dependent upon the dose rate.

Experiments with isobutane-ethylene, isobutane-propylene, isobutane-butylene, n-butane-ethylene, aniline-ethylene, and butylene-propylene indicate that there were no significant reactions in these mixtures using gamma radiation.

I. INTRODUCTION

The following study of the effect of gamma radiation on various petrochemical reactions was undertaken for Standard Oil Company of Indiana. The work was done under the auspices of the Engineering Research Institute of the University of Michigan, Project No. 2420. The present report is a continuation of the work reported in the annual report to Standard Oil Company of Indiana of August, 1955 to July, 1956, Effect of Gamma Radiation on Various Petrochemical Reactions, and covers the work period from July, 1956 to January 1st, 1957.

The program, in the six month period covered, consisted of four separate phases. The first was a continuation and analysis of the catalytic cracking studies of cetane. The second dealt with the reaction of para-xylene with ethylene and propylene using gamma radiation. The third phase consisted of a study of the effects of gamma radiation on the addition of ethyl mercaptan to ethylene and propylene. The last phase consisted of the study of alkylation and polymerization effects of gamma radiation on:

a) isobutane, ethylene

b) isobutane, propylene

c) n-butane, ethylene

d) iso-butane, butylene

e) butylene, propylene

f) ethylene, aniline

II. SUMMARY OF RESULTS

A. Catalytic Cracking of Cetane

From the results of the experiments conducted, it is possible to conclude that the irradiated experiments showed no differences from the non-irradiated experiments greater than 3 %, which is the probable experimental error. However, the work was not sufficiently detailed or comprehensive to rule out the possibility that small effects could have been masked by experimental and analytical variables.

B. Para-Xylene Experiments

(1) Ethylene

Ethylene will polymerize at pressures of 500-900 psig at room temperature in the presence of gamma radiation. It will not polymerize at these conditions without gamma radiation. However, this polymerization at the above conditions is inhibited by para-xylene. Due to the small quantities of solid product recovered, a quantitative statement cannot be made.

(2) Propylene

Since no component boiling higher than p-xylene was found in the distillation of the liquid from the p-xylene-propylene reaction, it was concluded that gamma radiation produced no detectable polymer or addition product in the propylene and para-xylene mixture.

C. Ethyl Mercaptan Reactions

(1) Ethylene

Ethylene will not react with ethyl mercaptan at room temperature and pressures from 450-1500 psig. However, this reaction will take place with gamma radiation forming predominately diethyl sulfide at a conversion of from 90 to 98 per cent in 72 hours at a dose rate of 59 kilorep per hour.

(2) Propylene

Propylene will react with ethyl mercaptan at temperatures from 20-50°C and pressures of 80-170 psig only under the influence of gamma radiation. When 1:1 molal ratios of propylene and ethyl mercaptan are present, the reaction is of the first order with respect to total pressure. The reaction rate constant is dependent upon the dose rate. The liquid samples contained from 96-99.7 per cent ethyl propyl sulfide. The reaction had a 95-100 per cent conversion of the ethyl mercaptan.

D. Alkylation and Copolymerization

Reactions with isobutane-ethylene, isobutane-propylene, isobutane-butylene, n-butane-ethylene, aniline-ethylene and butylene-propylene indicate that there were no significant reactions using gamma radiation at room temperature. However, the work was not sufficient to draw any definite conclusions. The preliminary work did indicate that the small amount of products formed was due to polymerization of the olefin and not due to a reaction between the olefinic molecule and the saturated molecule.

III. CATALYTIC CRACKING OF CETANE

A. Discussion of Results and Conclusions

Fig. 1 is a plot of the percentage of unconverted cetane recovered in the liquid product. The data applies to both the irradiated and non-irradiated runs at different space velocities. The data can be used as a direct measure of the amount of cracking that took place. It can be seen from Fig. 1 that there is no evidence to indicate that gamma radiation either inhibits or promotes the cracking of the cetane molecule.

Fig. 2 is a plot of the weight per cent of material lighter than cetane in the liquid product. There is no trend to indicate that gamma radiation has changed the product distribution resulting from the catalytic cracking reaction.

Fig. 3 is a plot of the carbon deposit on the catalyst per 100 grams of feed against space velocity. Again there is no trend to indicate that gamma radiation has an effect on the amount of carbon deposit on the catalyst.

Fig. 4 compares the gas produced at different space velocities. It shows that in every case more gas was produced in the non-irradiated runs than in the corresponding irradiated runs at the same space velocity. Two hypotheses were postulated in an effort to explain this result:

(1) The reaction mechanism for the irradiated runs tended to crack the cetane molecule near the center thereby producing a shift in product distribution resulting in less of the light gaseous hydrocarbon molecules and more of the heavier liquid molecules.

(2) Gamma radiation promoted polymerization of the light olefins to produce heavier liquid compounds and thereby reducing the volume of gas.

The analyses of the gas collected during the course of the runs as shown in Table I , indicate that the molecular weights and product distribution for the irradiated and non-irradiated runs at the same space velocity are nearly identical.

These run gas analyses present the strongest evidence to refute the two proposed theories since for either proposed theory to be valid, the gas from the irradiated and non-irradiated runs must have different product distributions and also would be expected to have different molecular weights.

From the results of runs conducted, it is possible to conclude that gamma radiation has no appreciable effect on catalytic crack-

ing. However, the work was not sufficiently detailed or comprehensive to rule out the possibility that small effects could have been masked by experimental and analytical variables.

B. Results

Table II is a summary of the experimental conditions and results of the 23 catalytic cracking runs. Of the 23 experiments, 11 were made with gamma radiation. The other twelve were used as control runs to better determine any effects of the radiation. The average temperature recorded in Table I was taken as the integral average of the temperature profile across the catalyst bed. As can be seen from Table I, there was no significant pressure drop observed in any of the runs reported. The radiation dose reported was calculated as shown in the Appendix, pages 34-35, of the Annual Report from August, 1955 to July, 1956. The space velocity in the Table is defined as:

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

The data in the column headed, Material Lighter than Cetane, %, was obtained from a liquid product analysis determined by gas chromatography by Standard Oil (Indiana).

Runs 1c through 8c were conducted with 1.2 inches of catalyst bed. However, it was decided that more accurate data could be obtained if more gas was formed during the run. Therefore, 3.6 inches of catalyst bed was used for runs 9c to 23c which resulted in decreased space velocities. However, only runs 16c through 23c are plotted in the following Figures 1 through 4 since these were the only runs where consistent conditions were maintained. The data for these runs were collected after modifying the equipment to permit a uniform method of duplicating the irradiated and non-irradiated runs. The temperature difference (max. 15°C) was neglected in making the plots.

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 was controlled by establishing a given temperature profile in the catalyst before each run was started. With these difficulties overcome, it can be noted (runs 18c-23c) that for runs at the same space velocity the temperature difference was only 1°C. The operation at different feed rates resulted in different temperature profiles in the catalyst bed and accounts for the range in average catalyst bed temperatures from 519 to 543°C.

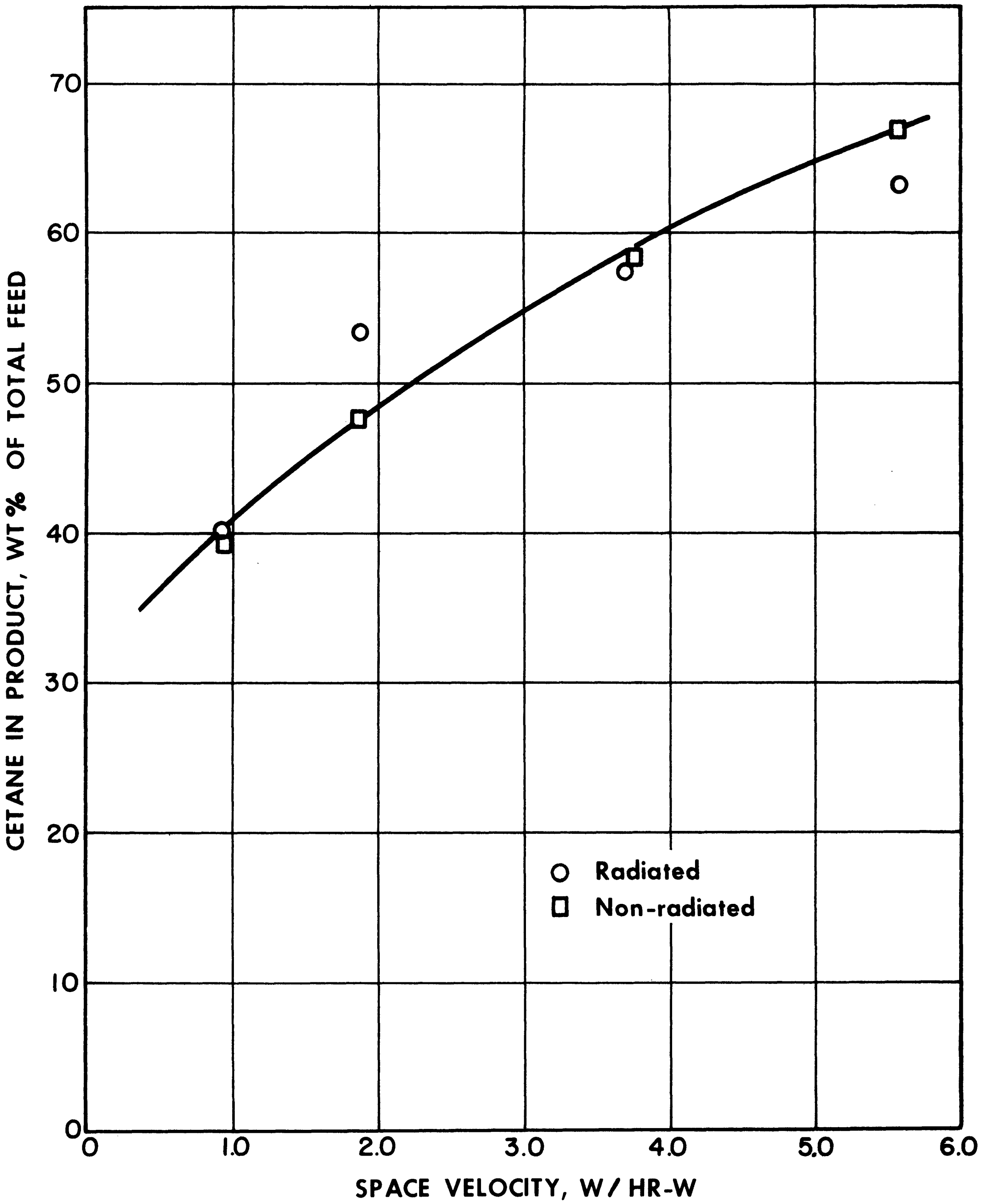


Figure 1. Cetane in Product, Wt. % of Total Feed vs. Space Velocity

Runs 16c through 23cγ plotted

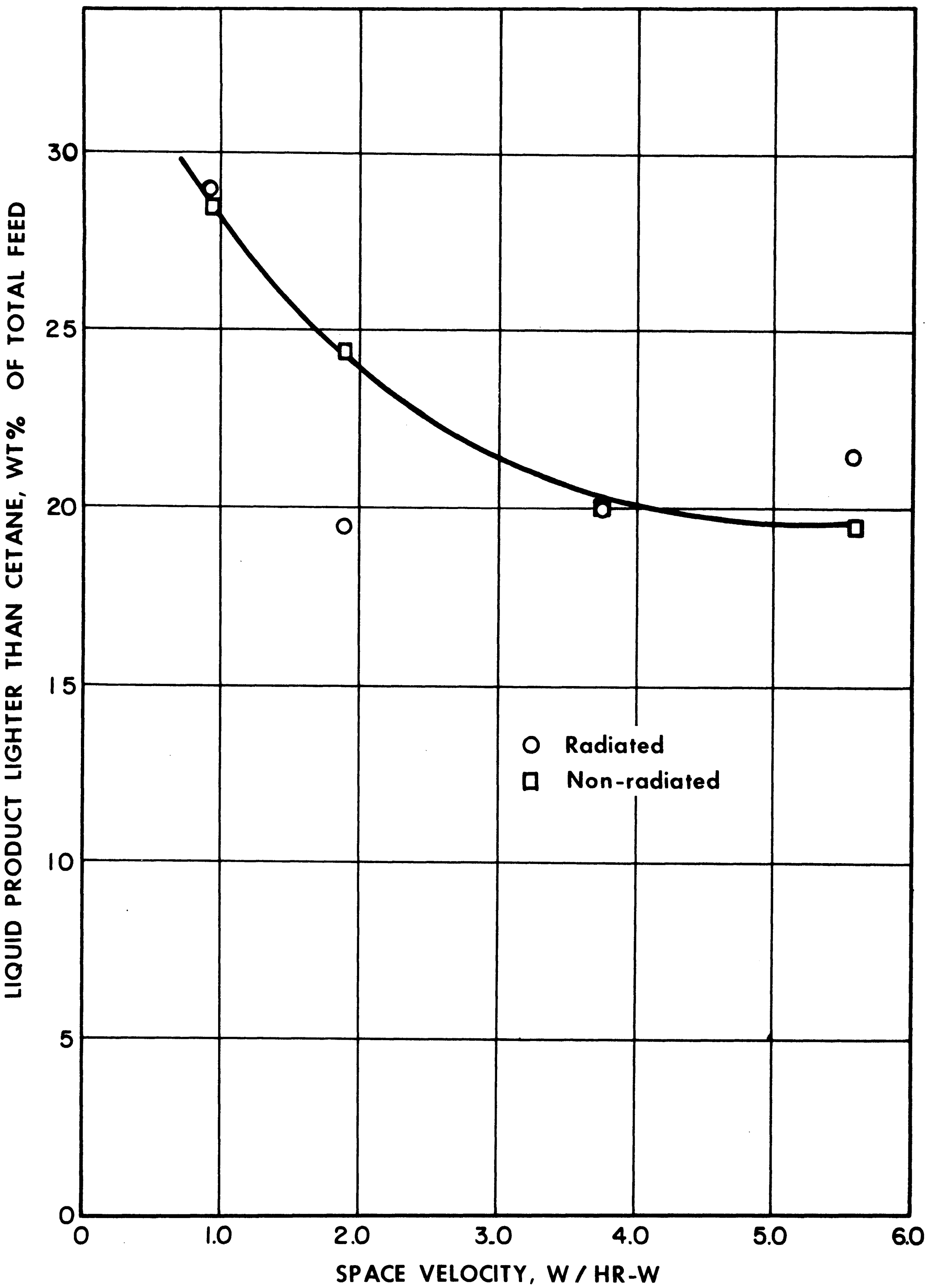


Figure 2. Liquid Product Lighter than Cetane, Wt. % of Total Feed vs. Space Velocity

