

# High-Octane Isoparaffinic Fuels

## Production by the Addition of Olefins to Isoparaffins

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**T**HE reaction of olefins with the lower isoparaffins recently described by the authors (2) has proved to be general with regard to olefins; all those examined, with the exception of ethylene, react with considerable ease to give products consisting essentially of isoparaffins.

Whether addition is effected by heat and pressure alone, with the aid of active halides, or in the presence of sulfuric acid, the primary reaction, involving the direct combination of the olefin and isoparaffin, is invariably accompanied by side and secondary reactions. As a result the final product is a complex mixture of hydrocarbons, almost entirely paraffinic and boiling over a relatively wide range. Adding further to the complexity of the product is the possibility that the pri-

In the presence of concentrated sulfuric acid the lower olefins, with the exception of ethylene, react with isobutane to give a product from which a fully saturated fraction (boiling from 27° to 185° C.) may be isolated by distillation. This material apparently consists entirely of isoparaffins ranging from isopentane to isodecanes and higher. Its high octane rating, roughly 90+, coupled with its low sulfur content, renders it an excellent component for 100-octane aviation gasoline. The reaction is not limited to isobutane and has been extended to isopentane and 2-methylpentane, but the lower octane ratings of the gasoline fractions obtained from these isoparaffins render them less suitable as components for 100-octane fuels.

The effect of varying the reaction conditions upon the yield and nature of the product is outlined. As satisfactory starting materials for commercial operation the unsaturated four-carbon cut obtained from normal cracking operations may be employed together with an isobutane concentrate taken from natural gasoline stabilization. The heat evolved in the reaction and acid consumption are briefly discussed.

mary reaction itself may produce one or more isomers, depending upon the manner in which addition takes place. This is well illustrated by the work of Frey and Hepp (6) who found that the addition of ethylene to propane resulted in the formation of both normal and isopentanes, depending upon whether the mechanism of addition involved either a primary or secondary hydrogen atom in the propane molecule.

The secondary reactions may include isomerization, degradation of the primary products, and the addition to them, or to the secondary products derived from them, of further olefin molecules. These reactions, particularly those responsible for the formation of higher and lower molecular weight hydrocarbons, may be suppressed to an appreciable extent by employing a large excess of the isoparaffin. Even under the most favorable conditions, however, a considerable part of the primary product undergoes secondary changes.

Probably the most important of the secondary reactions is isomerization. This may result, particularly in the presence of active halides, in almost complete rearrangement of the primary product—for example, in the reaction of ethylene with isobutane. When heated under pressure, a mixture of these hydrocarbons was found by Frey and Hepp to give considerable amounts of 2,2-dimethylbutane; however, with either activated boron fluoride or aluminum chloride present, only small amounts of this hydrocarbon and 2-methylpentane (another expected product) were obtained by Ipatieff and Grosse (8). Instead they found that 70 to 90 per cent of the hexane fraction from their product consisted of an isomerization product, 2,3-dimethylbutane. Isomeric changes of a similar nature appear to take place in the presence of sulfuric acid.

Both higher and lower molecular weight hydrocarbons are formed as the result of secondary reactions of a different type. The mechanism of these reactions is obscure but appears to involve cleavage of the paraffin molecule, with the formation of radicals followed by the disproportionate recombination of the latter. Normal and isoparaffins both undergo this reaction in the presence of aluminum chloride; the more highly branched isoparaffins—2,2,4-trimethylpentane, for example—are particularly susceptible (7). Similar reactions take place in the presence of sulfuric acid, but since this is much less drastic in its action, probably only the more complex isoparaffins are affected. [Tafel (12) appears first to have commented upon the fact that certain isoparaffins prepared by the electrolytic reduction of substituted acetoacetic esters had a wider boiling range after treatment with concentrated sulfuric acid than before.] Both 2,2,4-trimethylpentane and the hydrogenated copolymer of butene and isobutene (B. I. B.)—mainly 2,2,3-trimethylpentane—are readily attacked by sulfuric acid on prolonged intimate contact at room temperatures, with the formation of higher and lower isoparaffins, including considerable amounts of isobutane (Figure 1). [The ease with which certain isoparaffins are attacked by concentrated sulfuric acid indicates the inadvisability of employing this reagent in their purification. Whether the "impurities" isolated from the crude synthetic isooctane (2,2,4-trimethylpentane) by Brooks, Cleaton, and Carter (4) originated from acid treatment in this way or as a

result of a similar type of reaction at the surface of the catalyst during hydrogenation is unknown (cf. Birch, Pim, and Tait, 3).]

The third type of secondary reaction, the addition of a further olefin molecule to the primary reaction products, was considered by Frey and Hepp to be largely responsible for the higher boiling hydrocarbons formed in their experiments. To what extent such reactions take place when active halides or sulfuric acid is employed is, however, doubtful. Certainly no addition was observed when diisobutene was added to a vigorously agitated mixture of 2,2,4-trimethylpentane and sulfuric acid. Although this is an isolated example, it seems

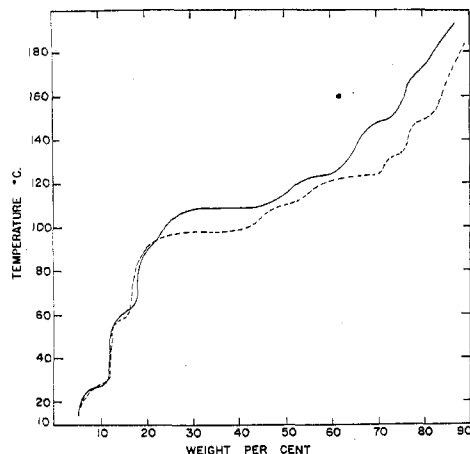


FIGURE 1. DISTILLATION CURVES (25-PLATE COLUMN) OF LIQUID PRODUCTS FROM ACTION OF 97 PER CENT SULFURIC ACID ON GASOLINES

— Hydrogenated polymer gasoline (105.5-112° C.)  
 --- Isooctane

unlikely that the more complex isoparafrins formed in these reactions will combine with a further olefin molecule. On the other hand, there is little doubt that isoparafrins formed as a result of the degradation of the primary products react in this way; isopentane, for example, a secondary product from isobutene and isobutane reacts readily with olefins.

