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Catalytic Cracking of Pure Hydrocarbons

Secondary Reactions of Olefins

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The secondary reactions of olefins—isomerization, hydrogen transfer, polymerization, and aromatization—were found to be extensive and to influence greatly the nature of the products from catalytic cracking. Isomerization, both double-bond shift and chain-branching, occurred rapidly under conditions of catalytic cracking. Saturation by hydrogen transfer was shown to be faster for tertiary than for secondary olefins. This, together with the rapid chain-branching isomerization of olefins, affords an explanation of the high ratios of iso- to normal paraffins observed in catalytic cracking. Molecular hydrogen had no more influence than nitrogen on the saturation of olefins; both acted as inert diluents. Polymers were readily formed from lower olefins, but were rapidly converted to other products at the usual conditions for catalytic cracking. Such products from the treatment of normal butenes were found to include benzene, toluene, xylenes, and higher boiling aromatics in important quantities.

THE four previous papers (*6, 7*) in this series described individually and compared as classes the catalytic cracking of many paraffin, olefin, naphthene, and aromatic hydrocarbons of a wide variety of types and molecular weights. A total of fifty-six hydrocarbons was tested with a silica-alumina-zirconia catalyst under conditions similar to those used in the commercial cracking of petroleum fractions. In addition to the primary cracking reactions involving the severance of carbon-to-carbon bonds, a number of secondary reactions were shown to participate to an important extent in the hydrocarbon transformations observed in catalytic cracking systems; they consequently exerted a substantial influence upon the nature of the products obtained.

The majority and the most important of these secondary reactions are those characteristic of the ethylenic double bond, either in the original hydrocarbon or in the products resulting from cracking. This consideration led to a series of experiments on the secondary reactions of olefins in the catalytic cracking system, in the following respects: the nature and extent of olefin isomerization; olefin saturation via hydrogen transfer, and the effect on saturation of the variables of temperature, flow rate, and diluents; the effect of olefin structure upon hydrogen transfer reactions; Decalin and Tetralin as hydrogen donors; a comparison of hydrogen transfer and catalytic hydrogenation; the production of polymers and aromatic hydrocarbons from olefins.

In addition to the silica-alumina-zirconia cracking catalyst (U.O.P. type B) used in most of the experiments, commercial synthetic silica-alumina, a silica-alumina-magnesia, and activated natural clay cracking catalysts were used in some cases and gave similar results.

In addition to the terminology previously applied, the following definitions are required: "Hydrogen transfer" is the saturation of an ethylenic double bond by direct catalytic transfer of hydrogen to the bond from another hydrocarbon, with no essential participation of free molecular hydrogen; "self-saturation" or "autosaturation" is a special case of hydrogen transfer in which a single hydrocarbon provides both acceptor and donor molecules; "hydrogen donor" is any hydrocarbon which provides hydrogen for the general case of hydrogen transfer; and "hydrogen acceptor" is any compound containing an ethylenic double bond which becomes saturated via hydrogen transfer. "Coke" is the carbonaceous deposit remaining on the catalyst after the reactor is purged with nitrogen; it is measured by the carbon dioxide and water in the regeneration gases after conversion of carbon monoxide to the dioxide. "Reactor purge" is material collected by condensation and by combustion of noncondensables over copper oxide during a 20-minute purge of the catalyst with nitrogen.

Differing slightly in temperature limitations from previous definitions, "gas" is all material boiling below 25° C., and "liquid product" is any material boiling above 25° C. "LHSV" (liquid hourly space velocity) is the liquid input per volume of catalyst space per hour at room temperature, usually about 25° C. "Amount cracked" includes gas, liquid boiling below the original, and coke, summed on a no-loss basis.

EXPERIMENTAL PROCEDURE

A vertical, fixed-bed reactor system was used for the experiments. The hydrocarbon feeds were metered, pumped into the top of the reactor, and passed over the catalyst. Products left the reactor through a condenser and were collected in a still kettle

TABLE I. DOUBLE-BOND-SHIFT ISOMERIZATION OF 1-BUTENE

Catalyst		U.O.P.-B					Nalco No. 300			Filtrol		Nalco No. 300
Temperature, ° C.		205	162	162	104		500	400	270	400		150
Time after start, min.		12	10	80	30		10–16	3–27	0–6	5–15		0–31
Flow rate, moles/l./hr.		68	55	55	16		95	32	191	95		21
LHSV		6.4	5.2	5.2	1.5		9	3	18	9		2
Gas, mole %	Feed	Products				Feed	Products				Feed	Product
Below C_4	0.0	...	...	...	...	0	5.7	9.4	...	1.1	0.0	....
Iso-C_4H_8	0.1	...	...	...	...	0	8.6	13.4	...	4.6	0.7	0.7
1-C_4H_8	93.0	31.2	42.4	57.8	54.3	98	27.1	21.2	19.0	21.4	99.3	34.7
trans-2-C_4H_8	5.8	38.5	30.5	22.2	23.1	1	58.6	53.2	...	71.7	0.0	30.9
cis-2-C_4H_8	1.1	30.3	27.1	20.0	22.6						0.0	33.7
C_4H_{10}	0.0	...	...	...	...	1	0.0	2.8	...	1.2	0.0	0.0
Liquid, wt. % of feed	..	Present	Present	Present	Present	..	5.0	24.3	>8	8.0	..	Present
2-C_4H_8 in product as % of equil. concn.	..	79	64	47	49	..	98	96	98	102	..	72

or distillation. Gas was composited from noncondensables and distillation gas. The usual conditions were: temperature, 400° C.; flow rate, 0.5 to 3.0 LHSV; process period, 15 minutes; catalyst volume, 25 to 75 cc. All experiments were at atmospheric pressure. The usual cycle of operation was as follows:

> Heat the reactor to temperature and flush the system with nitrogen; process hydrocarbon feed for 15 minutes; shut off feed and drain reactor for 3 minutes; connect reactor outlet to cold trap followed by copper oxide furnace and water and carbon dioxide absorbers; purge reactor with nitrogen up to 550° C. for 20 minutes; regenerate catalyst with air free of carbon dioxide and water, and collect water and carbon dioxide evolved in absorbers after the copper oxide furnace; debutanize liquid product and distill in precision column equivalent to ten theoretical plates at 10 reflux ratio.