Runs 16c through 23 cγ plotted

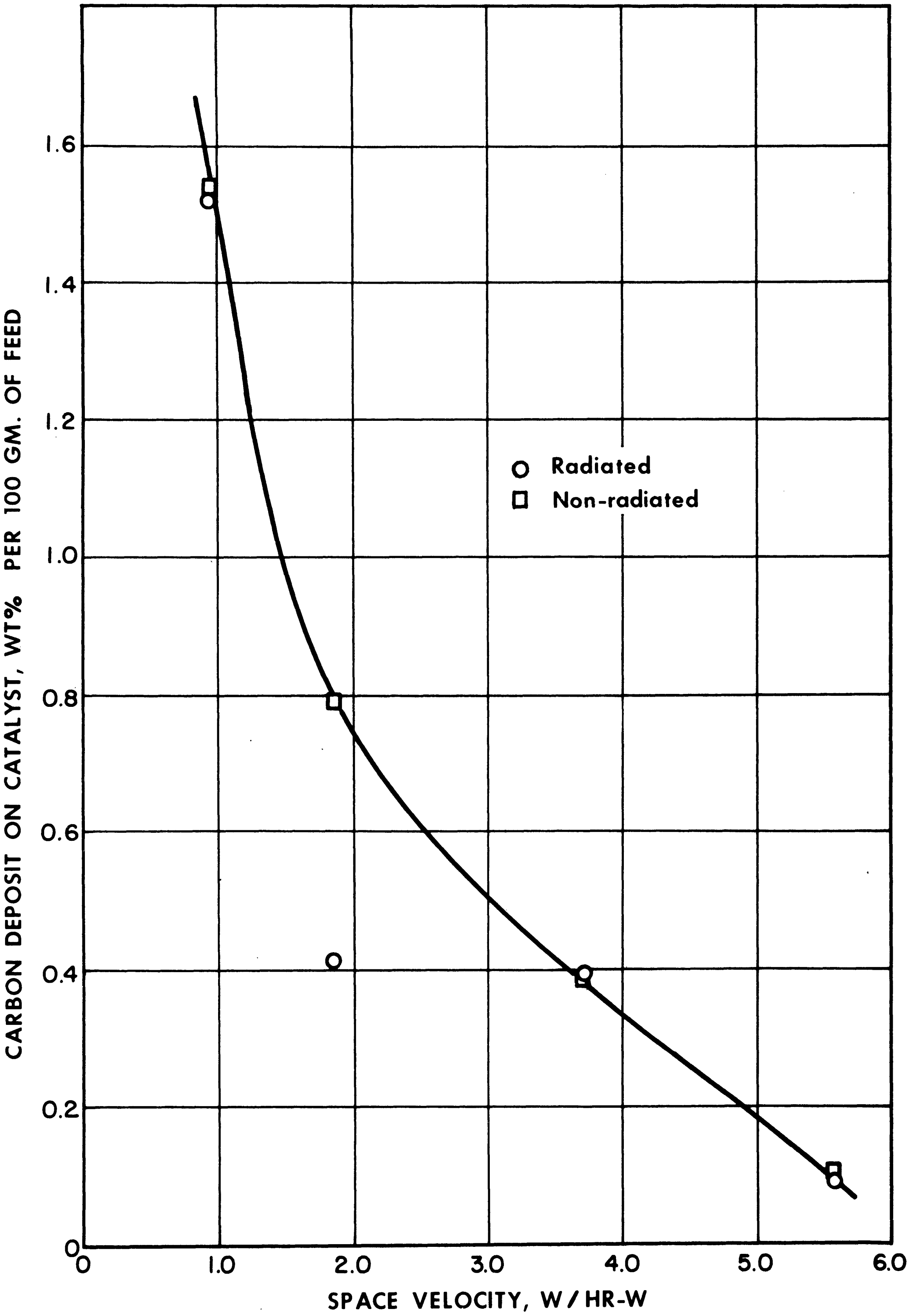


Figure 3. Carbon Deposit on Catalyst, Wt. % per 100 grams of Feed vs. Space Velocity
Runs 16c through 23cγ plotted

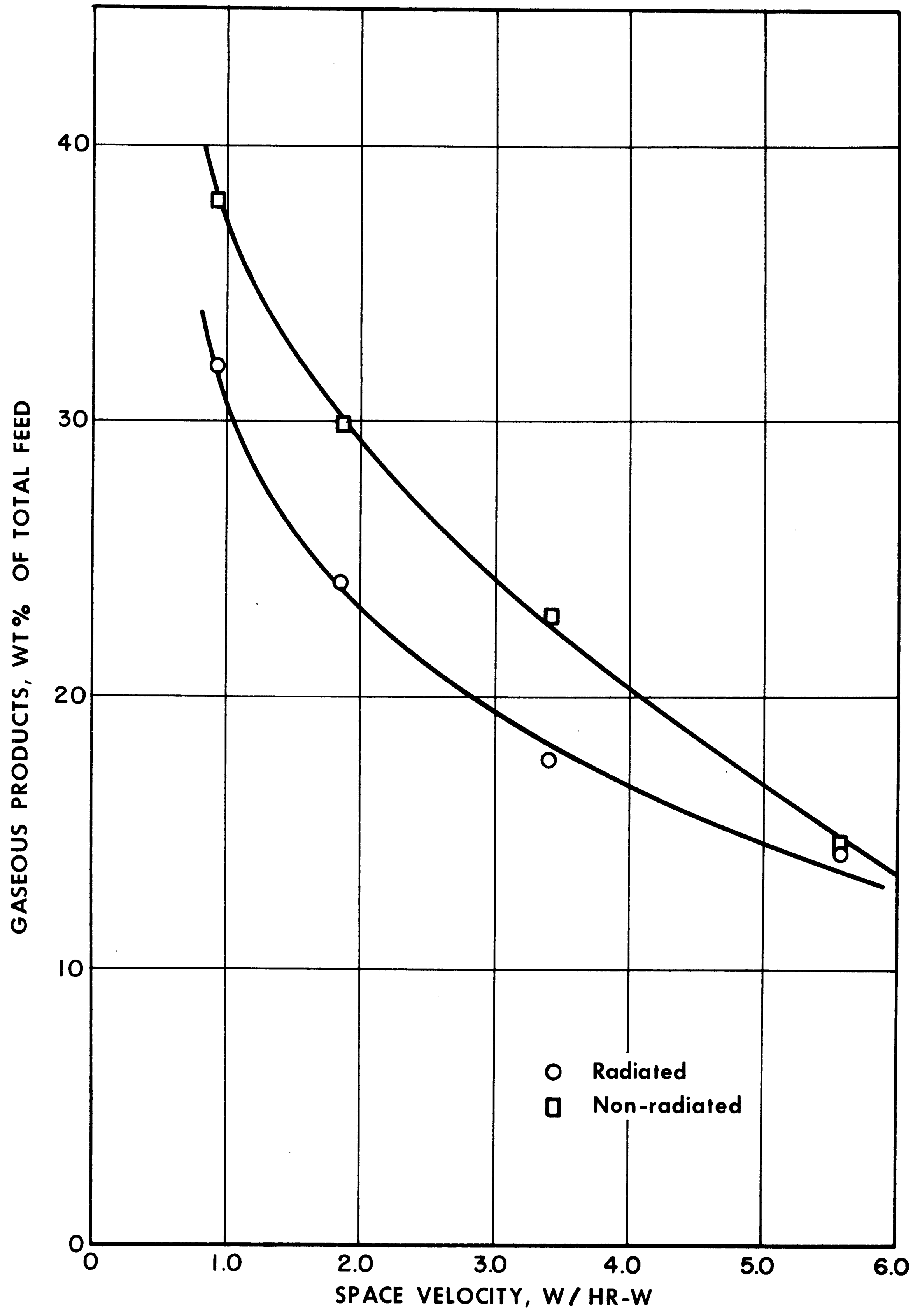


Figure 4. Gaseous Product Wt. % of Total Feed vs. Space Velocity.

Runs 16c through 23cγ plotted

TABLE I. PRODUCT DISTRIBUTION AND AVERAGE MOLECULAR WEIGHTS OF GAS SAMPLES FROM CATALYTIC CRACKING OF CETANE

Run Number	16c	17cγ	18c	19c	20cγ	21cγ	22c	23cγ
Space Velocity	3.73	3.71	5.58	1.86	1.87	5.58	0.933	0.932
C_6 Olefins and Napthenes	0.2	0.1	0.1	0.4	0.1	0.1	0.1	
C_5 Olefins and Napthenes	3.3	2.0	2.9	3.6	2.7	2.5	1.7	2.1
Normal Pentane		0.1	0.1		0.1	0.2	0.2	.3
Isopentane	1.9	1.3	1.4	2.0	1.8	1.4	1.4	1.4
Normal Butane	2.6	2.5	1.8	2.1	1.8	2.0	2.2	1.9
Isobutane	5.3	5.7	5.1	5.3	5.3	4.6	5.2	5.5
Butenes	21.8	20.1	21.0	19.8	18.6	20.2	14.9	15.8
Propane	7.9	8.9	7.4	7.5	7.2	6.5	8.3	8.4
Propylene	30.6	33.4	33.6	28.5	31.0	33.2	28.4	26.9
Ethane	3.0	3.2	3.6	4.6	5.0	3.6	5.2	4.7
Ethylene	9.4	8.9	9.4	9.7	11.0	11.9	12.8	12.1
Methane	4.8	4.5	5.2	6.8	6.8	5.2	9.2	9.3
Hydrogen	9.2	9.2	8.3	9.8	8.7	8.4	10.5	11.5
Total	100.0	99.9	99.9	100.1	100.1	99.8	100.1	99.9
Specific Gravity	1.439	1.417	1.426	1.401	1.386	1.401	1.300	1.297
Average Molecular Weight	41.6	40.2	41.4	40.7	40.2	40.6	37.7	37.6

TABLE II. SUMMARY OF CATALYTIC CRACKING OF CETANE

Run Number Date	1c 5/24/56	2c 5/25/56	3c γ 5/28/56	4c 5/29/56	5c 5/31/56	6c * 6/2/56	7c 6/4/56	8c ^ 6/6/56	9c 6/11/56	10c 6/12/56	11c ^ 6/12/56
Depth of bed, inches	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	3.6	3.6	3.6
Average Temp., °C.	495	495	500	534	542	544	542	541	475	482	486
Middle of bed Temp., °C.	500	500	505	539	547	549	547	543	475	495	492
Bottom of bed Temp., °C.		499					547	538	463	471	487
Top of bed Temp., °C.		477					536	533	440	487	487
Pressure drop, psig.	0	0	0	0	0	0	0	0	0	0	0
Approx. rad. dose krep/hour	-	-	42	-	-	42	-	42	-	-	38
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
Feed rate, cc/hour	120	120	120	120	120	120	120	120	120	120	120
Total run time, hour	1.0	1.0	0.834	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
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
Total feed, moles	0.409	0.409	0.340	0.409	0.409	0.409	0.409	0.409	0.409	0.409	0.409
Space velocity, W/hr/W	11.29	11.20	13.20	11.31	11.61	11.51	11.51	11.40	3.70	3.77	3.68
Liquid product, gm.	-	93.5	55.4	92.0	-	-	-	-	-	79.2	61.3
Off gas, SCF	0.0188	0.0249	0.00	0.0560	0.0938	0.00	0.0758	0.0802	0.1460	0.1345	0.0042
Weathered gas, SCF	-	-	-	-	-	-	-	0.011	0.0300	0.0143	0.0229
SCF 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
Gm-mole gas/-mole feed	0.055	0.0729	0.00	0.197	0.274	0.00	0.221	0.266	0.516	0.435	0.0793
Material lighter than cetane, %	7	8	6	9	12	10	12	9	14	13	13
Catalyst: (gas chromatography)											
% Carbon on sample											
% Volatile on ash											
% Carbon on ash											
Average molecular weight (off gas)	-	44.4	-	42.9	-	-	38.3	41.7	50.8	42.2	-
Off gas, gms.											
Weathered gas, gms.(mol.wt.58 assumed)***											
Purge gas, gms.**											
Material balance, weight %											
Gas products, weight % (input basis)											
Liquid products, weight % (input basis)											
Cetane converted, weight % (input basis)											
Cetane converted, weight % (output basis)											

