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H. J. HEPP

2,816,150

INTEGRATED CRACKING-ALKYLATION PROCESS

Filed Dec. 14, 1953

4 Sheets-Sheet 1

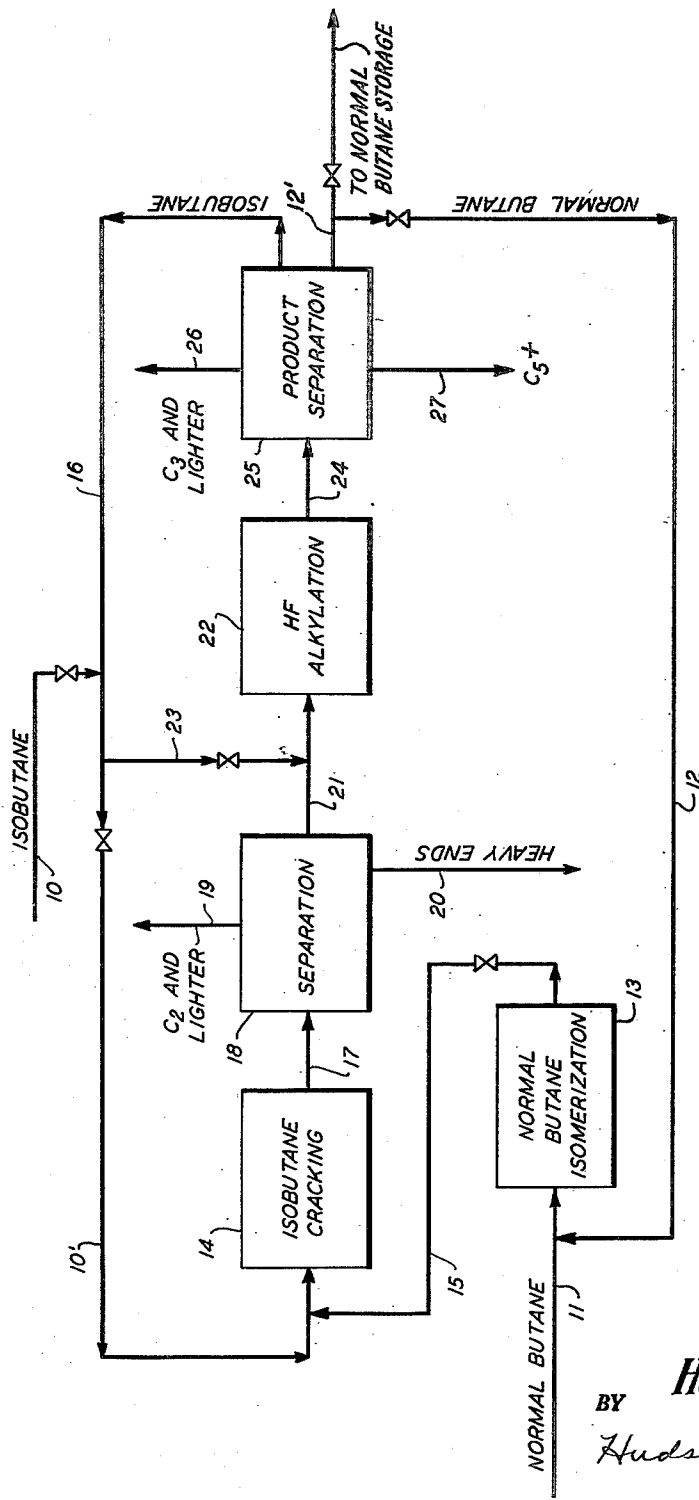


Fig. 1.

