Purification, Purity, and Freezing Points of 20 API Standard and API Research Hydrocarbons

ANTON J. STREIFF, LAWRENCE H. SCHULTZ, AURA R. HULME, JAMES A. TUCKER, NED C. KROUSKOP, and FREDERICK D. ROSSINI

Petroleum Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pa.

▶The purification and determination of freezing points and purity are described for the following 20 hydrocarbons of the API Standard and API Research series: 2,2-dimethyl-3-ethylpentane; 2,4-dimethyl-3-ethylpentane; cycloheptane; 3-methyl-1-hexene; 4-methyl-*trans*-2-hexene; 2,4-dimethyl-1-pentene; 3,3-dimethyl-1-pentene; 3,4-dimethyl-*cis*-2-pentene; 3,4-dimethyl-*trans*-2-pentene; 2-methyl-*trans*-3-heptene; 2,5-dimethyl-*trans*-3-hexene; 2-methyl-3-ethyl-1-pentene; 3-methyl-1,2-butadiene; 1-methylcyclopentene; 1-methylcyclohexene; 1-ethylcyclohexene; cyclohexylcyclohexane; cyclohexylbenzene; 3-cyclopentyl-1-propene (allylcyclopentane); and phenylbenzene (biphenyl).

THIS investigation is a continuation of the work of producing highly purified hydrocarbons of the API Standard and Research series (*1*, *5–10*). This paper describes the purification and determination of purity and freezing points of 20 hydrocarbons, which include two paraffins, one cycloparaffin, nine monoolefins, one diolefin, three cyclo-olefins, one dicycloparaffin, one cycloparaffin-aromatic, one cycloparaffin-olefin, and one dinuclear aromatic. The final lots of material labeled API Standard are sealed in vacuum in glass ampoules and made available as API Standard samples of hydrocarbons by the Carnegie Institute of Technology. The material labeled API Research is made available in appropriate small lots through the American Petroleum Institute Research Project 44 for loan to qualified investigators for the measurement of needed physical, thermodynamic, and spectral properties.

Table I gives the names of the 20 compounds, the laboratories providing the starting material, details concerning the first and succeeding distillations, the character of the plot of the freezing point of the hydrocarbon part of the distillate as a function of its volume, and the volumes of the final lots of API Standard and Research material.

The procedures followed in the process of purification and determination of purity were the same as described in previous papers (*2*, *5–10*) except that phenylbenzene (biphenyl) was purified using the process of zone melting (*3*). Details of the distillation apparatus and operations have been described (*4*, *11*).

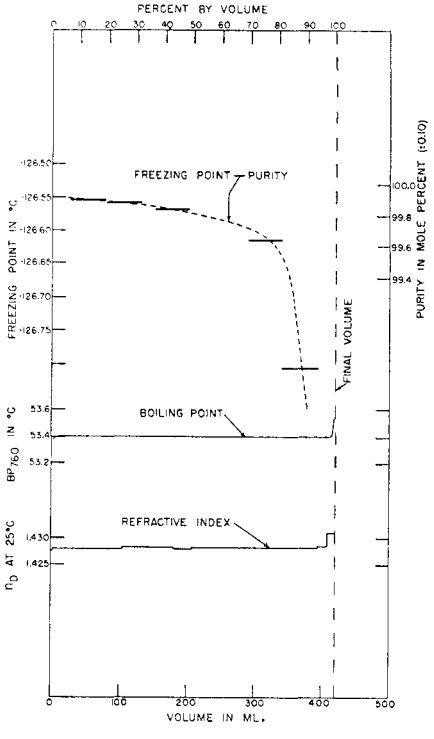

Figure 1. Results of azeotropic distillation of 1-methylcyclopentene with methanol

Figures 1, 2, and 3 show graphically the results of some typical distillations. They represent the cases where the purest material is, respectively, largely in the forepart of the distillation, in the middle of the distillation, and in the after part of the distillation. In each figure plots are given for refractive index, boiling point, freezing point, and purity as a function of the volume of the hydrocarbon part of the distillate.

