Catalytic Cracking of Rosin[2]

BY IRA T. CLARK AND ELWIN E. HARRIS

Rosin was converted to lower molecular weight compounds, chiefly aromatic hydrocarbons, by catalytic cracking over silica–zirconia–alumina catalyst. The aromatic content of the oil product increases with temperature to 100% aromatics at 450 to 500°, and the total yield of oil product decreases with increase of temperature. Five to seven per cent. of the product was phenols or organic acids. The remainder was aromatic hydrocarbons with some naphthenes and hydroaromatic compounds. Constituents shown to be present were methylcyclopentane, dimethylcyclopentanes, benzene, toluene, xylenes. diethylbenzenes, trimethylbenzenes, naphthalene, methyl- and dimethylnaphthalenes, and anthracene.

Rosin was converted to lower molecular weight compounds, chiefly aromatic hydrocarbons, by catalytical cracking with silica–zirconia–alumina catalyst at atmospheric pressure. The effects of temperature and catalyst–contact–time variables were determined in a series of runs in which the temperature was varied from 350 to 500°, and the liquid hourly space velocity (LHSV) of the molten rosin feed was varied from 0.4 to 1.2 milliliters per hour per milliliter of the catalyst. See Fig. 1.
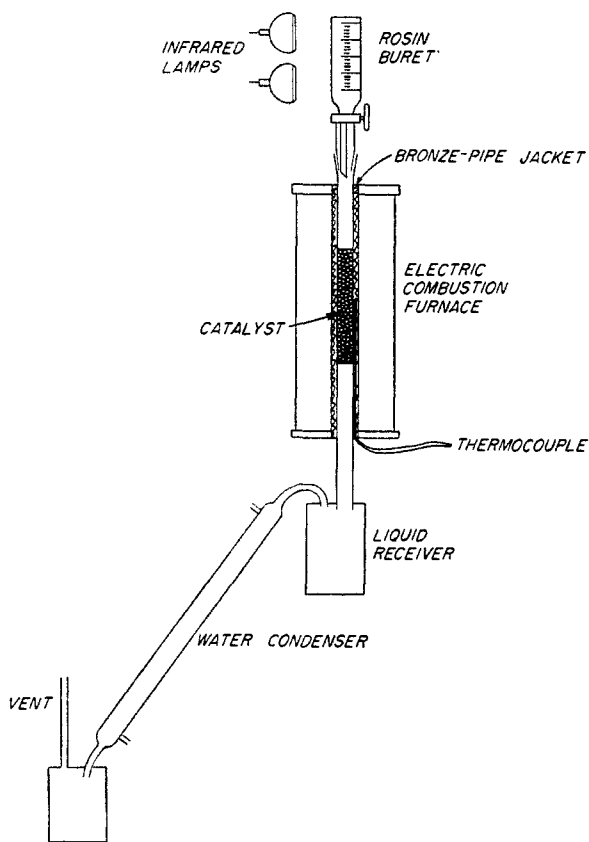

Fig. 1.—Apparatus used for catalytic cracking of rosin.

Increasing the cracking temperature from 350 to 500° caused an increase in non-condensable gaseous products and water and also in the aromatic content of the oil product. Temperatures of 500° yielded 53 to 58% of the weight of rosin as an oil containing 100% aromatics at any LHSV used. At 450°, the yield was 58 to 62% of oil having an aromatic content of 80 to 90%.

(1) Maintained at Madison, Wis., in coöperation with the University of Wisconsin.

(2) Research and Marketing Act Studies, Report No. 40.

