THE NON-CATALYTIC POLYMERIZATION
OF ETHYLENE DISSOLVED IN NAPHTHALENE
by
Clyde Kempton Smith
A.B., Stanford University
1933
and
Ben T. Woodruff
B.S., University of Chicago
1932
Submitted in Partial Fulfillment of the Requirements
for the degree of
MASTER OF SCIENCE
from the
Massachusetts Institute of Technology
1935
Signatures of Authors

Department of Chemical Engineering, July 10, 1935
Professor in Charge of Research
Chairman of Departmental Committee on Graduate Students
Massachusetts Inst. of Technology
Cambridge, Mass.
July 10, 1935

Professor W. G. Whitman
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

Dear Professor Whitman:

In accordance with the regulations of the Department of Chemical Engineering governing thesis work, we herewith submit a thesis entitled, "The Non-Catalytic Polymerization of Ethylene Dissolved in Naphthalene", in partial fulfillment of the requirements for the Master of Science Degree.

Respectfully submitted,

\[\text{\underline{Clyde Kempton Smith}}\]

\[\text{\underline{Ben T. Woodruff}}\]

\[203844\]
Acknowledgement

The authors wish to express their gratitude to Professor Hottel for his helpful advice and counsel on the investigation of this problem. They also wish to thank Mr. F. R. Russell for his willing direction and assistance in the work.
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Problem</td>
<td>1</td>
</tr>
<tr>
<td>Summary</td>
<td>2</td>
</tr>
<tr>
<td>Introduction</td>
<td>4</td>
</tr>
<tr>
<td>Previous Work by Other Investigators</td>
<td>5</td>
</tr>
<tr>
<td>Summary of Procedure</td>
<td>8</td>
</tr>
<tr>
<td>Discussion of Results</td>
<td>12</td>
</tr>
<tr>
<td>Conclusions</td>
<td>16</td>
</tr>
<tr>
<td>Recommendations</td>
<td>18</td>
</tr>
<tr>
<td>Appendix</td>
<td></td>
</tr>
<tr>
<td>Description of Apparatus</td>
<td>20</td>
</tr>
<tr>
<td>Procedure</td>
<td>24</td>
</tr>
<tr>
<td>a. Operating Procedure</td>
<td>24</td>
</tr>
<tr>
<td>b. Analytical Procedure</td>
<td>26</td>
</tr>
<tr>
<td>c. Calibrations</td>
<td>31</td>
</tr>
<tr>
<td>Sample Calculations</td>
<td>34</td>
</tr>
<tr>
<td>Experimental Data</td>
<td></td>
</tr>
<tr>
<td>Literature Cited</td>
<td>37</td>
</tr>
</tbody>
</table>
The Problem

The purpose of this investigation was to study the polymerization of ethylene in the presence of an inert, non-catalytic hydrocarbon solvent. The solvent was to exist in a liquid phase as well as a gas phase under the conditions of reaction. Calculations were to be made to determine a constant for the rate of reaction, and some study was to be made of the products of polymerization. The problem is part of a broad program of study of the mechanism of polymerization of hydrocarbons.
Summary

In this investigation the primary concern was the determination of the reaction rate constant for the polymerization of ethylene dissolved in naphthalene with both liquid and gas phases present, although as a corollary the change of the constant with temperature and the nature of the products formed were also investigated. The method of finding the reaction rate constant consisted in making runs for varying lengths of time at a constant temperature of 780°F. An indication of the change of the constant with temperature was obtained by varying the temperature while holding the time of the runs constant. By analytical means it was possible to determine the extent to which the polymerization had taken place, as well as to find in a general way the nature of the products formed.

The fact that two phases were present rendered it impractical to express the ethylene concentration during the run. Another complication was the exceeding complexity of the reactions taking place in the later stages of the runs. An expression for the reaction rate constant similar in form to the second order type of reaction was obtained by plotting data on percent of original ethylene left
against time of reaction. The original concentration of ethylene was about 6 mol per cent, (according to fugacity calculations). Data on the nature of the products formed indicate that hexylene is the principal gaseous olefine formed. They indicate too that certain amounts of paraffinic hydrocarbons are formed during the reaction.
Introduction

Interest in polymerization of olefinic hydrocarbons has increased markedly in the past few years, particularly in the petroleum industry. It appears in cracking as troublesome coke and gum formation. On the other hand it is a very useful tool in the production of synthetic resins, solvents, and high grade motor fuels. Especially in connection with the latter two groups of compounds investigators are doing extensive work.

In extending the scope of the work of polymerization of ethylene begun by Mr. Russell, it was planned to investigate the problem under conditions such that both liquid and gas phases were present. Only a very limited amount of work is reported in the literature on the non-catalytic polymerization under these conditions. Primary interest was in finding the conditions under which such polymerization would occur, in determining the reaction rate constant for the polymerization, and in gaining an indication of the change of the constant with temperature. With the limited time available it was decided to investigate the problem by arbitrarily fixing two of the four primary variables, namely, the extent of the liquid phase and the initial pressure of ethylene. Runs were made at constant temperature for varying lengths of time and for varying temperature with constant lengths of time.
Previous Work by Other Investigators

Although much work has been done on the gas phase polymerization of ethylene, with and without the use of catalysts, the problem of polymerization with a liquid hydrocarbon phase present has received but a limited study. A review of the literature for several years back yielded only two patents of somewhat contradictory nature.

The first one, which was issued to A. S. Ramage in 1925, states that ethylene compressed into kerosene at 0°C. and 80 lbs. per square inch pressure showed about seventy-five per cent conversion to a product which was mainly butylene. (The time of the reaction was indeterminate from a description of the process.) He also states that higher temperatures and pressures can be used, and that the only requirement is that the ethylene dissolves in the liquid phase. Considering all the data on polymerization which requires an elevated temperature, the other patent, which was issued to H. D. Elkington in 1930, seems more consistent with the facts. He states that 95 grams of ethylene heated in an autoclave with 300 grams of paraffin oil, at 45 atmospheres and 420°C. yielded 50 grams of a light naphtha. His claims state that pure ethylene is not necessary, and that it is thus possible to use gaseous
cracking products containing ethylene, to make useful polymers.

