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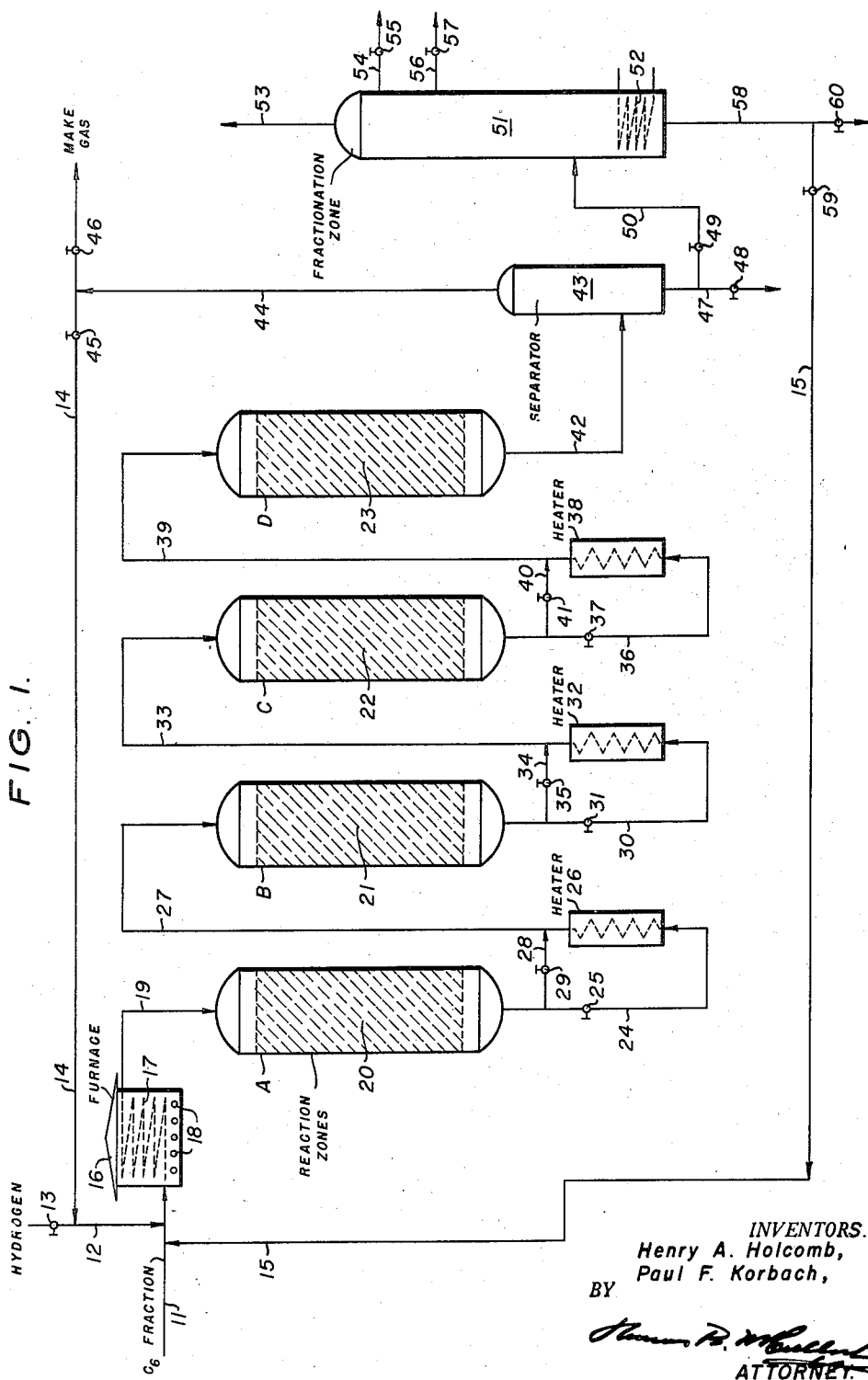
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2,863,826