Dilution of the sulfuric acid after reaction leads to the separation of an oil consisting of comparatively high-boiling, highly unsaturated hydrocarbons closely resembling those normally formed when olefins are treated with concentrated acid [cf. Ormandy and Craven (11), Nametkin and Abakumovskaja (10), Ipatieff and Pines (9)]. These hydrocarbons are formed as the result of a peculiar reaction (termed by Nametkin "hydropolymerization") in which the olefin becomes partly polymerized and partly converted into a mixture of saturated hydrocarbons (mainly high-boiling parafrins) and highly unsaturated hydrocarbons. (It is doubtful whether the unsaturated products of hydropolymerization occur as such in the acid. A more likely explanation is that they are formed by the breaking down on dilution of unstable sulfuric esters.) It would appear reasonable to assume that, during the addition of olefins to isoparafrins in the presence of sulfuric acid, hydropolymerization of the olefin also occurs as a side reaction to a greater or less extent, depending upon the conditions. The high-boiling parafrins and polymers formed as a result of this reaction would be found in the hydrocarbon layer with the products of the main addition reaction and probably constitute an appreciable part of the higher boiling fractions.

Similar high-boiling unsaturated oils separate when acid

which has been stirred with 2,2,3- or 2,2,4-trimethylpentanes for a prolonged period is diluted. Their formation is not easy to explain. Possibly the olefin-isoparafrin addition is to some extent reversible in the presence of sulfuric acid, and the oils result from the hydropolymerization of the olefin formed by the reverse reaction.

Whether similar compounds are formed when active halides are used to effect additions has not been reported.

Even when carried out under the simplest conditions—i. e., heat and pressure alone—it is obvious that olefin-parafrin addition is by no means a simple reaction. Apart from the primary, secondary, and side reactions already mentioned, there are others which may occur and appreciably influence the course of the reaction. Isomerization, for example, is not necessarily confined to the reaction products but may equally well affect one or both of the reactants prior to addition. Thus it is doubtful whether a normal parafrin would react at ordinary temperature unless first isomerized to the more reactive isoparafrin. Again, the similarity of the final products from isobutene and normal butenes when allowed to react with isobutane in the presence of sulfuric acid indicates that isomerization of olefins can also occur.

### Olefin-Isoparafrin Reaction in Presence of Sulfuric Acid

We doubt whether the term "alkylation" is satisfactory in view of the complex nature of the olefin-isoparafrin reaction and have avoided its use. Some account has been published (2) of the use of sulfuric acid in effecting reaction between certain olefins and isoparafrins. This may be summarized as follows: With pure hydrocarbons it has been shown that the reaction in the presence of sulfuric acid may be applied generally to the lower olefins with the exception of ethylene. Thus propylene, isobutene, 1- and 2-butene, trimethylethylene, together with the lower polymerides of isobutene, di- and triisobutene, and the butene-isobutene copolymer (B. I. B.) have all been shown to react with isobutane to give good yields of saturated products boiling between 27° and 185° C. and possessing octane numbers of 90 +. Of the parafrins investigated, isobutane, isopentane, and isohexane (2-methylpentane) reacted smoothly, although the octane number of the saturated product fell off rapidly with increasing length of the carbon chain of the isoparafrin used, as was to be expected. Neither *n*-butane nor isooctane (2,2,4-trimethylpentane) appeared to react; the latter presumably failed to do so because of some steric effect. (Rather unexpectedly methyleyclohexane did not react with diisobutene in the presence of sulfuric acid.)

The reaction is conveniently carried out in the liquid phase by adding the olefin over a definite period of time to the vigorously agitated isoparafrin and acid. Since the effective carrying out of the reaction is determined to a considerable extent by the intimacy of mixing achieved, conditions favorable for fine acid-isoparafrin emulsion formation are essential—i. e., a high acid-hydrocarbon ratio and efficient agitation. Insufficient mixing, whether due to poor agitation or too small acid-hydrocarbon ratios, results in polymerization rather than addition.

Since the most convenient temperature range for the reaction is between -10° and +30° C. except when working with isobutane, the reaction may be carried on without pressure. However, the reaction is exothermic and means must be provided to remove the heat evolved. It is also possible to work with isobutane in the liquid phase at ordinary pressures by employing temperatures slightly below its boiling point, but much more satisfactory results are obtained at 20° C. in a pressure reaction vessel.

Early experiments were carried out in a glass vessel fitted with an efficient bell stirrer, metal coil condenser, thermometer, and delivery tube. Reactions with isopentane or other hydrocarbons which can be conveniently handled at ordinary temperatures were carried out with the reaction vessel surrounded by an ice bath. When working with isobutane, this was replaced by a bath containing solid carbon dioxide and acetone, which enabled the temperature to be steadily maintained slightly below the

and weighed, and the hydrocarbon layer forced into glass siphons (I) which could be conveniently weighed.]

After separation of the acid (usually pale brown in color which rapidly darkened on contact with air), the product was neutralized with sodium hydroxide and distilled to recover unchanged isobutane and any *n*-butane that may have been

present originally. (This procedure is only possible if we start with isoparaffins boiling outside the range of the product. Isoparaffins such as 2-methylpentane must be recovered by subsequent fractionation.) The residual material was water-white in color, and possessed a pleasant odor characteristic of isoparaffins and a low bromine number. Bromine numbers were determined by the Francis method (5). Distillation was then continued until the column head temperature reached 185° C. The gasoline fraction so obtained had a sweet odor and an extremely low sulfur content, and was entirely saturated. The high-boiling residue remaining was usually pale yellow to brown in color and consisted largely of isoparaffins together with some olefins.