Some of the pertinent facts concerning gas-phase polymerization would be expected to apply to the liquid-phase work, at least to a certain extent; they will be discussed briefly. Ipatiev heated ethylene in an iron tube under high pressure, and found that polymerization began at 325°C and was quite rapid at 380 - 400°C. Hague and Wheeler found that ethylene polymerized readily between 400 and 700°C, yielding butylene. They used a silica bulb and heated it for three hours. According to Sachanen and Tilicheyev the polymerization of olefines to form higher olefines is thermodynamically possible up to 500°C. This is brought out graphically by Francis and Kleinschmidt who plotted the changes in free energy occurring versus the absolute temperature. The change in slope of the curve shows a tendency for ethylene to polymerize below 425°C and to crack at higher temperatures. Isomerization to cycloparaffins is possible below 425°C.

Other facts, some of which were corroborated by this investigation, are mentioned briefly below. Pressure seems to have only a small effect during the first stages of the reaction. Its main purpose is to keep the ethylene
in the liquid phase. The effects of temperature and time are similar; a short time at a high temperature shows about the same results as a long time at a lower temperature. Polymerization is generally bi-molecular, or a reaction of the second order, in contrast to cracking which is a first order process. Many chain reactions may follow initial polymerization.
Summary of Procedure

The problem resolved itself into one of making various runs under pressure with a solvent present. Naphthalene was used as the solvent because of its aromatic, non-cracking character, relative inactivity, and high critical temperature. There were four primary variables in the experiments; they may be taken as: (1) the extent of the liquid phase; (2) the concentration of ethylene in the liquid phase; (3) temperature; and (4) time of reaction. It was obviously necessary to limit the scope of the work, and some of the variables had to be eliminated. For this reason all of the runs were made with the same liquid-gas ratio, and at the same initial concentration of ethylene. For comparison some runs were made with only the gas phase present. The required amount of naphthalene was estimated from fugacity data to give a liquid phase of about one ninth of the reactor volume. Previous work in the literature reported a negligible effect of pressure on the reaction, and since this determines the concentration of ethylene, the amount of ethylene originally put into the system was arbitrarily chosen and kept constant. Runs at a constant temperature were made for times varying from fifteen minutes to three hours. These two variables, temperature and time,
were the ones mainly investigated, although a run was made to determine if the iron, of which the system mainly composed, had any catalytic effect. This was accomplished by putting steel wool in the reactor to obtain a large iron surface.

The extent to which the reaction had proceeded was determined by measuring the amount of gas left after the materials had been allowed to react, and analyzing it for ethylene. The amount of ethylene disappearance indicated the extent of polymerization. Supplementing the above work, the nature of the products formed was sought as an indication of the mechanism of the reaction. An analysis of the reaction gases revealed the amounts of higher olefins, and of inert paraffinic hydrocarbons and hydrogen formed. Gas density data were obtained both on the reaction gas, and upon the residual gas after removal of all olefins. From these results it was possible to calculate the average molecular weights of the higher olefins and of the residual gas. Further data as to the nature of the products was obtained by a quantitative analysis of the residual gas for carbon and hydrogen by combustion.

As previously mentioned, the attack of the problem necessitated the use of high pressures. In addition to this, the high temperatures used made it necessary to employ
materials which would hold their strength under the severe conditions of reaction. A high pressure reactor was available which was suitable. It was heated by a winding of resistance wire. The heads of the reactor were removed after every run to take out the mixture of naphthalene and liquid polymer, and to add fresh naphthalene. The measure of the amount of ethylene originally added to the system was made with a low range pressure gage. During all the runs where a liquid phase was present, the reactor was shaken to maintain equilibrium conditions.

The procedure in making a run was to add naphthalene to the reactor, mount the latter, evacuate the system, and put the ethylene in from a cylinder under pressure. Current was then put on the heating element of the reactor. Initial heating was at a high rate to minimize the correction for reaction during the heating period. Temperatures were controlled by means of two thermocouples, the first one a chromel-alumel junction on the outside wall of the reactor which was used to indicate heating rate, and the second one a copper-constantan couple which extended to the center of the reactor and measured the actual operating temperature. Both pressure gages and thermocouples were calibrated against appropriate standards. Readings of temperature and pressure were made at frequent intervals during the runs.
Upon completion of the time previously decided upon for the length of the run, heating was discontinued, the lagging with which the reactor was covered was taken off, and an electric fan was turned on the reactor to cool it rapidly. When the conditions indicated that the naphthalene had solidified, the gas was vented off and measured. A special type of gas collection apparatus was used which allowed the measurement of the gas under atmospheric pressure. It was collected over saturated brine which was also saturated with ethylene.

A Williams gas analysis apparatus was used for the gas analysis. The first pipette contained 87% sulfuric acid to remove higher olefins. The second pipette contained bromine water which removed ethylene. The residue, after being passed through caustic solution, was assumed to be a mixture of paraffinic gases and hydrogen.

Gas-density data was obtained by weighing the gases in calibrated gas-density flasks. In determining the density of the gases inert to bromine water, these latter were separated from the olefinic gases by bubbling through towers containing bromine and caustic solutions.
Discussion of Results

The principal information to be drawn from this work is in regard to the rate of reaction and the effect of naphthalene on polymerization. The data from the constant temperature runs were sufficient to allow calculation of the reaction rate constant. The fact that two phases were present made it difficult to express this data in terms of concentration of ethylene. Therefore, the percent of the original ethylene left after a given time was used as a basis for calculation. Another complication was encountered in the complexity of the reactions taking place after initial polymerization. The reaction rate constant was figured on the assumption that during the early part of the run the reaction was of the simple second order type. This gives an integration of the form:

\[
\left( \frac{1}{E_2} - \frac{1}{E_1} \right) = K \theta
\]

where \( K \) is the reaction rate constant, \( E \) is percent ethylene left, and \( \theta \) is time of reaction in minutes. The initial slope of the curve of the reciprocal of the percent ethylene left versus time indicated the constant. (Figs. 1, 2.) This gave a value of 0.00064. It was hoped to get enough data to show how \( K \) changes with temperature, but the few runs at constant time and varying temperature did not allow this.
The time used in all of these runs was so long as to be in the portion of the curve where the assumption of a second order reaction did not apply.

