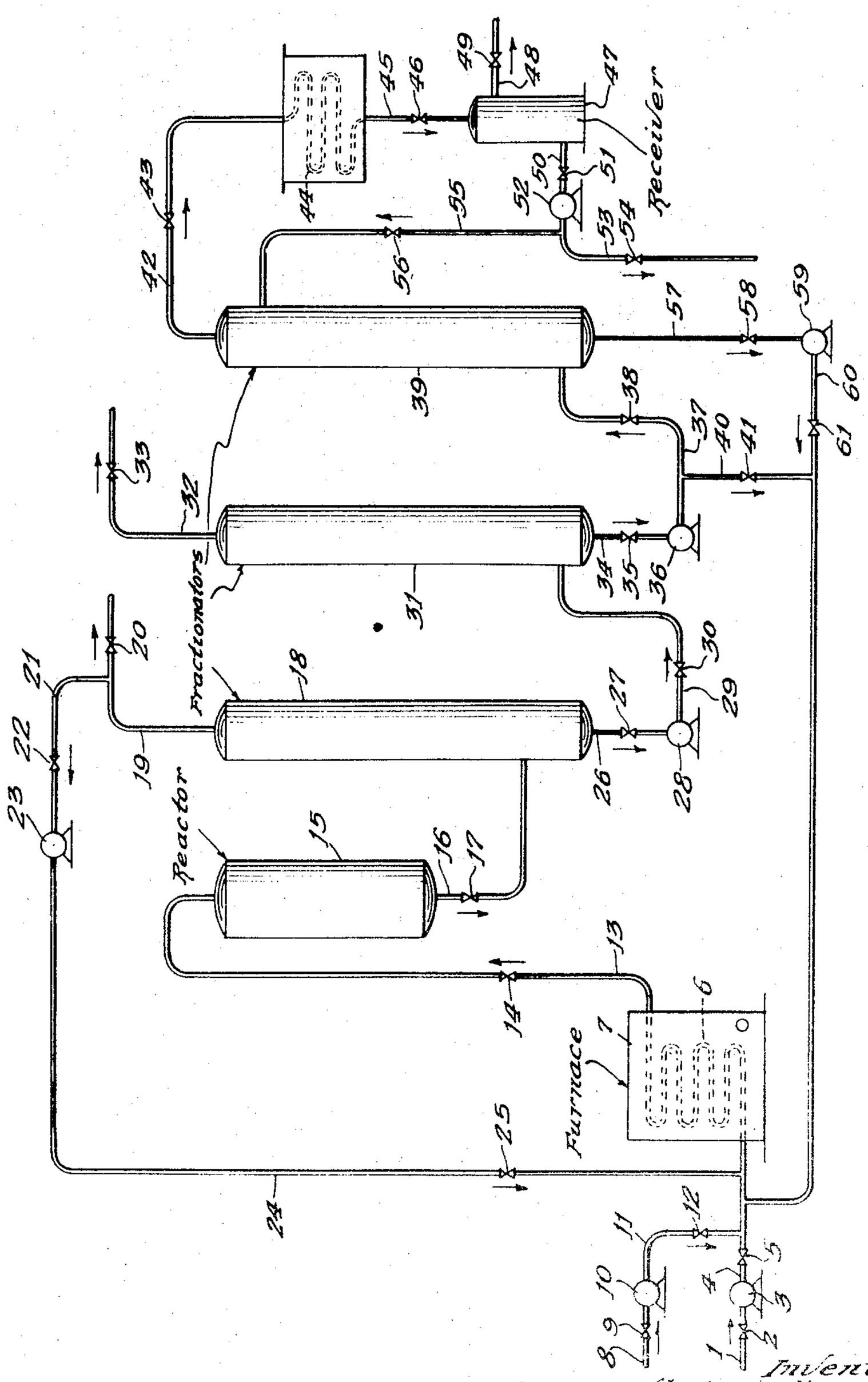
May 18, 1948. V. HAENSEL ET AL 2,441,663

PROCESS FOR PURIFYING SATURATED HYDROCARBONS INVOLVING SELECTIVE DEMETHYLATION

Filed Sept. 21, 1946



Inventors
Vladimir Haensel
Vladimir N. Ipatieff
By Maynard P. Venema
Attorney

Patented May 18, 1948 2,441,663

UNITED STATES PATENT OFFICE

2,441,663

PROCESS FOR PURIFYING SATURATED HYDROCARBONS INVOLVING SELECTIVE DEMETHYLATION

Vladimir Haensel, Clarendon Hills, and Vladimir N. Ipatieff, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application September 21, 1946, Serial No. 698,442

7 Claims. (Cl. 260—666)

1

This application is a continuation-in-part of our co-pending application Serial No. 508,278, filed October 30, 1943, now abandoned.