CATALYTIC CONVERSION OF PARAFFINS

Filed Aug. 27, 1956

2 Sheets-Sheet 1



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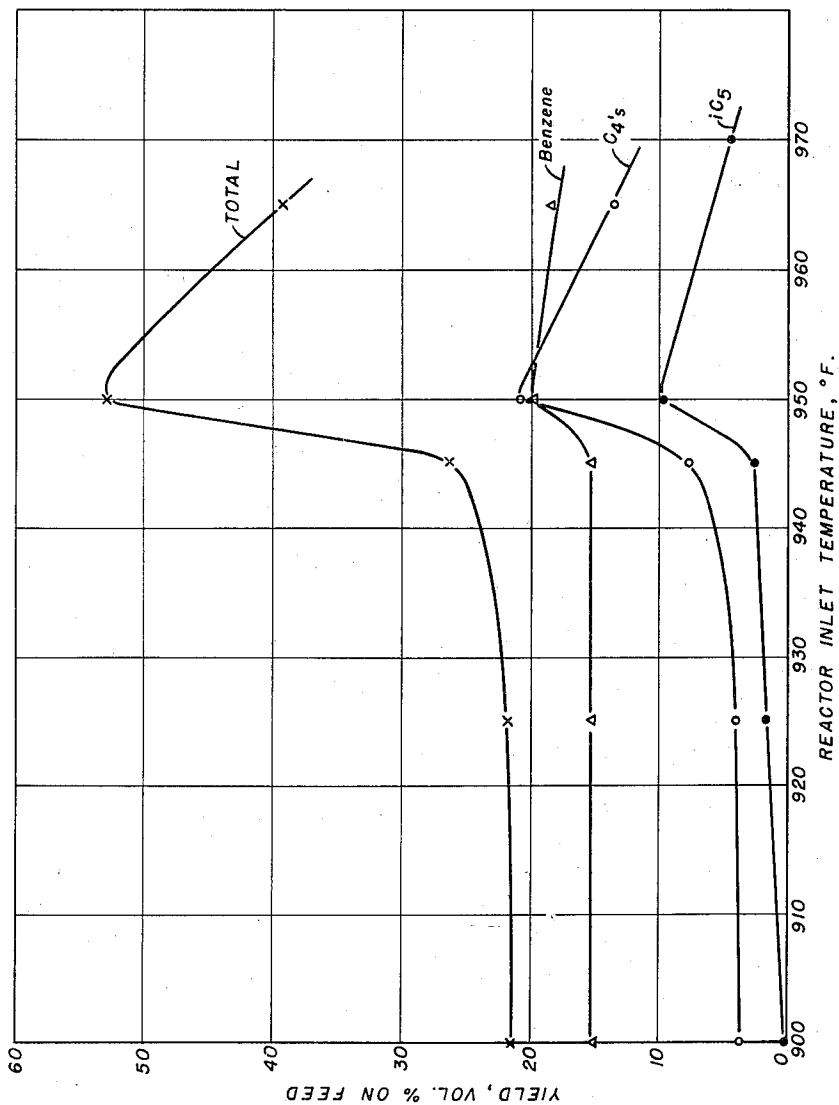
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FIG. 2.



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CATALYTIC CONVERSION OF PARAFFINS

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7 Claims. (Cl. 208—138)

The present invention is directed to a method for converting paraffins. More particularly, the invention is directed to a method of producing high yields of high octane number hydrocarbons from paraffinic hydrocarbons. In its more specific aspects, the invention is directed to converting paraffin hydrocarbons to major amounts of high octane number components.

The present invention may be briefly described as a method for producing high yields of high octane number hydrocarbons from paraffinic hydrocarbons boiling in the range from about 105° to about 180° F. The paraffinic hydrocarbons in this boiling range are contacted with a platinum catalyst at a temperature of 950° F. in the presence of a free hydrogen-containing gas and under conditions of pressure and space velocity to form a converted product containing a major amount of high octane number components. The high octane number components are recovered from the product.

The catalyst employed in the present invention is a platinum catalyst and preferably is a supported platinum on alumina catalyst. The amount of platinum on the catalyst is preferably 0.6% by weight but amounts of platinum in the catalyst from about 0.1% to 2.0% by weight may be employed. In some cases as much as 4.0% by weight may be used although the lesser range is preferred. The support is preferably highly purified aluminum oxide. The aluminum oxide may suitably be a gamma alumina or an eta alumina derived from conventional sources of alumina hydrates or from specially derived alumina hydrates, such as those obtainable from aluminum alcoholates, phenolates, etc.

The temperature employed in the practice of the present invention is critical and an inlet temperature of 950° F. must be employed to obtain maximum yields of high octane number components from the feed stock. Actually, because of the endothermic nature of the reaction, the average catalyst temperature in adiabatic reactors may be less than 950° F. However, it is important that the inlet temperature be at 950° F. for desirable results.

The feed stock is a paraffinic hydrocarbon fraction boiling in the range from 105° to 180° F. and preferably is a paraffinic fraction consisting of hydrocarbons having six carbon atoms in the molecule. The six carbon atom paraffinic hydrocarbons consist essentially of hexane and its isomers.

A feed stock suitable for the practice of the present invention may have the composition set out in Table I.

Table I

	Percent by volume
2,3-dimethyl butane	3.8
2-methyl pentane	6.6
3-methyl pentane	15.6
2,2-dimethyl butane	1.2
2,4-dimethyl pentane	3.0
Normal hexane	42.9
Cyclohexane	3.0
Methylcyclopentane	18.2
Benzene	5.7

100.0

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Pressure employed in the practice of the present invention may range from about 200 to about 500 pounds per square inch gauge. A suitable and preferred pressure is about 300 pounds per square inch gauge.