As to the effect of the naphthalene, the liquid phase does not seem to be as important as the mere presence of naphthalene itself. It does not seem to react with the ethylene, because it distilled off in a fairly pure state when the distillations were made on the naphthalene containing the polymers. The increased polymerization due to the presence of even naphthalene vapor is seen in comparing the ethylene disappearance in runs 3 and 4. (See Calculated Data.) From the way in which the pressure varied during the run it appears that in pure ethylene runs an induction period of about half an hour is required before polymerization occurs after which it takes place fairly rapidly. (Fig. 4) The converse seems to hold with the naphthalene for most of the polymerization occurs during the first half hour. (Fig. 5)

Certain conclusions can be drawn in regard to the nature of the products formed in the runs in which time is a variable. The weight per cent of ethylene which polymerized to heavy polymers in the naphthalene followed a curve just the inverse of the per cent ethylene remaining. (Fig. 1) The amount of inert hydrocarbons, which were found to be a mixture of paraffins and hydrogen, increased uniformly until
about two hours had passed and then slowly decreased. The gaseous olefines formed were at a maximum at forty minutes, and then decreased slowly as more of them went to heavy polymers. The fact that the molecular weights of the gaseous polymers were all between 65 and 85 except in one case indicates that they were probably mixtures of butylenes and hexylenes. The last conclusion to be drawn is in regard to the apparent inhibitive effect of iron surface. The data on the steel wool run (See Fig. 1 and Calculated Data.) seems conclusive enough to indicate that a large surface of iron definitely inhibits the polymerization of ethylene, at least under the conditions of this investigation.

With regard to the reproducibility of the data, check runs were made at one half hour and constant tempera-
ture giving results which agreed within five per cent. Granting that the runs were all carried out with the same amount of care as these two, this seems to be the limit of the accuracy of the data. The temperature measurements were reproducible to better than three degrees Fahrenheit. The assumption made that no ethylene remained in the solidified naphthalene after the run, was verified by making a check on the reactor volume. The system was filled with ethylene under operating pressure, the naphthalene was melted, and
and then the gas was vented off. This checked the other calibrations within 2 per cent.
# Calculated Data

<table>
<thead>
<tr>
<th>Run No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conditions</td>
<td>naphth.</td>
<td>naphth.</td>
<td>naphth.</td>
<td>naphth.</td>
</tr>
<tr>
<td>Effective Time</td>
<td>106 min.</td>
<td>85.6</td>
<td>142</td>
<td>123</td>
</tr>
<tr>
<td>Effective Temperature</td>
<td>750°F</td>
<td>767°F</td>
<td>750°F</td>
<td>750°F</td>
</tr>
<tr>
<td>Gas In (cu.ft.)</td>
<td>.180 cu.ft</td>
<td>.262</td>
<td>.258</td>
<td>.216</td>
</tr>
<tr>
<td>Gas Out (cu.ft.)</td>
<td>.1441</td>
<td>.1462</td>
<td>.0999</td>
<td>.075</td>
</tr>
<tr>
<td>C₂H₄ In (cu.ft.)</td>
<td>.1788</td>
<td>.2601</td>
<td>.2563</td>
<td>.2142</td>
</tr>
<tr>
<td>Analysis of Gas Out:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% C₂H₄ Out</td>
<td>83.2</td>
<td>75.45</td>
<td>63.7</td>
<td>77.75</td>
</tr>
<tr>
<td>% Gaseous Olefins</td>
<td>7.3</td>
<td>14.03</td>
<td>13.25</td>
<td>9.02</td>
</tr>
<tr>
<td>% Inert Hydrocarbons</td>
<td>9.5</td>
<td>10.52</td>
<td>23.05</td>
<td>13.23</td>
</tr>
<tr>
<td>C₂H₄ Out (cu.ft.)</td>
<td>.1198</td>
<td>.1103</td>
<td>.0636</td>
<td>.0584</td>
</tr>
<tr>
<td>% Ethylene Disappear.</td>
<td>33.0</td>
<td>57.6</td>
<td>70.5</td>
<td>72.8</td>
</tr>
<tr>
<td>Mol. Weight of Gas Out</td>
<td>----</td>
<td>36</td>
<td>33.5</td>
<td>29.2</td>
</tr>
<tr>
<td>Mol. Weight of Gaseous Olefins</td>
<td>----</td>
<td>83.5</td>
<td>67.9</td>
<td>40.0</td>
</tr>
<tr>
<td>Mol. Weight of Inert gases</td>
<td>----</td>
<td>30.3</td>
<td>29.2</td>
<td>28.8</td>
</tr>
<tr>
<td>Wt. % C₂H₄ Left</td>
<td>67</td>
<td>42.4</td>
<td>29.5</td>
<td>27.2</td>
</tr>
<tr>
<td>Wt. % as Gaseous Olefins</td>
<td>----</td>
<td>23.32</td>
<td>10.07</td>
<td>4.5</td>
</tr>
<tr>
<td>Wt. % as Inerts</td>
<td>----</td>
<td>6.38</td>
<td>6.73</td>
<td>4.7</td>
</tr>
<tr>
<td>Wt. % as Liquid Polymers</td>
<td>----</td>
<td>28.0</td>
<td>53.7</td>
<td>63.7</td>
</tr>
<tr>
<td>Remarks</td>
<td>No gas densities obtained</td>
<td>Small losses of gas obtained</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### CALCULATED DATA