Over the range studied, the rate of rosin feed had a less pronounced effect than temperature upon the yield of products (Figs. 2 and 3). Slower rates resulted in a higher aromatic content in the oil product and favored the formation of substituted benzenes. Faster flow rates favored a slight increase in formation of naphthalene and acidic products and in total oil yields.
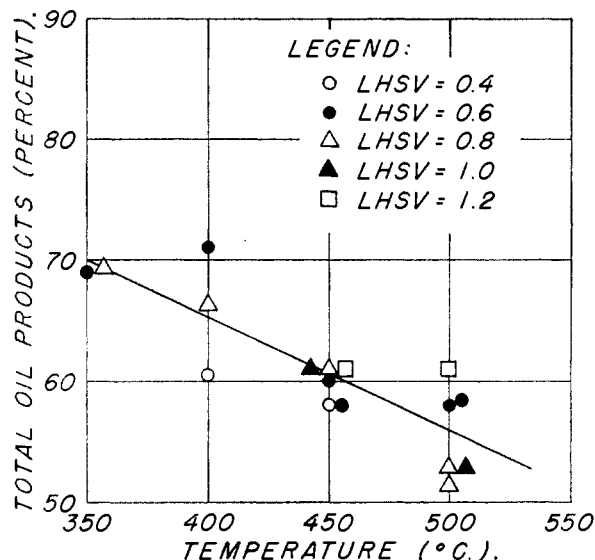

Fig. 2.—Effect of temperature and rate of rosin feed upon the yield of oil products from cracked rosin.

The oil product, which had a specific gravity of 0.90 to 0.91 at 25°, was a complex mixture, chiefly hydrocarbons with some phenolic and acidic materials, and distilled over a range 40° at atmospheric pressure to above 180° at 1.8 mm. To separate the oil into its constituents, acidic materials were removed by extraction with aqueous alkali, and neutral oils were separated by fractional distillation, chromatographic adsorption, and crystallization at −30°.

The composition of 350 g. of oil obtained by runs made at 500° and 1.2 LHSV is given in Tables I and II. The constituents varied slightly with the temperature and flow conditions used. A typical distillation curve of the hydrocarbon fraction is shown in Fig. 4.

The variety and type of compounds identified and the undoubted presence of certain other types would seem to show that not only did the opening of carbon-to-carbon bonds take place, but also that rearrangement and disproportionation occurred under the cracking conditions used.
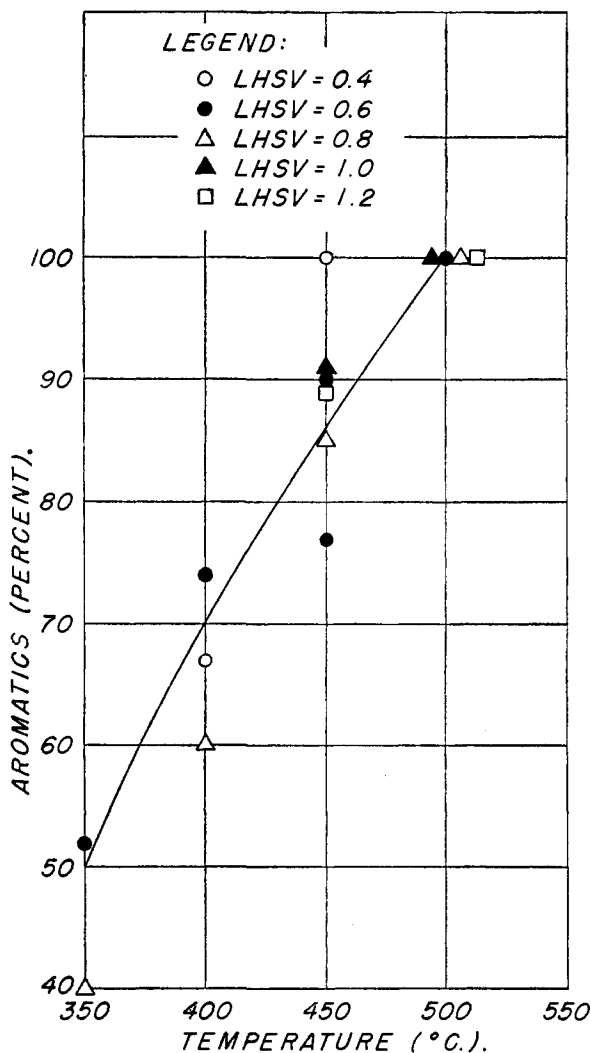
Fig. 3.—Effect of temperature and rate of rosin feed upon the aromatic content of the oil product from cracked rosin.