Run Number Date	12c 7/8/56	13c γ 7/9/56	14c ^ 7/12/56	15c ^ 7/13/56	16c 7/16/56	17c γ 7/19/56	18c 7/31/56	19c 8/7/56	20c γ 8/9/56	21c γ 8/13/56	22c γ 8/16/56	23c 8/20/56
Depth of bed, inches	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6	3.6
Average Temp., °C.	525	522	529	526	527	520	535	533	-	-	-	530
Middle of bed Temp., °C.	532	527	534	531	531	525	534	526	527	533	519	519
Bottom of bed Temp., °C.	515			506	506		520	494	-	-	-	481
Top of bed Temp., °C.	523			521	521		515	531	-	-	-	525
Pressure drop, psig.	0	0	0	0	0	0	0	0	0	0	0	0
Approx. rad. dose krep/hour	-	42	42	42	-	42	-	-	42	42	42	-
Catalyst charged, gm.	25.20	25.54	25.20	25.20	25.20	25.20	25.20	25.20	25.20	25.20	25.20	25.20
Feed rate, cc/hour	120	122.4	122.2	122.1	122.6	121.3	182.9	61.05	61.15	183.1	30.55	30.50
Total run time, hour	1.0	1.0	1.0	1.0	1.0	1.0	1.0	2.0	2.0	1.0	2.0	2.0
Total feed, cc.	120	122.4	122.2	122.1	122.6	121.3	182.9	122.1	122.3	183.1	61.1	61.0
Total feed, gm.	92.6	94.4	94.1	93.9	94.0	93.5	141	93.9	94.3	141	47.1	47.0
Total feed, moles	0.409	0.416	0.415	0.414	0.415	0.413	0.621	0.414	0.415	0.621	0.208	0.207
Space velocity, W/hr/W	3.68	3.70	3.74	3.72	3.73	3.71	5.55	1.86	1.87	5.58	0.933	0.932
Liquid product, gm.	72.0	50.7*	61.4	62.15	68.75	67.27	116.7	59.04	62.03	115.24	26.13	24.90
Off gas, SCF	0.399	0.2965	0.279	0.280	0.362	0.295	0.359	0.4665	0.425	0.363	0.294	0.2965
Weathered gas, SCF	0.028	0.0121	0.0074	0.0313	0.0265	0.0154	0.025	0.0505	0.038	0.015	0.018	0.0475
SCF total gas/gm-mole feed	1.056	0.746	0.690	0.750	0.941	0.752	0.618	1.30	1.12	0.609	1.50	1.67
Gm-mole gas/-mole feed	1.265	0.594	0.825	0.896	1.125	0.900	0.737	1.55	1.33	0.727	1.79	2.00
Material lighter than cetane, %	17	15	15	25	20	20	19	24	19	23	28	27
Catalyst: (gas chromatography)												
% Carbon on sample	1.157	0.694	1.003	0.714	0.460	0.476	0.194	0.971	0.511	0.175	0.827	0.936
% Volatile on ash	3.35	2.75	4.24	3.66	3.37	3.41	2.56	2.38	3.01	2.14	2.64	2.58
% Carbon on ash	1.196	0.713	1.046	0.740	0.496	0.492	0.199	0.994	0.526	0.179	0.953	0.962
Average molecular weight (off gas)	42.9	42.5	40.9	40.8	41.6	40.2	41.0	40.4	39.9	40.3	37.4	37.2
Off gas, gms.	21.6	15.3	12.3	12.6	18.1	13.7	17.6	22.7	19.5	18.5	13.1	13.4
Weathered gas, gms.(mol.wt.58 assumed)***	2.05	0.84	0.50	2.2	2.0	1.4	1.7	3.5	2.7	1.0	1.25	3.3
Purge gas, gms.**	1.2	1.1	-	1.1	1.2	1.5	1.5	0.8	0.5	0.6	0.8	1.2
Material balance, weight %	105	73.4	101.0	83.3	96.0	89.6	97.5	91.8	89.7	96.0	87.5	91.0
Gas products, weight % (input basis)	26.8	19.5	14.65	17.0	22.7	17.7	14.7	29.6	24.1	14.3	32.0	38.1
Liquid products, weight % (input basis)	13.2	7.85	12.95	16.5	13.6	14.4	15.6	15.1	12.5	18.8	15.5	14.3
Cetane converted, weight % (input basis)	40.0	27.3	27.6	33.5	37.3	32.1	30.5	44.9	36.6	33.0	47.5	52.3
Cetane converted, weight % (output basis)	38.8	37.3	27.6	40.1	38.9	33.6	31.3	47.9	40.8	34.4	54.3	57.3

* Spill

** Purge gas - 2000 cc of N_2 passed through reacting system after each run

*** Weathered gas- gases evolved from liquid product on warming from 0°C to 20°C.

C. Experimental Procedure

The equipment and procedure followed in the catalytic cracking studies are fully defined in the Annual Report, August, 1955 to July, 1956. The details are listed on pages 26 through 27 of that report. Fig. 19, Catalytic Cracking Unit Flow Diagram, of the above report, shows the same equipment that was used for all catalytic cracking and Fig. 21, Catalyst Arrangement in Reactor without Spacer, is a diagram of the reactor used for experiments 9c through 23c, since it was desired to use a larger catalyst bed. The catalyst was obtained from Standard Oil of Indiana, No.3A5427 W.S.

The radiation facilities for the experiments are described in detail on pages 1 through 4 in the above report.

IV. PARA-XYLENE EXPERIMENTS

A. Ethylene and Para-Xylene

(1) Discussion of Results and Conclusions

Ethylene will not polymerize by itself or in the presence of para-xylene at room temperature and at pressures from 500-900 psi. However, at these conditions and with gamma radiation, ethylene does polymerize in the presence of para-xylene or by itself. Table III indicates that this polymerization is inhibited by para-xylene. But due to the small quantities of solid product recovered, a quantitative statement cannot be made.

(2) Results

The run conditions and results are reported in Table III. In most cases a white emulsion was present in the liquid product after venting off the gas. Most of the liquid was then distilled off at 138°C, the boiling point of para-xylene. The remaining emulsion was then placed on a watch glass and allowed to evaporate, leaving a solid product. In the distillation there was no fraction obtained with a boiling point higher or lower than 138°C.

The reactions containing ethylene, without para-xylene present, yielded a white fluffy polymer. The reactions containing para-xylene and ethylene yielded a dense polymer after distillation and solidification. It will be noted in Table III that some products are listed as being brown in color. However, it is believed that the product was initially white and that the distillation was carried too far and caused discoloration.

The products are now being analyzed at the Standard Oil Laboratories in Whiting.

TABLE III. ETHYLENE & PARA-XYLENE, SUMMARY OF RESULTS

Run Number Date	1 8/24/56	2 8/24/56	3 8/24/56	4 8/27/56	5 8/31/56	6 8/31/56	7 8/31/56	8 9/11/56	9 9/15/56	10 10/31/56
Volume of para-xylene, cc	25	0	12.5	0	25	12.5	3.0	0	70	35
Ethylene, gm	11.2	5.15	8.0	12.6	21.65	18.20	14.73	15.3	11.4	27.5
Initial pressure, psig	530	510	509	875	810	810	810	810	760	870
Initial Temperature, °F	72	72	80	90	77	77	77	68	64	77
Final Pressure, psig	530	100	480	860	805	795	800	810	430	870
Final Temperature	77.5	77.5	75.5	76	72	72	72	72	72	72
Ethylene gas phase, gm (recovered)	3.8	5.15	4.35	12.6	9.25	10.8	12.4	15.3	1.31	27.5
Solid product, gm	0.1835	-	0.0912	0.33	0.2754	0.2178	0.2433	0.37	0.065	0.22
Dose, megarep	5.12	4.2	4.95	3.59	4.17	4.17	4.17	4.32	4.20	4.3
Gm product per gm C_2H_4 charged	0.0163	-	0.0114	0.0262	0.0129	0.0119	0.0165	0.0242	0.0057	0.0080
Remarks	brown waxy solid		brown solid	white soft powder	dense white solid	dense white solid	dense white solid	white soft powder	brown sludge	white solid

(3) Equipment and Procedure

A 100 cc stainless steel reactor equipped with a pressure gauge was used. This reactor is the same as shown on page 12, Fig. 7 of the Annual Report, August, 1955 to July, 1956. The reactor was filled with para-xylene by means of a pipette. The para-xylene and reactor were then cooled down to -76°C. The ethylene loaded mechanism was attached as shown in Fig. 5 of the present report. After the reactor was cooled, a vacuum of approximately 300 microns was established in the system. The desired amount of ethylene, as calculated from the pressure drop of the loading vessel, was then condensed into the reactor from the 300 cc loading vessel. The reactor was then closed and removed from the loading system.

Comparable reactions were run so that they would have a constant initial pressure with varying amounts of para-xylene and consequently, varying amounts of ethylene. The experiments were carried out at the temperature of the source room.

B. Propylene and Para-Xylene

(1) Discussion of Results and Conclusions

Since no component was found in the liquid product distillation between that of p-xylene and the added high boiler, it was concluded that gamma radiation produced no detectable results on the propylene and para-xylene mixture. The experiments were discontinued.

(2) Results

The four para-xylene-propylene runs are listed in Table IV. The experiments were so designed that the only variable would be the amounts of propylene and para-xylene present. The radiation was held constant for each run. The vials were all irradiated at the temperature of the source room.

An analysis of the liquid left in the glass vials after the propylene was allowed to vent off was attempted in a Podbielniak Column with cetane being added as a high boiling liquid. For reactions 1_p-3_p no component with a boiling point between p-xylene and cetane was detected. Run 1_p was not distilled but the p-xylene was allowed to evaporate and a few drops of viscous liquid was obtained as a product.

(3) Equipment and Procedure

The 100 cc vials for the propylene and para-xylene experiments are the same as those described on page 5, Fig. 5, of the Annual Report, August, 1955 to July, 1956. The apparatus shown