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Conditions</th>
<th>Effective Time</th>
<th>Effective Temperature</th>
<th>Gas In (cu.ft.)</th>
<th>Gas Out (cu.ft.)</th>
<th>C₂H₄ In (cu.ft.)</th>
<th>Analysis of Gas Out:</th>
<th>C₂H₄ Out (cu.ft.)</th>
<th>% Ethylene Disappearance</th>
<th>Mol. Weight of Gas Out</th>
<th>Mol. Weight of Gaseous Olefins</th>
<th>Mol. Weight of Inert Gases</th>
<th>Wt. % C₂H₄ Left</th>
<th>Wt. % as Gaseous Olefins</th>
<th>Wt. % as Inerts</th>
<th>Wt. % as Liquid Polymers</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>100 gms. naphth.</td>
<td>131 min.</td>
<td>819°F.</td>
<td>.216 cu.ft.</td>
<td>.0428 cu.ft.</td>
<td>.2144 cu.ft.</td>
<td>40.0</td>
<td>.0161 cu.ft.</td>
<td>92.4</td>
<td>31.56</td>
<td>31.1</td>
<td>-</td>
<td>7.6</td>
<td>2.2</td>
<td>11.63</td>
<td>78.5</td>
<td></td>
</tr>
<tr>
<td>7 A</td>
<td>100 gms. naphth.</td>
<td>138 min.</td>
<td>780°F.</td>
<td>.208 cu.ft.</td>
<td>.0655 cu.ft.</td>
<td>.2069 cu.ft.</td>
<td>51.0</td>
<td>.0335 cu.ft.</td>
<td>83.8</td>
<td>32.38</td>
<td>27.6</td>
<td>16.2</td>
<td>9.3</td>
<td>11.9</td>
<td>62.65</td>
<td>68.4</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>100 gms. naphth.</td>
<td>38.6 min.</td>
<td>780°F.</td>
<td>.2092 cu.ft.</td>
<td>.0853 cu.ft.</td>
<td>.2078 cu.ft.</td>
<td>75.55</td>
<td>.0644 cu.ft.</td>
<td>69.0</td>
<td>33.05</td>
<td>30.5</td>
<td>31.0</td>
<td>11.83</td>
<td>5.56</td>
<td>51.61</td>
<td>73.6</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>100 gms. naphth.</td>
<td>68.8 min.</td>
<td>780°F.</td>
<td>.2083 cu.ft.</td>
<td>.0837 cu.ft.</td>
<td>.207 cu.ft.</td>
<td>73.6</td>
<td>.0654 cu.ft.</td>
<td>68.4</td>
<td>32.95</td>
<td>32.95</td>
<td>31.6</td>
<td>11.0</td>
<td>8.61</td>
<td>48.79</td>
<td>H/C analysis made Ratio=3.9:1</td>
<td></td>
</tr>
</tbody>
</table>

Remarks

Traps installed.
Small gas loss
## Calculated Data

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Conditions</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 gms.</td>
<td>100 gms.</td>
<td>Naphth.</td>
<td>100 gms.</td>
<td>naphth. &amp; steel wool naphth.</td>
</tr>
<tr>
<td>Effective Time</td>
<td>15.4 min.</td>
<td>37.5</td>
<td>33.7</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td>Effective Temperature</td>
<td>780°F.</td>
<td>780°F.</td>
<td>780°F.</td>
<td>780°F.</td>
<td></td>
</tr>
<tr>
<td>Gas In (cu.ft.)</td>
<td>.2158 cu.ft.</td>
<td>.2176</td>
<td>.2113</td>
<td>.2087</td>
<td></td>
</tr>
<tr>
<td>Gas Out (cu.ft.)</td>
<td>.1318</td>
<td>.085</td>
<td>.1308</td>
<td>.0573</td>
<td></td>
</tr>
<tr>
<td>C₂H₄ In (cu.ft.)</td>
<td>.2143</td>
<td>.2162</td>
<td>.2097</td>
<td>.2073</td>
<td></td>
</tr>
<tr>
<td>Analysis of Gas Out:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% C₂H₄ Out</td>
<td>90.57</td>
<td>74.7</td>
<td>88.34</td>
<td>55.0</td>
<td></td>
</tr>
<tr>
<td>% Gaseous Olefins</td>
<td>6.12</td>
<td>12.5</td>
<td>7.44</td>
<td>10.72</td>
<td></td>
</tr>
<tr>
<td>% Inert Hydrocarbons</td>
<td>3.31</td>
<td>12.8</td>
<td>4.22</td>
<td>34.28</td>
<td></td>
</tr>
<tr>
<td>C₂H₄ Out (cu.ft.)</td>
<td>.1192</td>
<td>.0645</td>
<td>.1038</td>
<td>.0315</td>
<td></td>
</tr>
<tr>
<td>% Ethylene Disappearance</td>
<td>44.3</td>
<td>70.6</td>
<td>45.0</td>
<td>85.0</td>
<td></td>
</tr>
<tr>
<td>Mol. Weight of Gas Out</td>
<td>30.4</td>
<td>33.5</td>
<td>30.0</td>
<td>35.2</td>
<td></td>
</tr>
<tr>
<td>Mol. Weight of Gaseous Olefins</td>
<td>(65.8)</td>
<td>70.3</td>
<td>(54.0)</td>
<td>90.4</td>
<td></td>
</tr>
<tr>
<td>Mol. Weight of Inert Gases</td>
<td>---</td>
<td>29.4</td>
<td>---</td>
<td>29.4</td>
<td></td>
</tr>
<tr>
<td>Wt. % C₂H₄ Left</td>
<td>55.7</td>
<td>29.4</td>
<td>55.0</td>
<td>15.0</td>
<td></td>
</tr>
<tr>
<td>Wt. % as Gaseous Olefins</td>
<td>8.85</td>
<td>12.4</td>
<td>8.95</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Wt. % as Inerts</td>
<td>2.18</td>
<td>5.3</td>
<td>2.85</td>
<td>9.94</td>
<td></td>
</tr>
<tr>
<td>Wt. % as Liquid Polymers</td>
<td>33.27</td>
<td>52.9</td>
<td>33.2</td>
<td>65.4</td>
<td></td>
</tr>
</tbody>
</table>