CATALYSTS. The following were used, with analyses as weight per cent of ignited sample, unless otherwise stated: U.O.P. cracking catalyst, type B, from Universal Oil Products Company. The sample used in this work was found to contain 86.2% silica, 9.4% zirconia, and 4.3% alumina, and was in the form of 3 × 3 mm. cylindrical pellets. Nalco No. 300, a silica-alumina-magnesia catalyst from National Aluminate Corporation, was used in the form of 8–14 mesh granules. An earlier batch of this catalyst contained 8.1% magnesia and 18.1% alumina. Filtrol (No. X-189) is an activated bentonitic clay from the Filtrol Corporation and was used in the form of $^1/_8$-inch extruded pellets. A chromia-alumina hydrogenation-dehydrogenation catalyst was prepared by impregnating 8–14 mesh granular Alorco grade A alumina with chromic acid and contained 13.7% chromium. A silica-alumina catalyst, made by the Davison Chemical Company, contained 11.9% alumina and 0.09% ferric oxide and lost 19.3% on ignition. This catalyst was calcined for 3 hours at 550° C.; it was in the form of $^3/_{16}$-inch pellets.

HYDROCARBONS. These are arranged in the order of increasing molecular weight. 1-Butene was obtained by careful fractionation of butenes resulting from the dehydration of *n*-butanol over Alorco activated alumina. Mixed normal butenes were made by dehydration of *sec*-butanol; they analyzed about 99% normal butenes. The main lot contained 24.4% 1-butene and 75.6% 2-butenes. Another lot, used only for the run at 500° C., contained 65.4% 1-butene and 33.3% 2-butenes. Isobutene made by dehydration of *tert*-butanol analyzed 98.1% isobutene and 0.8% propylene plus normal butenes. Normal pentenes were prepared by dehydration of *sec*-amyl alcohol over Alorco activated alumina at 350° C. The product was fractionally distilled, and the portion from 30–38° C. was used. Cyclohexene from the Dow Chemical Company had a boiling range of 83–84° C., $d_4^{20} = 0.8044$, $n_D^{20} = 1.4461$. Hexenes used were better than 95% olefinic and were obtained from the distillation of propylene polymer from Shell Oil Company, Inc. The boiling range was 59–76° C., and bromine number was 189. 2,3-Dimethyl-2-butene was made by dehydrochlorination (and simultaneous isomerization) of 1-chloro-3,3-dimethylbutane. Boiling range was 71–73.5° C., $n_D^{20} = 1.4111$, bromine number 173. Tetralin from Eastman Kodak Company, after being fractionally distilled, had a boiling range of 206–207° C., $d_4^{20} = 0.9714$, $n_D^{20} = 1.5427$. Decalin from Eastman had $d_4^{20} = 0.8827$, $n_D^{20} = 1.4795$.

ISOMERIZATION REACTIONS

Olefins are extensively isomerized over cracking catalysts under the normal commercial operating conditions. Several types of molecular isomerization may be distinguished, only two of which will be dealt with: (I) a change in the position of the double bond, which involves the breaking of carbon-hydrogen bonds and the movement of hydrogen atoms and (II) a change in the original configuration of the carbon skeleton, which involves the breaking of carbon-carbon bonds and the movement of alkyl groups. This latter type may be subdivided into case (*a*) in which the number of terminal carbon atoms is changed (for example, normal to isobutene) and case (*b*) in which the number of terminal carbon atoms is unchanged (for example, 2-methyl-1-pentene to 3-methyl-1-pentene). In view of analytical limitations, this paper is concerned primarily with types I and II*a*, which are called "double-bond shift" and "chain-branching", respectively. Other types of olefin isomerization, such as *cis-trans* and optical stereoisomerism, are not taken into consideration.

Isomerizations of types I and II*a* usually reach equilibrium under the conditions of commercial catalytic cracking, according to the analyses available and the limited data on the equilibria. In the C_4 fraction the rapid double-bond-shift isomerization causes the normal butenes to have an equilibrium composition of about 30% 1-butene and 70% 2-butenes at 500° C. Likewise the chain-branching isomerization of butenes proceeds close to equilibrium, for isobutene is 34 to 40% of the total butenes in catalytic cracking of a variety of pure hydrocarbons and petroleum fractions at 500–550° C., with depths of cracking varying from 30 to 80%. The estimated equilibrium between isobutene and the normal butenes is in the same range (*4*).

The C_5 fraction from the catalytic cracking of a Los Angeles Basin heavy gas oil over a silica-alumina catalyst at 550° C. showed the following distribution of olefinic components:

C_5 Olefin	Per Cent
1-Pentene	8
2-Pentene	27
2-Methyl-1-butene	26
3-Methyl-1-butene	7
2-Methyl-2-butene	32

The content of tertiary olefins, 58% of the total C_5 olefins, is representative of products from catalytic cracking. Data from several petroleum gas oils, cracked to the extent of 20 to 85% at 500° to 550° C., show tertiary olefins to be 54 to 60% of the total C_5 olefins, and this is believed to be essentially equilibrium. Further, the distribution of the methylbutenes listed compares fairly well with that calculated for this temperature from the free-energy equations of Ewell and Hardy (*3*), who measured approximate equilibria at somewhat lower temperatures. The data are as follows:

C_5 Olefin	% of Total Methylbutenes Observed	 Calculated
2-Methyl-1-butene	40	33
3-Methyl-1-butene	11	5
2-Methyl-2-butene	49	62

Experiments with pure hydrocarbons that gave definite information on the olefin isomerization reactions are described in the following two sections. Analyses were made by infrared absorption, distillation, and sulfuric acid absorption.

Double-Bond Shift. This isomerization was tested with 1-butene over several cracking catalysts. Results are presented in Table I. The isomerization to *cis*- and *trans*-2-butenes was very rapid; at 270° C. equilibrium was reached over Nalco No. 300 catalyst with a flow rate of 191 moles per liter of catalyst per hour. Even at 100° to 150° C. the isomerization proceeded at quite a high rate over Nalco No. 300 and U.O.P. type B catalysts. There can be little doubt that equilibrium among the isomeric normal butenes will be reached in present commercial catalytic cracking.

The data in Table I are presented only to give the order of magnitude of the isomerization rate. Accurate material balances are not available for several of the runs. Some cracking and conversion to isobutene occurred at temperatures of 400° to 500° C., while some polymerization took place in most of the runs. Mention of the presence of liquid in the product may mean anything from 0 to 30% by weight of the feed.

At the lower temperatures (100–200° C.) it was found that the extent of isomerization depended markedly on the process period, even though practically no coke was formed. This is exemplified by the run at 162° C. with U.O.P. type B catalyst, in which the conversion after 80 minutes was much less than it was at 10 minutes. A likely explanation for the deactivation is accumulation of polymer on the catalyst.