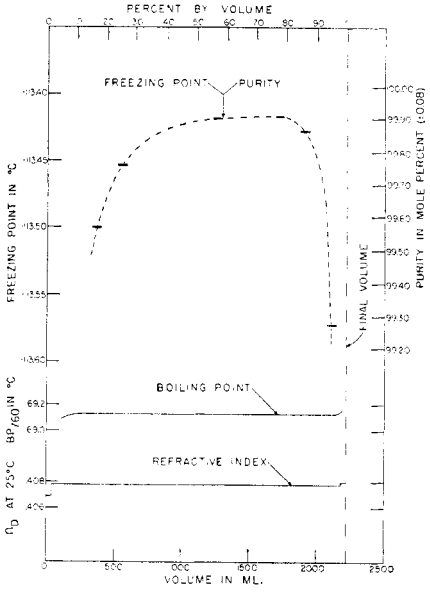

Figure 2. Results of azeotropic distillation of 3,4-dimethyl-*trans*-2-pentene with ethyl alcohol

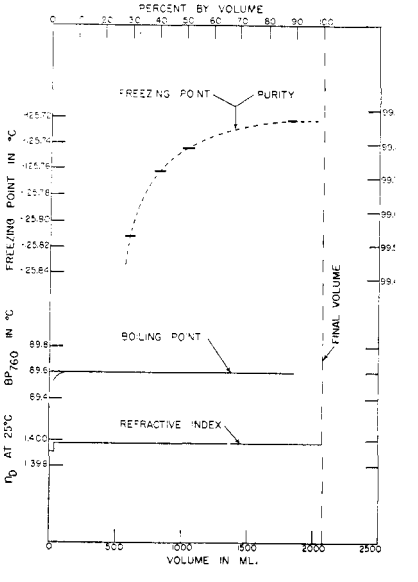

Figure 3. Results of regular distillation of 4-methyl-*trans*-2-hexene

Table I. Purification of 20 API Standard and API Research Hydrocarbons

Compound	Laboratory[a] Providing Starting Material	Hydrocarbon Charged for Distillation		Distillation[b]							Volume of Selected Sample	
		Vol., liters	Purity, mole %	Kind[c]	Azeotrope-forming substance[d]	Amt. hydrocarbon in azeotropic distillate[e], vol. %	No. of equivalent theoretical plates in distilling column[b]	Rate of collection of distillate, ml./hour	Time of distillation, hours	Location of purest material in distillate[f]	API Standard, ml.	API Research, ml.
2,2-Dimethyl-3-ethylpentane	NBS Auto. Sec.	1.05	...	Reg. and Azeo.[g]	... Me Cell	.. 61	200 200	4 4	336 144	A M	560	165
2,4-Dimethyl-3-ethylpentane	NBS Auto. Sec.	0.68	99.3±0.2	Reg. and Azeo.[g]	... Me Cell	.. 63	200 200	3 4	336 264	M F	425	85
Cycloheptane	APIRP45	2.99 2.38	99.97±0.01 99.988±0.008	Reg. Azeo.	... Me Cell	.. 64	200 200	4 4	864 1224	A A	... 1075	... 330
3-Methyl-1-hexene	APIRP45	4.18 2.60	... ...	Reg. Azeo.	... Ethyl alcohol	.. 69	200 200	4 4	1224 1032	M M	... 1150	... 340
4-Methyl-*trans*-2-hexene	APIRP45	5.60 2.90	95.4±0.3 98.0±0.2	Reg. Azeo.	... Ethyl alcohol	.. 67	200 200	7 7	1104 792	M M	... ...	... ...
		2.15	99.6±0.1	Reg. and Azeo.[g]	... Ethyl alcohol	.. 67	200 200	7 7	432 192	A F	950	210
2,4-Dimethyl-1-pentene	APIRP45	3.42[h] 3.44[h] 2.65	98.9±0.2 98.9±0.2 [i]98.8±0.2	Reg. Reg. Azeo.	... ... Ethyl alcohol	 73	200 200 200	7 7 7	672 624 600	M M M	... ...	... ...
		2.30[j]	[i]98.0±0.2	Azeo.	Ethyl alcohol	73	200	7	600	M	...	...
		2.70[k]	99.72±0.12	Azeo.	Ethyl alcohol	73	200	7	768	M	1085	325
3,3-Dimethyl-1-pentene	APIRP45	5.93 4.38	99.59±0.12 99.78±0.10	Reg. Azeo.	... Ethyl alcohol	.. 75	200 200	4 4	1584 1920	A A	... ...	... ...
		3.50	99.86±0.08	Reg.	...	..	200	7	600	A	1430	360
3,4-Dimethyl-*cis*-2-pentene	APIRP45	3.45	99.64±0.12	Reg. and Azeo.[l]	... Me Cell	.. 86	200 200	7 4	... 1440	.. M	... ...	... ...
		1.35	98.2±0.1	Azeo.	Ethyl alcohol	62	200	4	624	M	...	...
		1.86[k]	99.90±0.07	Azeo.	Ethyl alcohol	62	200	4	912	M	1175	360
3,4-Dimethyl-*trans*-2-pentene	APIRP45	3.18[h] 2.31[k]	96.8±0.02 99.44±0.12	Reg. Azeo.	... Ethyl alcohol	.. 64	200 200	7 7	504 672	M M	... 945	... 245
2-Methyl-*trans*-3-heptene	APIRP45	3.78	99.75±0.08	Azeo.	Me Cell	77	200	4	1440	A	1170	345