**Remarks**
Fig. 1.

Weight Percent of Original Ethylene in Final Products Plotted Versus Time

- Ethylene Remaining
- Higher Gaseous Olefins
- Liquid Polymers
- Paraffinic Hydrocarbons and Hydrogen

Temp. = 780°F
Reciprocal Curve for Calculation of Reaction Rate Constant

Temp. = 780°F.

\[
\kappa = \left( \frac{1}{E - 0.01} \right) \frac{1}{\theta} = 0.00064
\]
Wt. % of Original Ethylene as Final Products Plotted Versus Temperature at a Constant Time of 2 Hours.
Change in Pressure at Constant Temp. of 750°F.

Run No. 1

Diagram showing change in pressure over time with time in minutes on the x-axis and pressure in lbs/sq.in. abs. on the y-axis.
Change in Pressure
At Constant Temperature of 780°F.

Run No. 13

Time-Minutes

Pressure Less/Sq. In. A.B.S.
CONCLUSIONS

1. Ethylene gas polymerizes readily under suitable conditions of pressure and temperature without the use of catalysts.

2. The presence of an amount of naphthalene insufficient to produce a separate liquid phase increased the amount of polymerization.

3. The presence of a liquid phase of naphthalene does not seem to increase the polymerization above that in the case where there was a gas phase of naphthalene with the ethylene.

4. An increased temperature causes more ethylene disappearance and a larger percentage of heavy liquid polymers.

5. Ethylene disappearance increases continuously with time but gives evidence of approaching a constant value different from 100%.

6. The polymerization of ethylene starts as a second order reaction but becomes more complex as higher polymers are formed.

7. Gaseous products of polymerizations in the presence of naphthalene include olefins other than the ethylene, and hydrocarbon gases which are inert to bromine.

8. The difficulty of good temperature control when only a gas phase is present prevents the comparison of reaction
rate with that where a liquid phase is also present.

9. Duplication of data is possible as was found by the close checking of runs under identical conditions.

10. Pressure readings during reaction suggest the conclusion that there is an induction period before polymerization begins when ethylene alone is used, and the converse conclusion that with naphthalene present most of the polymerization takes place during the early part of the reaction period.

11. A large iron surface, obtained with steel wool, very decidedly inhibits polymerization of ethylene under the conditions of this investigation.

12. An empirical equation of the second order can be fitted to the data of this investigation at a constant temperature of 780°F. The integrated form is:

\[ K \theta = \frac{1}{E_2} - \frac{1}{E_1} \]

where \( E \) is the per cent ethylene left, \( \theta \) is the time of reaction in minutes, and \( K \) is a constant equal to .00064.
RECOMMENDATIONS

In making recommendations for further work on this problem the following are suggested:

1. More work should be done on ethylene alone, the results of which could be compared with liquid phase data.

2. Further work with a liquid phase should include short runs at a constant time and varying temperatures so that the variation of reaction rate with temperatures could be observed.

3. Different solvents should be studied.

4. The effect of the filling pressure might be investigated.

5. Any effect of the amount of liquid phase present might be investigated, but it appears to be negligible.

6. Since such striking effects were noticed with an increased iron surface, this should be further investigated.

Improvements in apparatus for this type of work would be advisable for any further investigation. These are as follows:

1. The use of iron cones and iron tubing where there are severe temperature conditions would doubtless reduce trouble from leaks while under operation, but there would be
an increased danger of shattering in case of explosion.

2. It would be advisable to use a reactor and method of heating which would afford more uniform temperature conditions inside the reactor. This is particularly necessary in the runs where there is no liquid phase, because the gas does not mix readily, and local overheating or underheating may occur in the system. This could best be done by having a uniform, constant temperature source of heat since direct agitation of the gas is impracticable with a high pressure system.
DESCRIPTION OF APPARATUS

For protection against possible explosion the reactor and its accompanying apparatus were mounted behind a sheet steel booth of three sides. It was about five feet high and securely fastened to the floor. The outsides served as operating panels and mountings for control apparatus. High pressure connections were mounted on the inside, and valve handles extended through holes to the outside. The hookup of the various component parts of the apparatus is indicated on an accompanying flowsheet.

Reactor and Thermocouples

The reactor was available and was made from mild steel high-pressure pipe. The flanges and heads were cut from round stock and held by vanadium steel bolts. The heads were pressure-sealed with thin copper gaskets. Details of construction are given on an accompanying scale drawing. Two thermocouples were used for temperature measurement. The inside copper-constantan couple was made from high pressure copper tubing with a fine constantan wire in the bore. The couple, which extended into the center of the reactor, was soldered at the tip with "Sil-Fos", and the constantan wire was insulated from the rest of the copper tubing by a Pyrex glass capillary. A chromel-alumel couple was
placed on the outside wall of the reactor. It was made by fusing No. 30 chromel and alumel wires in an arc. Both couple leads were insulated outside of the reactor with asbestos tubing. For the cold junction the wires were taken directly to U tubes filled with mercury and placed in a water bath outside the reactor. This made it easy to disconnect the couples when the reactor was taken down without affecting the junction. The temperature of the water bath was recorded with a thermometer. A portable Leeds and Northrup potentiometer was used in measuring the E.M.F., and contact was to the couples through a double-pole double throw switch. The heater was made by winding 34 feet of 1/8 inch chromel ribbon (0.207 ohms/ft.) over a layer of asbestos paper and a layer of alundum cement. The winding was covered by another layer of alundum cement and wound with asbestos tape. The body of the reactor was insulated with removable pipe lagging. The head with no connections to it was insulated with a cap which slipped on and off and was molded from asbestos paper and magnesia. The other head was wrapped with asbestos paper and tape.

