CATALYTIC CRACKING OF PURE HYDROCARBONS

Aromatics and Comparison of Hydrocarbon Classes

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The cracking of twenty-two aromatic hydrocarbons over a silica-zirconia-alumina catalyst is reported. A wide range of behavior is observed, from nearly inert compounds like toluene or biphenyl to highly reactive ones such as aromatics with substituent alkyl or cycloalkyl groups containing three or more carbon atoms, for which the removal of the whole substituent group is the chief cracking reaction. Results from catalytic cracking of the various hydrocarbon classes are reviewed. The stability of compounds of a given carbon number in processing over the cracking catalyst increases in the order: olefins, aromatics with C_3 or larger substituent groups, naphthenes, polymethyl aromatics, paraffins, and unsubstituted aromatics. This order differs substantially from that found in thermal cracking.

PREVIOUS papers of this series described the cracking of a number of paraffins, olefins, and naphthenes over a silica-zirconia-alumina catalyst under conditions similar to those employed in the commercial cracking of petroleum fractions (*4*, *5*, *6*). Results are given here from the cracking of various kinds of aromatics. As before, an effort is made to compare the catalytic with the thermal cracking of the same compounds. Thomas, Hoekstra, and Pinkston (*13*) studied the catalytic cracking of some alkylbenzenes, and reported results similar to ours.

The catalyst employed was described previously (*4*); it was obtained from Universal Oil Products Company, and was designated as UOP cracking catalyst, type B. The sample was found to contain 86.2% silica, 9.4% zirconia, and 4.3% alumina, by weight, and was in the form of 3 × 3 mm. cylindrical pellets. This catalyst gives results similar to those from the synthetic silica-alumina catalysts currently employed on a large industrial scale.

The experimental procedure, definitions, and terminology were given in an earlier paper (*4*). The preferred conditions of operation of the reaction system, which was arranged for flowing the hydrocarbon vapor over a fixed bed of catalyst, were: catalyst volume 50 cc. of pellets, atmospheric pressure, temperature 500° C., process period one hour, and flow rate about 13.7 moles of hydrocarbon per liter of catalyst per hour. The last three conditions were altered in many cases to attain suitable extents of reaction. The aromatics chosen covered a fairly wide range of structural types, and included compounds from C_7 to C_{15}. Properties and sources of materials follow, with compounds arranged in the order of increasing molecular weight:

Toluene was Baker's C.P. grade, further purified by treatment over a dehydrogenation catalyst and distillation. It had a boiling point of 110.7° C., d_4^{20} 0.8664, n_D^{20} 1.4964.

Ethylbenzene from Eastman Kodak Company had b.p. 136.3° C., d_4^{20} 0.8677, n_D^{20} 1.4958.

p-Xylene from Eastman had b.p. 138.0° C., d_4^{20} 0.8581, n_D^{20} 1.4950.

Indan (or hydrindene) from Eastman had b.p. 177.5° C., d_4^{20} 0.9499, n_D^{20} 1.5321, bromine number 4.3.

Mesitylene from Eastman had b.p. 165.0° C., d_4^{20} 0.8644, n_D^{20} 1.4982.

Isopropylbenzene from the Dow Chemical Company had a boiling range (5–95%) of 152–153° C., d_4^{20} 0.8621, n_D^{20} 1.4912.

n-Propylbenzene from Dow had a boiling range (5–95%) of 155–158° C., d_4^{20} 0.8617, n_D^{20} 1.4917.

Pseudocumene, Eastman technical grade, had a boiling range (5–95%) of 167–175° C., d_4^{20} 0.8871, n_D^{20} 1.5038, and probably did not contain over 50% pseudocumene. A second, purer sample from methylation of *p*-xylene had b.p. 168–169° C., d_4^{20} 0.8744, n_D^{20} 1.5047.

Tetralin from Eastman was purified by fractional distillation. The portion used had a boiling range of 205.9–206.8° C., n_D^{20} 1.5405–1.5435 (average 1.5419), d_4^{20} 0.9714, sulfur 0.0006% by weight.

n-Butylbenzene from Eastman had a boiling range of 181–182.5° C., d_4^{20} 0.8564, n_D^{20} 1.4882.

sec-Butylbenzene from Eastman had a boiling range of 173–174° C., d_4^{20} 0.8605, n_D^{20} 1.4901.

tert-Butylbenzene from Eastman had a boiling range of 168–169° C., d_4^{20} 0.8648, n_D^{20} 1.4930.

Methylnaphthalenes: Eastman practical grade α-methylnaphthalene was distilled in a 60-cm. Vigreux column, and the fraction 243–244° C. was used. Judging by the properties, it was a mixture of α- and β-methylnaphthalenes, along with impurities. The sulfur content was 0.98%, nitrogen about 0.25%. It had d_4^{20} 1.0188, n_D^{20} 1.6073.

Cyclopentylbenzene was prepared by condensation of cyclopentene with benzene in the presence of aluminum chloride. It had a boiling range of 210–215° C., d_4^{20} 0.9451, n_D^{20} 1.5269.

Pentamethylbenzene from Eastman had a melting range of 45–60° C., while the melting point of the pure compound is 54° C. Fractional distillation showed the presence of about 50% tetramethylbenzenes, probably durene (melting point 79.3° C.). The mixture as received was used for the cracking experiment.

Amylbenzenes, from Sharples Chemicals Inc., were said to contain at least 90% secondary amyl structures, with the rest tertiary. The sample had a boiling range of 185–195° C., d_4^{20} 0.8611, n_D^{20} 1.4885.

Biphenyl from Eastman melted at 68.9° C.

Cyclohexylbenzene, prepared by the condensation of cyclohexene with benzene in the presence of aluminum chloride, had a melting range of 5.0–5.8° C., boiling range of 230–233.5° C., d_4^{20} 0.9417, n_D^{20} 1.5252.

Triethylbenzenes from Dow were fractionated under vacuum and a middle fraction boiling from 158–161° C. at 200 mm. was taken, n_D^{20} 1.4960.

1,1-Diphenylethane from Dow had boiling range (5–95%) of 272.1–274.6° C., d_4^{20} 0.9882, n_D^{20} 1.5658.

tert-Butylnaphthalene was made by aluminum chloride alkylation of naphthalene with isobutene. The monobutylnaphthalene, probably largely beta-substituted, was recovered by fractionation, with d_4^{20} 0.9648, n_D^{20} 1.5757.

Amylnaphthalenes from Sharples were said to be 100% beta-substituted, and to contain at least 90% secondary amyl structures with the rest tertiary. They had a boiling range (initial, 95%) of 279–306° C., d_4^{20} 0.9645, n_D^{20} 1.5727.

INDIVIDUAL CRACKING BEHAVIOR

TOLUENE. Tests at 500° and 550° C. showed toluene to be very stable over the catalyst at these temperatures (Table I). Gas production was very small, and even at 550° there was only a trace of lower-boiling liquid. The total cracking in this run at 550° was estimated to be about 1.2% by weight of the charge. The recovered toluene had a refractive index of 1.4967, compared to 1.4964 for the charged toluene, and was therefore nearly free of condensation products. It was light yellow in color. The run at 500° C., low space velocity, and short process period, was perhaps as severe as that at 550°, but a careful balance of toluene showed that only 1.7% or less disappeared, confirming the high degree of stability. An experiment reported by Natanson and Kagan (*8*), however, showed about 25% disproportionation of toluene to benzene and xylenes in treatment over silica-alumina at 430° C. and the very low flow rate of 0.5 mole per liter per hour.