Degrees of approach to equilibrium for the products in Table I are based on the following experimental values (*12*):

Temperature, ° C.	% 1-Butene in Total *n*-Butenes at Equilibrium
100	7
200	13
300	19
400	25
500	30

Table II. Chain-Branching Isomerization of Isobutene at 500° C.

Catalyst		Nalco No. 300		U.O.P.-B
Process period, min.		20	18	23
Flow rate, moles/l./hr		30	91	30
LHSV		3	9	3
Ratio, gas out/gas in		0.99	1.01	0.91
Liquid product		None	None	None
	Feed	Products		
Gas analysis, mole %				
Below C_4	0.5	6.1	Trace	11.7
Iso-C_4H_8	48	21.2	33.3	12.4
n-C_4H_8	1	14.7	10.7	10.6
C_4H_{10}	50	53.5	53.1	60.3
Above C_4	0.5	4.5	2.9	5.0
% Isomerization of iso-C_4H_8 to n-C_4H_8	....	33	21	21

Chain-Branching Isomerization. Conversion of isobutene to normal butenes was tested with U.O.P. type B and Nalco No. 300 catalysts. A feed containing 48% isobutene and 50% butanes was used for the experiments, which are reported in Table II. Conversion to normal butenes was extensive but did not reach equilibrium at 500° C. with a flow rate of 30 moles per liter per hour. Reactions to form products of lower and higher molecular weights accompanied the isomerization.

Examples of the conversion of normal butenes to isobutene are listed in Table I, where data for runs over Nalco No. 300 catalyst at 400° and 500° C. show appreciable production of isobutene. Chain-branching isomerization of butenes was also noted in publications and patents by a group of investigators of the Universal Oil Products Company (*2*, *11*).

The chain-branching isomerization of butenes proceeds at a rate that is of the same order of magnitude as the rate of catalytic cracking of typical gas oils at about 500° C. The butenes from such catalytic cracking are usually, but not always, at equilibrium. At temperatures much below 500° C. the isomerization is slower. In the butenes saturation experiments at 400° C., this isomerization was never close to equilibrium.

Table III. Chain-Branching Isomerization of n-Pentenes

Catalyst	..	U.O.P.-B	Filtrol	Nalco No. 300
Temperature, ° C.	..	500	500	475
Process period, min.	..	30	30	60
Flow rate, moles/l./hr	..	28	28	93
LHSV	..	3	3	10
Material balance, wt. % of charge				
C_5	..	61.2	69.3	88.8
Higher liquid	..	16.0	11.8	8.4
Carbon	..	2.6	1.8	
Gas	..	19.1	15.5	2.8
Loss	..	1.1	1.6	
	Feed[a]	Products		
C_5 analysis, mole %				
tert-Olefins	4	47.3	54	58.0
sec-Olefins	96	30.3	..	38.0
Saturates	0	22.4	..	4.0
tert-C_5H_{10} as % of feed	..	29	37	51

[a] Average, since the feeds were not quite the same in all experiments.

Pentenes were found to undergo chain-branching isomerization much more readily than the butenes. Data are presented in Table III for experiments with U.O.P. type B, Filtrol, and Nalco No. 300 catalysts. The isomerization appears to have reached equilibrium (represented by about 58 to 60% tertiary olefins in the total C_5 olefins) in all the runs, including that at 475° C. with a flow rate of 93 moles per liter per hour. Isomerization was accompanied by cracking, saturation, and formation of higher boiling products, but these secondary reactions were reduced to minor percentages at the highest flow rate.

Another example of chain-branching isomerization is found in the conversion of cyclohexene to methylcyclopentenes, which is rather readily effected over cracking catalysts. Bloch and Thomas (*1*) found 29% conversion of cyclohexene to methylcyclopentenes at 300° C. and 4 LHSV with a silica-alumina-thoria catalyst. The isomerization reaction was more rapid than polymerization, cracking, or saturation of this hydrocarbon.

HYDROGEN TRANSFER REACTIONS

Hydrogen transfer reactions in the catalytic cracking system cause a partial saturation of the olefins and lead to an increased production of isoparaffins. These reactions are especially important in the retreatment of olefinic cracked gasolines over cracking catalysts to produce less olefinic gasolines of higher lead susceptibility. Thomas (*10*) presented interesting data on the self-saturation of normal octenes by hydrogen transfer. Hydrogen transfer was studied by the authors in more detail.

Effect of Operating Variables on Self-Saturation of Hexenes. A mixture of hexenes derived from propylene polymer, consisting predominantly of 2-methyl-2-pentene and 3-methyl-2-pentene, provided the base material for a series of experiments. The hexenes are of sufficiently high molecular weight to display cracking as well as saturation and polymerization tendencies. Furthermore, since hexenes are formed in ordinary commercial catalytic cracking, this mixture is of practical interest. Study was made of the effects of temperature, flow rate, and diluents upon the self-saturation.

Temperature. Operating successively at 350°, 400°, and 450° C. demonstrated that increasing temperature results in more extensive formation of both lower and higher boiling products, as shown in Table IV. Examination of the products showed that

TABLE IV. EFFECT OF TEMPERATURE ON SELF-SATURATION OF HEXENES

(Catalyst, U.O.P.-B; process period, 15 minutes; flow rate, 16.4 moles/l./hr.; LHSV, 2.0)

Temperature, ° C.	350	400	450
Fate of hexenes, wt. %			
Cracked	12	21	26
Saturated	25	26	28
Higher boiling	15	18	20
Recovered as hexenes	48	35	26
Saturates in C_6 cut, wt. %	35	43	52
Ratio of cracked plus higher boiling to C_6 saturated	1.08	1.50	1.64
Gaseous product			
Moles/mole of charge	0.170	0.196	0.310
Vol. % H_2	3.4	6.8	9.0
Saturates	34.5	36.9	34.6
Olefins	62.1	56.3	56.4
Material balance, wt. % of charge			
Gas	8.3	10.5	16.5
Liquid product			
<50° C.	0.0	4.6	3.4
50–75° C.	69.9	56.5	49.7
>75° C.	14.2	16.7	18.7
Carbon in coke	3.4	4.3	4.2
Hydrogen in coke	0.3	0.3	0.2
Reactor purge	0.6	5.6	0.9
Loss (to 100%)	3.3	1.5	6.4
Bromine No.[a] of liquid products			
50–75° C.	124.0	108.5	90.5
>75° C.	...	60.1	...
Whole liquid product	120.5	...	85.5

[a] Rosenmund method used throughout this work, expressed as grams bromine per 100 grams hydrocarbon.

the saturation of the C_6 fraction increased about 50% over this temperature range, but the accompanying increase in C_6 disappearance acted to reduce the total C_6 recovered by some 25%, and the net result was a very small increase of C_6 saturates as weight per cent of charge. At a given total conversion of the hexenes, judging from these results and the flow rate series, saturation was greatest at the lowest temperature.