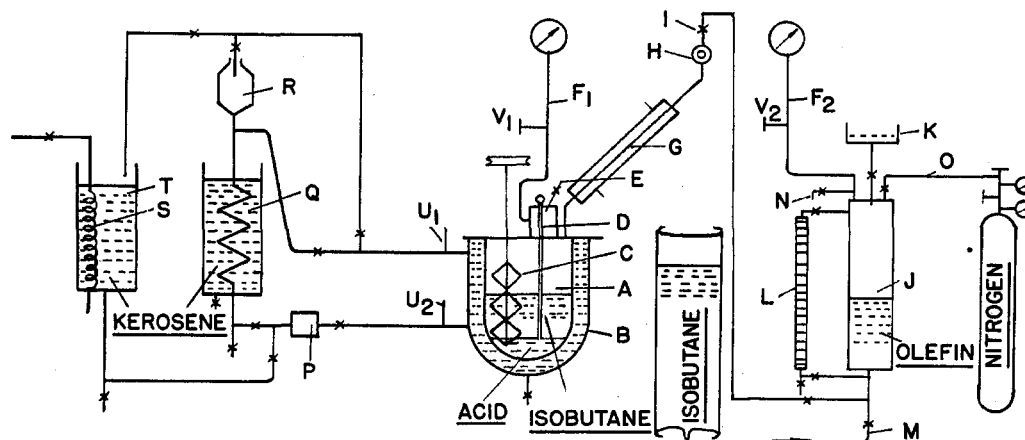


FIGURE 2. AUTOCLAVE AND ACCESSORIES

- A. Lead-lined autoclave
- B. Jacket
- C. Stirrer
- D. Thermometer pocket
- E. Blowoff
- F<sub>1</sub>, F<sub>2</sub>. Pressure gage
- G. Condenser
- H. Sight feed
- I. Valve controlling feed
- J. Feed vessel
- K. Funnel

- L. Sight glass, calibrated
- M. Isobutane line
- N. Blowoff valve
- O. Pressure line
- Q. Circulating pump
- R. O<sub>2</sub>-kerosene cooling tank
- K. Balance vessel
- S. Steam coil or immersion heater
- T. Kerosene
- U<sub>1</sub>, U<sub>2</sub>. Thermometer pockets
- V<sub>1</sub>, V<sub>2</sub>. Safety disks

boiling point of the isobutane but above the freezing point of the acid. Similar coolants were used to surround the metal coil condenser. The reaction was carried out by adding the olefin to the vigorously agitated isoparaffin and acid sufficiently slowly to avoid any marked rise in temperature.

Later a lead-lined pressure vessel was employed, equipped with stirrer, thermometer pocket, valves, and pressure gage, and provided with a jacket through which either hot or cold kerosene could be circulated (Figure 2). A device was also provided by means of which the olefin could be added as liquid during the operation against any pressure in the reaction vessel. A sight feed enabled the rate at which the olefin was added to be observed and checked from time to time.

The following description of a run with isobutane and isobutene is typical of the procedure adopted: After the autoclave had been carefully dried by a stream of warm air, the thermometer pocket was removed and the sulfuric acid added (1600 cc. of 97 per cent acid). The desired volume of isobutane, previously placed in the feed vessel, was then forced by nitrogen pressure into the autoclave, the valve being closed immediately on completion of the transfer. Stirring was commenced and the vessel brought to the required temperature by the circulation of hot or cold kerosene. The nitrogen pressure on the feed vessel was released, and the calculated volume of isobutene placed in it. This was then added to the vigorously agitated acid and isobutane with the aid of a nitrogen pressure in excess of the isobutane pressure in the reaction vessel. The rate of olefin feed was so adjusted that addition would be complete in a definite time, usually 90 minutes. Since the reaction is exothermic, it was necessary to circulate cold kerosene through the jacket during the operation in order to maintain a constant reaction temperature. At 20° C. the pressure was 45 to 50 pounds per square inch at the beginning of the experiment; it dropped as reaction proceeded, to an extent depending upon whether an excess of the isoparaffin was being used. When all the isobutene had been added, stirring was continued 30 minutes longer. Finally agitation was stopped and cold kerosene circulated during settling to cool the reaction products to roughly -10° C.; it was thus easier to handle the products without excessive loss. To remove the contents of the autoclave, the thermometer pocket was replaced by a tube reaching to the bottom and a slight nitrogen pressure applied. [When an accurate weight balance was required, the acid was first removed

### Chemical Composition of Gasoline Fraction

Since attention has mainly been concentrated on the addition of the three- and four-carbon olefins to isobutane, the available information on the composition of the hydrocarbons formed is largely confined to the products from these reactions. Owing to the complex nature of these products and the difficulties encountered in separating the isomeric hydrocarbons present, this work is far from complete.

From their physical properties it appears that, irrespective of olefin and isoparaffin involved, the hydrocarbons formed consist substantially, if not entirely, of isoparaffins. Confirmation of this, at least so far as the hydrocarbons obtained in the isobutene or polyisobutene-isobutane reaction is concerned, is given by the consistently high octane numbers of the fractions obtained on rough fractionation (Table I).

TABLE I. VARIATION OF OCTANE NUMBER WITH BOILING RANGE

Fraction, <sup>a</sup> Boiling Range, C.	Octane No.	Fraction, <sup>a</sup> Boiling Range, C.	Octane No.	Fraction, <sup>a</sup> Boiling Range, C.	Octane No.
50-65	92.2	115-120	92.7	152-165	83.5
65-90	89.7	120-125	92.2	165-170	85.1
90-98	93.4	125-130	89.3	170-175	85.6
98-105	97.5	130-145	79.7	175-185	86.6
105-115	90.0	145-152	85.2	185-190	87.3

<sup>a</sup> From the diisobutene-isobutane reaction product; olefin:isoparaffin = 1:2.

More accurate fractionation with a twenty-five-plate column has enabled some of the individual hydrocarbons formed to be identified. The mechanism by which certain of them

TABLE II. EFFECT OF VARIATION IN OLEFIN-ISOPARAFFIN RATIO

Run No.	Olefin	Isoparaffin	Ratio, Olefin: Isoparaffin	Crude Product <sup>a</sup>		Gasoline (B. P. 27-185° C.)		Residue (B. P. >185° C.)		Isooctane Fraction Yield
				Yield <sup>b</sup> %	Final B. P. ° C.	Yield <sup>b</sup> %	Octane No.	Yield <sup>b</sup> %	Bromine No.	
51	Diisobutene	Isobutane	1:2 <sup>c</sup>	167	264.5	142	90.5	20	10	33.5
99			1:8 <sup>c</sup>	177	204	168	93.6	8	9	63.0
62	2-Butene	Isobutane	1:1	164	258	148	90.2	14.8	10	36.0
122			1:4	199	204	181	93.0	14.6	4	72.0
97	1-Butene	Isobutane	1:1	159	254	139	89.1	20.0	3	69.0
124			1:4	183	203	169	92.9	13.0	3	69.0

<sup>a</sup> After removal of isobutane.<sup>b</sup> Based on weight of olefin taken.<sup>c</sup> See footnote, page 888.

have been produced is by no means clear, and they are probably the result of the secondary reactions.