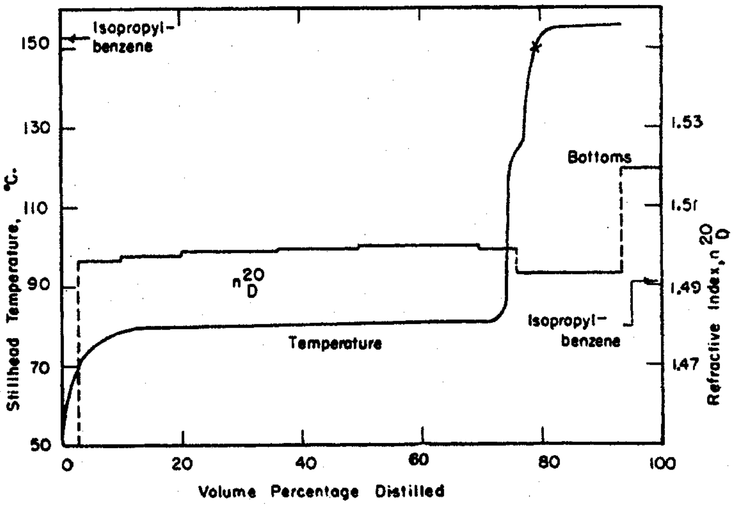

Figure 1. Distillation Curve for the Liquid Product from the Catalytic Cracking of Isopropylbenzene at 500° C.

ETHYLBENZENE. Results from the cracking of ethylbenzene at 500° C. showed the main reaction was scission next to the ring to yield benzene and ethylene. About 1.5% of toluene was formed compared to 6% benzene, indicating a minor amount of cracking within the side chain. The refractive index of the remaining material above toluene showed a styrene content, if present, of less than 3%.

n-PROPYLBENZENE. Cracked at 500° C., *n*-propylbenzene yielded almost exclusively propylene and benzene by scission next to the ring. The *n*-propylbenzene was 43% decomposed. Some of the propylene initially formed was saturated to propane.

ISOPROPYLBENZENE. Figure 1 is a distillation curve for the liquid product. The main reaction was scission next to the ring to yield benzene and propylene. This proceeded very extensively (about 80%) at 500° C. and a flow rate of 13.7 moles per liter per hour. The efficiency of benzene production, computed from the amount of feed cracked, was 90%. The mechanism is thus particularly well defined for a cracking reaction. Products other than propylene and benzene were present in much smaller amounts; there was no toluene, and C_9 aromatics were only about 3% of the charge. Isopropylbenzene decomposed nearly twice as extensively as *n*-propylbenzene.

BUTYLBENZENES. Three isomeric butylbenzenes (normal, secondary, and tertiary) were cracked under mild conditions—namely, 400° C. and 12.5 moles per liter per hour flow rate—to compare the relative stabilities. The results show that the structure of the alkyl group had a marked effect on the extent of cracking; *tert*-butylbenzene was 80.4% decomposed while *n*-butylbenzene was only 13.9% decomposed and *sec*-butylbenzene fell between with 49.2% decomposed. It is improbable that these marked differences in extents of cracking can be ascribed to differences in thermodynamic equilibria; rather, it is believed that they are mainly the result of rate differences caused by the several unique structures of the butyl group. Although free-energy limitations indicate that dealkylation cannot be 100% complete under the conditions used, an unlisted experiment with *n*-butylbenzene, at half the flow rate used for the run listed in Table I, gave nearly twice the dealkylation (about 24% decomposition compared to 13.9%), showing that equilibrium was not limiting the reaction in the latter run. With all three compounds the chief reaction was dealkylation to benzene and butenes. This was followed by a certain amount of secondary reaction of the butenes, which are known under these conditions to give lighter gas, isomerized butenes, butanes, and higher-boiling material. Distillation and spectrophotometric analysis of the cuts indicated that toluene was less than 1% of the liquid product in all the runs. Combined C_7, C_8, and C_9 aromatics were not over 4% by weight of the charge for any of the runs.

AMYLBENZENES. The amylbenzenes, a mixture of secondary and tertiary monoamylbenzenes, were cracked at 500° C. The extensive reaction, chiefly to give pentenes and benzene, was similar to those of the butyl- or propylbenzenes. A loss of 13% in the distillation of the liquid product made the distribution of the products somewhat uncertain, but it appeared that benzene recovery was 94% of the theoretical for the simple splitting to benzene and pentenes, based on the disappearance of amylbenzenes. The C_5 material actually recovered (50% of the theoretical amount based on disappearance of charge) contained 86% olefins. Distillation clearly showed that liquids other than

TABLE I. CATALYTIC CRACKING OF MONOALKYLBENZENES

Hydrocarbon	Toluene		Ethyl-benzene	*n*-Propyl-benzene	Isopropyl-benzene	*n*-Butyl-benzene	*sec*-Butyl-benzene	*tert*-Butyl-benzene	Amyl-benzenes
Temperature, ° C.	500	550	500	500	500	400	400	400	500
LHSV[a]	0.53	1.44	1.69	1.93	1.91	1.95	1.91	2.05	2.38
Flow rate, moles/l./hr.	5.0	13.6	13.8	13.8	13.7	12.5	12.3	13.2	13.8
Process period, min.	15	60	60	60	60	45	45	45	60
Gaseous product									
Moles/mole charge	0.020	0.033	0.069	0.373	0.700	0.124	0.441	0.694	0.195
Vol. % H_2	31.8	45	24.6	5.6	2.5	12.7	4.4	0.6	17.1
CH_4	...	...	...	3.5	3.0	0.0	0.0	...	23.4
C_2H_4	...	...	32.5	2.0	0.6	1.8	0.3	0.2	6.7
C_2H_6	...	...	...	1.7	3.5	0.0	0.3	...	7.5
C_3H_6	...	...	...	76.2	86.2	13.7	5.4	3.5	19.0
C_3H_8	...	...	...	7.4	0.8	10.0	1.1	1.1[c]	3.4
Iso-C_4H_8	...	...	...	1.0	1.2	10.0	3.6	76.7	8.1
n-C_4H_8	...	...	...	1.0	2.1	11.8	73.4	7.3	7.1
C_4H_{10}	...	...	...	1.6	0.1	40.0	11.5	10.6	7.7
Total olefins	33.3	16	51.5	80.2	90.1	37.3	82.7	87.7	40.9
Total saturates	34.9	39	23.9	14.2	7.4	50.0	12.9	11.7	42.0
C No. of saturates[b]	2.0	2.2	2.5	...	...	...	...	...	...
Material balance, wt. % of charge									
Gas	0.9	0.5	1.7	12.1	23.3	4.3	17.5	28.7	4.0
Liquid below original b.p.	0.0	0.6	7.7	27.8	50.7	8.5	31.0	50.7	(78)
Remaining liquid	96.0	94.8	86.8	55.4	15.3	83.4	45.1	15.6	(12)
Carbon	0.6	4.1	1.3	1.5	3.9	1.1	0.7	1.0	3.0
Loss	2.5		2.5	3.2	6.8	2.7	5.7	4.0	3

[a] Liquid hourly space velocity. [b] Carbon No. = *n* in C_nH_m. [c] C_1, C_2, and C_3 saturates, carbon No. 2.5.