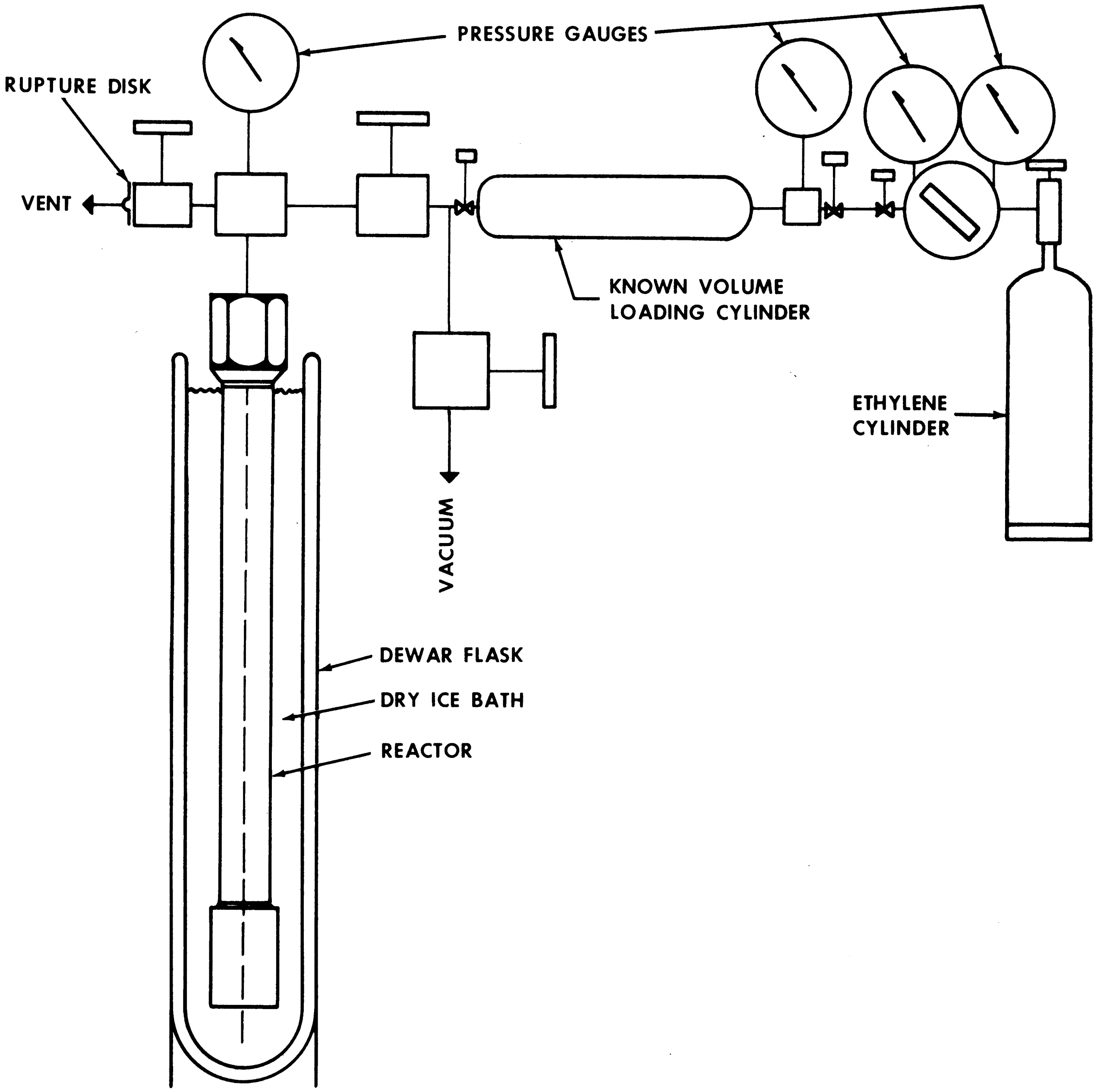


Figure 5. Ethylene Loading Apparatus

in Fig. 6 was used to load the vials with propylene and para-xylene.

The first step in the procedure was to evacuate the complete system to a pressure of 150 microns. The desired amount of propylene was then condensed in the vial at a temperature of -76°C (dry ice-chloroform-carbon tetrachloride mixture). Para-xylene was then injected into the vial by means of a syringe through the rubber serum stopper on one of the lead-out ports of the glass vial utilizing the vacuum of the system. The vial was then glass sealed with a flame and removed from the system.

The amount of propylene condensed was calculated from the specific gravity of liquid propylene at this temperature and the volume of the vial.

Recovery was attempted by breaking open the glass vials and letting the propylene evaporate. The para-xylene was then collected.

TABLE IV. PROPYLENE & PARA-XYLENE

Run Number	1_p	2_p	3_p	4_p
Date	9/6/56	9/6/56	9/7/56	9/7/56
Volume p-xylene, cc at 76°F	7.5	15	22.5	0
Volume of propylene, cc at -76°C(-103°F)	22.5	15	7.5	26
Dose, megarep	9.0	9.0	9.0	9.0

V. ETHYL MERCAPTAN EXPERIMENTS

A. Discussion of Results and Conclusions

(1) Ethylene

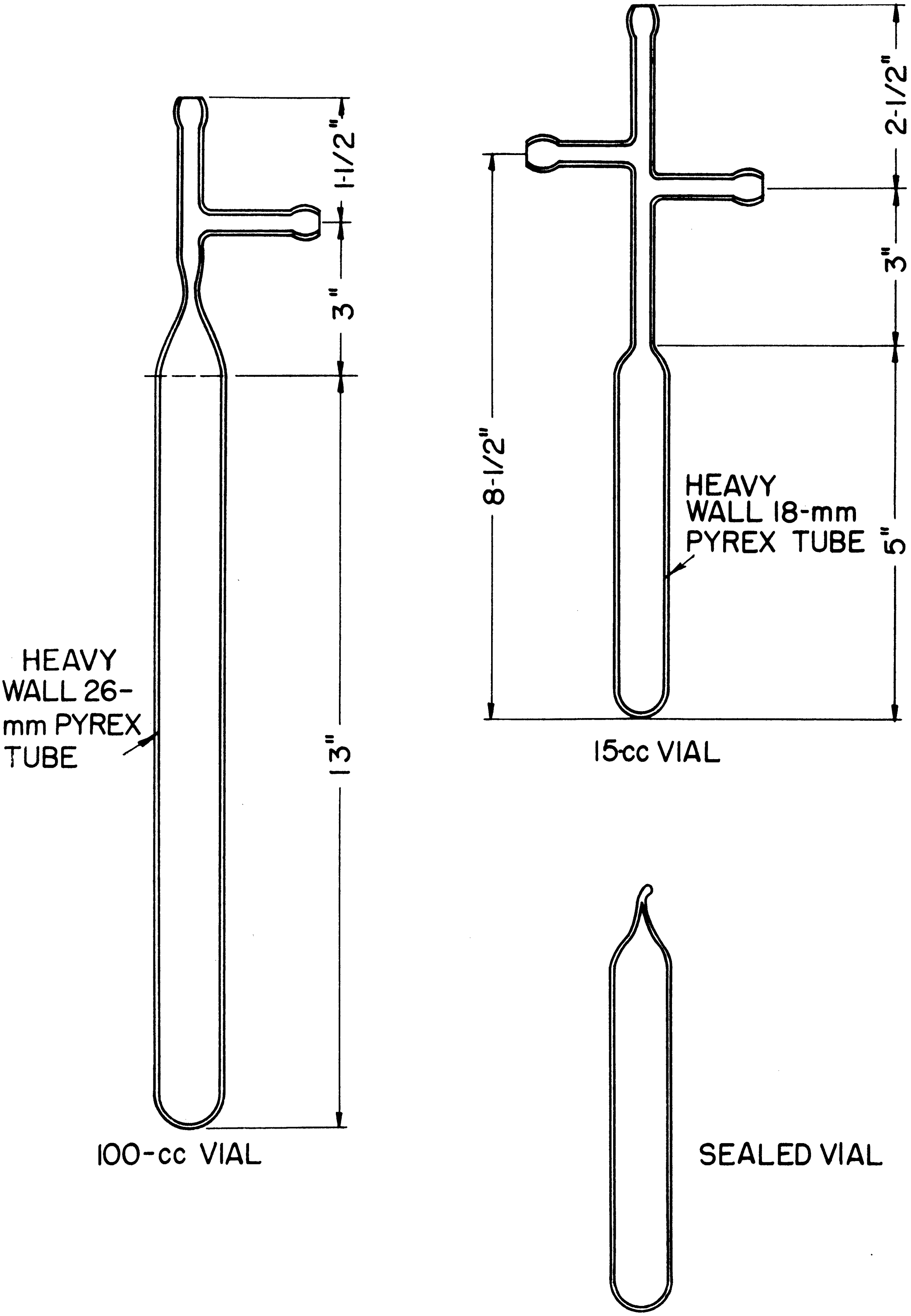
A study of the structure of ethyl mercaptan and ethylene indicates that any of the following reactions or combinations thereof are possible:

$$C_2H_5SH + C_2H_4 \rightarrow C_2H_5SC_2H_5$$

$$2C_2H_5SH \rightarrow C_2H_5S\text{-}SC_2H_5 + H_2$$

$$C_2H_5SC_2H_5 + C_2H_4 \rightarrow C_4H_9SC_2H_5$$

$$nC_2H_4 \rightarrow (-C_2H_4-)_n$$



100-cc VIAL

15-cc VIAL

SEALED VIAL

Figure 6. Glass Vessels for Propylene-Para-Xylene Experiments

However, from the analysis of the liquid products, it can be seen that the addition of ethylene to ethyl mercaptan tended to form diethyl sulfide (C_2H_5-S-C_2H_5). This reaction was definitely predominate even though a very small amount of the ethyl mercaptan did react with itself forming ethyl sulfide. However, the latter reaction only resulted in from 0.5 per cent to 7.0 per cent of the sample. It should also be noted in Run No. 3 that 10 per cent of the liquid sample was the compound $C_6H_{14}S$, believed to be $C_4H_9SC_2H_5$. There is no explanation as to why there is a greater amount of this higher sulfur compound formed in this case as compared to the other runs (per cent of higher sulfur compounds are listed in the miscellaneous column).

It should be noted here that the reaction will not take place without gamma radiation. A reactor was filled under the test conditions and allowed to stand for three days. During this time there was no reaction. However, when the reactor was irradiated, a reaction took place. It is concluded, therefore, that for ethylene to react with ethyl mercaptan at room temperature, the reaction must be initiated by gamma radiation. However, the data given in Table V do not permit other conclusions since there were not sufficient experiments conducted.

(2) Propylene

Rate studies were made on the addition of propylene to ethyl mercaptan at temperatures of 20°C and 50°C. The results are shown in Table VI and in Fig. 7 and 8. The graphs are plots of the concentration of propylene vs the radiation time for experiments No. 4 and 5 in Table VI. The concentration was calculated from the pressure of the reaction at different radiation times. (See Appendix-Sample Calculations, page 31). The log concentration versus radiation time for both runs plot as a straight line, indicating a first order reaction, depending on the concentration of the mercaptan. It is believed that the reaction rate constant is not a strong function of temperature but is dependent on dose rate. The latter is supported by the fact that without radiation there was no reaction. If temperature had an effect on the reaction rate constant, it would be expected to increase the constant, not decrease it as the data shows. However, the discrepancies in the two reported reaction rate constants, 0.0371 1/hr as compared to 0.0326 1/hr, is believed to be due to the fact that the reactor received different dose rates caused by the necessity of a constant temperature bath for the 50°C reaction (59K-rep/hr and 40K-rep/hr respectively).

The log concentration versus radiation time plot for Run No. 5 was a straight line with a reaction rate constant of 0.0326 1/hr for the first part of the reaction and a straight line of different slope with a reaction rate constant of 0.0213 1/hr for the latter part of the run. The change in rate constants

TABLE V. ETHYLENE + ETHYL MERCAPTAN, SUMMARY OF RESULTS

Run Number Date	1 9/18/56	2 9/18/56	3 9/19/56	4 9/26/56	5 9/28/56	6 9/29/56	7 10/9/56
1. Ethyl mercaptan charged, gms) S.G.=0.915 @ -75°C)	18.3	18.3	18.3	18.3	18.3	18.3	22.8
2. Ethylene charged, gms	23.8	11.9	**	0	20.0	35.0	0
3. Moles C_2H_4/moles C_2H_5SH	2.90/1	1.44/1	**	-	2.43/1	4.25/1	-
4. Vented gas, gms (MW=28)	10.72	5.58	6.78	0	10.3	26.0	0
5. Liquid product, gms	27.20	24.30	19.45	15.1	23.45	22.94	18.64
6. Initial pressure, psig	620	490	460	0	610	1450	0
7. Final pressure, psig	480	270	350	0	460	750	0
8. Temperature, °F	70	70	70	70	70	70	70
9. Dose, megarep	4.2	4.2	4.2	4.2	4.2	4.2	4.2
10. Liquid product analysis (mole %)							
Ethylene	*	-	-	*	-	-	-
Ethyl mercaptan	*	-	3.5	*	-	9.0	
Ethyl sulfide	97.5	97.0	79.0	*	97.0	87.0	-
Ethyl Disulfide	1.25	2.0	7	*	0.5	1-2	-
Miscellaneous***	1.25	1.00	10.0	*	2.5	1-2	
11. % Recovery of reactants	*	99	-	82.5	88	92	-
A value		7,250	6,900	-	7,050	7,100	-

* No analysis made due to contamination
** Reactor had to be vented to relieve pressure
*** Indicates higher molecular weight sulfur compounds