This invention relates to a process for purifying hydrocarbons. More specifically, the invention is concerned with a method for increasing the concentration of a difficultly demethylatable hydrocarbon in a narrow boiling range mixture with a more readily demethylatable hydrocarbon.

An object of this invention is the production of a difficultly demethylatable saturated hydrocarbon from a narrow boiling range hydrocarbon mixture containing said saturated hydrocarbon.

Another object of this invention is the treatment of a narrow boiling range hydrocarbon fraction containing a difficultly demethylatable saturated hydrocarbon by reacting said fraction and hydrogen in the presence of a hydrogenation catalyst at a temperature of from about 150° to about 350° C. and at which the more readily demethylatable hydrocarbons are demethylated more rapidly than the described saturated hydrocarbons.

A further object of this invention is the treatment of a narrow boiling heptane fraction containing a major proportion of triptane with hydrogen in the presence of a hydrogenation catalyst at conditions of operation at which triptane undergoes demethylation to only a small extent but at which other branched chain heptanes of closely related boiling points are demethylated substantially to paraffinic hydrocarbons of lower molecular weight, and separating said paraffinic hydrocarbons by fractional distillation from a higher boiling fraction containing a greater concentration of triptane than present in the heptane fraction charged to the process.

A still further object of this invention is the treatment with hydrogen of a saturated hydrocarbon fraction of narrow boiling range containing a major proportion of cyclohexane and smaller proportions of methyl cyclopentane, dimethyl pentanes and methyl hexanes in the presence of a hydrogenation catalyst at conditions of operation at which cyclohexane undergoes demethylation to only a small extent but at which the other saturated hydrocarbons admixed therewith are demethylated to saturated hydrocarbons of lower molecular weights and separating the said saturated hydrocarbons of lower molecular weight from a higher boiling fraction containing a greater concentration of cyclohexane than present in the saturated hydrocarbon fraction charged to the process.

One specific embodiment of the present invention comprises a process for increasing the concentration of a difficultly demethylatable hydrocarbon in a narrow boiling range mixture with a more readily demethylatable hydrocarbon which comprises subjecting said mixture to reaction with hydrogen in the presence of a hydrogenation catalyst at a temperature of from about 150° C. to about 350° C. to convert a substantial portion, at least, of said more readily demethylatable hydrocarbon into lower boiling hydrocarbon, and fractionating the thus treated mixture to separate said lower boiling hydrocarbons from the unconverted difficultly demethylatable hydrocarbon.

2

Another embodiment of this invention comprises a process for increasing the concentration of a difficultly demethylatable saturated hydrocarbon in a narrow boiling range mixture with a more readily demethylatable saturated hydrocarbon, which comprises subjecting said mixture to reaction with hydrogen in the presence of a hydrogenation catalyst at a temperature of from about 150° C. to about 350° C. to convert a substantial portion, at least, of said more readily demethylatable saturated hydrocarbon into lower boiling saturated hydrocarbons, and fractionating the thus treated mixture to separate said lower boiling saturated hydrocarbons from the unconverted difficultly demethylatable saturated hydrocarbon.

A further embodiment of this invention comprises a process for increasing the concentration of a difficultly demethylatable saturated hydrocarbon in a narrow boiling range mixture with a more readily demethylatable saturated hydrocarbon, which comprises subjecting said mixture to reaction with hydrogen in the presence of a nickel catalyst at a temperature of from about 150° C. to about 350° C. to convert a substantial portion, at least, of said more readily demethylatable saturated hydrocarbon into lower boiling saturated hydrocarbons, and fractionating the thus treated mixture to separate said lower boiling saturated hydrocarbons from the unconverted difficultly demethylatable saturated hydrocarbons.