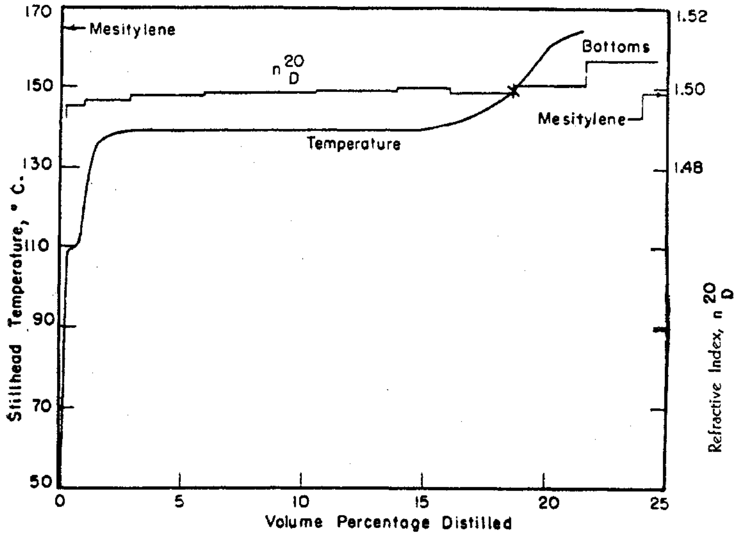

Figure 2. Distillation Curve for the Liquid Product from the Catalytic Cracking of Mesitylene at 500° C.

pentenes, benzene, and uncracked amylbenzenes were small in amount—about 5% from 40–75° C. and the same from 85–180° C.

p-Xylene. This compound was treated under more severe conditions than were normally employed—namely, at 550° C. and a flow rate of 4 moles per liter per hour (Table II). Decomposition was quite extensive, only 47.1% by weight of the charge being recovered as xylenes. Besides 23.8% of lower-boiling liquid, chiefly toluene, there was also formed 16.1% higher-boiling liquid, chiefly C_9 aromatics. A disproportionation or methyl-group transfer must therefore have taken place. Analysis of the remaining xylenes showed that isomerization to approximately an equilibrium mixture had occurred, as follows:

Isomer	% in Xylene Fraction	
	Exptl. from *p*-xylene	Theoretical at 550° C.(*10*)
Para	27.4	21
Meta	47.3	58
Ortho	25.3	21

The analysis of the xylene fraction was made by ultraviolet absorption.

Mesitylene (1,3,5-Trimethylbenzene). Mesitylene reacted to a moderate extent when passed over the catalyst at 500° C. The distillation curve in Figure 2 shows that the chief reaction was removal of one methyl group. No benzene was formed, only a trace of toluene, and considerable xylenes. A fair amount of condensation product was indicated by the elevated refractive index of the recovered mesitylene fraction (1.5073 compared to 1.4982 for mesitylene), and further distillation led to isolation of 6.3% by weight on the charge of bottoms above 185° C., with n_D^{20} 1.5305. Isomerization of mesitylene was not examined. The gas analysis showed appreciable amounts of C_2, C_3, and C_4 compounds, believed to have been formed by the combination of C_1 fragments initially removed from mesitylene.

Pseudocumene (1,2,4-Trimethylbenzene). Technical pseudocumene decomposed about as extensively as mesitylene when cracked at 500° C. The lower-boiling products were toluene and xylenes, in about equal amounts. The fact that the feed was a technical grade casts doubt on the results. In another run at 550° C. a pure pseudocumene from the methylation of *p*-xylene was charged. The high temperature coupled with the low flow rate of 3.2 moles per liter per hour caused the conversion of over 60% of the pseudocumene to other products. The gas was 5.5% by weight and was chiefly methane and hydrogen, although small amounts of C_2, C_3, and C_4 were also present, an indication of secondary recombination reactions. Toluene and xylenes amounted to 4 and 22% by weight of the charge, respectively. There was little or no benzene. Since the xylene product was an equilibrium mixture of the isomers, no conclusion can be reached as to which methyl group was most readily removed from the pseudocumene. About 13% of the pseudocumene charged appeared as higher-boiling material, over 80% of which distilled within 40° C. above the boiling point of the feed and was, therefore, presumably tetramethylbenzenes or other C_{10}–C_{11} aromatics. The bottoms above 209° C., amounting to 2.3% by weight of the charge, contained 42% of material boiling in the range 209–230° C., with n_D^{20} 1.5657.

Pentamethylbenzene. The trimethylbenzenes cracked much more readily than toluene. To ascertain the extent of this trend for benzenes with even more methyl groups, the behavior of pentamethylbenzene was studied. Unfortunately, the sample of pentamethylbenzene used was of poor quality, containing much tetramethylbenzene. The amount of cracking, which could be gaged only approximately, was of the order of the amounts for the trimethylbenzenes under equivalent conditions—namely, about 20% by weight of the feed. The cracked gas was chiefly methane, and the lower-boiling liquid, C_9 and C_{10} aromatics.

Triethylbenzenes. The cracking behavior of triethylbenzenes was between those of monoalkylbenzenes and poly-

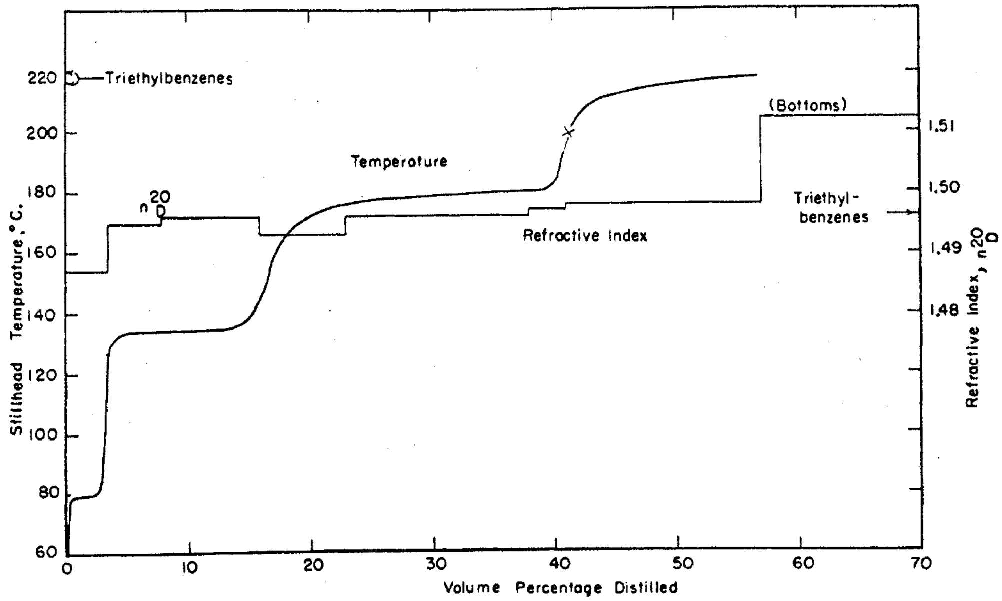

Figure 3. Distillation Curve for the Liquid Product (79% Yield by Weight) from the Catalytic Cracking of Triethylbenzenes at 500° C.

TABLE II. CATALYTIC CRACKING OF POLYALKYLBENZENES

(Process period 60 minutes)

Hydrocarbon	*p*-Xylene	Mesitylene	Pseudocumene[a]		Pentamethylbenzene	Triethylbenzenes
Temperature, ° C.	550	500	500[a]	550	500	500
LHSV	0.50	1.9	1.9	0.46	2.4[b]	2.6
Flow rate, moles/l./hr.	4.0	13.7	13.0	3.2	13.6	13.7
Gaseous product						
Moles/mole charge	0.508	0.084	0.140	0.460	0.170	0.606
Vol. % H_2	49.8	24.6	41.3	23.0	10.6	29.0
CH_4	40.2	58.9	...	71.6	...	5.1
C_2H_4	2.9	3.4	...	1.4	...	12.2
C_2H_6	3.2	3.0	...	1.7	...	7.3
C_3H_6	2.6	1.9	...	0.8	...	17.9
C_3H_8	0.3	4.7	...	0.9	...	4.6
Iso-C_4H_8	1.0	0.1	...	0.3	...	1.9
n-C_4H_8		0.5	...		...	14.5
C_4H_{10}		2.9	...	0.3	...	7.5
Total olefins	6.0	5.9	21.3	2.5	10.5	46.5
Total saturates	44.2	69.5	37.4	74.5	78.9	24.5
C No. of saturates	1.1	...	1.7	...	1.2	...
Material balance, wt. % of charge						
Gas	5.2	1.1	2.1	5.5	2.1	11.3
Liquid below original b.p.	23.8	17.6	14.6	30.0	(15)[c]	31.2
Remaining liquid	63.1	77.9	76.8	51.2	(75)[c]	48.0
Carbon	2.1	1.6	3.2	8.8	2.9	3.5
Loss	5.8	1.8	3.3	4.5	5.0	6.0

[a] Technical grade in run at 500° C.
[b] Based on liquid at 100° C.
[c] See text.

methylbenzenes. The removal of one or more side chains gave rise to a little benzene, considerable ethylbenzene, and even more diethylbenzene. The distillation curve in Figure 3 also shows that no toluene was formed. The presence of large amounts of C_3 and C_4 material in the gas suggests that C_2 fragments initially cracked off underwent further reaction, perhaps a combination on the catalyst surface.