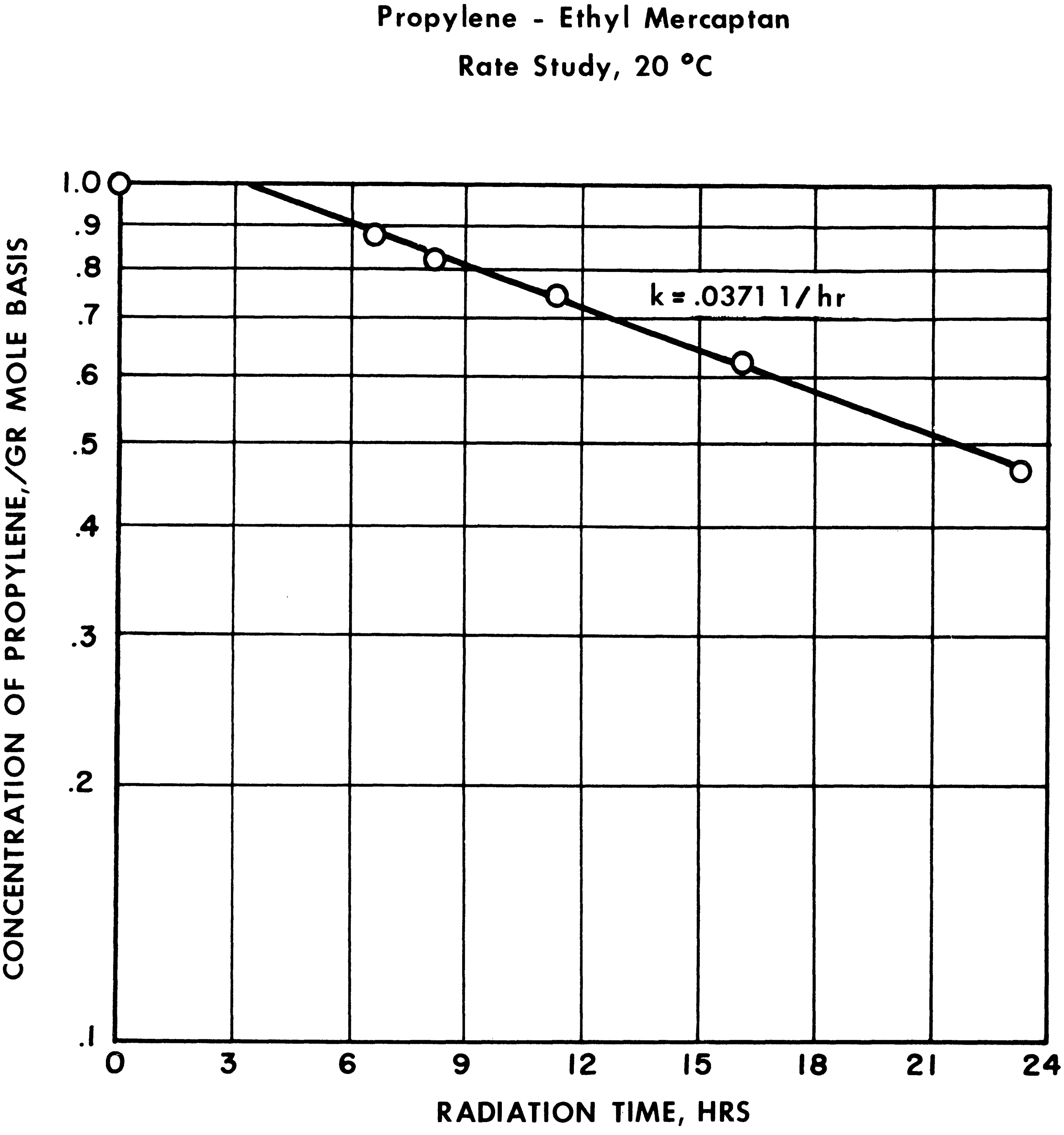


Figure 7. Run No. 4 Propylene and Ethyl Mercaptan
1/1 mole ratio at 20°C
Dose rate 59 K-rep/hr.

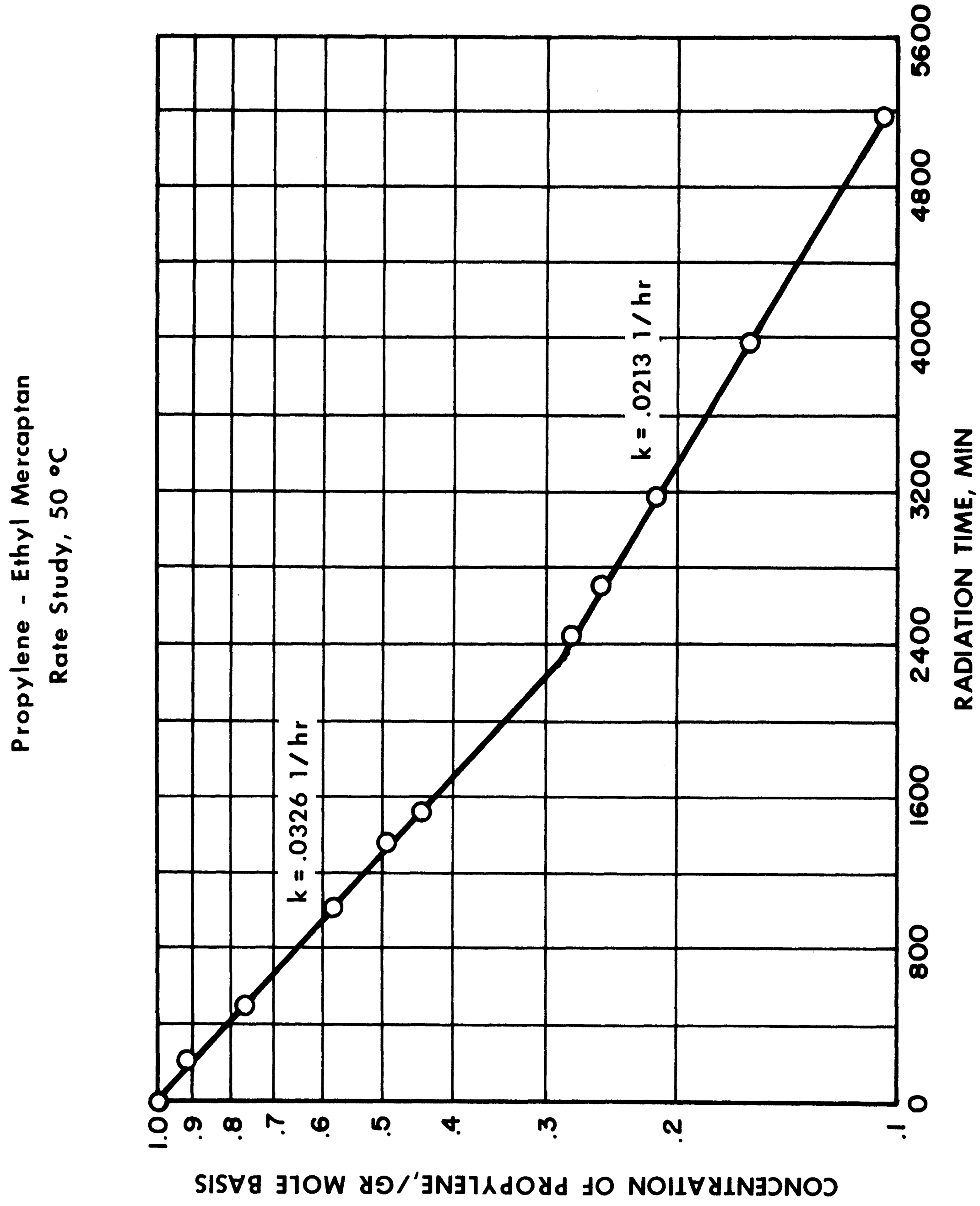


Figure 8. Run No. 5 - Propylene and Ethyl Mercaptan
1/1 mole ratio at 50°C
Dose rate 40K-rep/hr.

is believed to be caused by accidently moving the reactor during its radiation time resulting in a decreased dose rate and thereby causing a lower reaction rate constant.

Two reactors were loaded and run under test conditions without radiation, one at 20°C and one at 50°C, for a two day period without any evidence of a reaction. However, when these same reactors were radiated a reaction took place. It was concluded, therefore, that the reaction between propylene and ethyl mercaptan will take place in the temperature range of 20-50°C only when initiated by gamma radiation.

The addition of propylene to ethyl mercaptan takes place almost exclusively with the propylene adding to the sulfur atom. The liquid samples analyzed indicated that the ethyl propyl sulfide formed from this reaction constituted from 96-99.7 per cent of the liquid sample while other sulfur compounds completed the total.

B. Results

The results of the seven experiments with ethylene and ethyl mercaptan are reported in Table V. The five experiments with propylene and ethyl mercaptan are given in Table VI. The ethylene experiments were conducted with constant amounts of ethyl mercaptan and constant radiation time. However, in the propylene experiments these quantities were varied. In addition the temperature of Runs 4 and 5 of the propylene experiment was varied to study the possible rate effects.

A distillation was attempted on the liquid product from Run No. 1 of the ethylene experiments. Since approximately 90 per cent of this product was distilled over in a boiling range from 84 to 95°C, a reaction was indicated. The boiling point of ethyl mercaptan is 37°C. Another distillation was attempted on the liquid product from Run No. 4 of the ethylene experiments. This run consisted of radiating pure ethyl mercaptan, and the distillation showed that all the product distilled over at 37°C.

The liquid products of Runs No. 3 and 4 of the propylene experiments were also distilled. All the liquid from Run No. 3 distilled at a constant temperature of 114°C. Six cc of the liquid from Run No. 4 distilled at 37°C (the boiling point of ethyl mercaptan) and 36 cc distilled in a temperature range of 116-119°C. This boiling point range corresponds to the boiling points of the possible addition products of the reaction.

In most of the ethylene experiments there was a certain amount of solid poly-ethylene found in the liquid product. There

TABLE VI. PROPYLENE & ETHYL MERCAPTAN, SUMMARY OF RESULTS

Run Number Date	1 10/6/56	2 10/7/56	3 10/17/56	4 11/3/56	5 11/13/56
1. Ethyl mercaptan charged, gms	19.8	8.94	19.0	29.4	29.8
2. Propylene charged, gms	13.45	25.2	28.1	20.2	20.2
3. Molar ratio, $\frac{\text{Propylene}}{\text{Mercaptan}}$	1/1	4.17/1	2.18/1	1/1	1/1
4. Liquid product, gms	32.21	13.00	27.75	40.02	48.0
5. Gas vented, gms (M.W.=42.1)	0	22.5	14.3	8.04	0.175
6. Initial pressure, psig	80.0	100	-	80	168
7. Final Pressure, psig	0	60	0	43	20.7
8. Dose, megarep	4.2	4.2	4.2	1.37	3.0
9. Temperature, (°C)	21	21	21	20	50
10. % Recovery of reactants, gms. products/gms feed	96.8	104	89.2	97	98.5
11. Liquid product analysis (mole %)					
Ethyl disulfide		1.3	0.3		
Ethyl propyl sulfide		96.0	99.7		
Miscellaneous *		2.0	-		
A value	4,200	3,020	3,080	7,420	5.750

* Indicates higher molecular weight sulfur compounds

was no attempt made to recover the solid product from the liquid. The complete product was sent to the Standard Oil Laboratories at Whiting for analysis.

C. Equipment and Procedure

The experiments were carried out in the same 100-cc stainless steel pipe reactors as mentioned earlier and shown on page 12, Fig. 7, of the Annual Report.

The procedure for loading was to first evacuate the system to approximately 300 microns and then immerse the reactor in a liquid nitrogen bath. In the ethylene experiments, ethylene was condensed in the reactor from the 275 cc loading vessel as shown in Fig. 5. After the desired amount of ethylene, as calculated from the pressure drop of the loading vessel, was condensed, the reactor and its cooling bath were removed from the loading system. A rubber serum stopper attached to a glass tube was then connected to the reactor. Ethyl mercaptan was introduced into the reactor from a syringe utilizing the vacuum in the reactor at liquid nitrogen temperature.

The procedure for loading propylene was very similar in that the system was first evacuated and then immersed in a dry ice bath. The desired amount of propylene was then condensed in the calibrated vial as shown in Fig. 9. The dry ice bath on the calibrated vial was removed and the propylene was allowed to condense in the reactor. Ethyl mercaptan was introduced into the reactor in the same manner as for the ethylene experiments.

The amount of ethylene charged was calculated from the pressure drop of the loading vessel as shown in the Appendix. The accuracy of this measurement is believed to be approximately ± 10 per cent. The accuracy of the propylene loading measurement are considered better since they were based on liquid volume measurements at a known specific gravity.

The ethyl mercaptan was cooled to 0°C before any attempt was made to work with the compound. A rubber serum stopper was attached to the top of the bottle containing the compound, and the ethyl mercaptan was withdrawn using a syringe.

After the reactor was irradiated, it was cooled in a dry ice bath. The reactor was then allowed to warm to room temperature while the gas was vented through a wet test meter and measured. A gas sample was taken at dry ice temperature and at room temperature for the ethylene series.

