Purification, Purity, and Freezing Points of 31 Hydrocarbons of the API-NBS Series

By Augustus R. Glasgow, Jr., Evelyn T. Murphy, Charles B. Willingham, and Frederick D. Rossini

This report describes the purification and determination of freezing points and purity of 31 hydrocarbons of the API-NBS series, including 2 pentanes, 5 hexanes, 2 heptanes, 1 octane, 3 alkylcyclopentanes, 3 alkylcyclohexanes, and 15 alkylbenzenes.

I. Introduction

In May 1943, the Advisory Committee for the American Petroleum Institute Hydrocarbon Research Committee, operating the API Hydrocarbon Research Project at the Ohio State University, requested the American Petroleum Institute Research Project 6 at the National Bureau of Standards to begin purification of a series of hydrocarbon compounds of the highest practicable purity, under the label API-NBS hydrocarbons. This work was begun July 1, 1943, with a large number of compounds of relatively high purity being supplied by the API.

Hydrocarbon Research Project for further purification. During the first year of operation, the purification of 31 compounds of the API-NBS series was completed. This report describes the purification and determination of freezing points and purity of these hydrocarbons, which are being made available on loan to qualified investigators for the measurement of needed properties.

1 The allocation of these samples, by loan to qualified investigators for the measurement of needed properties, is handled by the Advisory Committee for the API Research Project 44 at the National Bureau of Standards on the "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons" (W. E. Kuhn, chairman, Otto Beeck, Gustav Egloff, and S. Kurtz, Jr., with F. D. Rossini as Supervisor of the Project).

1 This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons.
2 Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.
3 On September 1, 1944, this project became the American Petroleum Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low-Molecular Weight", with Cecil E. Board continuing as Supervisor and Robert F. Marschner becoming chairman of the Advisory Committee. D. P. Barnard was chairman of the former API Hydrocarbon Research Committee, which was merged on September 1, 1944, with the API Advisory Committee on Fundamental Research on the Composition and Properties of Petroleum, of which J. Bennett Hill was chairman.
II. Materials and Purification

The starting materials were supplied as follows:  

By the API Hydrocarbon Research Project, now the API Research Project 45 on the "Synthesis and Properties of Hydrocarbons of Low-Molecular Weight", at the Ohio State University, under the supervision of Cecil E. Boord: Cyclopentane, ethylcyclopentane (A), methylcyclohexane (approximately half), ethylcyclohexane, m-xylene (A), p-xylene (A), 1,3,5-trimethylbenzene, n-butylbenzene (A), isobutylbenzene (A), sec-butylbenzene (A), and tert-butylbenzene (A).

By the Barrett Division of the Allied Chemical and Dye Corporation: Cyclohexane, methylcyclohexane (approximately half).

By the Standard Oil Co. (Indiana) and the M. W. Kellogg Co.: 2,3-Dimethylbutane.

By the General Motors Corporation: 2,2,3-Trimethylbutane.

By the Houdry Process Corporation: Methylcyclopentane.

By the Humble Oil & Refining Co.: Toluene.

By the Monsanto Chemical Co.: Ethylbenzene, isopropylbenzene.

By the Standard Oil Development Co.: o-Xylene (A).

By the Dow Chemical Co.: n-Propylbenzene (A).

By the API Research Project 6: n-Pentane, isopentane, n-hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, n-heptane, 2,2,4-trimethylpentane, benzene, 1,2,3-trimethylbenzene (A), 1,2,4-trimethylbenzene (A). In this group, the stocks of the following compounds were obtained by purchase of commercially available materials: n-Pentane, isopentane, and 2,2-di-

methylbutane from the Phillips Petroleum Co.; n-heptane from the Westvaco Chlorine Products Co.; 2,2,4-trimethylpentane from the Rohm & Hass Co.; benzene, from the Koppers Co.

Information regarding the volume of the starting material, details of the purification by distillation, and volume of the selected "best" lot, is given in table 1. Additional details of the distilling columns are given in preceding reports [1, 2].