Flow Rate. As the flow rate decreased from 2.9 to 0.5 LHSV, the hexenes disappearance increased rather regularly. The extent of saturation of the C_6 fraction increased markedly, with the sharpest rise between 1.5 and 1.0 LHSV. The greatest efficiency for the production of hexanes occurred at the low LHSV of from 0.5 to 1.5 (Table V).

TABLE V. EFFECT OF FLOW RATE ON SELF-SATURATION OF HEXENES

(Catalyst: U.O.P.-B; process period, 15 minutes; temperature, 400° C.)

LHSV	0.5	1.0	1.5	2.0	2.9
Fate of hexenes, wt. %					
Cracked	38	30	24	21	18
Saturated	46	45	31	26	23
Higher boiling	14	17	19	18	16
Recovered as hexenes	2	8	26	35	43
Saturates in C_6 cut, wt. %	96	84	54	43	36
Ratio of cracked plus higher boiling to C_6 saturated	1.13	1.04	1.39	1.50	1.48
Gaseous product					
Moles/mole of charge	0.280	0.278	0.225	0.196	0.182
Vol. % H_2	15.9	11.8	8.5	6.8	6.2
Saturates	57.0	45.8	39.2	36.9	29.6
Olefins	27.1	42.4	52.3	56.3	64.2
Material balance, wt. % of charge					
Gas	13.9	14.1	12.1	10.5	10.2
Liquid product					
<50° C.	4.8	4.6	3.8	4.6	4.3
50–75° C.	41.5	50.0	52.8	56.5	61.5
>75° C.	12.0	15.6	17.3	16.7	14.5
Carbon in coke	13.9	8.5	5.6	4.3	2.8
Hydrogen in coke	0.7	0.7	0.4	0.3	0.2
Reactor purge	10.7	5.8	4.2	5.6	1.6
Loss (to 100%)	2.5	0.7	3.8	1.5	4.9
Bromine No. of liquid cuts					
50–75° C.	7.5	28.2	85.5	108.5	119
>75° C.	6.9	22.8	43.9	60.1	...
Whole liquid product	...	...	...	...	119

Diluents. The preceding data showed a large effect of flow rate on the self-saturation of hexenes. The higher the flow rate, the shorter the residence time of the hydrocarbon, and the less the saturation. A similar but lesser effect can be produced at constant LHSV of hydrocarbon feed by adding a diluent. Two diluents—hydrogen and nitrogen—were used, each in equimolal mixture with hexenes. Results (Table VI) show there was no significant difference in the effects of these two gases. This important observation establishes the fact that free molecular hydrogen does not enter into the saturation reaction.

The effect of diluents on saturation was marked. The bromine number of the whole liquid product was 17 at 0.45 LHSV of hexenes with hydrogen added or at 0.68 LHSV of hexenes alone (by interpolation), and about 52 at 0.8 LHSV of hexenes with hydrogen or nitrogen added or at 1.25 LHSV of hexenes alone (by interpolation). In other words, it appears that equimolal dilution under these conditions has approximately the same effect as a 50% increase in the LHSV of the hexenes alone.

Use of the bromine number of the whole liquid product in roughly evaluating the degree of saturation of the hexenes is justified because the C_6 cuts (50–75° C.) made up about 75% of the whole liquid products, and because close agreement was found in those runs for which both the C_6 fractions and the whole liquid products were analyzed (Tables IV and V).

EFFECT OF OLEFIN STRUCTURE

Analysis of the products from the catalytic cracking of a normal paraffin such as cetane reveals a high ratio of iso- to normal paraffins, particularly in the butane and pentane fractions. The rate of isomerization of paraffins over a cracking catalyst is negligible (*6*, *7*). Therefore, the large amounts of isoparaffins found in the cracked products cannot be attributed to the isomerization of the corresponding normal (or less highly branched) paraffins or to the isomerization and subsequent cracking of higher paraffins. Since hydrogen transfer and isomerization were shown to occur extensively with olefins, an explanation was sought in the isomerization of olefins to branched structures followed by saturation to paraffins via hydrogen transfer. In addition it was observed that the ratio of iso- to normal paraffins usually exceeded the equilibrium ratio of the corresponding iso- and normal olefins. To illustrate, ratios of iso- to *n*-butane commonly obtained with the usual commercial cracking catalysts range from 2 to 6 at about 525° C. At this temperature the equilibrium ratio of iso- to normal butenes is only about 0.65. Studies were therefore initiated to explain these observations by the hypothesis that the rate of saturation of a given olefin via hydrogen transfer is dependent upon the structure, with particular emphasis upon the comparison of secondary and tertiary olefins.

BUTENES. Preliminary experiments not reported here in detail, on the self-saturation of pure iso- and normal butenes at 400° C. and a flow rate of 7.6 moles per liter per hour, showed the rate of formation of total butanes to be twice as great with isobutene. However, since the iso- and normal butanes in the product were not separated and there must have been some concomitant isomerization of the original olefins, the full extent of the difference in the rates of saturation of iso- and normal butenes was not clearly defined.

To determine the difference in rates of saturation, a mixture of butenes approximating the thermodynamic equilibrium at 400° C. (namely, 42 isobutene-58 *n*-butenes) was tested under conditions similar to those of the preliminary experiments. The data in Table VII show that the recovered total C_4 fraction, 50 mole % of the C_4 feed, contained 46% butanes with an iso-normal ratio of 7. This means that the rate ratio of saturation was greater than 7, since isobutene was more nearly used up than were the normal butenes. Isomerization was not so rapid as saturation. More complete data on this experiment are presented in Table VII. The following table shows the saturation of butenes at 400° C., using U.O.P. type B catalyst, a process period of 15 minutes, and a flow rate of 7.6 moles per liter per hour:

C_4 Fraction, Mole %	Feed	Product
Iso-C_4H_8	39.9	10.1
n-C_4H_8	54.3	43.7
Iso-C_4H_{10}	4.2	40.4
n-C_4H_{10}	1.6	5.8

Table VI. Saturation of Hexenes and Equimolal Diluent-Hexene Mixtures

(Catalyst, U.O.P.-B; temperature, 400° C.; process period, 15 minutes)

Feed	LHSV of Hexenes	Bromine No. of Whole Liquid Product
Hydrogen + hexenes	0.45	17.3
Hydrogen + hexenes	0.81	53.5
Nitrogen + hexenes	0.77	51.0
Hexenes	0.45	5.4
Hexenes	1.0	34.5
Hexenes	1.5	68.0

Another experiment at 500° C. and flow rate of 6.9 moles per liter per hour with pure normal butenes gave a ratio of iso- to n-butane of 3.5. Here isomerization preceded part of the saturation. In this experiment only 38.2% of the feed was recovered as total C_4 fraction, and only 7% as normal butenes (Table VII). The following table shows the saturation of normal butenes at 500° C., using U.O.P. type B catalyst, a process period of 15 minutes, and a flow rate of 6.9 moles per liter per hour.