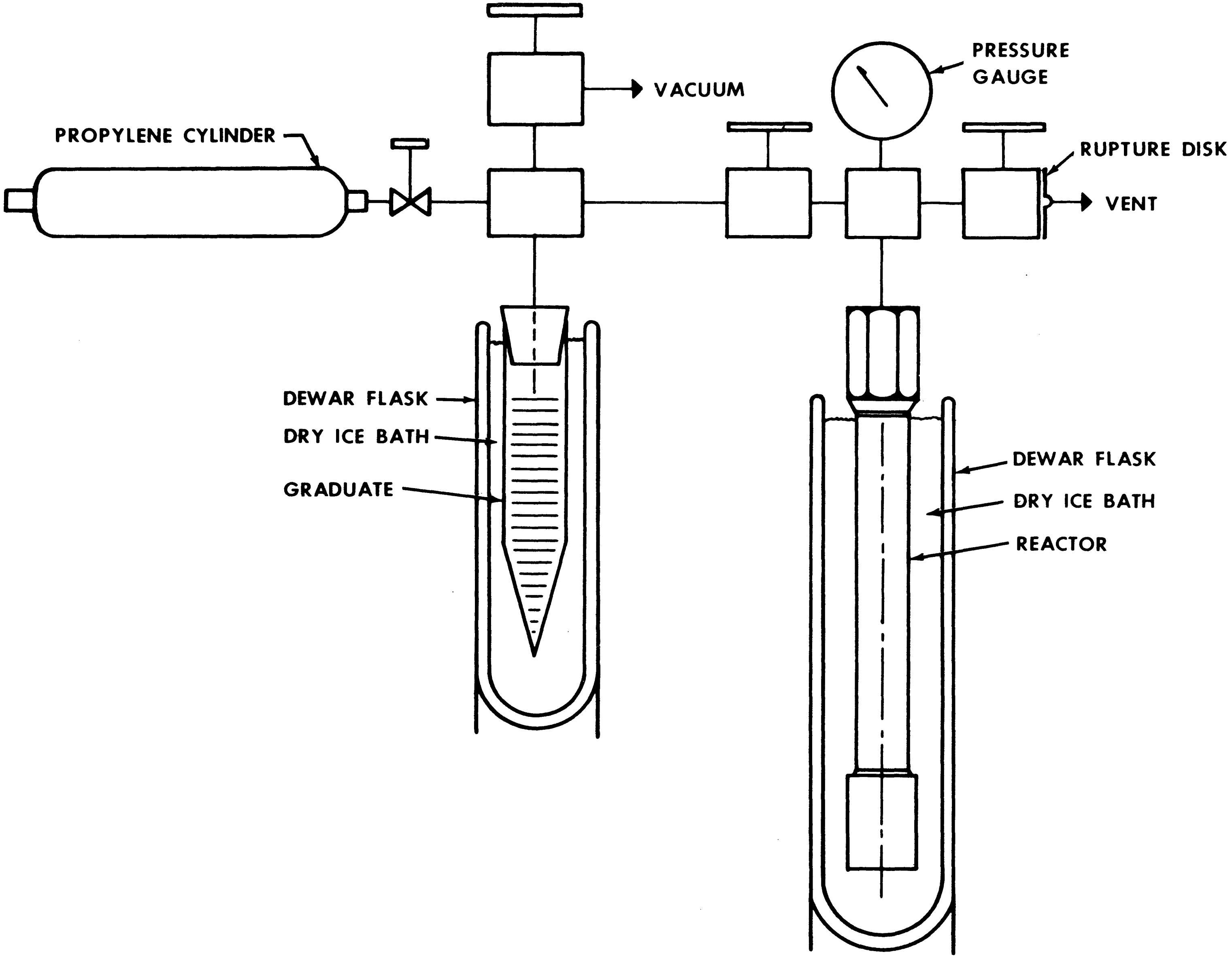


Figure 9. Propylene Loading Apparatus

VI. ALKYLATION AND COPOLYMERIZATION

A. Discussion of Results and Conclusions

The results of the various alkylation and copolymerization experiments are shown in Table VII. It should be noted from the table that there were no significant reactions with gamma radiation. The small amount of products formed seem to be a result of the olefin, for example ethylene, polymerizing by itself without any reaction with the saturated molecule. Also, in the case of propylene and butylene, it is believed that the residues left in the reactor were polymerization products of the olefins.

The large amount of product reported in the aniline-ethylene experiment is the weight of the aniline that was originally charged into the reactor and then recovered.

The only copolymerization experiment reported, butylene-propylene, showed no significant results.

It is believed that further work on the alkylation reactions must be conducted before any conclusions can be reached.

B. Results

(1) Isobutane

(a) Ethylene

Ethylene and isobutane, 20 gms and 22.1 gms respectively, were loaded into the reactor. This corresponds to a mole ratio of ethylene to isobutane of 1.87:1. The reaction received a dose of 6.9 megarep at room temperature, 70°F, the pressure remained constant at 510 psig. A white, fluffy product was recovered that weighed 2.3 grams and resembled polyethylene. It had a melting point of 127°C. In addition another isobutane-ethylene experiment was made. Since there was an error made in loading, it is not known how much isobutane was loaded with the 17.2 gms of ethylene. The reaction received 82 hours of radiation at an unknown dose rate which is indeterminate due to moving of the reactor. A solid was recovered weighing 0.21 gms and having a melting point of 123-127°C.

(b) Propylene

Two experiments were run at approximately 1:1 mole ratio. The first experiment contained 20.4 grams of isobutane and 14.9 grams of propylene and was held at 80 psig at 70°F. The mixture received a dose of 8.67 megarep. There was no liquid product.

TABLE VII. SUMMARY ALKYLATION EXPERIMENTS

	Olefins				
	Ethylene		Propylene		Butylene
	Run 1	Run 2	Run 1	Run 2	Run 1
1. Isobutane					
Amount of $1\text{-}C_4H_{10}$ loaded	22.1	-	20.4	26.8	21.2
Amount of olefin loaded	20	17.2	14.9	18.2	20.3
Mole ratio	1.87/1		1/1	1/1	1/1
Temperature (°C)	20	20	20	110	20
Pressure (psig)	510	-	80	2400	-
Radiation (megarep)	6.9	-	8.67	-	-
Product recovered (gm)	2.3	0.21	-	-	-
Description	white, fluffy solid	white, fluffy solid		oily residue	small amt. of liquid
2. N-Butane					
Amount of $n\text{-}C_4H_{10}$ loaded	22.2				
Amount of olefin loaded	19.8				
Mole ratio	1/1				
Temperature (°C)	20				
Radiation (megarep)	9.5				
Liquid product recovered	0.55				
Description	white, fluffy solid				
3. Aniline					
Amount aniline loaded	-				
Amount of olefin loaded	19.7				
Temperature (°C)	20				
Pressure	970				
Radiation (megarep)	4.2				
Liquid product	22.84				
Description	dark red liquid (pure aniline)				
4. Butylene					
Butylene loaded			14.1		
Amount of olefin loaded			10.6		
Mole ratio			1/1		
Temperature (°C)			100		
Pressure			405		
Radiation (megarep)			2.19		
Liquid product			-		
Description			small amt. viscous liquid		

The second experiment contained 18.2 grams of propylene and 26.8 gms of iso-butane and was conducted at a temperature of 110°C and at a pressure of 2400 psig. This received an unknown amount of radiation. An oily residue was left on the side of the reactor but there was not a sufficient quantity of it for recovery.

(c) Butylene

One experiment was conducted with butylene and iso-butane in 1:1 mole ratio. The reactor contained 21.2 gms of isobutane and 20.3 gms of butylene. After radiation, a small amount of camphorous smelling liquid was detected on the walls of the reactor.

(2) n-Butane

One experiment was carried out with 19.8 gms of ethylene and 22.2 gms of n-butane. The reaction was conducted under ambient conditions and received a dose rate of 9.5 megarep. A white, flaky solid was recovered that resembled polyethylene. The product weighed 0.55 gms. There was no liquid product present.

(3) Aniline and Ethylene

Twenty five cc of aniline was loaded into the stainless steel reactor. Then 19.7 gms of ethylene was charged into the reactor with a resulting pressure of 970 psig at 20°C. The experiment was conducted at ambient conditions and received a total dose of 4.2 megarep. A dark red liquid product was recovered that weighed 22.84 gms. However, it is believed that all of the product was pure aniline. Another experiment was conducted by irradiating pure aniline. In this case also a red liquid was recovered that distilled over at the boiling point of pure aniline.

(4) Butylene and Propylene

An experiment to determine the copolymerization effects of propylene and butylene was also made. A 1:1 mole ratio of the two materials (10.6 gm of propylene and 14.1 gms of butylene) was heated to 100°C with a resulting pressure of 405 psig. The reaction received a dose of 2.19 megarep. After venting the reactor, a small amount of viscous liquid was found at the bottom of the reactor. However, the amount was insufficient for recovery. In addition, there appeared a very small amount of brownish solid material attached to the sides of the reactor.

C. Procedure

The stainless steel bombs were used as reaction vessels. The system was as shown in Figure 10. The complete system was first evacuated to a pressure of 300 microns. The reaction vessel and calibrated vial were then immersed in a dry ice bath. The calculated amount of reactant was condensed in the calibrated vial. The dry ice bath was then removed from the vial, and the reactant was allowed to condense in the reaction vessel. This procedure was followed for each of the two reactants.

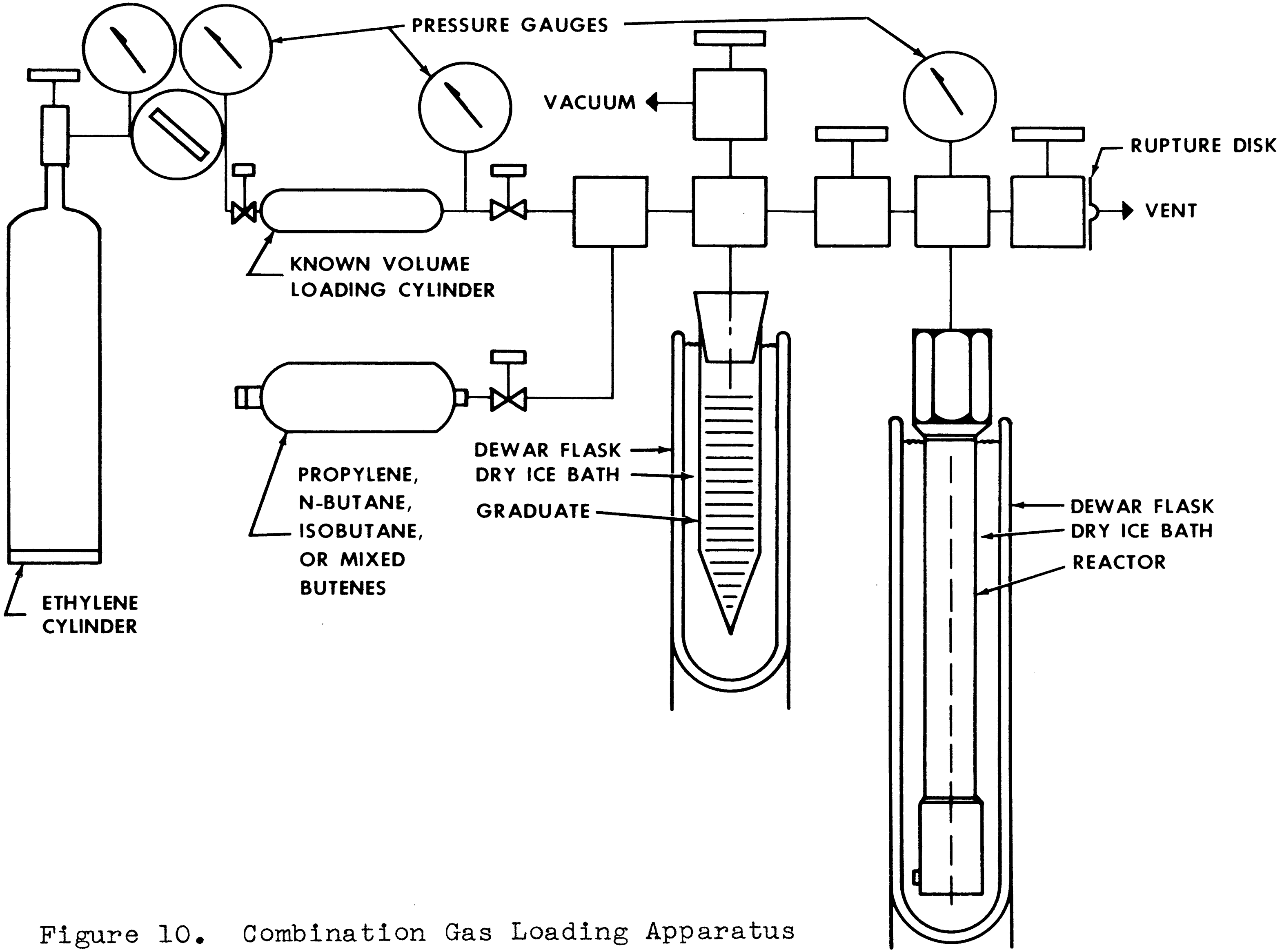


Figure 10. Combination Gas Loading Apparatus

APPENDIX

A. Sample calculations for Run No. 16c (Catalytic Cracking of Cetane)

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

Off gas. vol. = 0.362 S.C.F. (S.C.F. at 60°C and 1 atmosphere)
Off gas M.W. = 41.6 (Determined from mass spec. analysis)

$$\text{Off gas weight} = 0.362\ \text{S.C.F.} \times 1.197\ \frac{\text{gm moles}}{\text{S.C.F.}} \times 41.6\ \frac{\text{gm}}{\text{gm mole}} = 18.1\ \text{gm}$$