METHYLNAPHTHALENES. Redistilled α-methylnaphthalene when treated at 500° C. was about 10% reacted, chiefly to lower-boiling materials and coke (Table III). Naphthalene isolated by distillation was 3% of the charge. The 1.2% of liquid distilling from 80° to 200° C. was nearly 100% mononuclear aromatics, of which the origin is somewhat obscure, especially since the feed contained some impurities—for example, 0.98% sulfur in combined form and about 0.25% nitrogen; it may have been the nitrogen or sulfur compounds that cracked rather than the hydrocarbon.

***tert*-BUTYLNAPHTHALENE.** This compound, like other aromatic compounds with large alkyl groups, cracked very extensively. Products were gas, containing much isobutene and butane, and a solid (freezing point 66° C.), which was doubtless impure naphthalene. The run was interrupted after 15 minutes because the reaction system became clogged with solid product, and therefore the material balance is only approximate. The high carbon formation is in part explained by the short duration of the run.

AMYLNAPHTHALENES. Cracking was very extensive. Products were a small amount of gas, liquid which was entirely C_6 hydrocarbons and contained 91.5% olefins, and a solid (impure naphthalene freezing at 70.5° C.). The complete cracking of amylnaphthalenes contrasts with the low reactivity of methylnaphthalene; the difference is analogous to that between amylbenzenes and toluene.

BIPHENYL. This compound underwent practically no reaction in treatment at 550° C. Gas formation was very small. The lack of reaction was substantiated by the melting point of the recovered biphenyl sample, which was only 0.7° C. below that of the charge; this indicated only 1.4 mole % of substances other than biphenyl in the solid product. Some material was formed which colored the products yellow-orange; the feed was nearly colorless.

Cracking in the presence of hydrogen was tried in an effort to cause splitting to benzene. An equimolal mixture of biphenyl and hydrogen was treated at 550° C., but there was insufficient reaction to lower the melting point of the biphenyl more than 0.5° C. in this test.

1,1-DIPHENYLETHANE. This compound was not chosen as a likely representative of any petroleum hydrocarbons, but rather because of the information to be gained by studying a substance of its particular structure. Decomposition in cracking at 500° C. was very extensive (about 75%) and proceeded almost exclusively to benzene and ethylbenzene with only a trace of toluene. The benzene yield was 90% of the theoretical, based on the feed decomposed; the ethylbenzene fraction was 75% of theoretical. In the ethylbenzene fraction there was only 2–6% olefin, probably styrene. Since a simple cracking reaction would produce benzene and styrene, there was evidently much saturation of styrene over the catalyst by hydrogen transfer. Carbon formation was quite high; this usually accompanies hydrogen transfer reactions between olefins.

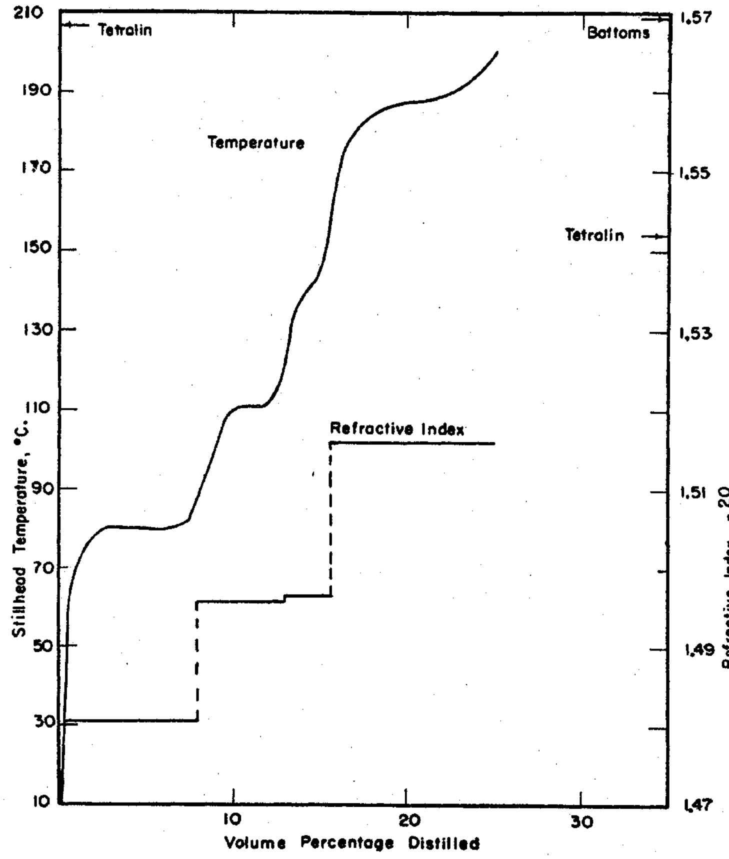

Figure 4. Distillation Curve for the Liquid Product from the Catalytic Cracking of Tetralin at 525° C.

TABLE III. CATALYTIC CRACKING OF BICYCLIC AROMATICS, BOTH RINGS AROMATIC

Hydrocarbon	Methylnaphthalenes	*tert*-Butylnaphthalene	Amylnaphthalenes	Biphenyl	1,1-Diphenylethane
Temperature, ° C.	500	500	500	550	500
LHSV	1.94	2.6	2.7	1.07[a]	1.26
Flow rate, moles/l./hr.	13.8	13.5	13.2	6.8	6.8
Process period, min.	60	15	60	60	60
Gaseous product					
Moles/mole charge	0.104	(0.51)	0.212	0.026	0.131
Vol. % H_2	58.9	15.0	26.5	...	28.7
Total olefins	10.3	48.6	33.1	...	31.8
Total saturates	30.8	36.4	40.4	...	39.5
C No. of saturates	1.5	4.2	2.0	...	1.9
Material balance, wt. % of charge					
Gas	0.9	(13)	3.0	...	1.7
Liquid below original b.p.	4.2	(71)[b]	18.8[c]	...	69.0
Remaining material	87.4		72.6[b]	...	13.9
Carbon	4.6	9.2	1.2	0.4[d]	4.6
Loss	2.9	6.8	4.4	...	10.8

[a] Based on liquid at 100° C.
[b] Solid
[c] Includes C_5 only.
[d] CO from regeneration not included.

INDAN (HYDRINDENE). When indan was cracked at 500° C. (Table IV), the amount of decomposition was rather small. The gas was 51.3% hydrogen. The lower-boiling liquid was almost wholly aromatic; it contained a little benzene, somewhat more toluene, and some C_9 aromatic material boiling below indan. This C_9 fraction contained no more than 10% olefins. The remaining liquid consisted chiefly of unchanged indan, but the bottoms from the distillation, which amounted to 26% of the charge to the run, had n_D^{20} of 1.5558 (indan 1.5383, indene 1.5768) and thus contained dehydrogenated or more highly condensed material. Carbon formation in the cracking of indan was fairly high (4.8% by weight of the charge).