The space velocity is preferably about 2.0 volumes of feed hydrocarbon per volume of catalyst per hour. However, space velocities may range from about 0.5 to about 5.0 v./v./hr.

The presence of hydrogen is required in the practice of the present invention and a preferred amount of hydrogen is about 4000 cubic feet of hydrogen per barrel of feed. The amount of hydrogen may range from about 2000 to 6000 cubic feet per barrel of feed.

The reaction is preferably conducted in a plurality of reaction zones with the supported catalyst arranged in beds therein. However, it is to be understood that the operation may be conducted with a fluidized type operation wherein a fluidized powdered catalyst of the nature described is suspended in the vaporized hydrocarbon. The reaction may be conducted under adiabatic or isothermal conditions.

The invention will be further illustrated by reference to the drawing in which:

Fig. 1 is in the form of a diagrammatic flow sheet of a preferred mode; and

Fig. 2 is a plot of data illustrating the criticality of the temperature.

Referring now to the drawing, numeral 11 designates a feed line by way of which a C₆ paraffinic hydrocarbon fraction of the type illustrated is introduced into the system from a source not shown. A free hydrogen-containing gas is introduced into line 11 by way of line 12 from a source, not shown, by opening valve 13 or by way of line 14 connecting to line 12. The source of the free hydrogen-containing gas in line 14 will be described further hereinafter. Introduced also into line 11 by way of line 15 is a recycle fraction of unconverted hydrocarbons. The C₆ fraction admixed with hydrogen is heated to 950° F. or slightly higher, such that the inlet temperature to the reaction zone, which will be described further, will be at 950° F., in a furnace 16 provided with a coil 17 and with gas burners 18. While it may be desirable and preferable to heat the hydrogen and hydrocarbon feed separately, for purposes of this description and for illustration only, the hydrogen and hydrocarbon feed are shown as being heated in a common furnace 16. The heated mixture is discharged from furnace 16 by way of line 19 and is contacted in a plurality of reaction zones A, B, C, and D with a supported platinum catalyst arranged in beds 20, 21, 22, and 23 in the several reaction zones. In reaction zone A, the heated mixture at an inlet temperature of 950° F. contacts the supported platinum catalyst therein and the converted product issues from the reaction zone A by way of line 24 controlled by valve 25 and is routed through a heater 26 and thence by way of line 27 into reaction zone B in contact with the bed of supported catalyst 21. The heater 26 provides a sufficient amount of heat to the partially converted product such that the partially converted product contacts the catalyst bed 21 in reaction zone B at an inlet temperature of 950° F. A bypass line 28 controlled by valve 29 allows the heater 26 to be bypassed if it is unnecessary to reheat the product issuing from zone A by line 24.

Similarly, the product from zone B discharges therefrom by line 30 controlled by valve 31 and is circulated through a heater 32 and thence by way of line 33 into reaction zone C in contact with the bed 22 of supported catalyst. A bypass line 34 controlled by valve 35 allows the heater 32 to be bypassed if desirable. The further converted product from reaction zone C is discharged

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therefrom by line 36 controlled by valve 37 and is circulated through a heater 38 and thence by way of line 39 into zone D in contact with the bed 23 of the supported catalyst. A bypass line 40 controlled by valve 41 is provided to interconnect lines 36 and 39 around the heater 38.

The product from zone D is discharged therefrom by line 42 into separator 43 wherein a separation is made between the free hydrogen-containing gas and the converted product, the free hydrogen-containing gas being withdrawn from separator 43 by line 44 and introduced into line 14 for recycling to line 12 by opening valve 45 or if the amount of hydrogen exceeds the amount required for discharge from the system by opening valve 46.

The converted product may be withdrawn from separator 43 by line 47 controlled by valve 48 and employed as a blending agent in gasoline. Preferably, however, valve 48 remains closed and valve 49 in line 50 is opened and the converted product is discharged thereby into a fractionation zone 51 which may be a plurality of fractional distillation towers equipped with suitable vapor-liquid internal contacting means, such as bell cap trays and the like, to obtain a precise separation between the high octane number components and the unconverted feed. The distillation zone 51 is also provided with all auxiliary equipment necessary for making such precise separations. This auxiliary equipment may include means for inducing reflux, cooling and condensing means, and the like.

Conditions of temperature and pressure in zone 51 are adjusted by a heating means 52 which may be a steam coil to recover an overhead fraction by way of line 53 and side stream fractions by way of line 54 controlled by valve 55 and line 56 controlled by valve 57 as may be desired. As will be clear, the converted fraction may be separated into the components thereof or may be withdrawn as a single overhead fraction, as desired. The unconverted minor amount is discharged from zone 51 by line 58 and preferably is recycled to line 11 by way of line 15 by opening valve 59. However, the unconverted product may be discharged from the system by opening valve 60 in line 58.