In the isobutene or polyisobutene-isobutane reaction the main products are 2,2,4-trimethylpentane and a mixture of isomeric octanes boiling between approximately 108° and 115° C., which has proved extremely difficult to separate. Repeated fractionation, however, indicated that 2,4- and 2,5-dimethylhexanes and 2,3,4- and 2,3,3-trimethylpentanes were probably present. In addition, smaller quantities of isopentane, 2,3-dimethylbutane, 2,3- and 2,4-dimethylpentanes, and 2,2,5-trimethylhexane have been isolated from this reaction, and the presence of 2-methylpentane and 2,2,6-trimethylheptane is suspected.

When an excess of isobutane is used, the product of the propylene-isobutane reaction consists mainly of two isomeric heptanes, 2,3- and 2,4-dimethylpentanes; but an appreciable quantity of 2,2,4-trimethylpentane is also formed.

### Effect of Reaction Conditions

The following summary of the effects produced by variation in reaction conditions is based upon results obtained by batch operation in the apparatus described mostly in connection with the diisobutene-isobutane reaction:

**ACID CONCENTRATION.** The most favorable concentration for the reaction is 96-97 per cent by weight. The use of higher concentrations generally results in considerable sulfur dioxide formation, coupled with charring and fouling of the acid. Higher acid concentrations, however (approximately 101 per cent), are necessary for the propylene-isobutane reaction in order to obtain satisfactory yields and avoid the formation of isopropylsulfuric esters which otherwise takes place. In general, lower concentrations favor polymerization at the expense of olefin-isoparaffin addition. It is noteworthy that the acid-soluble products normally formed have a much less adverse effect upon the course of the reaction than water in similar amounts.

**TEMPERATURE.** The temperature range for the reaction is approximately -10° to +30° C., the optimum being about 20° C. (Figure 3). Toward the lower limits of this range, polymerization of the olefin at the expense of reaction with the isoparaffin becomes very marked, and the amount of material boiling outside the gasoline range is considerably increased. This material not only has a higher olefin content (shown by its bromine number) than that formed when reaction is carried out at higher temperature, but it boils over a wider range and has a much higher end point. At the upper limit of the temperature range (30° C.) excessive oxidation and fouling of the acid occur with consequent increase in acid consumption. Attempts to obtain satisfactory yields with less concentrated acid by raising the reaction temperature to 40-50° C. were unsuccessful; oxidation and fouling of the acid were excessive. This applied not only to acid diluted with water (90-94 per cent) but also to acid from previous reactions so diluted with the normal acid-soluble reaction products that it

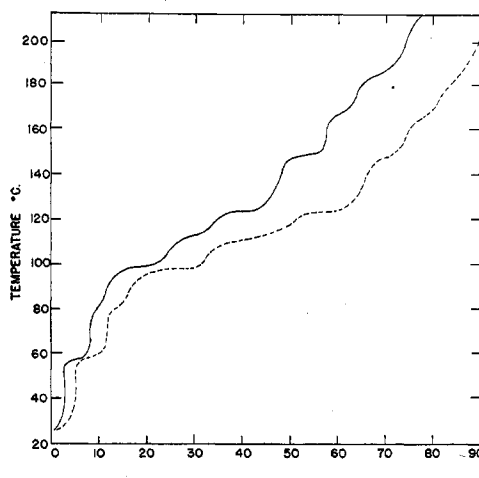


FIGURE 3. DISTILLATION CURVES (25-PLATE COLUMN) OF PRODUCTS FROM DIISOBUTENE AND ISOBUTANE (RATIO, 1:2)

— — — -10° C., run 28  
 - - - - 20° C., run 29

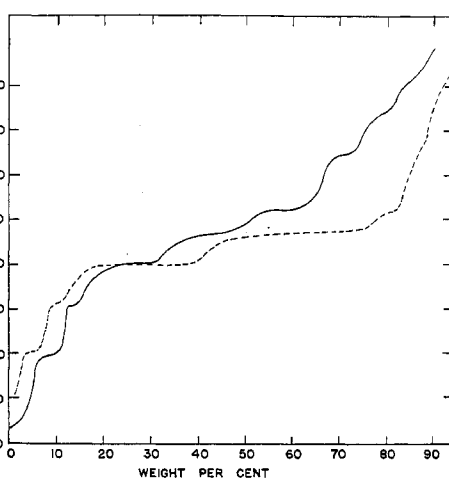


FIGURE 4. DISTILLATION CURVES (25-PLATE COLUMN) OF PRODUCTS FROM DIISOBUTENE AND ISOBUTANE AT 20° C.

— — — (C<sub>4</sub>H<sub>8</sub>)<sub>2</sub>:C<sub>4</sub>H<sub>10</sub> = 1:2 (run 29)  
 - - - - (C<sub>4</sub>H<sub>8</sub>)<sub>2</sub>:C<sub>4</sub>H<sub>10</sub> = 1:8 (run 96)

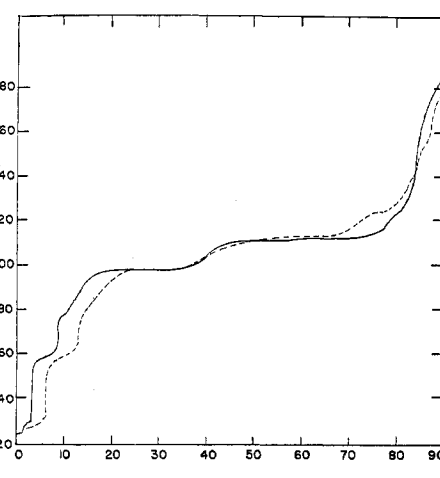


FIGURE 5. DISTILLATION CURVES (25-PLATE COLUMN) OF PRODUCTS FROM UNSATURATED FOUR-CARBON CUTS AND EXCESS ISOBUTANE (69 PER CENT) CONCENTRATE AT 20° C.