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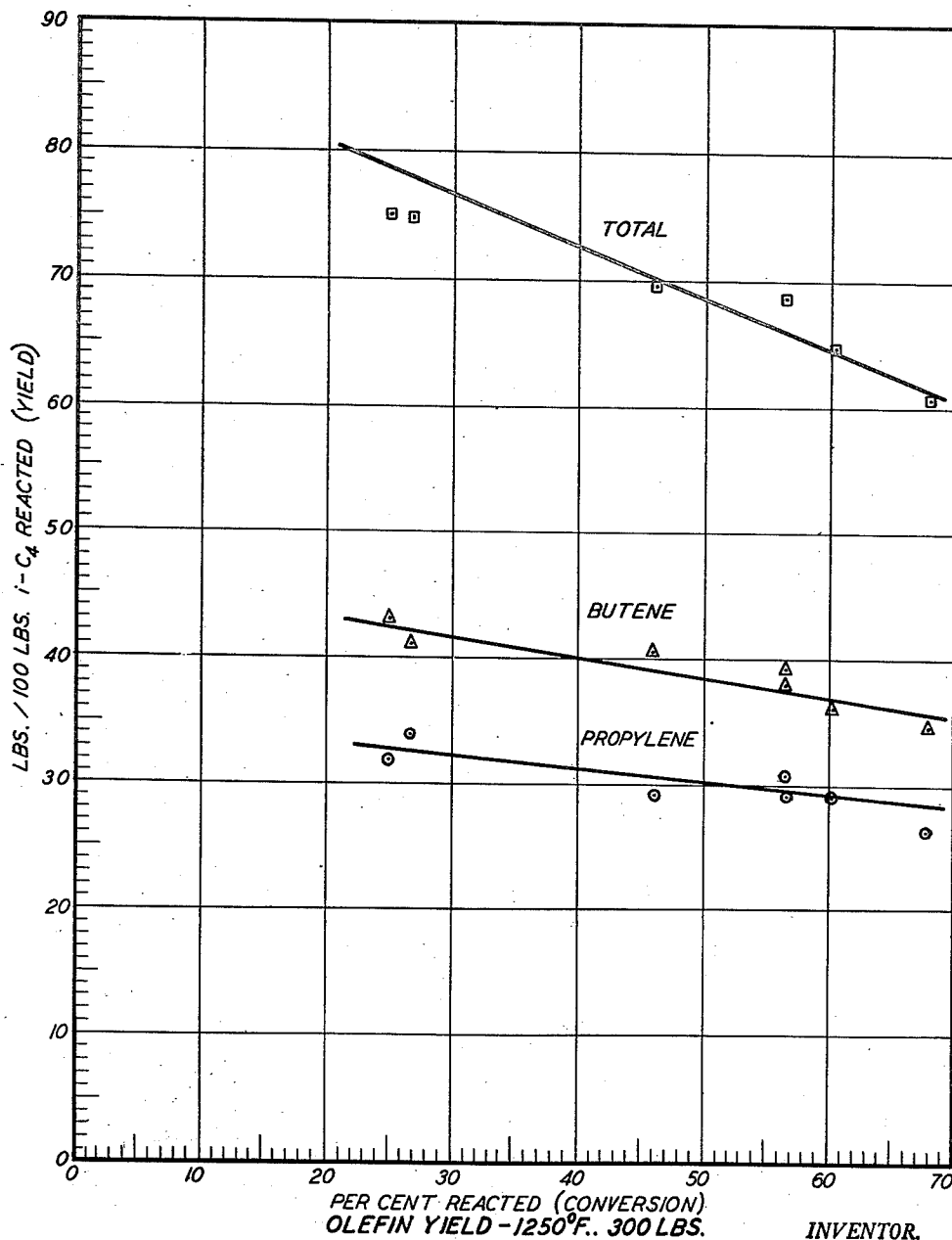
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Fig. 2.