TETRALIN (TETRAHYDRONAPHTHALENE). Cracking was carried out at 500° and 525° C. Figure 4 is a distillation curve for a typical liquid product. The cracking of Tetralin proceeded by a splitting of the naphthenic ring to produce monocyclic aromatic compounds. Benzene, toluene, and C_{10} aromatics were readily identified through the distillation curve, with smaller amounts of C_8 and C_9 aromatics also indicated. The gas contained considerable quantities of methane, C_3 and C_4 hydrocarbons, and small amounts of ethylene and ethane. The gas was fairly saturated. Dehydrogenation was evident, reflected in part by the hydrogen content of the gas. From the refractive index of the remaining liquid above 200° C. from the run at 525° C. (69% yield of such liquid, n_D^{20} 1.5694), it is apparent that naphthalene or condensation products of Tetralin must have been formed in the dehydrogenation reactions. Naphthalene (melting at 80.2° C.) was isolated from the product of this run in an amount equal to 16% of the charge. Transfer of hydrogen to the olefins produced also seems to have occurred, for although the monocyclic C_{10} aromatics from cracking Tetralin (which boil below Tetralin) should have unsaturated side chains, the C_{10} (175–195° C.) cut was found to contain only 2% olefins. It is also possible that some indan or methylindan was present in this cut. The low olefin content of the gas again points to saturation. Bloch and Thomas (*1*) gave more complete analyses of products from cracking Tetralin. Although obtained under somewhat different conditions, their results agree in a general way with ours.

CYCLOPENTYLBENZENE. Cyclopentylbenzene cracked rapidly over the catalyst; the chief reaction was scission at the link between the rings to give benzene and cyclopentene. The yield of benzene was practically quantitative at 1 mole per mole of feed cracked; but the yield of C_5 material was only about 0.35 mole per mole of feed cracked, so that it is necessary to postulate additional reactions, such as cracking off part of the cyclopentyl ring followed by dealkylation of the remainder to benzene, or secondary reaction of initially formed C_5 fragments. Yields of products were as follows:

Fraction, ° C.	Wt. % *of Charge*
25–57 (C_5)	11.9
57–85 (C_6)	46.8
85–208	9.5
208–218	8.5
Bottoms	9.5

The gas was rich in hydrogen. The C_5 fraction contained 64% olefins and was evidently a mixture of cyclopentene and cyclopentane. The C_6 fraction contained 90% benzene and 6% olefins. The small amount of material boiling above benzene but below the feed was probably alkylbenzenes. Distillaton bottoms with a high refractive index (n_D^{20} 1.5855) gave evidence of condensation products.

CYCLOHEXYLBENZENE (PHENYLCYCLOHEXANE). When cracked at 450° and 500° C., cyclohexylbenzene gave large yields of C_6 compounds, as Figure 5 shows. The principal reaction was splitting apart of the two rings; the C_6 fraction (66–82° C.) constituted almost the entire liquid product of lowered boiling point. It was made up of benzene, naphthenes, and small amounts of olefins and paraffins. Analysis of the C_6 fractions showed for the run at 450° C. (in per cent by weight): 6.5 olefins, 54.5 aromatics, 36 naphthenes, 3 paraffins; and for the run at 500° C.: 8 olefins, 48 aromatics, 41 naphthenes, and 3 paraffins. In conjunction with refractive index measurements, the flat portion of the distillation curve, rising gradually from 70° to 80° C., appears to indicate the presence of methylcyclopentane. Dehydrogenation appears again as an auxiliary but important reaction leading to hydrogen in the gas and highly aromatic substances in the distillation bottoms. The high degree of saturation of the gas, and especially of the C_6 fraction, is noteworthy; it indicates considerable hydrogen transfer to the initially formed olefinic products.

TABLE IV. CATALYTIC CRACKING OF BICYCLIC AROMATICS, ONE RING AROMATIC
(Process period 60 minutes)

Hydrocarbon	Indan	Tetralin			Cyclopentylbenzene	Cyclohexylbenzene		
Temperature, ° C.	500	500	500	525	500	450	500	500[a]
LHSV	1.68	0.87	1.87	1.86	1.12	1.16	1.11	0.24[b]
Flow rate, moles/l./hr.	13.5	6.4	13.7	13.7	7.2	6.8	6.5	1.43[b]
Gaseous product								
Moles/mole charge	0.149	0.310	0.516	0.322	0.302	0.144	0.358	0.116
Vol. % H_2	51.3	36.4	57	35.3	60.1	25.8	51.1	90.2
CH_4	14.2	7.5	...	4.7[c]	7.1	...	18.1	...
C_2H_4	4.2	2.7	...	3.2	5.4	...	5.7	...
C_2H_6	7.9	5.3	...	...	8.1	...	4.9	...
C_3H_6	10.6	9.4	...	17.3	6.8	...	7.9	...
C_3H_8	7.0	18.1	...	21.3	5.1	...	4.1	...
Iso-C_4H_8	0.5	1.5	...	0.6	0.6	...	0.4	...
n-C_4H_8	1.2	2.3	...	2.7	1.2	...	1.1	...
C_4H_{10}	3.1	16.8	...	14.9	5.6	...	6.7	...
Total olefins	16.5	15.9	16.3	23.8	14.0	16.7	15.1	6.3
Total saturates	32.2	47.7	26.7	40.9	25.9	57.5	33.8	3.5
C No. of saturates	...	...	2.9	...	...	2.9	...	3.1
Material balance, wt. % of charge								
Gas	2.2	6.6	7.8	7.2	3.3	3.3	3.7	0.5
Liquid below original b.p.	6.9	19.8	19.6	20.9	68.2	64.8	68.7	2.6
Remaining liquid	83.3	65.7	68.3	69.6	18.0	23.2	17.8	91.9
Carbon	4.8	1.9	1.0	0.8	1.5[d]	0.9[d]	1.4[d]	5.0
Loss	2.8	6.0	3.3	1.5	9.0	7.8	8.4	

[a] Thermal run.
[b] Based on heated free space of 70 cc.
[c] Including C_2H_6.
[d] CO from regeneration not included.

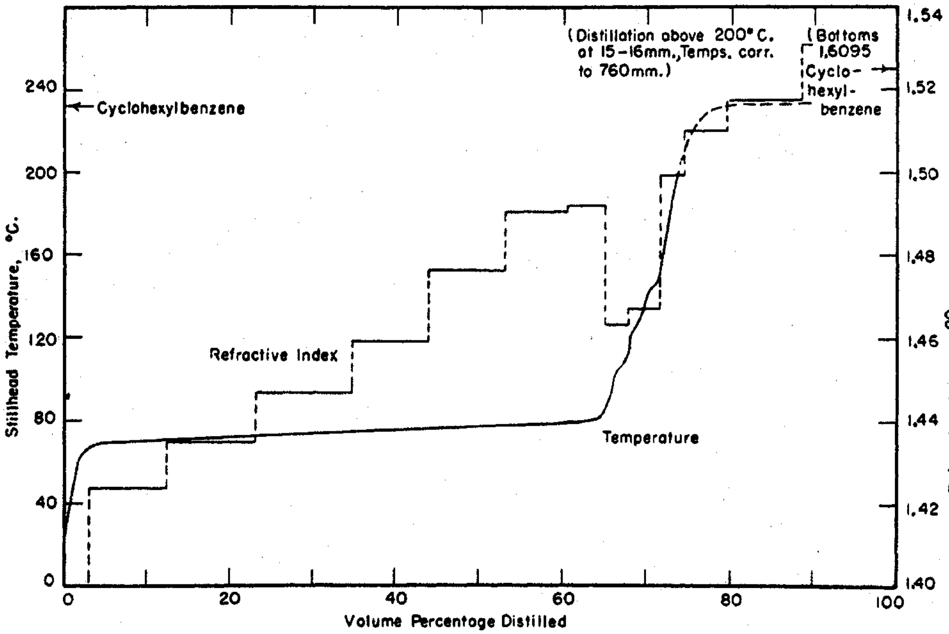

Figure 5. Distillation Curve for the Liquid Product from the Catalytic Cracking of Cyclohexylbenzene at 450° C.