The reactor was swung in a wooden frame with brass bearing surfaces. The axis was a pipe connected at right angles to the center of another pipe running the length of
the reactor. The long pipe was fastened into plates bolted to each head. Shaking was accomplished by fastening one end of a rod to the reactor and the other end to the edge of a face plate mounted on a shaft. The shaft was driven by an electric motor through reduction gears to give a complete cycle of swing about every five seconds.

Connections

The fact that naphthalene was used as the solvent necessitated the use of heated lines and valves. Both lines from the reactor were covered with asbestos tubing. A calculation assuming a reasonable coefficient of heat transfer from the tubes indicated a heat input of about four watts per foot. The total length of the main lines was about fifteen feet. These were wound with fifty-five feet of 1/16 chromel ribbon with a resistance of .68 ohms per foot, and covered with asbestos tape. A trap of about 2 c.c. capacity was installed in the high pressure gauge line and was heated with eight feet of the same chromel ribbon, connected in series with the line heaters. Direct current was supplied at 110 volts to the line heaters. All the block valves and both T-blocks were heated with 110 volt-150 watt strip heaters connected two in series to give a 38 watt heat output. These were bound on the blocks with asbestos tape. A glass trap was installed at the vent-off valve to catch the naphthalene
before it entered the cold vent-off line leading to the collection bottle.

Valves

The valves used were of the standard high pressure block type packed with graphite and asbestos, except the low pressure gauge valve which was a standard Hoke valve.

Gas Collection

For collecting the gas a three gallon bottle filled with ethylene-saturated brine was used. The gas displaced the brine, and the outlet tube was connected by rubber tubing so that it acted as an adjustable barometric leg to assure atmospheric pressure in the bottle. For putting the gas bottle under a head and for refilling, an auxiliary brine bottle was used also.

Analytical Apparatus

The analytical apparatus is described in the discussion of analytical procedure.
PHOTOGRAPHS OF APPARATUS
DETAILS OF PROCEDURE

Operating Procedure

Due to the fact that it was found impracticable to fill the reactor with melted naphthalene under pressure, which would have been necessary if the reactor were not to have been taken apart, one head of the reactor was removed after every run. The used naphthalene was removed, the reactor cleaned out and fresh naphthalene added. The head bolts were then securely tightened so that the copper gasket would flow and seal the reactor. Arbitrarily, 100 grams of naphthalene were added since this amount afforded sufficient liquid phase at the operating conditions. The reactor was then remounted, and ethylene was added at a pressure of 190 pounds per square inch by the low pressure gauge, which corresponded to 201 #/sq. in. absolute pressure. In this manner conditions of pressure, and therefore concentration, were kept nearly constant at any given temperature throughout the series of runs. Before filling, the reactor was pumped out with a Cenco Hy-Vac pump, filled with ethylene under a slight pressure, and then vented to remove all traces of air in the system.

After mounting, the shaking apparatus was started, and the heat applied slowly until the naphthalene was completely melted, as indicated by the inside thermocouple.
The temperature was held low until the pressure gauge indicated that equilibrium had been reached in the solution of ethylene into the naphthalene. Heating was then continued rapidly until the predetermined operating temperature was approached in the reactor. The heat was then cut down to prevent over-shooting by switching from 220v. to 110v. and regulating the rheostat. The ammeter in the line was used so that heat input could be kept constant. It generally took about 12.5 amperes to hold the temperature constant. A temperature difference of about 120° F. between the inside and outside thermocouples was found necessary to maintain the correct temperature in the reactor. Direct current was used in all heating to eliminate possible stray current effects on the thermocouple from alternating current.

Temperature, pressure, and time readings were taken at frequent intervals during a run. After the proper length of heating time, the heat was shut off from the reactor, leaving the lines and blocks hot so that they would not clog with naphthalene. The outside lagging on the reactor was quickly removed and a fan turned on the reactor to facilitate rapid cooling. Shaking was continued for a while until the temperature had fallen low enough to prevent any localized overheating. The reactor was allowed to cool
until the naphthalene had solidified.

When the reactor was cool, venting off of the gas was begun by slowly cracking the valve and allowing the gas to displace the brine in the collection bottle. The brine was collected in a graduated cylinder until the pressure in the system had been brought to atmospheric, and was measured to determine the volume of the gas. The temperatures of the gas in the bottle and in the reactor were recorded at this time. Knowing the conditions of pressure and temperature both before and after the run, and knowing the volume of gas in each case provided data for accurate calculations after the analysis of the gas was known.

To check calculations on the volume of the system, several gas determinations were made by filling with ethylene to a known pressure and temperature and then collecting the gas at atmospheric conditions both with and without naphthalene present in the reactor. One determination was made by melting the naphthalene and then allowing it to cool before venting off the ethylene. This was to verify the assumption that a negligible amount of ethylene remained dissolved in the solid naphthalene.

**Analytical Procedure**

The analysis of the products was fairly simple since no attempt was made to identify all of the constituents.
The first analysis was the volumetric determination of ethylene and other olefins. This was carried out in a regular Williams gas analysis apparatus. Brine saturated with ethylene was used for manipulating the gas. The absorption bulbs contained 87% H₂SO₄, 5% KBr solution saturated with bromine, and a 20% caustic solution respectively. The 87% acid preferentially absorbs all olefins other than ethylene, although a trace of ethylene is absorbed by it for which correction was made.