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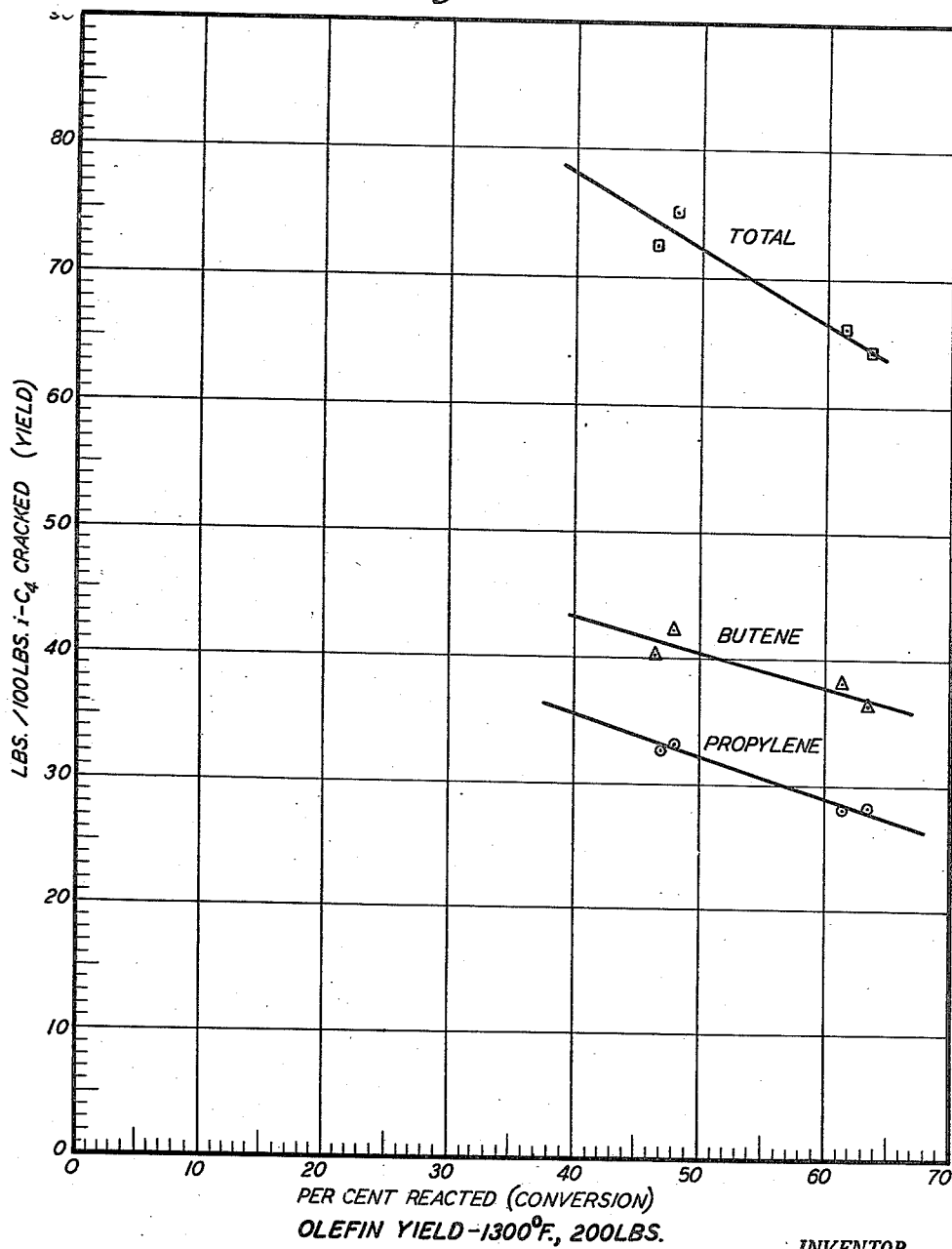
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Fig. 3.