Weathered gas vol. = 0.0285 S.C.F.
Weathered gas M.W. = 58 (assumed)

$$\text{Weathered gas weight} = 0.0285\ \text{S.C.F.} \times 1.197\ \frac{\text{gm moles}}{\text{S.C.F.}} \times \frac{58\ \text{gm}}{\text{gm mole}} = 2.0\ \text{gm}$$

Purge gas vol = 2000 cc (at 748 mm and 83°C)= 0.0623 S.C.F.
Purge gas composition = 35.4 wt % organic material + 64.6 % Nitrogen
Ave. M.W. of organic material = 45.6 (from mass spec.)

$$\text{Weight organics in purge gas} = 0.0623\ \text{S.C.F.} \times 0.354 \times 1.197\ \frac{\text{gm moles}}{\text{S.C.F.}} \times 45.6\ \frac{\text{gm}}{\text{gm mole}} = 1.2\ \text{gm}$$

Liquid product weight = 68.8 gms
Total product weight = 18.1+2.0+1.2+68.8=90 gms
Total feed = 94.0 gms

$$\text{Material balance} = \frac{90.2}{94.0} \times 100 = 96.0\ \%$$

$$\text{Gas product wt \% (input basis)} = \frac{18.1+2.0+1.2}{94.0} \times 100 = 22.7\%$$

Liquid lighter than cetane, wt % = 20 % from liquid analysis
Liquid lighter than cetane = 0.20 x 68.8 gms = 13.8 gms.

$$\text{Liquid products, wt \% (input basis)} = \frac{13.8}{94.0} \times 100 = 14.7\ \%$$

Cetane converted = 13.8 + 18.1 + 2.0 + 1.2 = 35.1 gms

$$\text{Cetane converted, wt \% (input basis)} = \frac{35.}{94.0} \times 100 = 37.3\ \%$$

$$\text{Cetane converted, wt \% (output basis)} = \frac{35.2}{90.2} \times 100 = 38.9\ \%$$

B. Sample Calculations for

Ethyl Mercaptan and Propylene Rate Study No. 2

$$C_2H_5SH + CH_2 = CH_2 \xrightarrow[\text{Rad.}]{50^\circ C} C_2H_5SC_2H_5$$

1. Activity Coefficient

P = Total Pressure, psia

P_v = Vapor Pressure, psia

r = Activity Coefficient

$x_p = x_m$ = Mole fraction propylene and mercaptan

$P = \Sigma r P_v x$

at 50°C Vap. Pressure C_3H_6 = 297 psia

Vap. Pressure C_2H_5SH = 23.8 psia

When equal mole quantities of C_3H_6 and C_2H_5SH were loaded into a reactor at 50°C the observed pressure was 182 psia.

$$182 = (r \times 297)(.5) + (23.8)(.5)$$

$r = 1.14$ (arbitrarily assuming activity coefficient for ethyl mercaptan = 1.0)

2. Mole % C_3H_6 and C_2H_5SH at any time

(a) It was assumed that the only reaction was an addition between C_3H_6 and C_2H_5SH and that the vapor pressure of the product is negligible.

(b) After 1510 minutes of radiation the pressure was observed to be 110 psia.

$96 = (279)\cdot(1.14)\cdot(X) + 23.8\ (X)$

X = mole % C_3H_6 and $C_2H_5SH = 0.304$

3. % Conversion and Concentration of C_3H_6 and C_2H_5SH

$a = 1$ = initial number of moles of C_3H_6 and C_2H_5SH

y = moles of C_3H_6 and C_2H_5SH reacted

n = moles of C_2H_5SH

$$\underset{a-y}{C_2H_5SH} + \underset{a-y}{C_2H_4} \longrightarrow \underset{y}{C_2H_5\text{-}S\text{-}C_2H_5}$$

At any time, the total number of moles = $2a-y$

$$X = \frac{2-y}{2a-y}$$

$$0.304 = \frac{1-y}{2-y}$$

$$y = 0.563 = \%\ \text{conversion}$$

$$n = .5 - .563\ (.5) = 0.218$$

4. Order of Reaction and Rate Constant

(a) If 1st order reaction

$$\frac{-dn}{dt} = k\,n$$

t = time, hr
k = rate constant, hr^{-1}.

upon integrating

$\log n = -kt + I$

Since a plot of log n vs. t was a straight line, the reaction is 1st order

(b) Rate Constant

$-k$ = slope of log n vs t

or $\log \frac{n_o}{n} = -kt$ n_o = initial C_2H_5SH = 0.500

$$\log \frac{0.500}{0.218} = -k \frac{1510}{60}$$

$$-k = 0.0328 \text{ hr}^{-1}$$

C. Ethylene Loading Calculation

Volume of measuring vessel = 274 cc. = 0.00968 ft^3

Initial pressure of measuring vessel = 600 psig

Final pressure of measuring vessel = 300 psig.

Temperature during loading = 60°F

Volume per pound of C_2H_4, $\overline{V}$; taken from Chem. Eng. Handbook by J. H. Perry

600 psig. = 615 psia. = 41.8 atmospheres

from Perry's Handbook: at 41.8 atm and 60°F

$$\overline{V_1} = 0.208 \text{ ft}^3/\text{lb}$$

Initial wt. of C_2H_4 charged $= \frac{V}{\overline{V_1}} = \frac{0.00968 \text{ ft}^3}{0.208 \text{ ft}^3/\text{lb}} = 0.0465$ lb.

300 psig = 315 psia = 21.4 atmospheres

from Perry's Handbook: at 21.4 atmospheres and 60°F

$$\overline{V_2} = 0.540 \text{ ft}^3/\text{lb.}$$

Final wt. of C_2H_4 charged $= \frac{V}{\overline{V_2}} = \frac{0.00968 \text{ ft}^3}{0.540 \text{ ft}^3/\text{lb}} = 0.0179$ lb.

wt. of C_2H_4 charged in reactor = (0.0465 lb-0.0179 lb)

$$454 \frac{\text{gm}}{\text{lb}} = 13.0 \text{ gm}$$

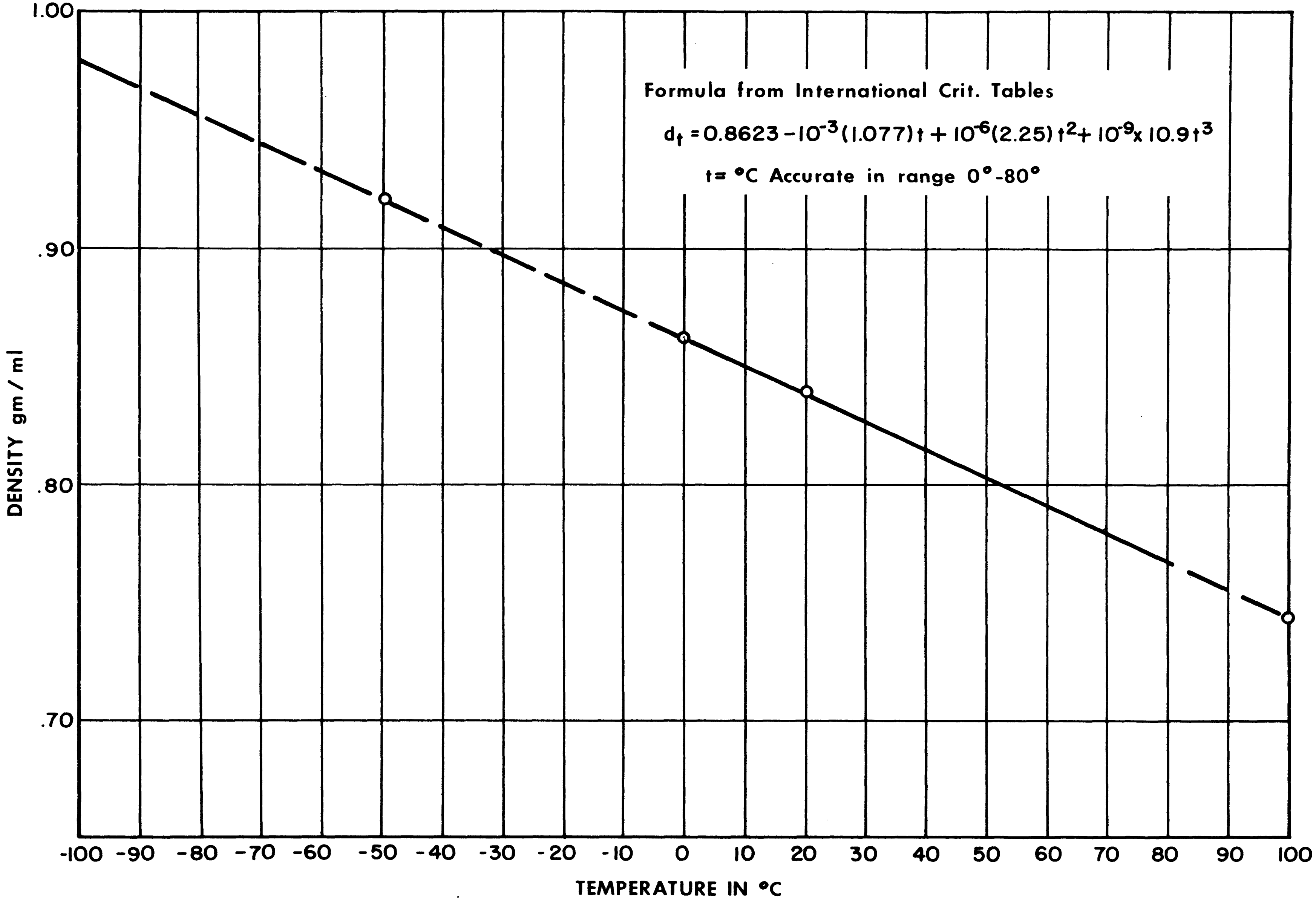


Figure 11. Density of Ethyl Mercaptan vs. Temperature

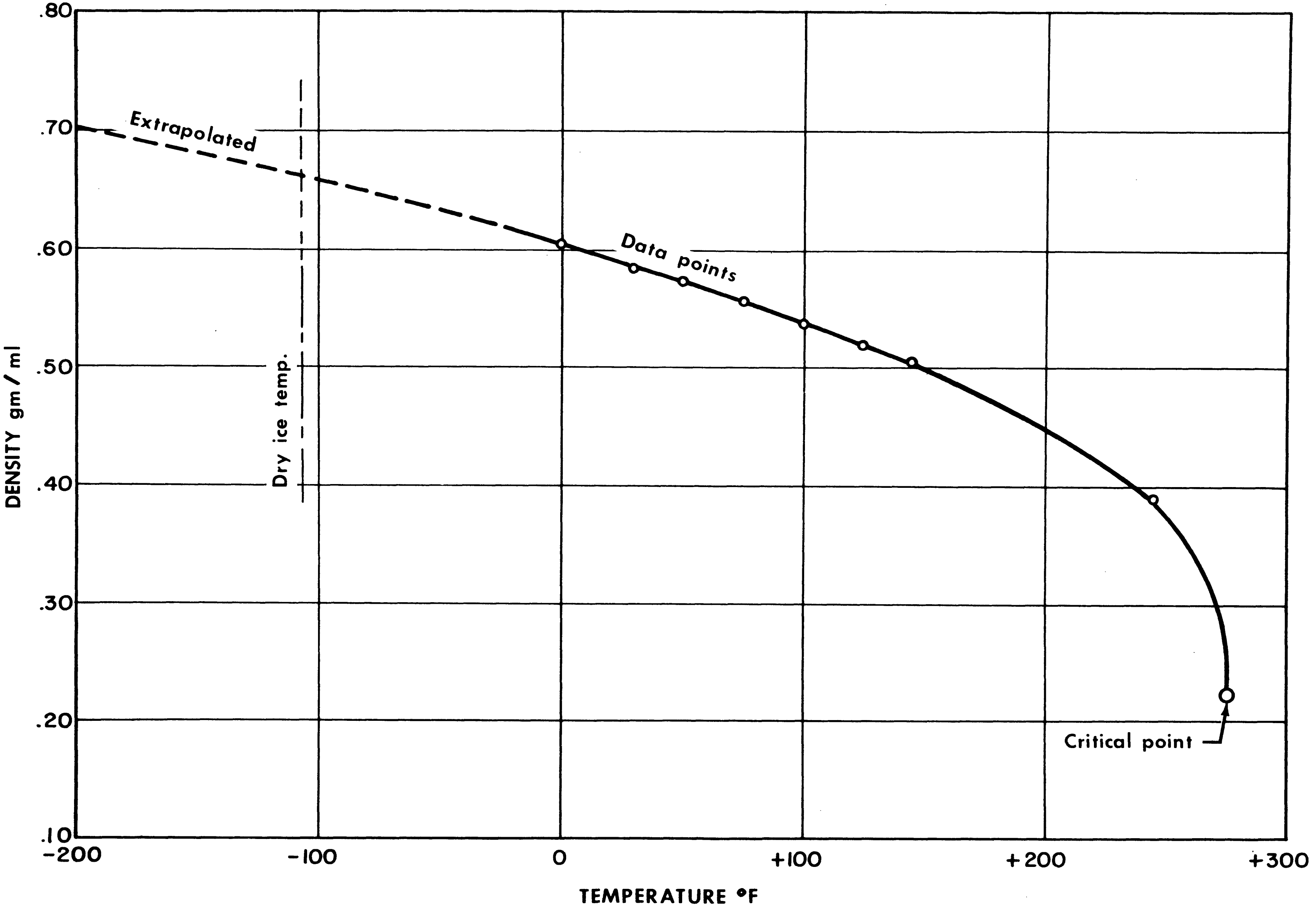


Figure 12. Liquid Density of Iso-Butane @ Saturated Pressure vs. Temperature °F - Data from Handbook of Butane Propane Gases