C_4 Fraction, Mole %	Feed	Product
Iso-C_4H_8	....	9.1
n-C_4H_8	98.7	18.7
Iso-C_4H_{10}	....	56.1
n-C_4H_{10}	....	16.1

Butenes in Presence of Cyclohexene. Experiments were made with butenes plus cyclohexene to determine the effectiveness of the cyclohexene as a hydrogen donor and the influence of the structure of the butenes. It was found that the latter effect was again quite marked and that no simple conclusions could be drawn as to the former.

Equimolal mixtures of cyclohexene and (a) normal butenes, (b) isobutene, and (c) a ratio of 45 n-butenes–55 isobutene were tested at 400° C. and 16.7 moles per liter per hour. The data obtained substantiate previous statements concerning the higher rate of saturation of iso- compared with normal butenes. Assuming a first-order rate law, it is calculated that the isobutene is saturated more than 10 times as rapidly under these conditions as are normal butenes. The following table shows saturation of butenes in the presence of cyclohexene, using U.O.P. type B catalyst, a temperature of 400° C., a 15-minute process period, and a total flow rate of 16.7 moles per liter per hour.

Feed (C_4 Fraction), Mole %	Equimolal Mixture of Cyclohexene and:		
	n-C_4H_8	Iso-C_4H_8	45 n-C_4H_8 55 Iso-C_4H_8
Iso-C_4H_8	2.5	12.5	13.5
n-C_4H_8	72.6	3.1	45.5
Iso-C_4H_{10}	9.9	84.3	34.6
n-C_4H_{10}	15.0	0.1	6.4
Ratio, iso-C_4H_{10}/n-C_4H_{10}	0.66	843	5.4

More complete data on these experiments are given in Table VIII. No correction was made for C_4 derived from cyclohexene, since this was estimated to be no more than 7% of the C_4 from the butenes. It is seen that the isomerization of normal to isobutene and vice versa is quite small under these conditions.

Table VII. Saturation of Olefins

Feed	n-Butenes	n-Pentenes	42 Isobutene–58 n-Butenes
Catalyst	U.O.P.-B	SiO_2-Al_2O_3	U.O.P.-B
Temperature, ° C.	500	500	400
Flow rate, moles/l./hr.	6.9	2.8	7.6
Process period, minutes	15	10	15
Moles of gas/mole of charge	0.862	1.387	0.670
Gas + C_5			
Vol. % H_2	9.8	3.9	2.9
CH_4	12.7	15.4	4.7[a]
C_2H_4	3.1	5.5	0.5
C_2H_5	3.5	4.3	...
C_3H_6	17.1	6.8	9.5
C_3H_8	6.8	12.0	...
Iso-C_4H_8	3.8	1.3	8.3
n-C_4H_8	7.8	2.1	36.0
Iso-C_4H_{10}	23.4	19.9	33.3
n-C_4H_{10}	6.7	3.9	4.8
tert-C_5H_{10}	1.2	1.9	...
sec-C_5H_{10}	0.7	0.8	...
Iso-C_5H_{12}	2.9	20.0	...
n-C_5H_{12}	0.5	2.2	...
Material balance, wt. % of charge			
Gas	61.0	36.7	64.7
Liquid product	20.7	39.4	10.3
Carbon in coke	13.7	20.6	13.2
Hydrogen in coke	0.7		2.7
Reactor purge	...	...	9.4
Loss (to 100%)	3.9	3.3	−0.3

[a] C_1–C_3 saturates.

Table VIII. Saturation of Butenes in Presence of Cyclohexene

(Temperature, 400° C.; catalyst, U.O.P.-B; process period, 15 minutes; equimolal mixtures)

Feed	Cyclohexene	Cyclohexene + n-Butenes	Cyclohexene + Isobutene	Cyclohexene + 45 Normal–55 Isobutenes
LHSV				
Cyclohexene	1.29	0.86	0.86	0.86
Butenes	...	0.78	0.78	0.78
Gaseous product				
Mole/mole of total charge	0.104	0.519	0.427	0.542
Vol. % H_2	24.6	18.7	12.3	6.5
C_1–C_3 saturates	...			6.6[a]
C_2H_4	7.5	5.9	3.1	15.1
C_3H_6	...			4.5
Iso-C_4H_8	31.3	1.9	10.6	9.1
n-C_4H_8		54.7	2.6	30.6
Iso-C_4H_{10}	36.6[b]	7.5	71.3	23.3
n-C_4H_{10}		11.3	0.1	4.3
Material balance, wt. % of charge				
Gas	3.6	37.4	33.3	38.0
Liquid product	82.8	47.7	56.8	46.8
Carbon in coke	6.7	6.0	7.7	5.5
Hydrogen in coke	0.4	0.5	0.4	0.6
Reactor purge	5.9	3.3	1.6	2.2
Loss (to 100%)	0.6	5.1	0.2	6.9

[a] Carbon number = 1.7.

[b] Total saturates, carbon number = 4.0.