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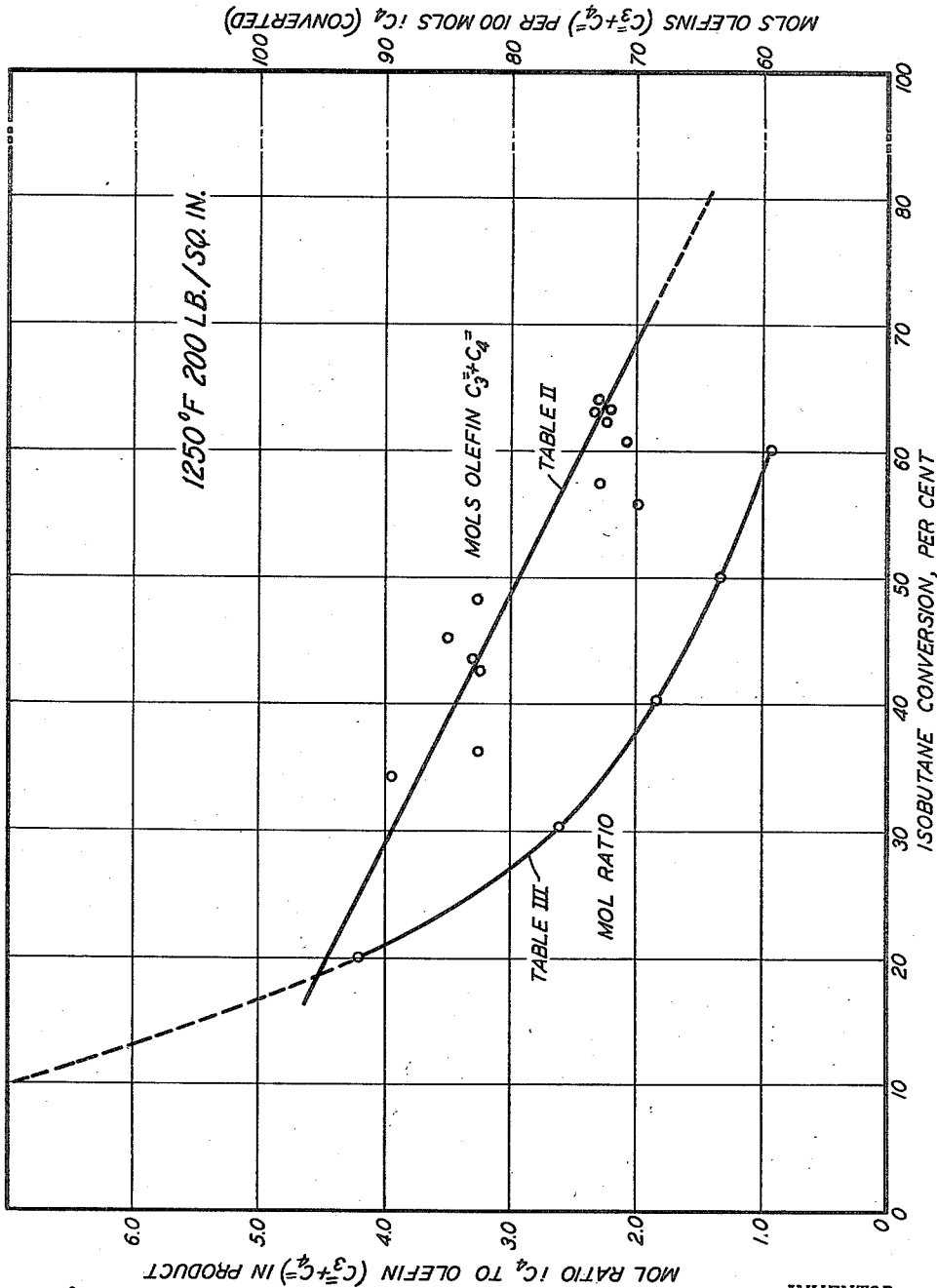


Fig. 4.

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INTEGRATED CRACKING-ALKYLATION PROCESS

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3 Claims. (Cl. 260—683.4)

This invention relates to the manufacture of hydrocarbons. In one aspect this invention relates to the manufacture of motor fuels. In one aspect this invention relates to the manufacture of olefins by reacting isobutane under selected conditions of pressure, temperature and per-pass conversion. In another aspect this invention relates to an integrated cracking-alkylation process wherein isobutane is cracked under specified conditions for producing effluent containing isobutane, propylene and butylene, in predetermined proportions, and, wherein said effluent is de-ethanized and then charged, subsequent to depentanization, if desired, as sole feed to an alkylation system and converted therein to hydrocarbons boiling in the gasoline range. In another aspect this invention relates to a process for cracking isobutane under pressure conditions to produce propylene and butylene in high ultimate yield and in a ratio to unreacted isobutane in the effluent such that the resulting effluent freed of materials lighter than propylene can be charged as sole feed to an alkylation system for conversion to motor fuel.