Experimental

Materials Used.—The rosin was grade N rosin, furnished by the Star Naval Stores Company at Hommersville, La.

The catalyst was type B cracking catalyst, furnished by the Universal Oil Products Company. It was in the form of 3- by 3-mm. pellets and contained 86.2% silica, 9.4% zirconia and 4.3% alumina.

Equipment.—The cracking apparatus, as shown in Fig. 1, consisted of a vertically mounted Pyrex combustion tube, 18 mm. inside diameter by 31 inches long. The tube was jacketed with a section of bronze pipe and heated by a standard electric combustion furnace, which was thermostatically controlled to ±2° of the desired operating temperatures. A liquid product receiver, which served also as a gas–liquid separator, was mounted directly below the catalyst tube. A second receiver for volatile fractions was connected to the first through a water condenser. A molten rosin feed buret, heated by infrared lamps, was attached to the top of the combustion tube by a standard taper groundglass joint.

Procedure.—Fifty milliliters of new catalyst and 50 g. of rosin were used for each run. Catalyst volume was determined by pouring the pellets into a graduated cylinder while tapping the cylinder to settle the catalyst. The pellets of catalyst were transferred to the catalyst chamber in the same manner.

Cracking was accomplished at atmospheric pressure by dropping a regulated flow of molten rosin at 180° directly upon the pelletted catalyst that had been previously heated to the reaction temperature. Attempts to use glass beads
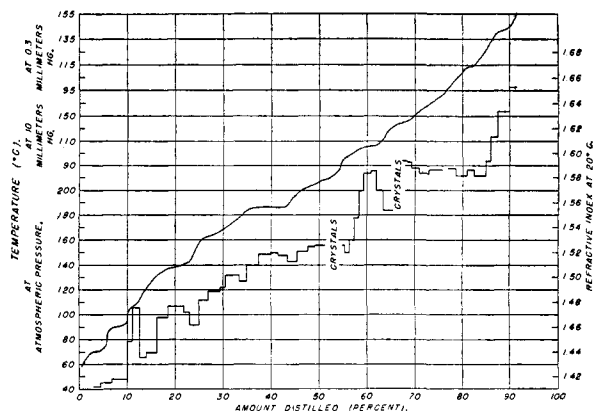

Fig. 4.—Upper curve, typical distillation curve of hydrocarbon fraction obtained from cracked rosin oil; lower curve, relation of amount distilled to refractive index.

TABLE I

COMPOSITION OF CRACKED ROSIN OIL (500°)

Constituents of cracked rosin oil	Content in rosin oil. %	Yield on original sample of rosin, %
Acidic and phenolic materials	7.3	3.9
Distillable to 188° (chiefly alkyl benzenes)	31.9	17.3
Distilling above 188° (up to 130° at 10 mm. (naphthalenes))	21.2	11.5
Distilling above 130° at 10 mm.	39.6	21.3
	100.0	54.0

TABLE II

CONSTITUENTS IDENTIFIED IN HYDROCARBON FRACTION OF CRACKED ROSIN OIL[a]

Identified constituents of hydrocarbon fraction	Content[b] rosin oil. %	Yield on original sample of rosin. %
Methylcyclopentane	5.0	2.7
Dimethylcyclopentanes	4.0	2.2
Toluene	2.5	1.4
Xylenes	8.0	4.3
Mesitylene	3.0	1.6
Pseudocumene	3.0	1.6
Diethylbenzenes	9.5	5.1
Naphthalene	10.0	5.4
Methylnaphthalenes	6.0	3.2
2.6-Dimethylnaphthalene	5.0	2.7
Anthracene	2.0	1.1
Hydrocarbons identified	58.0	31.3

[a] Fractions 2, 3 and 4 of Table I.   [b] Approximate (by distillation).

above the catalyst as a preheating surface resulted in excessive carbon deposits on the beads and were abandoned. Liquid hourly space velocity (LHSV), the milliliters of liquid-rosin flow per hour per milliliter of catalyst, was the basis used for comparison of flow rates.