We have found that alkanes, alkenes, alkylcycloalkanes, and alkyl aromatic hydrocarbons may be demethylated to saturated and aromatic hydrocarbons containing at least one carbon atom less than is present in the hydrocarbon charged to the process. This demethylation process comprises the treatment of a hydrocarbon or mixture of hydrocarbons of the above-named classes with hydrogen, or with a mixture of hydrogen and methane, in the presence of a hydrogenation

catalyst at a temperature of from about 150° to about 350° C. so maintained that methane is formed in approximately equivalent molecular proportion to the hydrogen consumed during the reaction. This process effects the removal of methane usually from the longest and least branched alkyl groups present in the hydrocarbon undergoing treatment. The more highly methylated hydrocarbons such as the polymethylalkanes are thus more stable under demethylating conditions than are other hydrocarbons with more nearly straight chain structures and, accordingly, we have found it possible to retreat a fraction containing more highly methylated hydrocarbons with hydrogen in another reactor containing a hydrogenation catalyst to obtain a hydrocarbon product containing a still higher concentration of polymethylated hydrocarbons. The reaction products from such a treating step are then separated by fractional distillation from incompletely converted hydrocarbons, and the latter are then recycled to further demethylation treatment.

By an alternative type of treatment, we are also able to obtain a fraction containing a high concentration of highly methylated hydrocarbons from a mixture of demethylation products and unconverted hydrocarbons. In order to obtain a small fraction containing a relatively high concentration of the desired demethylated hydrocarbons, the low boiling hydrocarbons are removed from the demethylation reaction product by fractional distillation, and a part of the distillation residue consisting of a mixture of the desired demethylated hydrocarbons and unconverted hydrocarbons is recycled to further demethylation treatment. The other portion of said distillation residue is subjected to another distillation whereby desired demethylated hydrocarbons are recovered from unconverted hydrocarbons, and the latter are also recycled to further demethylation treatment.

The attached drawing shows diagrammatically an arrangement of apparatus utilized in the production of a triptane fraction containing a relatively high concentration of this desirable difficulty demethylatable paraffinic hydrocarbon. Other types of apparatus may be employed alternately, and these various types of apparatus may also be utilized for treating other hydrocarbon fractions to increase their content of difficulty demethylatable hydrocarbons and accordingly the following description of the illustrative drawing is not limited to the treatment of trimethylpentanes to produce triptane.

A mixture of 2,2,3- and 2,3,4-trimethylpentane which is used as charging stock in the production of triptane is introduced through line 1 and valve 2 to pump 3 which discharges through line 4 and valve 5 into coil 6 which is heated by furnace 7. Simultaneously, hydrogen or a mixture of hydrogen and methane is directed through line 8 and valve 9 to compressor 10 which discharges through line 11 and valve 12 into line 4 and thence to coil 6, already mentioned. The mixture of hydrogen and trimethylpentane hydrocarbons which is so heated to a chosen reaction temperature is then directed from coil 6 through line 13 and valve 14 to reactor 15 containing a demethylation catalyst of the type herein described. The temperature of the catalyst in reactor 15 is maintained substantially constant by suitable means, such as the use of a heat transfer liquid such as tetralin in a jacket surrounding reactor 15. For example, use of such a jacketed reactor containing tetralin maintained under a particular vapor pressure serves as a means of accurately maintaining a desired temperature even though a considerable amount of heat is evolved as is true with the demethylation reaction.

From reaction 15 the reaction mixture of hydrocarbons and gases, the latter comprising essentially hydrogen and methane, is directed through line 16, and valve 17 to fractionator 18 of suitable design by which a mixture of hydrogen and methane is separated from normally liquid hydrocarbons. Said mixture of hydrogen and methane is discharged from fractionator 18 through line 19 containing valve 20 to waste, storage, or other use not illustrated in the drawing, but at least a portion of the mixture of hydrogen and methane which is being discharged through line 19 is directed therefrom through line 21 and valve 22 to compressor 23 which discharges through line 24 and valve 25 into line 4, already mentioned, through which the fresh hydrocarbon charging stock and hydrogen-methane mixture are charged to the process.

From fractionator 18 the mixture of normally liquid hydrocarbons is withdrawn through line 26 and valve 27 by pump 28 which discharges through line 29 and valve 30 into fractionator 31 in which low boiling liquid hydrocarbons are separated from a mixture of heptanes and unconverted trimethylpentane hydrocarbons. The vapors of the low boiling liquid hydrocarbons are discharged from fractionator 31 through line 32 and valve 33 to condensation and cooling not illustrated in the diagrammatical drawing. The higher boiling mixture of heptanes and unconverted trimethylpentane hydrocarbons is directed from fractionator 31 through line 34 and valve 35 to pump 36 which discharges through line 37 and valve 38 into fractionator 39.