In these cyclohexene experiments particular attention was given to the course of reactions other than saturation and to the resulting product distribution, material balance, and carbon and hydrogen balances. Information was thus obtained about reactions which liberate hydrogen for transfer. The liquid products comprised a large fraction at 60–90° C. and another large fraction above 150° C., with little intermediate material. The 60–90° C. fraction contained mostly saturates (chiefly methylcyclopentane), some olefins, and a little benzene. The benzene accounts for no more than 7% of the hydrogen transferred on the basis of the three runs considered here. Coke production ranged from 6 to 8 weight % of the charge but accounts for less than half of the hydrogen demand. Examination of the high boiling liquid product showed that 32% of the total liquid product from cracking cyclohexene alone (Table VIII) distilled above 200° C. and had a high refractive index; a small amount of naphthalene was isolated. Bloch and Thomas (*1*) identified 2,6-dimethylnaphthalene in the products from cyclohexene cracking at 400° C. The three experi-

TABLE IX. HYDROGEN BALANCE FROM CYCLOHEXENE AND CYCLOHEXENE-BUTENES RUNS

(Catalyst, U.O.P.-B; temperature, 400° C.; process period, 15 minutes; equimolal mixtures)

Feed	Cyclo-hexene	n-Butenes + Cyclo-hexene	Isobutene + Cyclo-hexene
C_6 product (60–90° C.), wt. %			
Of total liquid	65.3	59.5	44.5
Saturates in cut	96.8	77.4	77.3
Aromatics in cut	0.3	5.2	2.5
Higher liquid (>90° C.)			
n_D^{20}	1.5379	1.5219	1.5252
Moles of H_2 produced, computed as Tetralin	0.459	0.172	0.280
Estimated H_2 balance: moles of H_2 required for			
Gas[a]	0.115	0.142	0.249
C_6 saturates	0.565	0.132	0.117
Total	0.680	0.274	0.366
Estd. H_2 balance, moles of H_2 available from formation of:			
C_6H_6	0.004	0.021	0.008
Coke[b]	0.265	0.087	0.165
Higher aromatics	0.459	0.172	0.280
Total	0.728	0.280	0.453

[a] 1 mole of hydrogen required for 2 moles of gaseous aliphatic olefins formed from C_6H_{10}; computed for the cyclohexene experiment only.

[b] Moles of hydrogen produced, deducting remaining hydrogen in coke.

ments with mixtures of butenes and cyclohexene also contained much high boiling material; a third of it distilled between 160° and 180° C., corresponding to C_9 and C_{10} aromatics, whose presence was confirmed by high refractive index. The remainder, above 190° C., had physical properties corresponding to the analogous fraction from the test with pure cyclohexene. For the sake of calculation, the total fraction boiling above 90° C. was assumed to have the carbon to hydrogen ratio of Tetralin, in rough correspondence with the measured refractive indices.

Using the calculations shown in Table IX (based on experimental data in Table VIII) it is estimated for the case of the cyclohexene runs that the hydrogen transferred in saturation of total product up to 90° C. originated as follows: 35% from coke formation, 62% from formation of high boiling aromatics, and only 3% from direct dehydrogenation of cyclohexene to benzene. These results agree with observations of Bloch and Thomas (*1*) for treatment of cyclohexene alone.

NORMAL PENTENES. An experiment was made with the C_5 normal olefins at 500° C. and 2.8 moles per liter per hour over silica-alumina catalyst (Table VII). The total C_5 fraction recovered was 22.3 weight % of the charge; of this fraction, 89.2 mole % were pentanes with an iso- to normal ratio of 9.1. Over 99% of the original pentene was converted to other materials. A similar selective saturation was shown by the C_4 fraction (19.7 weight % of charge), which contained 87.5 mole % butanes with an iso- to normal ratio of 5.1. It may be concluded that preferential saturation of tertiary olefins produced by isomerization accounts for the high yields of isopentane and isobutane.

HEXENES. The total conversion to hexanes of a mixture of 2- and 3-methyl-2-pentenes was recorded under the section on operating variables. It is of interest to examine the composition of the product hexanes as an introduction to some further experiments on the relation of olefin structure to rate of saturation via hydrogen transfer. The total liquid product from the run at 2.9 LHSV and 400° C. in Table V was distilled in a forty-plate column at 42 reflux ratio, and the primary cuts were analyzed for bromine number, density, and refractive index. The greatest saturation was shown by those cuts in the range 52° to 65° C., bracketing the boiling points of 2- and 3-methylpentanes and 2,3-dimethylbutane. These cuts were washed with sulfuric acid to remove the remaining olefins, redistilled, and analyzed by infrared spectrophotometer for hexane isomers. This analysis only approximated the true composition when more than two isomers were present. The figures were used in preparing the following table showing hexanes derived from self-saturation of hexenes. The catalyst used was U.O.P. type B, with a 15-minute process period, LHSV of 2.9, and temperature of 400° C.:

	n-Hexane	2,2-Dimethylbutane	2,3-Dimethylbutane	2-Methylpentane	3-Methylpentane
Wt. % in total C_6 cut	0.8	0.8	7.3	14.8	14.1
Wt. % of hexenes fed	0.5	0.5	4.7	9.5	9.1
Wt. % of total hexanes	2.0	2.0	19.4	39.2	37.4
Calcd. equil. concn. at 400° C. of corresponding hexenes (*8*)	30	1	16	25	28

The chief point of interest for the present discussion is the nearly tenfold ratio of 2,3-dimethylbutane to n-hexane. It is likely that both these paraffins were formed by isomerization of the original methylpentenes followed by saturation. Although thermodynamic data are not very accurate, they indicate that the normal hexenes should equal or exceed in amount the 2,3-dimethylbutenes in equilibrium with them at 400° C. Therefore, this is another convincing case of preferential saturation of tertiary olefins.

An experiment was carried out to test the selectivity of saturation of dibranched as compared to monobranched hexenes. The feed stock comprised an equimolal mixture of methylpentenes and 2,3-dimethyl-2-butene. The methylpentenes were secured as a 65–70° C. fraction of the hexenes, and consisted chiefly of the 2- and 3-isomers. A self-saturation test was made at 400° C. and 2.8 LHSV (Table X). The resulting liquid product was distilled at 42 reflux ratio in a Stedman column of 6-mm. inside diameter, containing 256 screen cones, approximating 72 (theoretical) plates. The C_6 fraction analyzed 50.3% hexanes, 95.3% of which were 2-methylpentane, 3-methylpentane, and 2,3-dimethylbutane in the ratio of 2 to 1 to 2, respectively. These figures indicate that the dibranched olefin is no more rapidly saturated than the monobranched.

Examination of the distillation curve and analysis for individual components, however, identified less than 20% of the remaining hexenes as 2,3-dimethylbutenes. From this it may be concluded that the dibranched olefin undergoes saturation less rapidly than it does other reactions. Product analysis shows that at least 90% of the 2,3-dimethylbutene disappeared, but direct saturation could account for no more than 20%. Since cracking and polymerization were about the same as in the run with methylpentenes alone, apparently a large portion of the 2,3-dimethylbutene disappearance is accounted for by chain-branching isomerization to other hexenes. This statement is consistent with thermodynamic data, which indicate an equilibrium concentration at 400° C. of only 16.1% of 2,3-dimethylbutenes in total hexenes. It is concluded that saturation of the dibranched hexene actually may be two to three times as fast as that of the monobranched.