In addition to the purification by distillation, the benzene, m-xylene, and p-xylene were subjected to a purification by crystallization with centrifuging by B. J. Mair and A. J. Streiff of this laboratory [7].

For this group of 31 compounds, time was not available for the detailed examination of the purity, by measurement of freezing points, of the distillate as a function of its volume, and the best sample was taken as an appropriately selected "heart" cut (not necessarily the middle part of the distillate) having the volume given in the last column of table 1. This volume may be compared for each compound with the volume of the starting material given in the third column. The heart cut was selected largely on the basis of refractive index and boiling point, although, as will be shown in the next report on the purification of API-NBS hydrocarbons [3], this is a procedure which frequently results in the discarding of the best material. Each final lot was filtered through silica gel [4] to remove water and nonhydrocarbon impurities.

*Figures in brackets indicate the literature references at the end of this paper.

*In the next report on the purification of API-NBS and API-Standard hydrocarbons, in connection with the cooperative program of the National Bureau of Standards and the American Petroleum Institute on Standard Samples of hydrocarbons, a procedure will be described wherein enough freezing points are measured to determine the purity of the distillate as a function of its volume [3].
Table 1.—Information on the starting materials and purification

<table>
<thead>
<tr>
<th>Compound *</th>
<th>Starting material provided by laboratory *</th>
<th>Volume</th>
<th>Kind</th>
<th>Azeotrope-forming substance if used</th>
<th>Still No.</th>
<th>Number of theoretical plates at total reflux (approx.)</th>
<th>Reflux ratio (approx.)</th>
<th>Volume of selected sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARAFFINS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>APIRP 6</td>
<td>2.8</td>
<td>Regular</td>
<td></td>
<td>D</td>
<td>100</td>
<td>100/1</td>
<td>570</td>
</tr>
<tr>
<td>2-Methylbutane (isopentane)</td>
<td>APIRP 6</td>
<td>2.3</td>
<td>do.</td>
<td>Methanol</td>
<td>E</td>
<td>100</td>
<td>100/1</td>
<td>370</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>APIRP 6</td>
<td>1.2</td>
<td>Azeotrope.</td>
<td>Methanol</td>
<td>M</td>
<td>100</td>
<td>100/1</td>
<td>375</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>APIRP 6</td>
<td>1.0</td>
<td>do.</td>
<td>.do</td>
<td>E</td>
<td>100</td>
<td>100/1</td>
<td>325</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>APIRP 6</td>
<td>0.8</td>
<td>do.</td>
<td>.do</td>
<td>Q</td>
<td>100</td>
<td>120/1</td>
<td>255</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>APIRP 6</td>
<td>2.8</td>
<td>Regular</td>
<td>.do</td>
<td>H</td>
<td>110</td>
<td>120/1</td>
<td>255</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>Std. (Ind.); Kellogg</td>
<td>1.0</td>
<td>Azeotrope.</td>
<td>Methanol</td>
<td>M</td>
<td>100</td>
<td>100/1</td>
<td>275</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>APIRP 6</td>
<td>1.0</td>
<td>do.</td>
<td>Ethanol</td>
<td>8</td>
<td>130</td>
<td>145/1</td>
<td>380</td>
</tr>
<tr>
<td>2,2,3-Trimethylbutane</td>
<td>General Motors</td>
<td>1.3</td>
<td>do.</td>
<td>Methanol</td>
<td>9</td>
<td>135</td>
<td>165/1</td>
<td>380</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>APIRP 6</td>
<td>2.4</td>