A portion of the mixture of heptanes and unconverted trimethylpentane hydrocarbons being transmitted through line 37 is directed therefrom through line 40 and valve 41 to recycle line 60 and thence to line 4, already mentioned, through which the fresh trimethylpentane fraction is charged to the process. By proper regulation of valve 38, it is possible to control the amount of the hydrocarbon mixture to be returned through lines 40 and 60 to further demethylation treatment. The remainder of the mixture of demethylation product and unconverted trimethylpentane hydrocarbons which is directed to fractionator 39 is therein fractionally distilled and separated into demethylation products and unconverted trimethylpentanes. Vapors of the demethylation products are directed from near the top of fractionator 39 through line 42 and valve 43 to condenser 44 from which the condensed liquid hydrocarbons are directed through run-down line 45 and valve 46 to receiver 47 provided with conventional gas release line 48 containing valve 49. From near the bottom of receiver 47 the liquid demethylation product is directed through line 50 and valve 51 to pump 52 which discharges through line 53 and valve 54 to storage not illustrated in the drawing. In order to assist in controlling the temperature in fractionator 39 a portion of the demethylation product is directed from line 53 through line 55 and valve 56 to near the top of fractionator 39 to serve as reflux liquid therein. From near the bottom of fractionator 39 the higher boiling unconverted trimethylpentane hydrocarbons are withdrawn through line 57 and

valve 58 by pump 59 which discharges through line 60 and valve 61 into line 4, already mentioned. As hereinabove described, a portion of the mixture of demethylation products and unconverted trimethylpentane hydrocarbon withdrawn from the bottom of fractionator 31 is also recycled by way of lines 34, 37, 40 and 60 to line 4.

Hydrogenation catalysts useful in our hydrocarbon purification process comprise those catalysts which are commonly effective in the hydrogenation of olefinic hydrocarbons to paraffinic hydrocarbons. The hydrogenation catalysts which we prefer in our process comprise the metals and oxides of metals of the iron group and particularly nickel and cobalt. The metals iron, nickel, and cobalt or their oxides may be used as such, but they are preferably supported by a carrier such as alumina, silica, diatomaceous earth, crushed porcelain, or some other refractory material which has substantially no adverse influence on the demethylation reaction. In some instances, it is also desirable to composite one or more of the metals of the iron group or their oxides with freshly reduced copper to form a catalyst which is particularly active at relatively low reaction temperatures. Other hydrogenation catalysts useful in our process comprise platinum, palladium, and also the oxides and sulfides of elements selected from the metals of the left hand column of groups 5 and 6 of the periodic table and particularly the oxides and sulfides of vanadium, chromium, molybdenum, tungsten, and uranium.

A highly active nickel catalyst which we have used in the present process contains approximately 66% by weight of total nickel, 30% of diatomaceous earth, and 4% of oxygen, the latter present as nickel oxide. This catalyst is made by the general steps of suspending diatomaceous earth, also known as kieselguhr, in a dilute aqueous solution of nickel sulfate and then gradually adding thereto an excess of a hot saturated solution of sodium carbonate. This mixture of nickel sulfate soluton and diatomaceous earth is agitated vigorously while the sodium carbonate solution is introduced thereto to form a precipitate which is then removed by filtration, washed, dried, and reduced with hydrogen.

The resultant nickel-diatomaceous earth catalyst is employed in powder form when demethylation is effected in batch type treatment or with fluidized catalyst. When pelleted or formed catalyst particles are desired, the powdered mixture, preferably before being subjected to reduction with hydrogen, is mixed with graphite or some other lubricant and formed into pellets by a pilling machine. Other nickel-containing catalysts which may be employed similarly may be prepared to contain proportions of nickel different from those aforementioned.

Cobalt catalysts are produced by essentially the same series of steps as were used in producing nickel-diatomaceous earth catalyst composites. Diatomaceous earth and cobalt nitrate so proportioned as to give essentially the same ratio of cobalt to silica as of nickel to silica in the above described catalyst, were mixed with water and then treated with an excess of a hot saturated solution of sodium carbonate. The mixture of cobalt nitrate solution and diatomaceous earth suspended therein was agitated vigorously while the sodium carbonate solution was added thereto to form a precipitate which was then removed by filtration and washed, dried, and reduced to give an active cobalt-diatomaceous earth catalyst, utilizable in the form of powder or pellets in essentially the same manner as the nickel-diatomaceous earth catalyst.