[a] Abbreviations represent APIRP45, American Petroleum Institute Research Project 45, Ohio State University, Columbus, Ohio; APIRP6, American Petroleum Institute Research Project 6, Carnegie Institute of Technology, Pittsburgh, Pa.; NBS Auto. Sec., Automotive Section, National Bureau of Standards, Washington, D. C.; Penn State, Hydrocarbon Laboratory, Pennsylvania State University, University Park, Pa.; Standard (Indiana), Standard Oil Co. of Indiana, Whiting, Ind.

[b] See (*4*) and (*11*) for further details.

[c] Azeo, azeotropic; Reg., regular.

[d] Me Cell, methyl Cellosolve, ethylene glycol monomethyl ether; DPrG, dipropylene glycol.

[e] Approximate value obtained from actual volume of hydrocarbon recovered by extracting azeotrope-forming substance with water in separatory funnels.

[f] Designations refer to general location of purest material in hydrocarbon part of distillate as a function of its volume. F, fore or front of distillate; M, middle part of distillate; A, after part of distillate.

[g] Residue from regular distillation distilled azeotropically in order to recover it as distillate.

[h] One of two similar distillations.

[i] Purity of this material is lower than original because of rearrangement during regular distillation.

[j] Material from first distillation above.

[k] Material having substantially same composition from each of preceding two distillations.

[l] When half complete regular distillation was changed to azeotropic distillation.

[m] Second lot of 1-methylcyclopentene.

(*Continued on page 363*)

Table I. Purification of 20 API Standard and API Research Hydrocarbons (Continued)