The rosin flowed by gravity down over the catalyst surface, and the liquid products collected in the first receiver. Gaseous products were displaced as formed and passed through the water condenser to the second receiver. Noncondensable gases were vented.

Method of Analysis for Aromatic Content.—A modified method of the American Wood Preservers' Association,[3] which employed a triethyleneglycol–furfural mixture as a solvent for aromatic hydrocarbons, was used to determine

(3) American Wood Preservers' Assoc.. Report of Committee P-3 (1950).

the aromatic content of the oil product. While this solvent also dissolved olefins, the method was considered suitable for analysis in comparing the cracking runs. The analysis was performed by shaking 4 ml. of the hydrocarbon mixture with 9 ml. of a mixture of 40% (by volume) triethyleneglycol and 60% furfural for 2 minutes in a graduated centrifuge tube. The resulting solution was centrifuged, and the volume of the insoluble hydrocarbon layer read as an indication of the amount of non-aromatic compounds present in the original sample.

Separation of the Product.—For identification of the constituents of the cracked rosin oils, the products of a series of runs made from 350 to 500° were combined. Acidic materials (27 g. = 5.2%) were removed from the combined oil product of the cracking runs (519 g.) by extraction with 5% aqueous sodium hydroxide. These consisted of phenols, aliphatic acids and resin acids, which were not further identified.

The remaining oil product (492 g.) was fractionally distilled in a modified Stedman column to 150° at 0.3 mm. The column (13 mm. inside diameter by 4 feet long), when tested with n-heptane–methylcyclohexane mixture, was equivalent to 100 theoretical plates. The material distilling above 150° at 0.3 mm. was distilled to 200° at 1.8 mm. in a modified Stedman column, 10 mm. inside diameter by 8 inches long. The curve of the first distillation is given in Fig. 4. Liquid fractions of the distillation were further purified by chromatographic adsorption of the fraction on silica gel (28 to 200 mesh) in a column of suitable size. Refractive indexes were used for selection of the fractions from chromatographing for subsequent redistillation in a semimicro column.

Higher-boiling fractions not crystalline at room temperature were stored at −30°, and crystals that formed were filtered off at that temperature.

Ultraviolet analysis was performed on a Beckman model DU spectrophotometer. Infrared analysis was performed on a Baird recording spectrophotometer.

Identification of Constituents. (1) Methylcyclopentane.—The fraction that distilled at 70 to 71° (728 mm.). n^{20}D 1.4120, d^{20}_4 0.7530, after chromatographing and redistillation, was found to have an infrared spectrum identical with that of an authentic sample of methylcyclopentane.

(2) **Dimethylcyclopentanes.**—The fraction that distilled at 91.5 to 94° (728 mm.), n^{20}D 1.4180, after chromatographing and redistillation, was indicated by infrared analysis to be a mixture of $trans$-1,2-dimethylcyclopentane and $trans$-1,3-dimethylcyclopentane.[4]

(3) **Toluene.**—The fraction that distilled at 105 to 110° (728 mm.), n^{20}D 1.4760, was impure toluene. Oxidation with dilute potassium permanganate gave benzoic acid. Nitration gave dinitrotoluene.

(4) **Xylenes.**—The fraction that distilled at 137 to 141° (735 mm.), n^{20}D 1.4770, was a mixture of xylenes. Oxidation with dilute nitric acid[5] yielded p-toluic acid and a higher melting impurity believed to be terephthalic acid. Nitration[6] yielded 2,4,6-trinitro-m-xylene. A dimethylbenzene sulfonamide was obtained that melted at 146°. This could possibly be the 1,4-dimethyl-2-sulfonamide or the 1,2-dimethyl-4-sulfonamide reported in the literature to melt at 147 and 144°, respectively. It was concluded that meta and para xylenes were the main constituents of the fraction.