In order to obtain relatively high yields of desired demethylation products from a higher boiling saturated or aromatic hydrocarbon charging stock, it is necessary to carry out the process under correlated conditions of temperature, pressure, and partial pressure of hydrogen. With such correlated operating conditions, demethylation of the saturated hydrocarbons occurs as the principal reaction of the process. We have also found that the temperature of the demethylation reaction is controlled more readily when the partial pressure of hydrogen does not undergo considerable change throughout the reaction zone. Thus the normal excess of hydrogen relative to the hydrocarbon undergoing treatment appears to assist in dissipating the relatively high exothermic heat of reaction. The addition of methane and recycling of methane-hydrogen mixtures are other means of controlling the reaction temperature.

The following examples are given to illustrate the process of the invention although with no intention of unduly limiting the broad scope of the invention.

EXAMPLE I

A heptane fraction containing approximately 74% of triptane and 26% of essentially 2,2-dimethylpentane and 2,4-dimethylpentane was mixed with hydrogen and passed through a layer of granular nickel-diatomaceous earth catalyst contained in a steel reactor maintained at a temperature of 279° C. and at a pressure of 14.5 atmospheres. The heptane fraction which was charged at a rate of 1.7 liquid volumes per hour per volume of catalyst was thus treated with 4 molecular proportions of hydrogen and a liquid product was obtained in a yield of about 94% by volume of the heptane fraction charged to the process. Distillation of the recovered liquid products separated therefrom 25.6% by volume of hydrocarbons boiling below 75° C. and 74.4% of higher boiling hydrocarbons with a refractive index, n_D^{20}, of 1.3880. The 74.4% of higher boiling hydrocarbons crystallized upon being cooled to −78° C. and, accordingly, contained at least 83% of triptane as it is known that at least 83% of triptane must be present in a heptane fraction before it will freeze at −78° C.

Upon the basis of our experimental results, we have calculated that 16.5% of the triptane and 51.5% of the other heptanes present in the triptane fraction demethylated in the above-mentioned run.

These results show that it is possible to remove less branched hydrocarbons from a mixture with more branched hydrocarbons and thereby to concentrate the more highly branched hydrocarbons into a single fraction. As herein described, this reaction is not limited to a mixture of paraffinic hydrocarbons but is also applicable to a mixture of paraffins and cycloparaffins.

EXAMPLE II

A fraction containing about 74% of triptane and 26% of dimethylpentanes, namely, 2.2- and 2,4-dimethylpentane, was mixed with hydrogen and subjected to demethylation treatment at 282° C. catalyst temperature and at a pressure of 14 atmospheres in the same apparatus and in the presence of the catalyst as referred to in Ex-

ample I. Results of this run (run No. 2) are given in Table I which also contains experimental results obtained by recycling the product to further demethylation treatment in the presence of the same catalyst.

TABLE I

Treatment of triptane-dimethylpentane mixture with hydrogen in the presence of a nickel-diatomaceous earth catalyst

Run No.	2	3	4	5
Hydrogen: Heptane molar ratio	3.6	3.5	2.7	3.1
Hourly liquid space velocity of heptane	1.7	1.6	2.0	1.8
Duration of run, hours	28	3.2	6.4	2.8
Product:				
Vol. percent yield based on charge	96.0	97.5	97.0	94.0
Percent distilling below 75° C.	19.0		19.3	
Percent residue	81.0		80.7	
Triptane content of charge	74		83	
Triptane content of residue	83		91	
Exit gas, volume percent:				
Percent Hydrogen	91.7		------	
Percent methane	6.9		------	
Percent nitrogen	1.2		------	
Demethylation of triptane, percent	10.5		11.6	
Demethylation of the dimethylpentanes, percent	43.1		57.0	

The results given in Table I show that the triptane concentration was increased in the mentioned heptane fraction, particularly since the impurities, namely, 2,2- and 2,4-dimethylpentanes, are demethylated at about 4 to 5 times the rate of demethylation of the more highly branched hydrocarbon, triptane. The concentration of triptane in the reaction product was thus increased from 74 to 91% in two passes over the demethylation catalyst.