Unsaturated hydrocarbon:isobutane = 1:3  
 — — — C<sub>4</sub> cut, 95 per cent unsaturates, 22.7 per cent butadiene (run 110)  
 - - - - C<sub>4</sub> cut, 56 per cent unsaturates, 3.6 per cent butadiene (run 150)

TABLE III. EFFECT OF *n*-BUTANE ON THE DIISOBUTENE AND ISOBUTANE REACTION

Run No.	Isobutane Content, %	Ratio Isobutane: Diisobutene	Per Cent Based on Diisobutene Taken	
			Gasoline (B. P. 27-185° C.)	Residue (B. P. > 185° C.)
95	45	2:1	134	22.5
94	71		133	20.2
51	98		142	19.6
101	45	4.5:1	158	12.2
55	98	4:1	158	14.8
103	71	6:1	166	8.1
a	98		165	10

<sup>a</sup>These figures are interpolated from runs using isobutane:diisobutene ratios of 4:1 and 8:1.

was no longer capable of effecting efficient olefin-isoparaffin addition at 20° C. With even more dilute aqueous acid (75 per cent at 70-75° C.) no reaction between diisobutene and isobutane was observed; the product consisted entirely of higher boiling polymers.

**RATIO OF REACTANTS.** The ratio of reactants is probably the most important factor in determining the composition and characteristics of the product. In order to obtain efficient contact between the acid and the hydrocarbons, early recognized as necessary for the successful carrying out of the reaction, a high acid-hydrocarbon ratio was used throughout this work. The actual ratio is no doubt dependent upon the type of apparatus employed, the essential condition being the maintenance of good emulsification during reaction. Unsatisfactory agitation, especially when due to low acid-hydrocarbon ratios, leads to olefin polymerization without addition. Since an excess of olefin over that required for equimolecular reaction<sup>1</sup> results in the formation of hydrocarbons of high-boiling point outside the gasoline boiling range, this condition is to be avoided. On the contrary, increasing the isoparaffin-olefin ratio above that required for equimolecular reaction is definitely advantageous; the end point of the crude product is so lowered that, with the exception of a comparatively low-boiling residue, it boils almost entirely in the gasoline range. Accompanying this decrease in boiling range is an appreciable increase both in yield of useful material and in its octane number (Table II). In reactions where a large excess of isoparaffin is present, a much higher proportion of the direct addition product and its isomers is formed (Figure 4).

**PRESENCE OF NORMAL PARAFFINS.** In general, the presence of such diluents as normal paraffins does not seriously affect the course of the reaction, particularly when the isoparaffin present is in excess of equimolecular. The technical significance of this is obvious since it precludes the necessity of isolating isoparaffins in a state of comparative purity. At equimolecular olefin-isoparaffin ratios, however, the presence of appreciable amounts of the normal paraffin results in a slightly lower yield of useful material. The results of employing isobutane diluted with normal paraffin, mainly *n*-butane, in the diisobutene-isobutane reaction is shown in Table III.

**VARIATION IN TIME OF OLEFIN ADDITION.** In the batch method of operation used throughout this investigation, the olefin was added to the vigorously agitated isoparaffin and acid over a definite period of time. The rate at which such addition is most conveniently made, however, is largely dependent upon the apparatus and the quantities of reactants present. Consequently, apart from ensuring that the experimental procedure gave the optimum results obtainable with the apparatus, no very careful examination of the effect of varying addition rates, etc.,

<sup>1</sup> Since the polymers examined behaved as though they depolymerized to the equivalent monomeric olefin, in calculating the necessary amount of isoparaffin they have been regarded as such.

was made. It was established, however, that an optimum period for addition existed; rapid addition appeared to favor polymer formation with consequent decrease in yield of gasoline and increase in high-boiling residue. A too prolonged period of addition also resulted in a slightly lower yield of useful material, presumably owing to the breaking down of the primary product by the acid. A variation in the procedure, in which the olefin and isoparaffin previously mixed were added to the agitated acid, was also found to give an inferior yield of gasoline.

### The Isobutane-Butene Reaction

Substitution of normal butenes, either 1- or 2-butene, for isobutene in the reaction with isobutane was without marked effect upon the boiling range or octane number of the gasoline produced. Furthermore, fractionation indicated that apparently the same hydrocarbons were present in substantially the same amount in the product from all three olefins (2); the presence of 2,2,4-trimethylpentane was of special interest. It must be assumed either that the normal butenes are isomerized before addition to the isoparaffin or that rearrangement of an intermediate addition product occurs. Of these alternatives the former appears the most likely and is apparently confirmed by the formation of small amounts of di-*p*-*tert*-butylbenzene when the high-boiling residues from these reactions are treated with sulfuric acid and *tert*-butylbenzene (9).

If, instead of the simple four-carbon olefins the lower isobutene polymers, such as the di- and trimerides or the butene-isobutene copolymer (B. I. B.), are allowed to react with isobutane, addition proceeds smoothly and products are obtained identical with those formed from the olefins from which the polymers were derived. The gasolines from these reactions, like those from the simple olefins, are fully saturated and have an octane number of over 90. The similarity in their chemical composition is clearly shown by the twenty-five-plate column distillation curves which are practically superimposable.

The results obtained from the four-carbon olefins and their polymers (Table IV) show the striking similarity in the yields and characteristics of the products obtained.