Temperature increase from 450° to 500° C. caused a little more cracking and greater hydrogen production. The gasoline fractions formed at the two temperatures appeared to be nearly identical.

CRACKING OF AROMATICS

The aromatic hydrocarbons show a wide range of stability in catalytic cracking. At one extreme the wholly aromatic compounds, such as biphenyl and certainly benzene and naphthalene in view of the stability of toluene and methylnaphthalenes, are practically inert under normal cracking conditions. At the other extreme the aromatic compounds with large alkyl or cycloalkyl substituents are very reactive. When properly classified according to structure, the aromatics form a consistent picture.

Monoalkylbenzenes crack with increasing ease as the size of the alkyl group increases. Under fixed conditions, at 500° C. decomposition of toluene was about 1%, of ethylbenzene 11%, and of *n*-propylbenzene 43%. Isomeric structure has considerable effect, for isopropylbenzene was 83.5% decomposed under the same conditions. The marked effect of structure was also noted with the butylbenzenes, which at 400° C. were cracked to the following extents: normal, 13.9%; secondary, 49.2%; tertiary, 80.4%. The cycloalkylaromatics, cyclopentylbenzene and cyclohexylbenzene, behave much like the monoalkylbenzenes. All these compounds are cracked primarily at the link joining the substituent group to the aromatic ring, producing benzene nearly quantitatively. The groups removed are frequently altered by secondary reactions.

Polymethylbenzenes also crack with increasing ease as the molecular weight increases, but they are much less reactive than the isomeric monoalkylbenzenes. At 500° C. the cracking of toluene was about 1%, while that of mesitylene or pseudocumene at a higher flow rate and longer process period was about 20%. Pentamethylbenzene may be a little less stable than the trimethylbenzenes. Triethylbenzene appeared to combine the heightened reactivities arising from increased substitution and increased size of the alkyl group. A feature with the polymethylbenzenes is the mobility of the methyl groups, evidenced both by isomerization and by disproportionation. Associated with this phenomenon is the apparent combination of C_1 fragments from the methyl groups to yield C_2, C_3, and C_4 material in small amounts. The transfer of alkyl groups among aromatics in the presence of silica-alumina catalysts was recently described by others (*7*).

Substituted naphthalenes behave in much the same way as the analogous benzene derivatives. Diphenylethane cracked readily; it may be regarded as an analog of isopropylbenzene, with a methyl replaced by a phenyl group. Biphenyl, on the other hand, with no aliphatic groups, was almost inert.

The condensed ring bicyclic aromatics with only one aromatic ring (also designated as naphthene-aromatics) crack fairly readily and yield, as the chief lower-boiling products, benzene and some of its homologs. The ease of cracking evidently depends on the size and structure of the naphthenic ring, for Tetralin cracked more than twice as readily as indan under the same conditions. Although cracking tends to take place at the links to the aromatic ring, it does not occur there so exclusively as with the alkyl- and cycloalkyl- aromatics.

Aromatics are generally considered to be relatively unreactive in cracking, but the results of the present study show that some types are highly reactive over the catalyst. Therefore, it is essential to specify the types of aromatics concerned before attempting to predict the behavior of an aromatic fraction in catalytic cracking.

TABLE V. CHIEF LOWER-BOILING PRODUCTS FROM CATALYTIC AND THERMAL CRACKING OF AROMATICS

	Catalytic Cracking		Thermal Cracking		
Compound	Temp., ° C.	Chief products	Temp., ° C.	Chief products	Citation
Ethylbenzene	500	Benzene, ethylene	550–650	Styrene, toluene, benzene, hydrogen, methane	(*2, 9*)
n-Propylbenzene	500	Benzene, propylene	650	Toluene, ethylene	(*2*)
Isopropylbenzene	500–550	Benzene, propylene	600–650	Styrene, methane	(*2*)
Amylbenzenes	500	Benzene, pentenes	600–650	Toluene, styrene, gases	(*2*)
1,1-Diphenylethane	500	Benzene, ethylbenzene	675–700	Toluene, benzene, styrene	(*11*)
Methylnaphthalenes	500	Naphthalene, methane	450[a]	Naphthalene, methane	(*14*)
tert-Butylnaphthalene	500	Naphthalene, butene	650	Naphthalene	(*3*)
Tetralin	500–525	C_6, C_7, C_{10} aromatics	600	C_8, C_{10} aromatics	(*12*)
Cyclohexylbenzene	500	Cyclohexane, benzene	600	Styrene, alkylbenzenes, naphthalene, gases	(*3*)

[a] Autoclave at 25 atmospheres pressure.

COMPARISON WITH THERMAL CRACKING

The accelerative effect of the catalyst on the cracking of alkyl- or cycloalkyl-substituted aromatic compounds is great and comparison must be made with thermal cracking carried out at somewhat higher temperatures. Comparisons at the closest available temperatures used here or in the literature are listed below and followed by substantiative evidence. Compared to thermal cracking, catalytic cracking of these substituted aromatics is found (*a*) to be much faster, by factors of the order of 100 to 10,000; (*b*) to take place preferentially at the bond next to the aromatic ring, instead of in the substituent group; and (*c*) to give products of lower olefin content.

Table V lists the chief lower-boiling products obtained by catalytic and thermal cracking of typical substituted aromatics. The following detailed discussion of certain compounds brings out additional information.

ETHYLBENZENE. Thermal cracking at 550–600° C. gave chiefly styrene and hydrogen (*9*); catalytic cracking gave largely benzene and ethylene. According to the reaction velocity constant for the thermal reaction, the amount of ethylbenzene that would have decomposed thermally under the conditions used for catalytic cracking is about 0.01%. The observed amount was 11.8%. Thus the catalyzed reaction not only follows a different course but proceeds about a thousand times as fast as the thermal at 500° C. In another thermal study (*2*) at 650°, toluene and benzene were obtained in addition to styrene.

PROPYLBENZENES. Thermal experiments (*2*) showed that *n*-propylbenzene decomposed chiefly to toluene, and isopropylbenzene to styrene. In catalytic treatment both yielded almost exclusively benzene and propylene.

METHYLNAPHTHALENES. Thermal cracking (*15*) was observed at 450° C. in an autoclave at 25 atmospheres pressure. α-Methylnaphthalene cracked three to four times as fast as β-methylnaphthalene. Products were about equally divided among lower-boiling compounds, chiefly naphthalene and methane, and higher-boiling condensation products. The rate of thermal cracking at 500° C. is computed to be of the order of one hundredth that of catalytic cracking at the same temperature.

TETRALIN. In thermal cracking (*12*) there was no appreciable reaction at 550° C., with residence times twelve to twenty-four times those used for catalytic cracking. At 580° cracking was noticeable, and at 600–625° it proceeded fairly rapidly. Calculated first-order rate constants corrected to 500° (assuming an activation energy of 60 kg.-cal. per mole) indicate that the catalytic reaction is of the order of ten thousand times as fast as the thermal. Other comparisons, from the data in Table VI, show that catalytic cracking: (*a*) produces less hydrogen per mole cracked; (*b*) gives a gas lower in methane, and containing considerable amounts of C_3 and C_4 components which are virtually absent in the thermal gases, according to Sundgrén's analyses (*12*); and (*c*) gives a somewhat higher ratio of gas to lower-boiling liquid. The liquid products also differ considerably. Approximate analyses follow:

	Catalytic (This Work)			Thermal (*12*)		
Temp., ° C.	500	500	525	580	600	625
Flow rate, moles/l./hr.	6.4	13.7	13.7	0.55	0.55	0.55
Wt. % of lower-boiling liquid to 195° C.						
C_6 (70–95° C.)	29	36	34	10	7	10
C_7 (95–115° C.)	14	16	18	5	3	5
C_8 (115–145° C.)	16	9	18	36	22	48
C_9 (145–175° C.)		9		16	14	10
C_{10} (175–195° C.)	41	30	30	33	54	27
Olefin content, wt. % of fraction						
C_{10} (175–195° C.)	2	...	2	80	60	85

The catalytic liquid contains large amounts of C_6, C_7, and C_{10}; the thermal is predominantly C_8 and C_{10}. In both cases the liquids are made up of monocyclic aromatics, but in the thermal product the olefin content (C_8 and above) is much higher. It should again be pointed out, however, that the olefin content of the catalytic product is very dependent on operating conditions, and in some circumstances it might be quite high.