<td>do.</td>
<td>Ethanol</td>
<td>10</td>
<td>135</td>
<td>165/1</td>
<td>350</td>
</tr>
<tr>
<td>ALKYLCYCLOPENTANES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>APIRP 45</td>
<td>0.80</td>
<td>do.</td>
<td>Methanol</td>
<td>2</td>
<td>100</td>
<td>135/1</td>
<td>415</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>Houdry</td>
<td>1.8</td>
<td>do.</td>
<td>do</td>
<td>D</td>
<td>100</td>
<td>100/1</td>
<td>380</td>
</tr>
<tr>
<td>Ethylcyclopentane (A)</td>
<td>APIRP 45</td>
<td>0.40</td>
<td>do.</td>
<td>do</td>
<td>J</td>
<td>125</td>
<td>100/1</td>
<td>200</td>
</tr>
<tr>
<td>ALKYLCYCLOHEXANES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Barrett, APIRP 45</td>
<td>2.7</td>
<td>Regular</td>
<td>Ethanol</td>
<td>D</td>
<td>100</td>
<td>145/1</td>
<td>400</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>Barrett, APIRP 45</td>
<td>1.1</td>
<td>Azeotrope.</td>
<td>Cellosolve</td>
<td>9</td>
<td>135</td>
<td>165/1</td>
<td>450</td>
</tr>
<tr>
<td>Ethylcyclohexane</td>
<td>APIRP 45</td>
<td>0.92</td>
<td>do.</td>
<td>Cellosolve</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALKYLBENZENES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>APIRP 6</td>
<td>0.90</td>
<td>Regular *</td>
<td></td>
<td>I</td>
<td>125</td>
<td>100/1</td>
<td>450</td>
</tr>
<tr>
<td>Toluene</td>
<td>Humble</td>
<td>0.47</td>
<td>do.</td>
<td>Methyl Cellosolve</td>
<td>J</td>
<td>125</td>
<td>100/1</td>
<td>330</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Monsanto</td>
<td>0.82</td>
<td>Azeotrope.</td>
<td>Methyl Cellosolve</td>
<td>E</td>
<td>100</td>
<td>100/1</td>
<td>290</td>
</tr>
<tr>
<td>o-Xylene (A)</td>
<td>Std. Oil Dev.</td>
<td>0.60</td>
<td>Regular</td>
<td></td>
<td>J</td>
<td>125</td>
<td>100/1</td>
<td>240</td>
</tr>
<tr>
<td>m-Xylene (A)</td>
<td>APIRP 45</td>
<td>0.34</td>
<td>Regular *</td>
<td></td>
<td>I</td>
<td>125</td>
<td>100/1</td>
<td>330</td>
</tr>
<tr>
<td>p-Xylene (A)</td>
<td>APIRP 45</td>
<td>0.40</td>
<td>do.*</td>
<td></td>
<td>I</td>
<td>125</td>
<td>100/1</td>
<td>330</td>
</tr>
<tr>
<td>n-Propylbenzene (A)</td>
<td>Dow</td>
<td>0.48</td>
<td>do.</td>
<td>Cellosolve</td>
<td>J</td>
<td>125</td>
<td>100/1</td>
<td>220</td>
</tr>
<tr>
<td>iso-Propylbenzene</td>
<td>Monsanto</td>
<td>0.80</td>
<td>Azeotrope.</td>
<td>Cellosolve</td>
<td>M</td>
<td>100</td>
<td>100/1</td>
<td>350</td>
</tr>
<tr>
<td>1,2,3-Trimethylbenzene (A)</td>
<td>APIRP 6</td>
<td>0.45</td>
<td>do.</td>
<td>Methyl Carbitol</td>
<td>9</td>
<td>135</td>
<td>165/1</td>
<td>200</td>
</tr>
<tr>
<td>1,2,4-Trimethylbenzene (A)</td>
<td>APIRP 45</td>
<td>0.89</td>
<td>do.</td>
<td>Methyl Carbitol</td>
<td>10</td>
<td>135</td>
<td>165/1</td>
<td>400</td>
</tr>
<tr>
<td>1,3,5-Trimethylbenzene</td>
<td>APIRP 45</td>
<td>1.2</td>
<td>do.</td>
<td>do</td>
<td>8</td>
<td>130</td>
<td>145/1</td>
<td>200</td>
</tr>
<tr>
<td>n-Butylbenzene (A)</td>
<td>APIRP 45</td>
<td>0.94</td>
<td>do.</td>
<td>do</td>
<td>8</td>
<td>130</td>
<td>145/1</td>
<td>200</td>
</tr>
<tr>
<td>iso-Butylbenzene (A)</td>
<td>APIRP 45</td>
<td>1.1</td>
<td>do.</td>
<td>do</td>
<td>7</td>
<td>130</td>
<td>145/1</td>
<td>200</td>
</tr>
<tr>
<td>sec-Butylbenzene (A)</td>
<td>APIRP 45</td>
<td>1.1</td>
<td>do.</td>
<td>do</td>
<td>7</td>
<td>130</td>
<td>145/1</td>
<td>300</td>
</tr>
<tr>
<td>tert-Butylbenzene (A)</td>
<td>APIRP 45</td>
<td>1.1</td>
<td>do.</td>
<td>do</td>
<td>8</td>
<td>130</td>
<td>145/1</td>
<td>300</td>
</tr>
</tbody>
</table>