TABLE IV. REACTION OF FOUR-CARBON OLEFINS AND POLYMERS WITH ISOBUTANE UNDER OPTIMUM CONDITIONS<sup>a</sup>

Run No.	129	122	124	99	66	72 Butene-Isobutene Copolymer (95-120° C. Cut)
Olefin						
Product boiling above 27° C.:						
Yield based on olefin taken, %	183	199	183	177	181	181
Specific gravity, 15.6° C.	0.706	0.704	0.707	0.700	0.702	0.698
Bromine number	2	1	1	2	2	3
A. S. T. M. distillation, ° C.:						
Initial b. p.	41	51.5	58	43	32	34
2%	61	69	74	58	44	47.5
5%	75	83	84	69	53.5	59.5
10%	87	93.5	92	81.5	68	74.5
20%	97	100.5	99.5	95	89.5	93
30%	102	103.5	103	100.5	100.5	103.5
40%	106	106	105.5	104.5	107.5	108.5
50%	109.5	108	108	107	112.5	112
60%	113.5	110.5	110	110	118	117
70%	119	113	112.5	113	128.5	125
80%	130	118	117	119.5	149	140
90%	178	133	133	151.5	185	187
Final b. p.	242	204	203	202	227	224
Gasoline boiling between 27-185° C.:						
Yield based on olefin taken, %	166	181	169	168	164	157.5
Specific gravity, 15.6° C.	0.700	0.703	0.704	0.701	0.701	0.698
Bromine number	<1	<1	<1	<1	<1	<1
Octane number:						
Neat	93.4	93.0	92.9	93.6	90.9	91.4
Neat + 1.0 cc. (tetraethyllead) per Imperial gallon	103	102.3	100.7	100+	100 <sup>b</sup>	100.5 <sup>b</sup>
Residue boiling above 185° C.:						
Yield based on olefin taken, %	15	14.6	12.8	8	12.2	14
Specific gravity, 15.6° C.	0.771	0.766	0.768	0.777	0.782	0.778
Bromine number	5	4	3	9	15	14

<sup>a</sup> Isoparaffin:olefin (or monomeric equivalent) = 4:1; temperature, 20° C.; 97 per cent acid.

<sup>b</sup> Neat + 1.5 cc. TEL per Imperial gallon.

### Application of the Reaction to Refinery Products

The results so far described have been obtained with individual olefins. Further investigation showed that mixtures of olefins could be used with equally satisfactory results. Thus the crude polymer from the so-called cold acid polymerization of isobutene containing dissolved isobutene (in addition to the di- and trimerides) proved to be entirely satisfactory as a source of olefin.

The next logical step was the direct utilization of the four-carbon cut obtainable from cracking gases; a typical analysis is as follows:

Analysis of High-Pressure Cracking Gas	Per Cent by Vol.
C <sub>4</sub>	Trace
Isobutane	14.3
n-Butane	29.5
Isobutene	19.5
n-Butenes	32.2
Butadiene	3.6
C <sub>5</sub> +	1.2

Apart from the butadiene content, this material might be expected to form an excellent source of olefins, since all the olefins present have been shown to give satisfactory results. The ease with which butadiene is polymerized by concentrated sulfuric acid to form tarry products while at the same time fouling the acid seemed to offer a definite objection to its use. While means were being devised to remove it, however, a preliminary experiment was carried out on the untreated material. The result indicated that the presence of this amount of butadiene was apparently without effect, both yield and octane number of the gasoline being normal. Not only was this result confirmed, but later experiments in which an unsaturated four-carbon cut from low-pressure cracking operations containing 22.7 per cent butadiene was used gave equally satisfactory results. What happens to the butadiene, especially when it is present in comparatively large amounts, is an interesting problem for investigation since the distillation curves of the products seem to indicate that no hydrocarbons, other than those normally formed from the four-carbon olefins themselves, are present (Figure 5). Possibly during the course of the reaction the butadiene is partially hydrogenated to butene at the expense of isobutane which is itself dehydrogenated to isobutene in the process. If this is so, the mechanism may be somewhat similar to that which occurs in so-called hydropolymerization.

The yields and analytical data for the products from these experiments are shown in Table V.

be possible to precool the reactants to  $-10^{\circ}\text{C}$ . or even lower and allow reaction to proceed until the upper temperature limit is reached. Such a method of operation, however, has many disadvantages and cannot be applied to continuous operation when the capacity of the plant for absorbing heat can no longer be utilized. With a view to obtaining data for plant design, approximate determinations were made of the heat evolved for various olefin-isobutane reactions in the apparatus already described, the order of accuracy has been estimated at  $\pm 10$  per cent. The figures obtained with an acid concentration of 97.9 per cent are as follows:

Run No.	Olefin	Ratio, Olefin: Isobutane	Heat Evolved—Cal./gram olefin	B.t.u./lb. olefin
164	Isobutene <sup>a</sup>	1:3	284	512
64, 65	Diisobutene <sup>a</sup>	1:2	122	220
66	Triisobutene <sup>a</sup>	1:12	97	175
165, 166	Unsatd. C <sub>4</sub> cut <sup>b</sup> from high-pressure cracking operation	1:3	342	615

Total unsatd. content, 56%

<sup>a</sup> The isobutane used for these reactions contained 98 per cent isobutane.  
<sup>b</sup> An isobutane concentrate containing 67 per cent isobutane was used.

The figure of 615 B. t. u. per pound for the reaction involving the unsaturated four-carbon cut agrees reasonably well with a calculated value of 609 B. t. u. per pound, based on that found for diisobutene where due allowance is made for the isomerization of the normal butenes present.

### Acid Requirements

The high acid-hydrocarbon ratio employed throughout the present investigation was shown by the original preliminary experiments to be essential; without it the intimacy of mixing necessary for successful operation was not possible.

Although the part played by the acid in effecting combination of the olefin and the isoparaffin is apparently catalytic, during the reaction it becomes diluted with reaction products, presumably higher alkyl sulfuric acids. While the latter do not affect the ability of the acid to bring about the olefin-isoparaffin reaction to the same extent as would dilution with an equal quantity of water, they do nevertheless have an adverse effect upon its action. With prolonged use, therefore, the effectiveness of the acid decreases until finally it is no longer capable of producing an economical yield of the required material. The amount of acid required to produce a definite quantity of 90-octane gasoline thus becomes a factor of prime importance, upon which the technical feasibility of the process must eventually depend.

TABLE V. UNSATURATED FOUR-CARBON CUT FROM CRACKING UNIT STABILIZER<sup>a</sup>

Run No.	Unsaturated C <sub>4</sub> Cut			Gasoline Boiling at 27–185° C.					Residue (B. P. > 185° C.)		
	Cracking gas	Olefin content	Butadiene content	Yield <sup>b</sup>	Sp. gr. (15.6° C.)	Bromine No.	Octane No. Neat + 1 cc.		Yield <sup>b</sup>	Sp. gr. (15.6° C.)	Bromine No.
150	High-pressure	56.0	3.6	162	0.698	<1	90.7	98.0	16.0	0.781	15
119	Low-pressure	95.0	22.7	153	0.701	<1	91.8	99.7	11.0	0.795	24

<sup>a</sup> The quantities of these fractions were selected to give an olefin:isobutane ratio of 1:3, due allowance being made for isobutane content of unsaturated material.