It will be seen from the foregoing description taken with Fig. 1 that a simple and effective process is provided for converting paraffinic hydrocarbons.

In order to illustrate the invention further a number of runs were made with a feed stock as illustrated in Table I. This feed stock was contacted with a platinum on purified alumina catalyst which contained 0.6 weight percent of platinum at a space velocity of 2 v./v./hr., at a pressure of 300 pounds per square inch gauge, and in the presence of 4000 standard cubic feet of hydrogen per barrel. This hydrogen was recycled hydrogen. The feed stock was contacted with the catalyst in four equally packed adiabatic reactors arranged for sequential downflow.

Runs were performed at inlet temperatures of 800°, 900°, 925°, 945°, 950° and 965° F. with the results as shown in Table II:

Table II

Yield, Vol. Percent Fresh Feed	Reactor Inlet Temperature, °F.					
	800	900	925	945	950	965
iC ₄	0.1	2.2	2.3	4.0	1.6	7.2
nC ₄	0.3	1.5	1.6	3.3	19.3	6.2
iC ₅	0.2	1.8	1.4	2.5	9.8	4.4
Benzene	6.8	15.2	15.2	15.2	20.1	18.4
Toluene	0.1	.2	.3	.3	.6	.7
Other Aromatics5	.9	1.0	1.6	2.2
Total	7.5	21.4	21.7	26.3	53.0	39.1

From these results, it will be clear that a maximum yield comprising a major amount of desirable products was obtained at an inlet temperature of 950° F. It is

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to be noted that the yield of butanes, isopentane and benzene rose sharply to a maximum at 950° F. and fell sharply thereafter. In other words, these data show that an inlet temperature of 950° F. is critical for a feed stock of the nature described. The data in Table II are presented graphically in Fig. 2 which shows even more strikingly the criticality of the temperature.

In order to illustrate the effect of the improvement, the following values shown in Table III of research blending octane numbers (taken from API Project 45, 11th Annual Report (1950)) will illustrate the effectiveness of the present invention.

Table III

iC ₄	122
nC ₄	113
iC ₅	99
nC ₅	62
nC ₆	19
Benzene	99
Methylcyclopentane	107
Cyclohexane	110

Applying the data in Table III to the data in Table II, it may be shown, as set out in Table IV, that maximum yields of high octane number components are obtained at the 950° reactor inlet conversion operations.

Table IV

Material	Feed	800° F.	900° F.	950° F.
Vol. % on Feed Components having				
95+ Res. Cl. O. N.	26.9	23.1	23.8	51.5
Res. O. N.	105.6	105.3	103.5	105.2

It will be seen that at 950° F. conversion that 51.5 volume percent yield of the feed components having 95+ research clear octane number has been obtained. It will be seen from these data, shown in Fig. 2 and in the several tables, that a hexane-rich C₆ fraction may be converted or reformed at a critical temperature of 950° F. following which butanes, pentanes, and aromatics may be separated as high octane number material.

While the high octane number converted product is shown as being separated by fractional distillation, it is within the purview of this invention to use other separating means, such as adsorbents of the nature of molecular sieves in lieu of the fractional distillation zone. Illustrative adsorbents which may serve as molecular sieves are crystalline sodium and calcium aluminosilicates that have been heated to remove water of hydration.

The present invention is of considerable advantage and utility in that at a critical temperature of 950° F., it is possible to obtain maximum yields of high octane number components from C₆ fractions.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A method for producing high yields of high octane number hydrocarbons which comprises contacting a paraffinic hydrocarbon fraction boiling in the range from about 105° to about 180° F. with a platinum catalyst at a temperature of 950° F. in the presence of a free hydrogen-containing gas and at a pressure in the range from about 200 to about 500 pounds per square inch gauge and a space velocity in the range from about 0.5 to about 5.0 volumes of said hydrocarbon per volume of catalyst per hour to form a converted product containing a major amount of high octane number components, and recovering said components.

2. A method in accordance with claim 1 in which

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the paraffinic hydrocarbon fraction consists of hydrocarbons containing 6 carbon atoms in the molecule.

3. A method in accordance with claim 1 in which the paraffinic hydrocarbon consists essentially of hexane and its isomers.

4. A method in accordance with claim 1 in which the catalyst is platinum on alumina.

5. A method in accordance with claim 1 in which the catalyst is a supported catalyst.

6. A method in accordance with claim 1 in which the catalyst is platinum on purified alumina containing an amount of platinum within the range from about 0.1% to about 4.0% by weight.

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7. A method in accordance with claim 1 in which the catalyst is platinum on gamma alumina containing an amount of platinum within the range from about 0.1% to about 2.0% by weight.

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