* A letter A following the name of a compound indicates that subsequently a new and usually slightly purer sample (B) has been or is being prepared, the description of which will appear in a later report.

* The abbreviations represent the following laboratories:
APIRP 45: American Petroleum Institute Research Project 45 (formerly the American Petroleum Institute Hydrocarbon Research Project) on the "Synthesis and Properties of Hydrocarbons of Low Molecular Weight," at the Ohio State University, Columbus, Ohio; C. E. Boord, Supervisor.
Barrett; Barrett Division of the Allied Chemical & Dye Corporation, New York, N. Y.
Dow; Dow Chemical Co., Midland, Mich.

General Motors; General Motors Corporation, Detroit, Mich.
Humble; Humble Oil & Refining Co., Houston, Texas.
Kellogg; M. W. Kellogg Co., New York, N. Y.
Monsanto; Monsanto Chemical Co., Dayton, Ohio.
Std. Oil Dev.; Standard Oil Development Co., Elizabeth, N. J.
Std. (Ind.); Standard Oil Co. (Indiana), Whiting, Ind.
* Three separate distillations of this volume were made.
* See text regarding additional purification by crystallization.
* Methyl Cellosolve is ethylene glycol monomethyl ether; Cellosolve is ethylene glycol monophenyl ether; methyl Carbitol is diethylene glycol monomethyl ether.