<sup>b</sup> Based on the total unsaturated content (olefin + diolefin) of unsaturated C<sub>4</sub> cut.

Blended with 25 per cent of a special Iranian gasoline cut (octane number 70) together with 2.6 cc. of tetraethyllead per Imperial gallon, these gasolines provide an entirely satisfactory 100-octane aviation fuel.

### The Heat of Reaction

Although the reaction may be carried out over a range of  $-10^{\circ}$  to  $+30^{\circ}\text{C}$ ., the optimum temperature is in the neighborhood of  $20^{\circ}\text{C}$ . Since the reaction is exothermic, to maintain this temperature it is necessary to provide means for removing the heat evolved. In batch operation it would

Although a batch-operated process on a small scale does not lend itself to an accurate determination of acid consumption, an approximate figure can be obtained by leaving the acid in the reaction vessel and treating successive quantities of olefin and isoparaffin with it; only small samples of acid are withdrawn after each batch for analysis. Rough as the method is, it afforded figures which agreed quite well with those obtained later from a small pilot plant in continuous operation.

Table VI gives the results obtained in this way when 1600 cc. of 97 per cent acid were employed to treat eight successive

TABLE VI. EFFECT OF SUCCESSIVE ADDITIONS OF 800 GRAMS OF TECHNICAL DIISOBUTENE TO 5800 Cc. OF A 71 PER CENT ISOBUTANE CONCENTRATE AND A SINGLE BATCH OF 1600 Cc. OF 97 PER CENT SULFURIC ACID AT 20° C.

Run No.	111	111A	112	112A	113	113A	114	114A	115	115A	117	107	108
Strength of acid during run:													
Beginning	97	97	95.1	95.1	94	94	92.4	92.4	90.2	90.2	87.8	84.7	82.1
End	95.1	95.1	94	94	92.4	92.4	90.2	90.2	87.8	87.8	85.7	82.1	79.5
Product boiling above 27° C.:													
Yield based on olefin taken, %	176	189	190	190	181	183	182	182	178	173	173	149	128
Av. of 2 runs, %		183		190		182		182		176	...	...	...
A. S. T. M. distillation, ° C.:													
Initial b. p.	42.5	42.5	40	41	43	32	32	31.5	36	42	36	42	41
2%	62	57	52.5	52	58	42	44	45	47	57	48	58	54
5%	70	61	62	62	68	50	53	53.5	58	61	59	69	66.5
10%	81	71.5	75	75	80	62.5	65	65	68.5	72	71	81	81.5
20%	94	92	92	93	92.5	89	87	88	89.5	90	91	96.5	105
30%	101	99.5	100	100.5	100	99	97	100	100	99	102	108.5	118
40%	105.5	104	104	104.5	104.5	104.5	104.5	106	106.5	107	110	113	134
50%	107.5	107	108	108	108	108.5	109	110	110.5	110	117	122.5	153
60%	111.5	111	110.5	112	112	113	112	117	117.5	117	124.5	135	175.5
70%	115.5	115.5	116.5	117	117	119	120	125	126.5	125	144.5	162.5	199
80%	121	123	127	125	125	130	132	144	153	145	184	187.5	222
90%	161	167	170	168	166	177	177.5	187	193	190	220	222	259
Final b. p.	208	206	209	214	213	222	218	233	234	234	260	270	286
Gasoline boiling from 27-185° C.:													
Yield based on olefin taken, %	167	177	169	174	164	163	161	160	150	154	142	111	80
Av. of 2 runs, %		172		172		164		161		152			
Specific gravity, 15.6° C.	0.700	0.699	0.698	0.698	0.697	0.694	0.698	0.695	0.700	0.700	0.699	0.705	0.707
Bromine number	<1	<1	<1	<1	<1	<1	1	1	1.5	1	2.5	5	10
Octane number:													
Neat	92.4	92.7	92.4	92.5	92.5	92.2	92.6	92.2	89.7	89.9	88.9	91.3	91.8
Neat + 1.0 cc. TEL	101.6	101.7	101.6	101.8	101.5	101.5	100.7	102	98.1	98.4	97.9	100.2	100.0
Residue boiling above 185° C.:													
Yield based on olefin taken, %	6.1	7.1	12	9.5	12.2	14.8	16.8	18.6	19.6	16.4	28	34	48
Av. of 2 runs, %		6.6		10.8		13.5		17.7		18.0			
Specific gravity, 15.6° C.	0.780	0.779	0.777	0.783	0.777	0.780	0.780	0.781	0.785	0.785	0.787	0.786	0.791
Bromine number	15	13	12	14	13	9	13	15	23	25	33	34	49
Av. wt. % based on total olefin taken:													
Product boiling above 27° C.		183		186		185		184		183		181	171
Gasoline boiling from 27-185° C.		172		172		169		167		164		160	144
Residue boiling above 185° C.		6.6		8.7		10.3		12.2		13.3		15.8	22.1
Wt. % of 97% acid on total useful product	215		107		73		55		45		38.4	33.6	31.9

batches of technical diisobutene and isobutane. After a slight improvement with the second batch of hydrocarbon treated (probably due to some solvent effect of the fresh acid on the product from the first batch), with succeeding batches

there is a steady fall in yield of useful material and an increase in high-boiling residue. The rise in bromine number which accompanies the increase in the amount of residue formed indicates that polymerization is taking place at the expense

of the addition reaction. After the treatment of eight batches the yield of useful material had fallen to such an extent that it was no longer regarded as economical. Furthermore, the gasoline fraction possessed an appreciable bromine value and could no longer be regarded as saturated. At this stage the total amount of useful product based upon the weight of acid used was 314 per cent and upon the olefin, 152 per cent. This corresponds with an acid consumption of 31.9 per cent, the used acid having a concentration of approximately 82 per cent.