The following tabulation shows the percentages of the five hexane isomers derived from analysis of the C_6 fraction. The feed was an equimolal mixture of 2,3-dimethyl-2-butene and 2- and 3-methylpentenes. The catalyst used was U.O.P. type B, with a 15-minute process period, LHSV of 2.8, and temperature of 400° C.:

	n-Hexane	2,2-Dimethylbutane	2,3-Dimethylbutane	2-Methylpentane	3-Methylpentane
Wt. % in total C_6 cut	1.3	1.0	19.0	19.2	9.8
Wt. % of hexenes fed	0.7	0.5	9.7	9.8	5.1
Wt. % of total hexanes	2.6	2.1	37.6	38.2	19.5
Calcd. equil. concn. at 400° C. of corresponding hexenes (*8*)	30	1	16	25	28

HYDROGEN DONORS

The definition of hydrogen transfer in catalytic cracking systems stipulates that the hydrogen acquired by an ethylenic double bond shall come from other hydrocarbons present. The two previous sections showed that a single olefin as well as a mixture of two or more olefins may undergo extensive hydrogen transfer. In mixtures of olefins with other types of hydrocarbons commonly encountered in cracked petroleum fractions, the questions arise as to whether any components besides olefins may act as hydrogen donors, and whether these components will donate their hydrogen more or less readily than will the olefins themselves. The same general problem arises in the catalytic cracking of virgin petroleum fractions, in which the initial cracking immediately provides a mixture of olefins together with unreacted feed and nonolefinic cracked products. To examine these questions, and particularly to determine whether cyclic structures which may lose hydrogen by conversion to aromatics are effective hydrogen donors, experiments were undertaken.

TETRALIN AND DECALIN. To follow the behavior of these hydrocarbons as hydrogen donors, experiments were made with pure Decalin, Tetralin, hexenes, and mixtures of the latter with each of the first two. The total liquid product was quite saturated in the case of both Tetralin and Decalin but quite olefinic from the hexenes. When hexenes were mixed in equimolal amounts with either Tetralin or Decalin, the saturation of the total liquid product was considerably above that derived by simple additivity of the results from the pure materials. The degree of saturation was about the same in both cases—namely, 72.7 and 70.4% saturation of the corresponding C_6 fractions, compared with only 35.6% from hexenes alone. The Decalin and Tetralin, by cracking, contribute, at most, 6% to the C_6 fraction. A comparison of these two hydroaromatics as hydrogen donors is presented in the following table. The temperature was 400° C., the process period 15 minutes, and the catalyst U.O.P. type B; the mixtures were equimolal.

Feed	Decalin	Hexenes + Decalin	Tetralin	Hexenes + Tetralin	Hexenes
LHSV					
Hydroaromatic	3.9	4.0	3.9	4.0	...
Olefin	...	3.1	...	3.0	2.9
Bromine No. of whole liquid product	3.8	24.0	3.1	24.5	119
Olefins in C_6 cut, wt. %	...	27.3	...	29.6	64.4

Enough naphthalene was recovered from the Tetralin-hexenes experiment to account for 35% of the hydrogen needed to produce the hexanes observed; this was not all the naphthalene formed. Coke production ranged from 1.0 to 2.7 weight % of charge in the runs with mixed feeds; it provided but a small portion of the hydrogen demand. The major portion of the hydrogen evidently came from aromatic formation (Table X).

In another experiment normal pentenes were passed along with Decalin in an equimolal mixture at a partial olefin LHSV of 3.9. The pentanes recovered—37% by weight of the pentenes fed and 45% of the C_5 recovered—were over 95% isopentane, and probably not more than 2% of the pentanes came from the cracking of Decalin itself. This was another case of isoparaffin production by isomerization and selective saturation.

COMPARISON OF CATALYSTS

Hydrogen transfer over silica-alumina-zirconia cracking catalyst has now been shown to have the important characteristic of saturating tertiary olefins more rapidly than secondary olefins. The same effect is also obtained with the synthetic silica-alumina catalysts in commercial use. This selective reaction leads to the preferential formation of isoparaffins in the product, a great advantage with respect to the engine performance characteristics of the gasolines derived from them. To evaluate the degree of selectivity in comparison with straightforward hydrogenation of iso- and normal butenes with molecular hydrogen over an active hydrogenation-dehydrogenation catalyst, experiments were made with a chromia-alumina catalyst. The U.O.P. type B catalyst has already been indicated to have no appreciable activity for hydrogenation.

Starting with equimolal mixtures of hydrogen and either iso- or normal butenes at 400° C. and atmospheric pressure, both the secondary and the tertiary butenes hydrogenated at exactly the same rate, within experimental error, to the extent of 65% saturation. Isomerization was negligible, and there was little formation of cracked or higher boiling materials (Table XI). The conclusion to be drawn from these experiments is that the selective formation of isoparaffins in catalytic cracking systems is due to a specific property of the silica-alumina and similar cracking catalysts, which differentiates the tertiary from the secondary double bonds.

Another pertinent experiment presented in Table XI involved the use of an equimolal mixture of cyclohexene and 45 normal–55 isobutenes over the chromia-alumina catalyst with no added hydrogen. Here the cyclohexene was expected to yield free hydrogen by direct conversion to benzene, or might conceivably donate hydrogen directly to the olefins. The product gas contained 37 mole % of hydrogen, and the butenes were hydrogenated about 16%, indicating substantial dehydrogenation of the cyclohexene. Again, however, no preferential saturation of the tertiary butene could be observed, nor was there any appreciable isomerization of the C_4 components.

POLYMERIZATION REACTIONS

Catalysts of the silica-alumina type considerably accelerate the polymerization of olefins. At atmospheric pressure, however, the polymerization of an olefin such as a *n*-butene cannot exceed about 20% at 400° C. for thermodynamic reasons, and at higher temperatures it is even more limited. In catalytic cracking at 500–550° C. any polymer formed is rapidly converted to other products, so that very little true polymer is obtained as a final product. Nevertheless, the activity of the catalyst for polymerization is clearly shown by experiments at low temperatures, and it is possible that other products are formed by way of intermediate polymers at normal cracking temperatures.