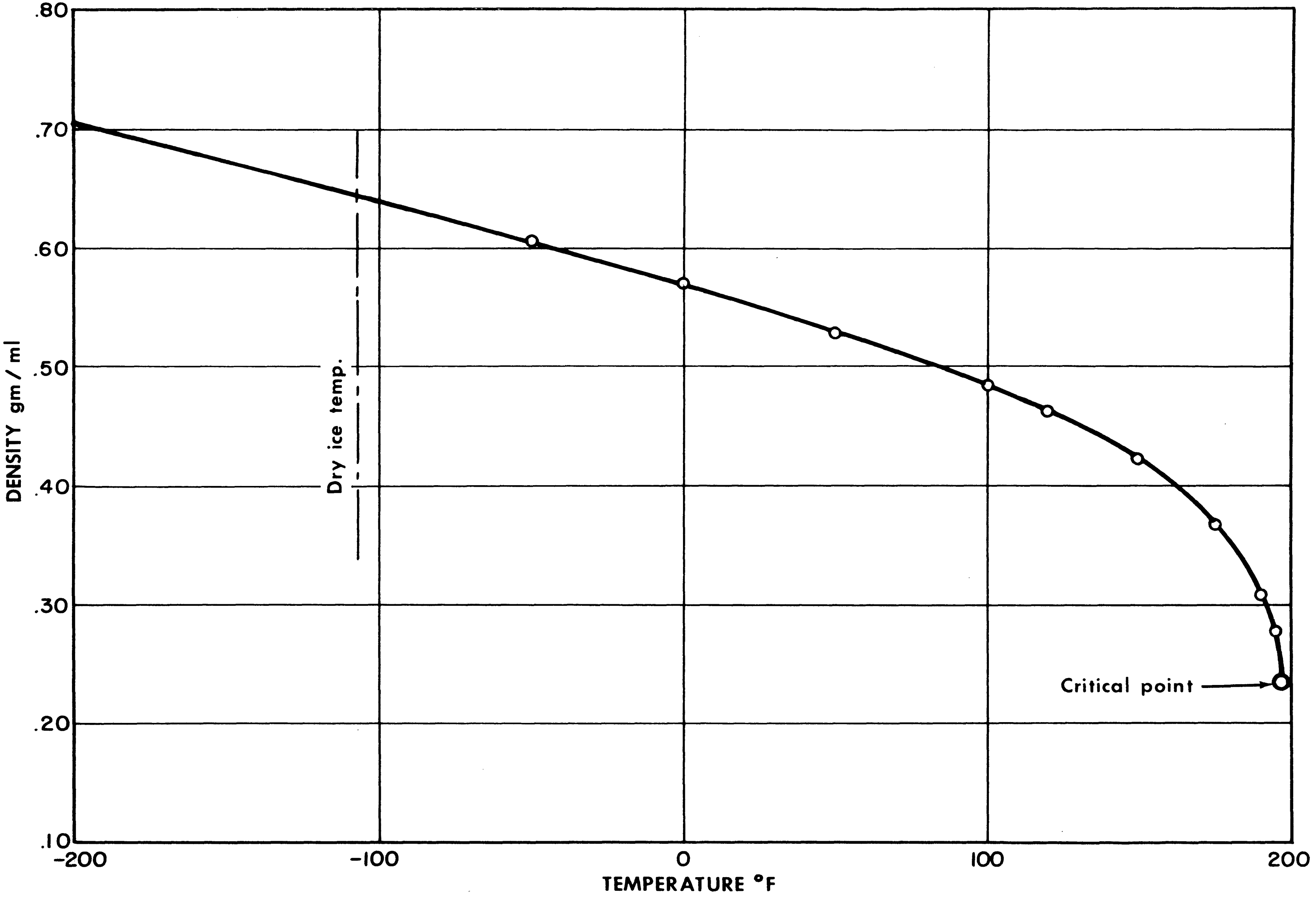


Figure 13. Liquid Density of Propylene Saturated Pressure vs. Temperature °F - Data from Handbook of Butane Propane Gases

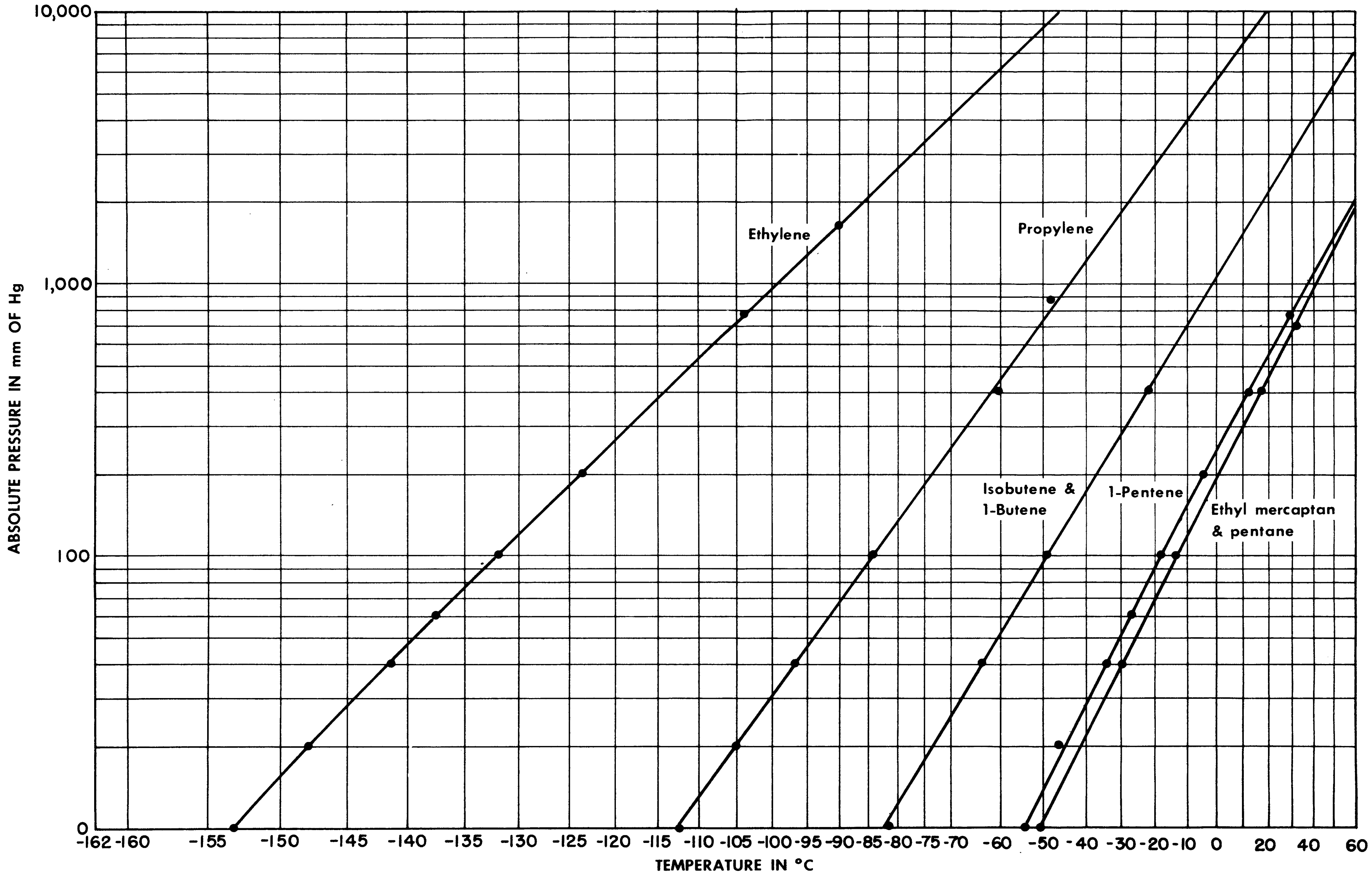


Figure 14. Vapor Pressure of Various Liquids vs. Temperature (Range: -162°C to +60°C) Data from Ind. Eng. Chem. 39, 518-550 (1947).

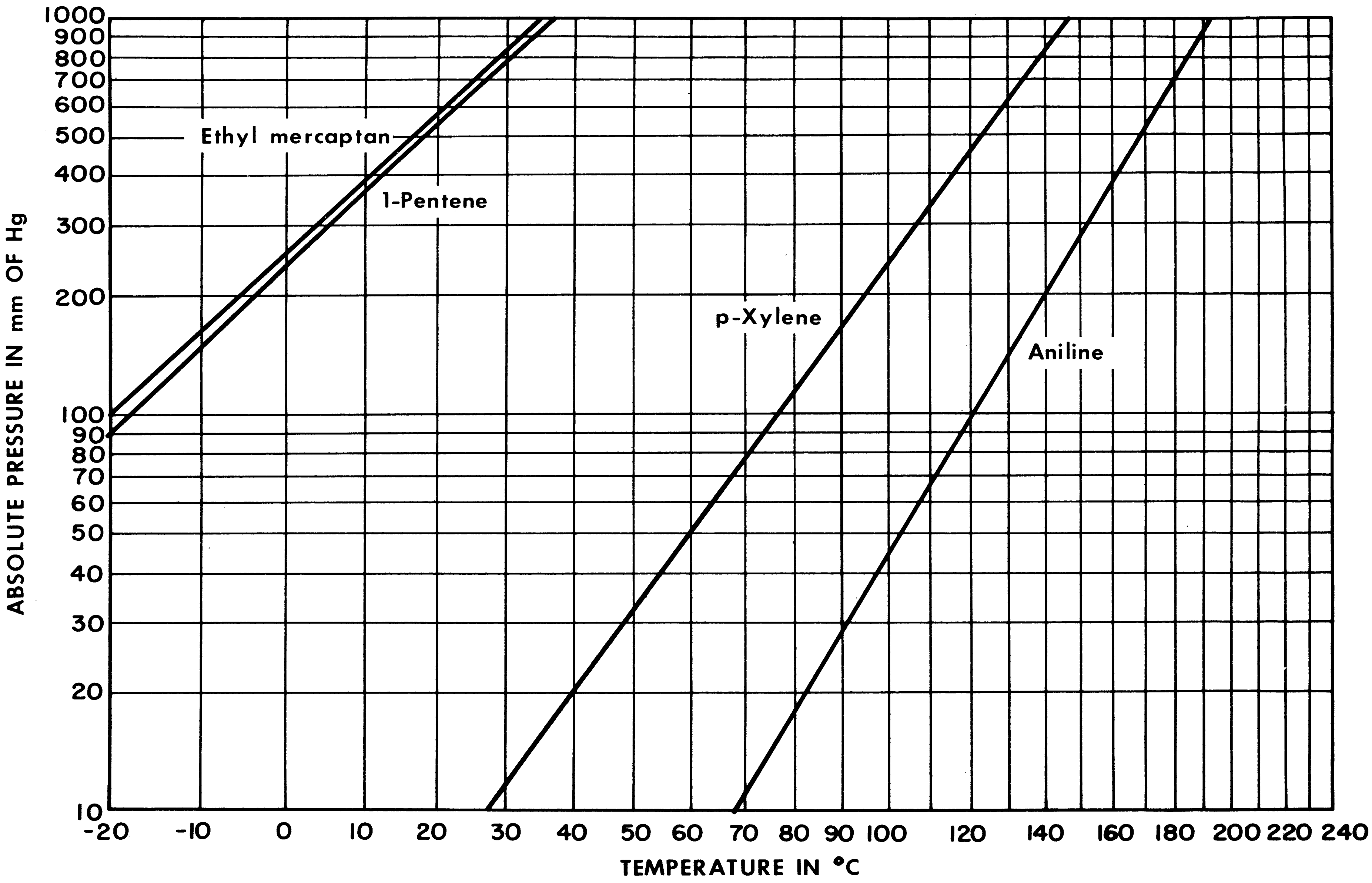


Figure 15. Vapor Pressure of Various Liquids vs. Temperature (Range: -20°C to 240°C) Data from Ind. Eng. Chem. 39, 518-550 (1947).

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