Similar results were obtained when a four-carbon cut containing 56 per cent unsaturates was used in place of technical diisobutene (Table VII). The sharp drop in yield which occurs when a definite stage has been reached was again observed. The over-all yield of gasoline at the point where the conversion was no longer considered economical corresponded closely to that obtained with diisobutene; it was 310 per cent by weight of the acid used. Since the concentration of the used acid also closely approximated that previously obtained, it would appear that this is the limiting concentration for the economical production of a saturated product from four-carbon olefins and isobutane.

TABLE VII. EFFECT OF SUCCESSIVE ADDITIONS OF 1320 GRAMS OF FOUR-CARBON CUT FROM HIGH-PRESSURE CRACKING GASES TO 4750 Cc. OF A 69 PER CENT ISOBUTANE CONCENTRATE AND A SINGLE BATCH OF 1600 Cc. OF 97 PER CENT SULFURIC ACID AT 20° C.

Run No.	150	151	152	153	154	155	156	157
Strength of acid during run:								
Beginning	97	94.6	93.4	91.4	90.5	88.9	86.4	83.7
End	94.6	93.4	91.4	90.5	88.9	86.4	83.7	79.8
Product boiling above 27° C. (yield based on olefin taken, %)	178	189	194	180	181	172	169	149
A. S. T. M. distillation, ° C.:								
Initial b. p.	34	31	38	38	33.5	36	35	33
2%	46	43	52	46	46	46.5	47	43
5%	56.5	53.5	62	54.5	57	56	53	51
10%	73	66	75	67	69	69	65	64
20%	94	92	94	89	91	90	88	91.5
30%	102	100	102	99	100	101.5	100.5	103.5
40%	106	106	107	106	106	106.5	107	108.5
50%	108.5	109.5	110	109	109.5	110.5	112	121
60%	112	113	114	115	115.5	115	117	131
70%	113	118	121	122	123.5	125	126	151
80%	129	127	136	137.5	144	140	151.5	194
90%	183	180	187	184	210	193	199	240
Final b. p.	229	227	258	232	250	229	251	268
Gasoline boiling from 27-185° C.:								
Yield based on olefin taken, %	161	170	166	158	157	150	139	114
Sp. gr., 15.6° C.	0.698	0.699	0.697	0.697	0.697	0.698	0.698	0.698
Bromine number	<1	<1	<1	<1	<1	<1	<1	1
Octane number:								
Neat	90.7	90.9	91.4	91.2	90.2	91.0	90.4	89.7
Neat + 1.0 cc. TEL	98.0	98.5	100.5	100.5	100.5	100.0	100.1	99
Residue boiling above 185° C.:								
Yield based on olefin taken, %	16	14.9	22	19	19.8	20	28.8	30.6
Sp. gr., 15.6° C.	0.781	0.778	0.779	0.781	0.783	0.781	0.778	0.790
Bromine number	15	17.5	15	18	30	28	27	58
Av. % based on total olefin taken:								
Product boiling above 27° C.	178	183	187	185	184	182	180	177
Gasoline boiling from 27-185° C.	161	165	166	164	162	160	157	152
Residue boiling above 185° C.	16	15.4	17.6	18	18.3	18.6	20	21.4
Wt. % of 97% acid on total useful product	244	119	79	59.5	48.3	41	35.6	32.2



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# Preparation of Cellulose Ethers

## Function of Alkali; Side Reactions

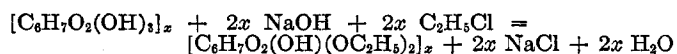
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The mechanism of cellulose etherifications based on the action of alkyl and aralkyl halides on alkali cellulose is described. One of the most important factors is the composition of alkali cellulose. The various ratios of the constituents (cellulose, sodium hydroxide, and water) greatly influence the initial speed, uniformity, and extent of etherification, and the character and speed of side reactions. In view of the topochemical and, in most cases, heterogeneous nature of the reaction, the mechanical conditions of uniform etherification, such as solvent effect of the medium, consistency

of the mix, type of agitation, etc., are pointed out. The changes of alkali concentration as the reaction proceeds greatly influence the course of etherification; the need for and methods of regulating this variable are shown. The side reactions of cellulose etherification have been studied experimentally in the case of the hydrolysis of benzyl chloride as influenced by such factors as concentration of the caustic solution, its ratio to benzyl chloride, temperature, time, speed of agitation, presence of solids and liquids of different character, etc.

OF THE various etherification methods known in organic synthesis, only a few can be applied to cellulose. In general, inorganic acid esters, such as dimethyl sulfate, propyl bromide, and benzyl chloride, are used as etherifying agents in the presence of an alkali to neutralize the acid formed in the reaction:



A notable exception is ethylene oxide (and its homologs), which enters into an addition reaction with cellulose to form a monoether of glycol (hydroxyethylcellulose). The alkali may be organic or inorganic. Pyridine has been used in tritylation (with triphenylchloromethane) (6, 22), and alkylations, as well as aralkylations, have been carried out in aqueous quaternary ammonium bases (1)—e. g., trimethylbenzylammonium hydroxide. The solubility of cellulose in these bases ensures a more uniform reaction, which may even become homogeneous when the alkylating agent (e. g., dimethyl sulfate) is also soluble in the base. In spite of the obvious

advantages of such reaction conditions as regards the quality of the product, economic reasons favor the use of inorganic alkalis.

In the production of the commercially important cellulose ethers (methyl, ethyl, and benzyl), the corresponding alkyl and aralkyl chlorides are the etherifying agents and sodium hydroxide the alkali. The cellulosic raw material is either cotton linters or wood pulp (high alpha-cellulose). Usually cellulose, sodium hydroxide, and water are first brought into intimate contact to form alkali (or soda) cellulose, which both for practical and scientific purposes may be considered as a unit in its interaction with the etherifying agent. A very uniform alkali cellulose is obtained according to the process used in rayon manufacture—viz., by immersing the cellulose in a large volume of sodium hydroxide solution of the desired concentration and removing the excess by pressing or centrifuging.

The composition of the alkali cellulose—i. e., the ratio of its constituents—is very important. The concentration of the sodium hydroxide (its ratio to water) influences the speed of