In accordance with this invention, isobutane is subjected to conversion at a pressure above about 80 p. s. i. g., so as to produce propylene and butylene in high ultimate yields, under which conditions total effluent can be produced containing isobutane, propylene and butylene in relative mol ratios such that resulting demethanized or de-ethanized conversion effluent is particularly applicable as sole feed to an alkylation system for conversion to isoparaffins boiling in the gasoline range. In accordance with one concept of this invention, total effluent from the above-described conversion is efficiently fractionated at its existing pressure to remove C_2 hydrocarbons and lighter materials therefrom (de-ethanization) and the resulting residual effluent is charged as sole feed, subsequent to depentanization, if desired, to an alkylation system and therein converted to isoparaffins boiling in the gasoline range.

Temperatures employed, in the conversion of isobutane to olefins in accordance with this invention are generally within the range of 1100–1400° F., although temperatures outside that range can be employed. More generally preferred temperatures are within the range of 1200–1350° F.

Pressures employed are those above 80 p. s. i. g., generally within 125–500 p. s. i. g., a still narrower range of about 150–300 p. s. i. g. being preferred because higher ultimate yields of olefin are obtained under these conditions, and relative ratios of isobutane, propylene and butylenes are obtained, which are especially suitable such that de-ethanized effluent can be advantageously charged as sole feed for conversion, by alkylation, to gasoline boiling-range hydrocarbons.

Time conditions employed are generally from about 0.03 to 150 seconds for a per-pass conversion of isobutane of from 10–70 mol percent at 1100 to 1400° F. and 125 to 500 p. s. i. g., and from about 0.2 to 12 seconds for a per-pass conversion of isobutane of from 25 to 55 mol percent at 1200 to 1350° F. and 150 to 300 p. s. i. g.

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This latter range of 25 to 55 mol percent per-pass conversion of isobutane provides high ultimate yields of propylene and butylene, and also suitable relative ratios of isobutane, propylene and butylene are obtained as sole feed to alkylation for conversion to motor fuels. The conditions of time, temperature and pressure must be correlated so as to give the desired per-pass conversion of isobutane.

When it is desired to carry out the integrated cracking-alkylation process of this invention, isobutane cracking is regulated so as to provide de-ethanized effluent containing isobutane in a mol ratio to olefins (after de-ethanization) in the range of about 1:1 to 10:1, more preferably from 4:1 to 6:1, under which conditions the said de-ethanized effluent can be charged as sole feed to alkylation for conversion to high quality motor fuels. The cracking operations required for achieving the above-described ranges of isobutane to olefin ratios are also those providing for highest ultimate yields of propylene and butylene. Isoparaffins other than isobutane give high yields of ethylene. Therefore, isobutane is the only possible feed for this process.

Although in carrying out the integrated cracking-alkylation process, the effluent from isobutane cracking is preferably de-ethanized and often advantageously depentanized prior to charging same as sole feed to alkylation, neither of these steps is required. Thus, the said effluent can be demethanized, and ethylene in the feed to alkylation can be utilized as an alkylating reactant, as for example when employing a 2-stage alkylation step, in the first of which steps ethylene is not converted, but is reacted with isoparaffins in the latter. The presence in the alkylation feed of any pentane and heavier hydrocarbon materials produced in the cracking process of the integrated cracking-alkylation process herein, is not generally desirable because of the effect of diolefins on catalyst consumption, i. e., to increase catalyst consumption to an unduly high rate, particularly when hydrofluoric acid or sulfuric acid are employed as catalysts.

A further advantage of my invention is provided with reference to preparation of total isobutane cracking effluent for alkylation. Because the cracking of isobutane is maintained at a pressure above about 80 p. s. i. g., generally from 125–500 p. s. i. g., the effluent from isobutane cracking can be efficiently fractionated for removal of materials lighter than propylene and to effect depentanization, without the need for pressurization, such pressures, particularly those exceeding 125 p. s. i. g. being advantageously employed in the removal of C_2 and lighter materials from cracking effluent. The elimination of the need for pressurization to separate C_2 and lighter materials, and to depentanize, provides a considerable saving in equipment and manpower requirements and thereby facilitates operation from the viewpoint of economics, thus adding to the economic feasibility of the process of this invention.