(5) **Mesitylene (1,3,5-Trimethylbenzene).**—The fraction that distilled at 160 to 165° (735 mm.), after redistillation,

yielded a fraction that distilled at 163 to 164°, n^{20}D 1.4900. Comparison of its infrared spectrum with that of an authentic sample indicated it to be mesitylene.

(6) **Pseudocumene (1,2,4-Trimethylbenzene).**—The fraction that distilled at 165 to 170°, after redistillation, yielded a fraction that distilled at 169° (735 mm.), n^{20}D 1.4972. Its infrared spectrum indicated it to be pseudocumene.[4]

(7) **Diethylbenzenes.**—The fraction that distilled at 184 to 187.5° (735 mm.), n^{20}D 1.5190, contained a small amount of an unidentified hydroxylated compound, which was removed by absorption on silica gel. After redistillation, infrared analysis indicated a probable mixture of alkyl benzenes.[4] Oxidation with 5% potassium permanganate yielded terephthalic acid. Oxidation with dilute nitric acid[7] yielded orthophthalic acid and 3,5-dinitroörthophthalic acid. Ultraviolet absorption curves confirmed these data by indicating that the fraction was a mixture of 1,4-diethylbenzene and 1,2-diethylbenzene.[8]

(8) **Naphthalene.**—The fraction distilling at 212 to 216.5° (740.5 mm.) crystallized in the receiver. Its melting point was 79°. It was identified as naphthalene by the mixed melting point method and by its characteristic odor.

(9) **Methylnaphthalenes.**—The fraction distilling at 106 to 107.5° (10 mm.), n^{20}D 1.5855, was indicated by these physical properties and by infrared analysis to be a mixture of 1-methylnaphthalene and 2-methylnaphthalene.[4]

(10) **2,6-Dimethylnaphthalene.**—The fraction distilling at 122.5 to 123.5° (10 mm.) crystallized in the receiver; melting point, 109 to 111°. *Anal.* C, 92.5; H, 7.62. Calcd. for 2,6-dimethylnaphthalene: C, 92.2; H, 7.75. Rast molecular weight was 152. These properties and its infrared spectrum indicated it to be chiefly 2,6-dimethylnaphthalene with a small quantity of impurities.[4]

Several succeeding fractions contained similar crystalline material whose melting points varied from 102 to 125°. The infrared spectra of these closely resembled that of 2,6-dimethylnaphthalene,[4] and the fractions were presumed to be mixtures with other dimethylnaphthalene isomers that fall in this distillation range.

(11) **Anthracene.**—A crystalline material was obtained from the fraction that distilled at 180° (1.8 mm.). After being recrystallized four times, it melted at 111 to 112°. *Anal.* C, 93.52; H, 6.44. Calcd. for anthracene: C, 93.55; H, 6.49. Anthroquinone was obtained by oxidation with chromic acid. The ultraviolet absorption curve of the crystalline material corresponded to that for anthracene.[4] It was concluded that the substance was a mixture of anthracene with anthracene derivatives.

(12) **Other Products.**—Oils distilling between 2,6-dimethylnaphthalene and anthracene yielded no crystalline products. The index of refraction of this fraction (1.58 to 1.65) and analysis (C, 91.2; H, 8.8) indicated the presence of substituted aromatic hydrocarbons or hydroaromatic compounds.

(4) American Petroleum Institute Infrared and Ultraviolet Spectrograms.

(5) Y. de Schepper, *Ann.*, **137**, 302 (1866) (Beilstein).

(6) E. H. Huntress and S. P. Mulliken, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 522.

(7) D. I. Legge, THIS JOURNAL, **69**, 2084 (1947).

(8) Ralph Stair, *J. Research Natl. Bur. Standards*, **42**, 587 (1949).