Compound	Laboratory[a] Providing Starting Material	Hydrocarbon Charged for Distillation		Distillation[b]							Volume of Selected Sample	
		Vol., liters	Purity, mole %	Kind[c]	Azeotrope-forming substance[d]	Amt. hydrocarbon in azeotropic distillate,[e] vol. %	No. of equivalent theoretical plates in distilling column[b]	Rate of collection of distillate, ml./hour	Time of distillation, hours	Location of purest material in distillate[f]	API Standard, ml.	API Research, ml.
2,5-Dimethyl-*trans*-3-hexene	APIRP45	4.17	99.75±0.08	Azeo.	Me Cell	76	200	4	1725	M	...	...
		2.92	99.85±0.06	Azeo.	Me Cell	76	200	7	528	M	1200	355
2-Methyl-3-ethyl-1-pentene	APIRP45	2.88	99.80±0.08	Azeo.	Me Cell	78	200	4	1080	M	1160	340
3-Methyl-1,2-butadiene	APIRP45	3.65	93.6±0.2	Reg.	...	..	200	7	624	M	1170	325
1-Methylcyclopentene	Penn State Standard (Indiana)[m]	2.30	97.8±0.2	Reg.	...	..	135	4	696	M	...	...
		1.81	97.9±0.2	Reg. and Azeo.[g]	...	..	200	4	504	A	...	...
		...	...		Methanol	60	200	4	192	F	...	...
		0.47	...	Azeo.	Methanol	60	200	4	336	F	...	...
		2.03[n]	99.32±0.14	Azeo.	Methanol	60	200	7	408	M	850	200
1-Methylcyclohexene	Penn State	3.00	...	Reg. and Azeo.[g]	...	..	200	4	670	A	750	195
		...	...		Ethyl alcohol	30	200	4	314	F		
1-Ethylcyclohexene	APIRP45	2.80[o]	...	Azeo.	Me Cell	53	200	7	1320	M	...	...
		2.84[o]	...	Azeo.	Me Cell	53	200	7	1008	M	...	...
		2.50[o]	...	Azeo.	Me Cell	53	200	7	936	M	...	...
		2.50[o]	...	Azeo.	Me Cell	53	200	7	1008	M	...	...
		2.64[p]	...	Azeo.	Me Cell	53	200	7	840	M	...	...
		1.87	96.4±0.2	Azeo.	Me Cell	53	200	7	840	M	...	...
		*1.20	97.8±0.2	Azeo.	Me Cell	53	200	9	336	F	...	...
		2.70[p]	...	Azeo.	Me Cell	53	200	9	696	M	...	...
		1.90	...	Azeo.	Me Cell	53	200	4	1344	M	...	...
		*1.01	98.2±0.1	Azeo.	Me Cell	53	200	9	336	F	...	...
		1.62[q]	99.49±0.12	Azeo.	Me Cell	53	200	4	1296	M	850	220
Cyclohexylcyclohexane	APIRP6[r]	7.62	...	Reg.	...	..	150	5	1656	A	...	...
		3.65	99.98±0.01	Azeo.	DPrG	58	150	5	1320	M	1525	480
Cyclohexylbenzene	APIRP6[r]	7.52	...	Reg.	...	..	150	5	1872	M	...	...
		3.60	99.89±0.07	Azeo.	DPrG	58	150	5	1200	M	1500	380
3-Cyclopentyl-1-propene (Allylcyclopentane)	APIRP45	2.22	99.84±0.11	Azeo.	Me Cell	62	200	7	576	A	1170	350
Phenylbenzene (Biphenyl)	APIRP6[r]	5.40	97.8±0.02	Zone melting[s]	...	..	...	...	...	..	1200	400

[n] Material from each of previous three distillations.
[o] One of four similar distillations.
[p] Material having substantially same composition from two of four similar distillations (see [o]).
[q] Material having substantially the same composition from two distillations above which are marked with (*).
[r] Obtained by purchase of commercially available material.
[s] Purified by fractionation by zone melting.

As emphasized in the previous reports, the blending of fractions of distillate for the preparation of material of the highest purity can be done safely only on the basis of the freezing points.

Table II gives the following information for the compounds measured: the kind of time-temperature curves, whether freezing or melting, used to determine the freezing point; the freezing point of the actual sample; the calculated value of the freezing point for zero impurity; the value of the cryoscopic constant, determined from the lowering of the freezing point on the addition of a known amount of a suitable impurity (*2, 4*); and the calculated amount of impurity in the API Standard and Research materials.