The invention is illustrated with reference to the drawing of Figure 1, which is a diagrammatic flow sheet illustrating one manner in which process of this invention can be carried out.

Figures 2, 3 and 4 are plots of curves setting forth data illustrative of process of this invention.

With reference to Figure 1, isobutane, or an isobutane-containing stream is passed via lines 10 and 10' to isobutane-cracking zone 14, as for example, a Selsas furnace. Isobutane, as feed in any desired proportion, can also be introduced via line 15 into line 10' from a normal butane isomerization zone 13, described hereinafter. Preferred isobutane-cracking conditions in zone 14, described hereinafter, are generally employed, namely a pressure in the range 150–300 p. s. i. g., a temperature in the range of about 1200–1350° F., and time conditions providing

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for 25-55 mol percent isobutane cracking, i. e., per-pass conversion. Effluent is withdrawn from zone 14 via line 17 at the existing pressure in zone 14 and introduced into separation zone 18, comprising any desired arrangement of fractional distillation equipment; although, if desired, other separation means may be employed in zone 18. In zone 18 effluent from zone 14 is de-ethanized, and the C₂ and lighter materials, principally ethane, ethylene, methane and hydrogen, are withdrawn via line 19. Heavy ends (pentanes and heavier) are withdrawn via line 20, and effluent from separation zone 18, in line 21, constitutes unreacted isobutane from zone 14 together with propylene and butylene formed therein. Effluent from zone 18, in line 21, contains isobutane, propylene and butylene in relative ratios suitable for charging the last said effluent as sole feed to an alkylation system for conversion to hydrocarbons boiling in the gasoline range, and is passed to alkylation zone 22, preferably an HF-alkylation unit, and therein converted to hydrocarbons boiling in the gasoline range, i. e., by alkylation of isobutane with propylene and/or butylene.

The following conditions are exemplary of those employed in conducting alkylation in zone 22, when employing HF as the alkylation catalyst.

	Broad Range	Preferred Range
Temperature, ° F.....	50-150	75-100
Pressure.....	(1)	(2)
Isoparaffin/Olefin, Mol ratio.....	3:1 to 10:1	4:1 to 10:1
Hydrocarbon/HF, vol. ratio.....	4:1 to 1:4	1½:1 to 1:1½
Acid Composition, HF, wt. percent.....	85-95	90-95
Contact time, Minutes.....	5-25	10-15

¹ Sufficient to keep reactants liquid.

Total effluent from alkylation zone 22 is passed via line 24 to product separation means 25 comprising any desirable means for separating hydrofluoric acid and hydrocarbon phases, and for then fractionating hydrocarbon phase into desired alkylation products and lighter hydrocarbons. C₃ and lighter materials separated in zone 25 are withdrawn via line 26; a C₅ and heavier hydrocarbon fraction, well-balanced for use as motor fuel, particularly with reference to distillation range (distribution) volatility and octane number, is withdrawn via line 27; isobutane unreacted in zone 22 is withdrawn via line 16, and any normal butane present is withdrawn via line 12 or 12' or both. Isobutane in line 16, present as a result of in situ build-up of isobutane in zone 22 can be recycled if desired via line 10' to zone 14, and/or via line 23 to HF alkylation zone 22. Normal butane in line 12 can be withdrawn to storage by way of line 12' or passed together with normal butane from any outside source, if the latter is desired, to normal butane isomerization zone 13 and therein converted to isobutane which can then be charged to isobutane cracking zone 14 via lines 15 and 10'.

Normal butane isomerization conducted in zone 13 can be in accordance with any method known in the art for isomerizing normal butane to isobutane such as for example, isomerization in the presence of aluminum chloride as a catalyst.