A sample of gas slightly less than 100 c.c. was drawn into the burette after thoroughly flushing the lines. It was passed through the acid until successive burette readings showed a constant difference. This difference was taken as the ethylene absorbed during each pass, and the net difference was the other olefins formed during the polymerization. The bromine would absorb all the olefins, but with the polymers removed the bromine absorption gave the amount of ethylene left in the gas. After several passes through the bromine, the gas was passed through the caustic solution to remove the bromine vapor, and then it was measured in the burette. This was repeated to constant readings. In every case there was some gas left after the ethylene was removed. It was thought to be a mixture of saturated hydrocarbons and hydrogen, but for convenience was termed the "inerts".
The rest of the analysis consisted of gas densities and combustions. The densities were measured gravimetrically by weighing a known amount of the gas. Two bulbs were used, one holding about 250 c.c. and fitted with one stopcock of glass, and the other holding about 100 c.c. and fitted with two stopcocks. For each analysis the bulb was weighed evacuated and then with air in it, the difference being the weight of that volume of air. The bulb was then re-evacuated and filled with the sample and then reweighed. If the temperatures of each weighing were the same, no corrections were necessary, and the molecular weight of the gas sample was determined directly by comparing with the molecular weight of air, 29. A desiccator was used to assure constancy in the weight of the empty bulb. First the gas as taken from the reactor was weighed, and then the so-called inerts were removed and weighed separately. This was accomplished by passing the gas slowly through an efficient bromine tower followed by a caustic tower. In this way the olefins were removed before passing into the evacuated bulb. Atmospheric pressure in the bulb was assured by filling under a slight pressure obtained by a few inches head of brine and then venting off to atmospheric pressure just before weighing. Therefore, knowing the molecular weight of the ethylene used, and the average molecular weights of
the gaseous polymers were calculated from a material balance on the gas.

A few combustion analyses on the inert gases were attempted, but only one or two were successful. A Shepard combustion apparatus was used for this but due to leaks around some of the stopcocks and inexperience of the experimentors in the technique of the operation of the apparatus, the results were not very conclusive. A measured volume of gas was ignited in a measured excess of oxygen. The resulting gas was measured to determine decrease on ignition and then passed through caustic to determine carbon dioxide. The remaining gas was supposedly all oxygen, but when absorbed in pyrogallic acid there was found to be a trace of gas left which was considered as nitrogen from air trapped in capillaries. From the resulting data, hydrogen-carbon ratios were calculated using material balances.

These three types of analysis gave sufficient data to make the necessary calculations and conclusions. In addition, however, a semi-qualitative distillation was made on the naphthalene from the reactor containing the non-volatile polymers. A variation of an Engler distillation was used, employing a steam jacketed condenser. It was found that no polymers were distilled before the naphthalene, and the naphthalene distilled over quite close to its boiling
point (218° C.). When the last few cubic centimeters remained in the flask, the boiling point rose rapidly to an end point of about 250°C. when the flask was dry. These heavy polymers seemed to be an oil of about the same quality as a gas oil and varied with the different samples in quantity rather than in quality. The distilled naphthalene was not pure white, but it was much lighter in color than before it was distilled. The residue was conversely a much deeper brown than the original sample. The naphthalene samples all had more or less of an odor of untreated petroleum products.
CALIBRATIONS

Thermocouples

In determining the calibrations of the thermocouples, the authors were fortunate to be able to use a secondary standard chromel-alumel couple calibrated by Mr. Walter Ullrich. Both of the couples used in the apparatus were put into a thermostatically controlled electric furnace, and readings made at several points. Unfortunately the copper-constantan junction was short circuited before being used and another had to be prepared. This was calibrated at the boiling points of water and of di-phenyl, and later at higher temperatures using the secondary standard previously referred to. In reading the temperatures from the chromel-alumel couple, the data as given in the chromel booklet of the Hoskins Company was used. A plot of this was available through Mr. Ullrich. Data for copper-constantan from the I.C.T. was plotted, and the curve for our junction was plotted with this as a standard. The curves are shown below.

Gages

The low pressure gage was calibrated up to 300 #/sq.in. the total range, by means of a dead weight gage belonging to the Mechanical Engineering Department of M.I.T. Points were taken every 5# for the first 100# and every 20# thereafter to 300#. Two such calibrations were made, the second after
the gage had been distorted by accidentally putting it under high pressure.

The high pressure gage was calibrated against the low pressure gage in the low ranges. This was accomplished by opening both instruments to the system after they were mounted. For the higher pressures the dead weight gage of the Chemical Engineering Department in the high pressure laboratory was used. Calibration curves for both gages are shown below.

**Reactor Volume**

The volume of the reactor was determined in three ways. It was first calculated from the dimensions of the reactor and the length of tubing used in the connections. It was then measured by filling the reactor with benzene and then measuring its quantity. Then a gas determination was made by filling the reactor with ethylene under pressure and measuring the amount vented off. By the use of Mu Charts, available through the Department of Chemical Engineering, the reactor volume was calculated. This was done both with 100 grams of naphthalene in the reactor and without any naphthalene. The results of these calculations are shown below.

**Results of Reactor Calibrations**

Volume from dimensions: 520 c.c. (Tubing included)

Volume from liquid measure: 512 c.c. (No tubing included)
Volume from ethylene measurement: 534 c.c. (Tubing and low pressure gage line included, no naphthalene.)

Volume of gas space left in system when 100 grams of naphthalene are present:

#1. 431 c.c.
#2. 439 c.c.
#3. 432 c.c.
#4. 421 c.c. (Naphthalene melted and then cooled.)

Average value: 431 c.c.

These results were considered as checking well enough since the pressure readings were accurate only to approximately one pound.
Run No. 9
Rate of Heating Curve
Temperatures Refer to
Inside Thermocouple

Fig. 6.

Time (Minutes)
RATE OF REACTION Vs. TEMPERATURE
Based on Assumption that Rate Doubles Every 25°F.
RATE OF REACTION VS. TIME

Fig. 8.

Used in Graphical Integration To Find Effective Time

Run No. 9

Area = 63.8 Squares
One Square = 10 Min. / Rate = 1
Effective Time = 68.8 Min.
Figure 9.
COPPER-CONSTANTAN
THERMOCOUPLE CALIBRATION

Temperature °F

Electromotive Force (E.M.F.) in Millivolts

500 600 700 800 900
Fig. 10.