The lower boiling hydrocarbon fractions produced in the demethylation treatments indicated in Table I represented about 19% of the reaction product and had the following composition:

	Per cent by volume
Condensible gas (butanes and neopentane)	4.6
Isopentane	8.2
Neohexane	60.2
2,3-Dimethylbutane and 2-methylpentane	27.0
Total	100.00

EXAMPLE III

A sample of technical cyclohexane containing approximately 89% of cyclohexane and 11% of a mixture of 2,4-dimethylpentane, 2,2-dimethylpentane, 3-methylhexane, normal hexane and methylcyclopentane was subjected to fractional distillation. Approximately 3% of the material boiled below 79° C. and about 95% distilled in the range of 79 to 81° C. A fraction taken at about the midpoint of the 79—81° C. plateau had a refractive index, n_D^{20}, of 1.4239 and a melting point of —1.6° C. Another sample of the original technical cyclohexane was then passed over a nickel on kieselguhr catalyst at 299° C. and 14.6 atmospheres in the presence of 4.1 moles of hydrogen per mole of hydrocarbon. The space velocity employed was 1 volume of liquid charge per volume of catalyst. 97.4% by volume of the liquid charge was recovered and subjected to fractional distillation. Approximately 18% of the product boiled below 79° C. and the remainder distilled in the range of 79 to 80.5° C. A fraction taken at about the midpoint of the 79–80.5° C. plateau had a refractive index, n_D^{20}, of 1.4253 and a melting point of +2.5° C. Another cut boiling at 80.5° C. had a refractive index, n_D^{20}, of 1.4260 and a melting point of +4.7° C. On the basis of the refractive indices and melting points, the calculated purity of the fraction distilled from the original charge was 92% while the two cuts obtained from the product had purities of 97 and 98.8% respectively.

We claim as our invention:

1. A process for increasing the concentration of triptane in a mixture of the latter with 2,2-dimethylpentane and 2,4-dimethylpentane, which comprises subjecting said mixture to reaction with hydrogen in the presence of a hydrogenation catalyst at a temperature of from about 150° C. to about 350° C. to convert a substantial portion, at least, of said dimethylpentanes into lower boiling hydrocarbons, and fractionating the thus treated mixture to separate said lower boiling hydrocarbons from the unconverted triptane.

2. The process as defined in claim 1 further characterized in that said catalyst comprises a metal of the iron group.

3. The process as defined in claim 1 further characterized in that said catalyst comprises nickel.

4. A process for increasing the concentration of cyclohexane in a narrow boiling range mixture of the latter with methylcyclopentane, dimethylpentanes, and methylhexane which comprises subjecting said mixture to reaction with hydrogen in the presence of a hydrogenation catalyst at a temperature of from about 150° C. to about 350° C. to convert a substantial portion, at least, of said methylcyclopentane, dimethylpentanes, and methylhexane into lower boiling hydrocarbons, and fractionating the thus treated mixture to separate said lower boiling hydrocarbons from the unconverted cyclohexane.

5. The process as defined in claim 4 further characterized in that said catalyst comprises a metal of the iron group.

6. The process as defined in claim 4 further characterized in that said catalyst comprises nickel.

7. A process for the treatment of a hydrocarbon mixture comprising 2,2-dimethylpentane, 2,4-dimethylpentane and a saturated hydrocarbon selected from the group consisting of triptane and cyclohexane to increase the concentration of said saturated hydrocarbon; said process comprising subjecting said mixture to reaction with hydrogen in the presence of a hydrogenation catalyst at a temperature of from about 150° C. to about 350° C. to convert a substantial portion, at least, of said dimethylpentanes into lower boiling hydrocarbons, and fractionating the thus treated mixture to separate said lower boiling hydrocarbons from the unconverted portion of said saturated hydrocarbon.

VLADIMIR HAENSEL.

VLADIMIR N. IPATIEFF.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,303,118	Frey	Nov. 24, 1942
2,342,074	Deanesly et al.	Feb. 15, 1944

OTHER REFERENCES

Zelinsky et al., Jour. Ind. Eng. Chem., vol. 27, 1209–11 (1935).

Kazansky et al., Comptes Rendus (Doklady) de l'Acad. des Sci. de l'U. R. S. S., vol. XXV, No. 7, 596–7 (1939).