Any known alkylation catalyst can be employed in zone 22, although as stated hereinabove it is preferred to use concentrated hydrofluoric acid or concentrated sulfuric acid as an alkylation catalyst. Among such alkylation catalysts that can also be employed in zone 22 are aluminum and zinc chlorides and bromides, mixed salts of aluminum chloride or bromide with various metal chlorides and bromides, such as an equimolar mixture of sodium and aluminum chlorides, boron fluoride, zirconium fluoride and the like. However, of these catalysts, sulfuric acid and concentrated hydrofluoric acid are preferred, because they appear to promote the union of propylene and butylenes with isobutane more selectively than other known alkylation catalysts.

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Data in the following tabulation show that, unexpectedly when cracking isobutane at elevated pressures in accordance with the present invention, yield of olefin is not substantially adversely affected.

Thus, in Table I are shown data obtained from cracking isobutane, demonstrating that no appreciable loss in olefin yield results from increasing the pressure of isobutane cracking from atmospheric to 200 p. s. i. g. at a given temperature and conversion level; the said tabulation also showing that at a given pressure and conversion, an increase in temperature within the cracking temperature range of this invention results in an increase in olefin yield.

TABLE I
Effect of temperature

Pressure, p. s. i. g.....	200	200	200
Temperature, ° F.....	1,200	1,250	1,300
Percent Conversion.....	50	50	50
Olefin Yield, lb./100 lb. i-C ₄ reacted:			
C ₃ H ₆	24.5	26.1	27.7
C ₄ H ₈	37.9	39.2	40.6
Total.....	62.4	65.3	68.3

Effect of pressure

Pressure, p. s. i. g.....	0	200	100	200	300
Temperature, ° F.....	1,200	1,200	1,250	1,250	1,250
Percent Conversion.....	50	50	50	50	50
Olefin Yield, lb./100 lb. i-C ₄ reacted:					
C ₃ H ₆	27.2	24.6	24.7	26.1	30.3
C ₄ H ₈	37.8	37.5	39.9	39.2	38.6
Total.....	65.0	62.1	64.6	65.3	68.9

Data obtained from isobutane cracking under process conditions of this invention are illustrated by way of the product yield curves, which show the olefin yields obtained at various conversion levels, at 1250° F. and 300 p. s. i. g. (Figure 2) and at 1300° F. and 200 p. s. i. g. (Figure 3).

The conversion levels required to give an isobutane cracking effluent stream containing isobutane, propylene and butylenes in relative proportions suitable for being directly charged as sole feed to the alkylation system are also the conversion levels at which ultimate yields of olefin are the highest.

Data obtained from cracking isobutane at 1250° F. and at 200 p. s. i. g., showing propylene and butylene yields at various conversion levels are tabulated in Table II and plotted in Figure 4.

TABLE II
Conversion of isobutane at 1250° F. and 200 p. s. i. g.,
Mols/100 mols

Percent Conv.	C ₃	C ₄	Total C ₃ +C ₄
57.8.....	31.5	40.8	72.3
55.7.....	32.2	37.2	69.4
63.2.....	35.1	37.8	72.9
34.2.....	46.7	42.8	89.5
45.0.....	42.6	42.6	85.2
48.5.....	39.4	43.0	82.4
62.0.....	38.0	37.7	75.7
62.4.....	37.6	34.2	71.8
63.2.....	37.0	34.3	71.3
64.1.....	36.6	35.8	72.4
36.2.....	39.7	42.7	82.4
42.9.....	41.1	41.1	82.2
43.3.....	41.4	40.8	82.2

In Table III and Figure 4 are data showing mol ratios of isobutane to olefin (propylene+butylene) obtained at various conversion levels when cracking isobutane at 1250° F. and 200 p. s. i. g.

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TABLE III

Mol ratio i-C₄ to olefin (propylene+butylene) at indicated conversion of isobutane

Percent Conversion	Mol Ratio i-C ₄ to olefin
20	4.2/1
30	2.6/1
40	1.8/1
50	1.3/1
60	0.90/1

Table IV is illustrative of product distribution of isobutane cracking in accordance with this invention at different conversion levels, particularly illustrating high propylene and butylene yields obtained over a broad range of conversions.