Chromel - Alumel Thermocouple Calibration
(Used with Standard Chart (Hoskins))
Corrections are additive
LOW PRESSURE GAGE CALIBRATION

Fig. 11.

[Graph showing relationship between True Absolute Pressure and Gage Pressure]
Sample Calculations

1. Reactor Volume:

Temp. in reactor = 69°F. = 529° R.
Temp. of gas collected = 69°F. = 529° R.
Partial press. of water over the brine = 13.5 mm Hg.
Gas collected = 6062 c.c. : 6062 x 746.5/760 = 5960 c.c.
Estimated volume of reactor = 430 c.c. + 90 c.c. of naphthalene = 520 c.c.
5960 + 430 = 6390 c.c. at 529° R. & 1 atmos. press.
Volume of gas in system at standard conditions:
6390 x 492/529 = 5970 c.c. = .2110 cu.ft.

By use of Mu Charts:
\[ V = \mu \frac{NRT}{P} \]
\[ P_r = \frac{P}{P_c} = \frac{201}{50.9} \times 14.7 = .269 \]
\[ T_r = \frac{T}{T_c} = \frac{529}{508} = 1.04 \]
\[ \mu = .917 \]
\[ V = .917 \times .211 \times 1545 \times 529/359 \times 201 \times 144 \]
\[ .01523 \text{ cu.ft. 431 c.c.} \]

2. Effective Time:

(See curves for graphical integration, Figs. 7, and 8.
Plot rate of reaction vs. temperature using the assumption that the rate doubles every 25°F., and let the effective temperature have a rate of 1. Then the area under the curve equals the effective time at the constant temperature which was given the rate of 1.)
3. Volume of Gas in: (Data from Run #9.)

\[ V = 0.01523 \text{ cu.ft.} \quad P = 201 \#/\text{sq.in.} = 28950 \#/\text{sq.ft.} \]
\[ T = 82^\circ \text{F.} \quad T_r = 1.065 \quad P_r = 0.269 \quad \mu = 0.91 \]
\[ N = \frac{PV}{\mu RT} = 28950 \times 0.01523/0.91 \times 1543 \times 542 = 0.00058 \text{ mols.} \]

Gas in = \(0.00058 \times 359 = 0.2083\) cu.ft.

Ethylene in = \(0.2083 \times 0.993 = 0.207\) cu.ft.

4. Volume of Gas out: (Data from Run #9.)

Gas vented off 2522 c.c.

Barometer correction = \(29.66/29.92 = 0.992\)

Partial pressure water over brine 20.5 m.m. Hg

Vol. = \((2522 \times 739 \times 422/760 \times 545) + (431 \times 492/660) \times 0.992 = 2514\) c.c. at s.c.

\[ = 153.3 \text{ cu.in.} = 0.0887 \text{ cu.ft.} \]

% Ethylene in vented gas = 73.6%

Ethylene out = \(0.736 \times 0.0887 = 0.0654\) cu.ft.

5. Ethylene disappearance:

\[ \text{In} = 0.2070 \quad \text{Out} = 0.0654 \quad \text{Disappear.} = 0.2070 - 0.0654 = 0.1416 \text{ c.} \]

\[ 100 \times 0.1416 / 0.2070 = 68.4\% \text{ disappearance} \]

6. Molecular Weights:

Bulb evacuated = 73.3589 gms.

" + air = 73.6406 "

" + gas = 73.6816 "

Molecular weight of gas = \((73.6816 - 73.3589) \times 29/(73.6406 - 73.3589) = 32.4\)

Molecular Wt. of Gaseous Olefins: M.W.Gas = 33.4

M.W.Ethylene=28: % = 73.6

M.W.Inert Gas=32.95±17.06

\[ \% \text{ Gas.Olefins} = 9.24 \]

\[ 33.4 - (0.736 \times 28 + 0.1706 \times 32.95) = 7.22 \]
7.33/.0934 = 76.9 = Mol. Wt. of Gaseous Olefins

7. Weight Percentages of the Products:

Wt. % in Liquid Polymers:

\[
\text{In} = .2070 \times 28 = 5.80 = \text{Lbs. } x 359
\]
\[
\text{Out} = .0887 \times 33.45 = 2.96 = \text{Lbs. } x 359
\]
\[
(5.80 - 2.96)/5.80 = .4879 = 48.79\%
\]

8. Hydrogen: Carbon Ratio:

Gas sample = 17.90 c.c.
Oxygen used = 55.45 c.c.
CO₂ formed = 28.00 c.c.

\[
28.00/17.90 = 1.56 \text{ atoms of carbon/molecule of gas}
\]
\[
55.45 - 28.00 = 27.45 \text{ c.c. of oxygen to water}
\]
\[
27.45 \times 4/17.90 = 6.14 \text{ atoms of hydrogen/molecule of gas}
\]
\[
6.14/1.56 = 3.94:1
\]
<table>
<thead>
<tr>
<th>RUN 1</th>
<th>RUN 2</th>
<th>RUN 3</th>
<th>RUN 4</th>
<th>RUN 5</th>
<th>RUN 6</th>
<th>RUN 7</th>
<th>RUN 8</th>
<th>RUN 9</th>
<th>RUN 10</th>
<th>RUN 11</th>
<th>RUN 12</th>
<th>RUN 13</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
<tr>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
<td>PMT</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL DATA SHEET**
Fig. 13.

VAPOR PRESSURE OF NAPHTHALENE
I.G.T. DATA

TEMP. DEG. F.

VAPOR PRESSURE - LBS./SQ. IN.

0 100 500 1000
LITERATURE CITED

3. Egloff and Schaad; J. Inst. Petroleum Tech., 19; 800-811 (1931)
4. Ellis, C.; "The Chemistry of Petroleum Derivatives"
5. Francis and Kleinschmidt; Oil Gas J. 28, 118, (1929).
8. Ipatiev; Ber., 44; 2978, (1911).
14. Tropsch and Philipovitch; Brennstoff Chemie, 4; 147-149, (1923).
15. International Critical Tables.