CYCLOHEXYLBENZENE. This compound was cracked thermally at 500° C. (Table IV). The rate of cracking was only about one four-hundredth that of catalytic cracking. There was a little lower-boiling liquid, which was not identified but was certainly not the almost exclusively C_6 material found in catalytic cracking. Much hydrogen was formed in thermal cracking. At 600° C. thermal cracking of cyclohexylbenzene gave monocyclic aromatics with aliphatic side chains including styrene and naphthalene (*3*). Again the contrast with catalytic cracking is evident.

COMPARISON OF HYDROCARBON CLASSES

The results accumulated on the cracking of pure hydrocarbons portray the behavior of the principal classes met in virgin petroleum—namely, paraffins, naphthenes, and aromatics. Although the isomers tested were not numerous for some classes, generalizations have been drawn which are felt to be reasonably valid for the structures present in petroleum. Recent unpublished data obtained by us for paraffins do indicate that their cracking may depend to some degree on isomeric structure; our generalizations are primarily for normal paraffins.

TABLE VI. CATALYTIC AND THERMAL CRACKING OF TETRALIN

Type Reaction and Source	Catalytic (This work)			Thermal (*12*)		
Temperature, ° C.	500	500	525	580	600	625
Rate, moles/l./hr.	6.4	13.7	13.7	0.55	0.55	0.55
Time, sec.[a]	7.7	3.6	3.5	92	90	84
% decomposed[b]	30.0	29.3	29.3	2.8	4.3	10.8
Products, % wt. of charge						
Gas	7.0	8.0	7.3	0.44	0.50	1.98
Liquid below original b.p.	21.0	20.2	21.2	1.89	3.22	7.10
Carbon	2.0	1.1	0.8	0.52	0.63	1.69
Gas analysis, vol. %						
H_2	36.4	57.0	35.3	56.2	66.6	84.7
CH_4	7.5	...	...	39.0	29.5	13.3
C_2H_4	2.7	...	3.2	4.1	3.9	2.0
Total olefins	15.9	16.3	23.8	4.1	3.9	2.0
Total saturates	47.7	26.7	40.9	39.0	29.5	13.3
Moles/mole charge decomposed						
H_2	0.37	1.00	0.39	1.31	1.37	4.56
Hydrocarbon gas	0.66	0.77	0.71	1.02	0.69	0.83

[a] Time of contact, assuming catalyst 100% void and allowing for expansion.

[b] To gas, lower-boiling liquid and carbon, on no-loss basis.

Figure 6 shows reactivities of representative hydrocarbons over the cracking catalyst, with percentages decomposed plotted against the number of carbon atoms in the molecule. At a given carbon number the paraffins are the most stable hydrocarbons in the figure, except toluene. Most stable of all are estimated to be the unsubstituted aromatics (not included in Figure 6), such as benzene, naphthalene, and biphenyl. The polymethylaromatics are somewhat more reactive than the paraffins, judging from data for the polymethylbenzenes. Next in order of increasing reactivity are the condensed-ring naphthene-aromatics (not in Figure 6) such as Tetralin, then the naphthenes, and finally the aromatics with large alkyl or alicyclic groups, among which only the monoalkylbenzene series is illustrated.

Olefins are important components of cracked and synthetic petroleum fractions, but cannot be directly compared with the other classes because of the lower reaction temperatures employed. Even at 400° C. the aliphatic olefins cracked more extensively than did the naphthenes at 500° C., an indication of their high reactivity. The alicyclic olefins or unsaturated naphthenes are similar in behavior.

The primary products from catalytic cracking of the several hydrocarbon classes are determined by the carbon-carbon bond ruptures which occur. These may be summarized as follows:

1. Paraffins are cracked preferentially at those links which yield fragments of three or more carbon atoms. With normal paraffins, cracking occurs at gamma carbon-carbon bonds or at those still nearer the center of the molecule, and the product gas is correspondingly low in methane and C_2. Long chains tend to crack simultaneously in several places and result in products comprising a molecular weight range very much lower than that of the feed.
2. Naphthenes also tend to give fragments of three or more carbon atoms. They are cracked in both the ring and the side

chain, especially when the latter contains three or more carbon atoms.

3. In substituted aromatics the link to the ring is selectively attacked, and in the simplest case of monoalkylaromatics the substituent group is sheared off to yield the bare aromatic and the complementary olefin. This reaction is very extensive with substituent groups of three or more carbon atoms.
4. Olefins are cracked in much the same manner as paraffins but much more readily.

In addition to the cracking reactions, there are secondary and auxiliary reactions which are important in determining the nature of the products. These include isomerization, saturation by hydrogen transfer, polymerization and condensation, cyclization to aromatics, dehydrogenation, and coke formation.

Isomerization is most pronounced with olefins, both aliphatic and cyclic. A shift in the position of double bonds has been determined in unreported experiments to be very rapid. Branching of the carbon skeleton of olefins, while less rapid, is also prominent. Saturation of olefins by hydrogen transfer is particularly important, and since it acts selectively on tertiary olefins, it leads preferentially to the formation of branched saturates. It is somewhat favored if high-molecular-weight naphthenes, such as Decalin, are present to act as donors of hydrogen. Direct isomerization of paraffins occurs to a very small extent.

Polymerization and condensation are prominent with olefins, and to a lesser extent with higher aromatics. Cyclization and condensation to aromatics is noticed with paraffins and aliphatic olefins, and seems particularly to lead to aromatics in the range C_8 to C_{10}. Dehydrogenation under catalytic cracking conditions is extensive only for the higher hydroaromatic compounds, such as Tetralin. Coke formation is invariably associated with catalytic cracking but is more marked with certain types of hydrocarbons, as will be outlined below.

Compositions of gases from catalytic cracking are surprisingly uniform, except for compounds such as the alkylbenzenes or the isobutylene polymers where the particular structure is of controlling importance. Gases are, in general, rich in C_3 and C_4 compounds because of the tendency to crack out large fragments. On the other hand, highly methylated chains such as 2,2,4-trimethylpentane tend to give moderately large amounts of methane. The degree of saturation of the gas depends on the conditions of cracking and on the efficacy of the parent hydrocarbon as a hydrogen donor. Hydrogen contents of gases are ordinarily low. This hydrogen does not necessarily imply direct dehydrogenation; often the major portion of it can be accounted for by the elimination of hydrogen in the condensation reactions that lead to coke formation, since most of the hydrocarbons have empirical formulas C_nH_n to C_nH_{2n+2}, whereas coke is about $C_nH_{0.5n}$.

Coke formation, measured by the carbon deposited on the catalyst, is fairly characteristic for different classes. Aliphatic olefins produce more carbon, evaluated as weight percentage of the original hydrocarbon, than do the naphthenes and paraffins, and the aromatics range in an intermediate position. The greatest amounts of coke are formed by cyclo-olefins, diolefins, and unsaturated aromatics such as styrene.

Comparison of catalytic and thermal cracking rates of the different hydrocarbon classes brings out the striking fact that the catalyst markedly changes the relative order of stability of the several classes. Thermally the stability for a given carbon number increases in the order: (1) paraffins and aliphatic olefins, (2) naphthenes, (3) alkyl aromatics, (4) unsubstituted aromatics. In catalytic cracking, stability increases in the order: (1) olefins, (2) aromatics with C_3 or larger substituent groups, (3) naphthenes, (4) polymethyl aromatics, (5) paraffins, (6) unsubstituted aromatics.