TABLE IV

Run	A	B
Temperature, ° F.	1,250	1,250
P. s. i. g.	200	200
Contact Time, Seconds	8.92	1.66
Conversion, Percent	63.2	34.2

MOLS PRODUCT/100 MOLS ISOBUTANE CONVERTED

Hydrogen	30.5	42.0
Methane	65.4	56.1
Ethylene	10.9	6.3
Ethane	3.4	0.8
Propylene	35.1	46.7
Propane	7.4	4.7
Butylene	37.8	42.8
Pentanes and heavier	4.8	0.6

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawings, and appended claims to the invention, the essence of which is that a process is provided for reacting isobutane at a pressure above about 80 p. s. i. g., generally from 125-500 p. s. i. g., so as to produce propylene and butylene in high ultimate yield under which conditions total effluent can be produced, which, subsequent to demethanization or de-ethanization, and depentanization when desired, is particularly applicable as sole feed to an alkylation system for conversion to isoparaffin hydrocarbons boiling in the gasoline range; in accordance with another concept, this invention providing for effecting the above-said de-ethanization at the substantially existing conversion pressure, thus eliminating necessity for pressurization to effect de-ethanization, and depentanization when desired; in accordance with another concept, this invention providing an integrated isobutane cracking-alkylation process, in which demethanized or de-ethanized effluent from isobutane cracking is charged, subsequent to depentanization, if desired, as sole feed to an alkylation system, preferably HF-alkylation, and converted therein to isoparaffins boiling in the gasoline range to form high quality motor fuels.

I claim:

1. An integrated cracking-alkylation process comprising passing isobutane into a cracking zone maintained at a temperature within the range of 1200-1350° F., under

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a pressure in the range of 150-300 p. s. i. g., for a period of time within the range of 0.2 to 12 seconds so as to maintain a per-pass conversion of isobutane within the range of 25-55 mol percent and thereby providing a total cracking effluent containing isobutane in a mol ratio to propylene plus butylene suitable for charging as the sole feed to an alkylation zone; passing total effluent from said cracking zone under substantially cracking pressure into a separation zone and therein separating, under said pressure, ethane and lighter materials, from said effluent; passing resulting de-ethanized effluent from said separation zone as sole feed to an alkylation zone and therein reacting same under alkylating conditions to produce normally liquid hydrocarbons boiling in the gasoline range, and recovering normally liquid hydrocarbons so produced as product of the process.

2. An integrated cracking-alkylation process comprising cracking isobutane at a temperature within the range of 1200-1350° F., at a pressure in the range of 150-300 p. s. i. g., for a period of time within the range of 0.2 to 12 seconds so as to (1) effect a per-pass conversion of isobutane of from 25-55 mol percent and (2) to provide total cracking effluent containing isobutane in a mol ratio to propylene plus butylene suitable for charging to an alkylation zone as the sole feed; passing total effluent from said cracking under substantially cracking pressure into a separation zone and therein separating, under said pressure, ethane and lighter materials and pentane and heavier materials from said total effluent; passing resulting de-ethanized and depentanized total effluent from said separation zone as sole feed to an alkylation zone and therein maintaining same in contact with liquid hydrofluoric acid under alkylating conditions to react isobutane with propylene and butylene to produce a motor fuel, and recovering motor fuel so produced.

3. An integrated cracking-alkylation process comprising passing isobutane into a cracking zone maintained at a temperature within the range of 1200-1350° F., under a pressure in the range of 150-300 p. s. i. g., for a period of time within the range of 0.2 to 12 seconds so as to (1) maintain a per-pass conversion of isobutane within the range of 25-55 mol percent and (2) to provide total cracking effluent containing isobutane in a mol ratio to propylene plus butylene suitable for charging as the sole feed to an alkylation zone; passing total effluent from said cracking zone under substantially cracking pressure into a separation zone and therein separating under said pressure, ethane and lighter materials from said effluent; passing resulting de-ethanized effluent from said separation zone as sole feed to an alkylation zone and therein reacting same under alkylating conditions to produce normally liquid hydrocarbons boiling in the gasoline range, recovering isobutane from effluent from said alkylation zone and recycling same to said cracking zone, and recovering normally liquid product from said alkylation zone.

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