TABLE X. SATURATION OF OLEFINS

(Process period, 15 minutes; temperature, 400° C.; equimolal mixtures; catalyst, U.O.P.-B)

Feed	Decalin	Hexenes + Decalin	Tetralin	Hexenes + Tetralin	*n*-Pentenes + Decalin	Methylpentenes + 2,3-Dimethyl-2-butene
LHSV						
Olefin	....	3.1	....	3.0	3.9	2.8
Hydroaromatic	3.9	4.0	3.9	4.0	5.7	....
Gaseous product						
Mole/mole charge	0.176	0.092	0.153	0.045	0.070	0.247
Vol. % H_2	....	5.8	14.1	19.8	....	2.7
Saturates	....	48.4	33.7	39.2	....	34.5
Olefins	....	45.8	52.2	41.0	....	62.8
Material balance, wt. % of charge						
Gas	5.1	4.5	5.4	1.7	3.3	14.3
Liquid product						
<50° C.	0.0	0.0	0.0	0.0	28.1	1.6
50–75° C.	3.1	24.2	2.9	31.2	67.7	57.7
>75° C.	85.1	65.8	86.6	62.2		21.0
Carbon in coke	1.1	2.1	0.6	0.9	0.5	3.0
Hydrogen in coke	0.2	0.6	0.1	0.1	0.1	0.2
Reactor purge	0.8	3.7	0.0	0.0	0.2	0.0
Loss (to 100%)	4.6	−0.9	4.4	3.9	0.1	2.2

TABLE XI. SATURATION OVER CHROMIA-ALUMINA CATALYST

(Temperature, 400° C.; catalyst, Cr_2O_3-Al_2O_3; process period, 15 minutes; equimolal mixtures)

Feed	*n*-Butenes + Hydrogen	Isobutene + Hydrogen	Cyclohexane + 45 Normal-55 Isobutenes
Total flow rate, moles/l./hr.	16.2	16.1	16.7
LHSV			
Cyclohexene	...	...	0.86
Butenes	0.76	0.75	0.78
Gaseous product			
Moles/mole of total charge	0.610	0.705	0.590
Vol. % H_2	20.0	19.9	37.2
C_1–C_3 saturates	1.4	4.7	1.5
C_2H_4	0.0	0.1	0.0
C_3H_6	0.1	1.1	0.4
Iso-C_4H_8	0.0	25.9	27.0
n-C_4H_8	27.5[a]	0.2	24.4
Iso-C_4H_{10}	0.6	47.4	4.6
n-C_4H_{10}	50.4	0.7	4.9
Material balance, wt. % of charge			
Gas	89.3	91.0	31.3
Liquid product	0.0	0.0	54.5
Carbon in coke	1.3	2.1	1.6
Hydrogen in coke	...	1.1	0.6
Reactor purge	3.6	5.8	8.6
Loss (to 100%)	5.8	0.0	3.4

[a] Includes 0.2% C_4H_6.

TABLE XII. POLYMERIZATION OF 1-BUTENE OVER NALCO NO. 300 CATALYST

Temperature, ° C.	210	250	270
Process period, min.	51	13	6
Flow rate, moles/l./hr.	5.3	95	191
LHSV	0.5	9	18
Liquid product, wt. % of feed	23	23	10

Gayer (*5*) found that alumina adsorbed on purified silica gel made an effective catalyst for the polymerization of propylene. He obtained 20% polymerization at 340° C., 2 LHSV, and atmospheric pressure. Polymerization of propylene and butenes with several cracking catalysts at 165–175° C. and elevated pressure was reported by Thomas (*9*). A few experiments with a silica-alumina-magnesia catalyst known as Nalco No. 300 are listed in Table XII and show polymerization at 210–270° C. and atmospheric pressure. The Nalco catalyst is similar in properties to U.O.P. type B catalyst and conventional silica-alumina cracking catalysts, and the results with Nalco are believed to be analogous to those with other cracking catalysts. In the polymerization of 1-butene at 270° C. or below, almost no gas below C_4 was formed. The polymer was a clear liquid, chiefly composed of C_8 material. This polymerization was much slower than the double-bond shift but faster than the chain-branching isomerization.

AROMATIZATION REACTIONS

Aromatic hydrocarbons of eight or more carbon atoms are formed in considerable quantities from the catalytic cracking of a wide variety of pure hydrocarbons and petroleum fractions. The results cited in earlier papers (*6, 7*) show that aromatics in the gasoline fraction may arise from the dealkylation of higher boiling aromatics or from the cracking and concomitant dehydrogenation assisted by hydrogen transfer from C_9 or higher naphthenes, especially those of the hydroaromatic type. However, these reactions in no way explain the presence of moderate quantities of aromatics in the products from the catalytic cracking of C_{10} and higher paraffins and aliphatic olefins (*6, 10*). One supposition is that aromatics are formed by dehydrocyclization of such aliphatics, analogous to the conversion of *n*-heptane or *n*-heptene to toluene over chromia-alumina catalyst. However, the rather weak dehydrogenation activity (to yield free hydrogen) of the cracking catalyst, together with the fact that no toluene is obtained from *n*-heptane under rather severe catalytic cracking conditions, led to a search for an alternative explanation for the production of aromatics from higher aliphatics with conventional cracking catalysts.

Since the primary production of lower olefins is common to all those catalytic cracking experiments which yielded aromatics from higher aliphatics, experiments were initiated using butenes as the feed stock.

NORMAL BUTENES. Operating at 500° C., 6.9 moles per liter per hour, and 15-minute process period, the disappearance of normal butenes amounted to 93%. Aromatic production amounted to 9.2 weight % of charge in a total liquid product of 20.7 weight % of charge. Of these aromatics, 39% comprised benzene, toluene, and xylene, and 32% corresponded to the 152° to 174° C. fraction, which was wholly aromatic by refractive dispersion. The remainder—29 weight %—was in the material above 174° C., which also appeared wholly aromatic by refractive index. The gas analysis and material balance for this run are presented in Table VII.

These results demonstrate, under experimental conditions conforming to normal catalytic cracking operations, that a wide range of aromatics may be derived from the butenes which are directly produced in the catalytic cracking of most petroleum fractions and in relatively large quantities from high boiling (above gasoline) aliphatic hydrocarbons. Propylene, pentenes, and hexenes can be expected to undergo similar aromatization reactions.

In addition to the foregoing, condensation reactions between aromatics and olefins or between two aromatic molecules are strongly indicated by various data obtained. Thus the experiments with butenes and cyclohexene gave large and highly aromatic fractions boiling between 160° and 190° C., corresponding to C_9 and C_{10} aromatics. Furthermore, the catalytic cracking of all alkylbenzenes above toluene yielded bottoms of enhanced refractive index, which indicate aromatic condensation products (*7*).

All these observations lead to, but do not rigorously prove, the conclusion that direct dehydrocyclization of aliphatics is not responsible for the large amounts of aromatics found in the products of catalytic cracking.

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