Purification of Hydrocarbons
### III. Freezing Points and Purity

For each of the compounds except 3-methylpentane, which failed to yield crystals, the freezing point of the actual sample was determined from table 2—freezing points and purity of 31 api-nbs hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Kind of time-temperature observations used to determine the freezing point</th>
<th>Freezing point of the actual sample, in air at 1 atm.*</th>
<th>Freezing point for zero impurity in air at 1 atm.</th>
<th>Calculated amount of impurity in the actual sample*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Paraffins</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-Pentane</td>
<td>F</td>
<td>+126.73°C</td>
<td>+126.73°C ± 0.015</td>
<td>0.15 ± 0.07</td>
</tr>
<tr>
<td>2-Methylbutane (isopentane)</td>
<td>F</td>
<td>+129.92°C</td>
<td>+129.890 ± 0.015</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>M</td>
<td>+133.24°C</td>
<td>+133.250 ± 0.010</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>F</td>
<td>+133.65°C</td>
<td>+133.660 ± 0.010</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>F</td>
<td>+128.47°C</td>
<td>+128.450 ± 0.010</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>1,2-Dimethylpentane</td>
<td>F</td>
<td>+128.47°C</td>
<td>+128.450 ± 0.010</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>Ethylcyclopentane</td>
<td>F</td>
<td>+126.57°C</td>
<td>+126.550 ± 0.010</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>M</td>
<td>+126.57°C</td>
<td>+126.550 ± 0.010</td>
<td>0.15 ± 0.06</td>
</tr>
<tr>
<td><strong>Alkylcyclohexanes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>F</td>
<td>+6.547°C</td>
<td>+6.547 ± 0.005</td>
<td>0.002 ± 0.002</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>M</td>
<td>+6.547°C</td>
<td>+6.547 ± 0.005</td>
<td>0.002 ± 0.002</td>
</tr>
<tr>
<td>Ethylcyclohexane</td>
<td>M</td>
<td>+11.02°C</td>
<td>+11.006 ± 0.015</td>
<td>0.006 ± 0.015</td>
</tr>
<tr>
<td><strong>Alkylbenzenes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>F</td>
<td>+5.089°C</td>
<td>+5.089 ± 0.010</td>
<td>0.072 ± 0.020</td>
</tr>
<tr>
<td>Toluene</td>
<td>F and M</td>
<td>+9.000°C</td>
<td>+9.000 ± 0.010</td>
<td>0.072 ± 0.020</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>M</td>
<td>+25.18°C</td>
<td>+25.175 ± 0.010</td>
<td>0.072 ± 0.020</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>M</td>
<td>+47.28°C</td>
<td>+47.267 ± 0.015</td>
<td>0.08 ± 0.015</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>M</td>
<td>+118.239°C</td>
<td>+118.236 ± 0.012</td>
<td>0.06 ± 0.015</td>
</tr>
<tr>
<td>n-Xylene</td>
<td>M</td>
<td>+99.839°C</td>
<td>+99.837 ± 0.015</td>
<td>0.05 ± 0.015</td>
</tr>
<tr>
<td>iso-Propylbenzene</td>
<td>M</td>
<td>+96.063°C</td>
<td>+96.028 ± 0.010</td>
<td>0.04 ± 0.015</td>
</tr>
<tr>
<td>1, 2, 3-Trimethylbenzene (A)</td>
<td>F</td>
<td>+25.494°C</td>
<td>+25.494 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>(A)</td>
<td>M</td>
<td>+43.919°C</td>
<td>+43.919 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>1, 2, 3-Trimethylbenzene (A)</td>
<td>M</td>
<td>+44.738°C</td>
<td>+44.736 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>n-Butylbenzene (A)</td>
<td>M</td>
<td>+87.994°C</td>
<td>+87.994 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>iso-Butylbenzene (A)</td>
<td>M</td>
<td>+51.327°C</td>
<td>+51.327 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>sec-Butylbenzene (A)</td>
<td>M</td>
<td>+75.577°C</td>
<td>+75.577 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
<tr>
<td>tert-Butylbenzene (A)</td>
<td>M</td>
<td>+87.872°C</td>
<td>+87.872 ± 0.010</td>
<td>0.03 ± 0.015</td>
</tr>
</tbody>
</table>


A Roman numeral 1 indicates that the value is for that crystalline form having the highest freezing point.

The values in this column were calculated as described in reference [5], using the values of the cryoscopic constants and freezing points for zero impurity given in the "z" tables of the American Petroleum Institute Research Project 44, reference [6]. For the 19 compounds for which values of the freezing point for zero impurity are reported in this paper, the values given in reference [6] are, at the time of this writing, identical to those in this table.

The amount of impurity in the 3-methylpentane was estimated by analogy with 2-methylpentane.

Grateful acknowledgment is made to the following persons and laboratories for supplying the materials for purification listed in table 1: C. E. Boord, Supervisor of the American Petroleum Institute Research Project 45 (formerly the API Hydrocarbon Research Project) at the Ohio State University, Columbus, Ohio; W. J. Sweeney, Standard Oil Development Co., New York, N. Y.; T. A. Boyd and W. G. Lovell, General Motors Corporation, Detroit, Mich.; E. A. Smith, Houdry Process Corporation, Marcus Hook, Pa.; R. R. Dreisbach, Dow Chemical Co., Midland, Mich.;

Especial acknowledgment is due George Calingaert, formerly chairman of the subcommittee on purification and properties under the API Hydrocarbon Research Project, who made the arrangements for starting the series of API–NBS hydrocarbons.

IV. References


WASHINGTON, April 3, 1946.