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Table II. Freezing Points and Purity of 20 API Standard and API Research Hydrocarbons

Compound	Kind of Time-Temp. Observations Used to Determine Freezing Point[a]	Freezing Point of Actual Material in Air at 1 Atm., °C. API Standard	Freezing Point of Actual Material in Air at 1 Atm., °C. API Research	Freezing Point for Zero Impurity in Air at 1 Atm., °C.	Cryoscopic Constant[a] A, Mole Fraction/Deg.	Calculated Amount of Impurity in Actual Material,[b] Mole % API Standard	Calculated Amount of Impurity in Actual Material,[b] Mole % API Research
2,2-Dimethyl-3-ethylpentane	M	−99.523	−99.511	−99.490±0.020	0.0407	0.13±0.08	0.08±0.08
2,4-Dimethyl-3-ethylpentane	M	−122.418	−122.396	−122.36± 0.03	0.0381	0.22±0.11	0.14±0.11
Cycloheptane	M	−8.124	−8.124	−8.100±0.020	0.0033	0.008±0.007	0.008±0.007
3-Methyl-1-hexene	..	...	...	...	...	[c](0.20±0.15)	[c](0.15±0.10)
4-Methyl-*trans*-2-hexene	M	−125.737	−125.723	−125.690±0.020	0.0388	0.18±0.08	0.13±0.08
2,4-Dimethyl-1-pentene	M	−124.087	−124.086	−124.060±0.020	0.0471	0.13±0.09	0.12±0.09
3,3-Dimethyl-1-pentene	M	−134.403	−134.402	−134.380±0.010	0.0466	0.11±0.05	0.10±0.05
3,4-Dimethyl-*cis*-2-pentene	M	−124.253	−124.251	−124.235±0.015	0.0477	0.09±0.07	0.08±0.07
3,4-Dimethyl-*trans*-2-pentene	M	−113.422	−113.417	−113.395±0.020	0.0412	0.11±0.08	0.09±0.08
2-Methyl-*trans*-3-heptene	M	−107.553	−107.552	−107.520±0.015	0.0483	0.16±0.07	0.15±0.07
2,5-Dimethyl-*trans*-3-hexene	M	−95.222	−95.220	−95.200±0.015	0.0424	0.09±0.06	0.08±0.06
2-Methyl-3-ethyl-1-pentene	M	−112.948	−112.948	−112.900±0.020	0.0396	0.19±0.08	0.19±0.08
3-Methyl-1,2-butadiene	M	−113.635	−113.635	−113.625±0.010	0.0368	0.04±0.04	0.04±0.04
1-Methylcyclopentene	M	−126.562	−126.556	−126.530±0.020	0.0427	0.14±0.08	0.11±0.08
1-Methylcyclohexene[d]	M	−120.441 (I)	−120.433 (I)	−120.400±0.020 (I)	0.0427	0.18±0.08	0.14±0.08
				−125.96± 0.03 (II) (u)	...	...	...
1-Ethylcyclohexene	M	−110.000	−109.984	−109.960±0.020	0.0430	0.17±0.09	0.10±0.09
Cyclohexylcyclohexane	M	3.649	3.651	3.670±0.010	0.0110	0.023±0.008	0.021±0.008
Cyclohexylbenzene	M	7.040	7.042	7.070±0.020	0.0245	0.07±0.05	0.07±0.05
3-Cyclopentyl-1-propene (allylcyclopentane)	M	−110.695	−110.688	−110.670±0.020	0.0538	0.13±0.11	0.10±0.10
Phenylbenzene (biphenyl)	M	68.961	68.964	68.970±0.010	0.0192	0.02±0.02	0.01±0.01

[a] M, melting. See (2) and (4) for experimental details and definition of cryoscopic constant.
[b] Values in this column, except as otherwise noted, were calculated as described in (2) and (4) using the values of cryoscopic constants and freezing points for zero impurity given in previous columns.
[c] Estimated by analogy with isomers subjected to similar purification.
[d] This hydrocarbon has more than one crystalline form. Forms indicated are labeled I and II in order of decreasing temperature of freezing point. Forms other than I will be, at their respective freezing points, in metastable equilibrium with the undercooled liquid, but will be unstable with respect to transition to some other solid form at the same temperature and pressure (1 atm.). Such metastable forms are indicated by (u) following Roman numeral.

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