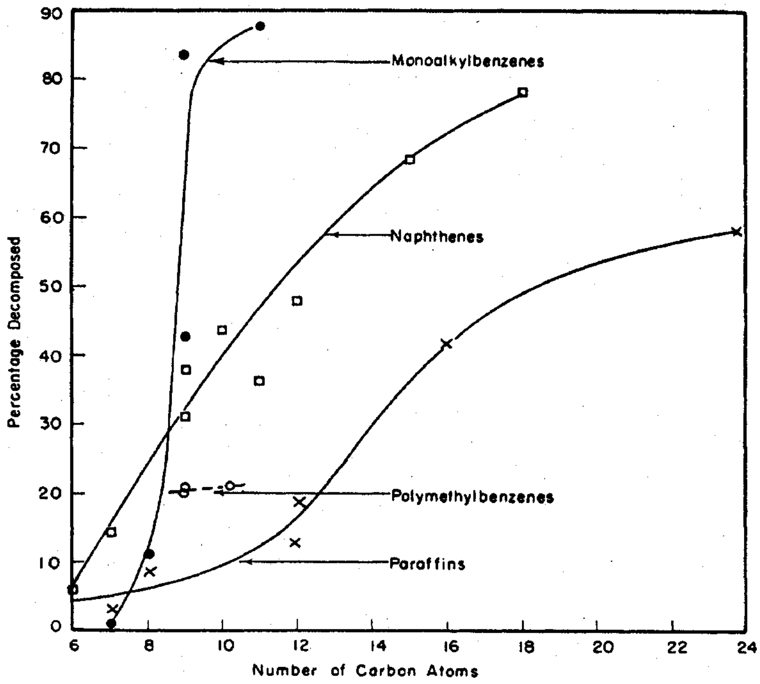

Figure 6. Catalytic Cracking of Various Hydrocarbon Classes

From treatment over silica-zirconia-alumina catalyst at 500° C. with flow rate of 13.7 moles per liter per hour for 1 hour; the percentage decomposed is the sum of gas, liquid boiling below the original b.p., and carbon.

These orders are based upon the assumption that the major portion of the molecule is of the class specified, and they represent only a rough segregation. For example, paraffins and olefins of the same carbon number are not necessarily identical in thermal stability, and actual rate ratios depend on conditions as well as on individual structures. For present purposes, however, the rates of thermal cracking of olefins and paraffins at atmospheric pressure and about 500° C. may be taken as roughly equal.

The change in the order of stability effected by the catalyst explains why petroleum cracking stocks cannot be rated uniformly for both catalytic and thermal cracking. Of particular practical importance is the paraffin-naphthene relation, since many virgin cracking stocks contain large amounts of these two hydrocarbon types. Catalytically, in the range C_{10} to C_{18}, naphthenes crack two to three times as fast as paraffins; thermally the naphthenes crack at about one twentieth the rate of the paraffins[1]. A factor of about 50 is thus introduced in the rate ratio of naphthenes compared to paraffins, in favor of catalytic cracking. This explains the preferred position of naphthenic oils as stocks for cracking with catalysts of these or similar characteristics.

A rough measure of catalysis for any class is obtained by comparing the first-order rate constants computed for catalytic and thermal cracking. As pointed out previously (*4*), such a comparison has only qualitative significance, and the ratios depend on the conditions for the catalytic reaction as well as on the assumptions applied in computing rate constants. Approximate ratios of catalytic to thermal decomposition rates are: paraffins, 6 to 60; naphthenes, about 1000; aromatics, up to 10,000;

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[1] The ratio of rates for thermal cracking of naphthenes and paraffins has been obtained from two sources: (*a*) a survey of the sparse data available from cracking at atmospheric pressure and about 500° C. and (*b*) the collections of Tilicheev (*14*), based largely on cracking in autoclaves. Both sources yield the same naphthene/paraffin rate ratio, although source *b* gives absolute rates two to ten times as high as source *a*.

olefins, over 1000. These values apply in the neighborhood of 500° C. The temperature coefficient of thermal cracking is much higher than that for catalytic cracking, which denotes a higher Arrhenius activation energy. Accordingly, the rate ratios cited will be altered by any substantial change in the reaction temperature.

In addition to the rate comparisons for the catalytic and thermal cracking of hydrocarbons, characteristic differences in reaction products have been shown in detail for individual compounds and for the major classes of hydrocarbons studied. An over-all comparison of these differences leads to several generalizations which help outline the nature of catalytic in contrast with thermal cracking of petroleum hydrocarbons in terms of the kinds of cracked products obtained. In summary, catalytic cracking gives rise to: (1) more selective cracking and relatively less of the smaller (C_1 and C_2) fragments; (2) more olefin isomerization, both of double bonds and carbon skeleton; (3) a more controllable saturation of double bonds, especially in the fractions of higher molecular weight; (4) greater production of aromatics (except at extreme thermal conditions); (5) less diolefin production; (6) relatively more coke.

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ANTISKINNING AGENTS . . . . .

DERIVED FROM NITROPARAFFINS

A number of nitroamines and polyamines have been tested as antiskinning agents for a badly skinning tung oil varnish. The results are given and are compared here with those from other antioxidants.

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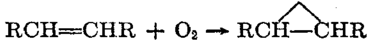
IN THE manufacture of paints and varnishes, the use of tung oil has always been a problem because of the gelling and skinning properties of the finished products before application. Tung oil (*9*, *14*) is obtained from the nuts of the tree, *Aleurites fordii*, which grows chiefly in China. It differs from other drying oils, except oiticica oil, in that it has conjugated double bonds which account for the characteristic waterproofness, fast drying, and durability it imparts to varnishes. The mechanism of drying and oxidation of oil films is still the subject of study and controversy (*12*). It is fairly well agreed that the reaction is complex and involves oxidation, polymerization, and colloidal gel formation. As Bradley (*1*) pointed out, it is generally believed that a certain amount of linear polymerization is characteristic of the fusible polymer which makes up the film-forming material before final application. Drying is then a mechanism by which the linear polymer is converted to a cross-linked polymer. Any agent or means of activation to bring about this conversion may be considered as a promoter.

The first step in the drying of the oil film is the addition of oxygen at the double bonds to form peroxides:

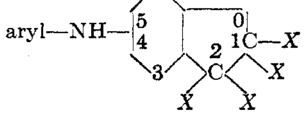


$$RCH{=}CHR + O_2 \rightarrow RCH{-}CHR\ (O_2)$$

The next steps in the mechanism are not clear. Elm (*6*) showed that, during the physical change of the oil, it is converted from a noncolloidal into a colloidal state upon exposure to oxygen. Just how the polymerization and/or association takes place has not been demonstrated. Later investigators (*1*, *11*) believe that oxidation followed by association is more likely in the light of the study of solvent action on the drying-oil film.

Irrespective of the mechanism, skinning and gelling of the paint or varnish are attributed to oxidation and/or polymerization in the presence of oxygen. The property of air hardening is necessary for the normal use of such paints and varnishes; obviously, then, attempts to eliminate skinning and related phenomena must at the same time avoid objectionable loss of air-hardening properties of the final film.

The literature reveals a number of patents on antioxidant compositions suitable for use in inks, paints, varnishes, and the like. Most frequently mentioned are polyhydroxy phenols and their derivatives (*4*). Other compounds are the azones (*5*)—i.e., organic compounds containing the tetravalent azono group —C=N—N; the arylaminodihydrobenzofuranes (*7*) of the general formula:



where aryl refers to the aryl nucleus of the benzene, naphthalene, or biphenyl series, and *X* is an alkyl group or hydrogen; and the arylamines (*8*) and alkylamino alcohols (*13*). One patent (*3*) discloses products of a nature somewhat similar to those discussed in this paper.

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