

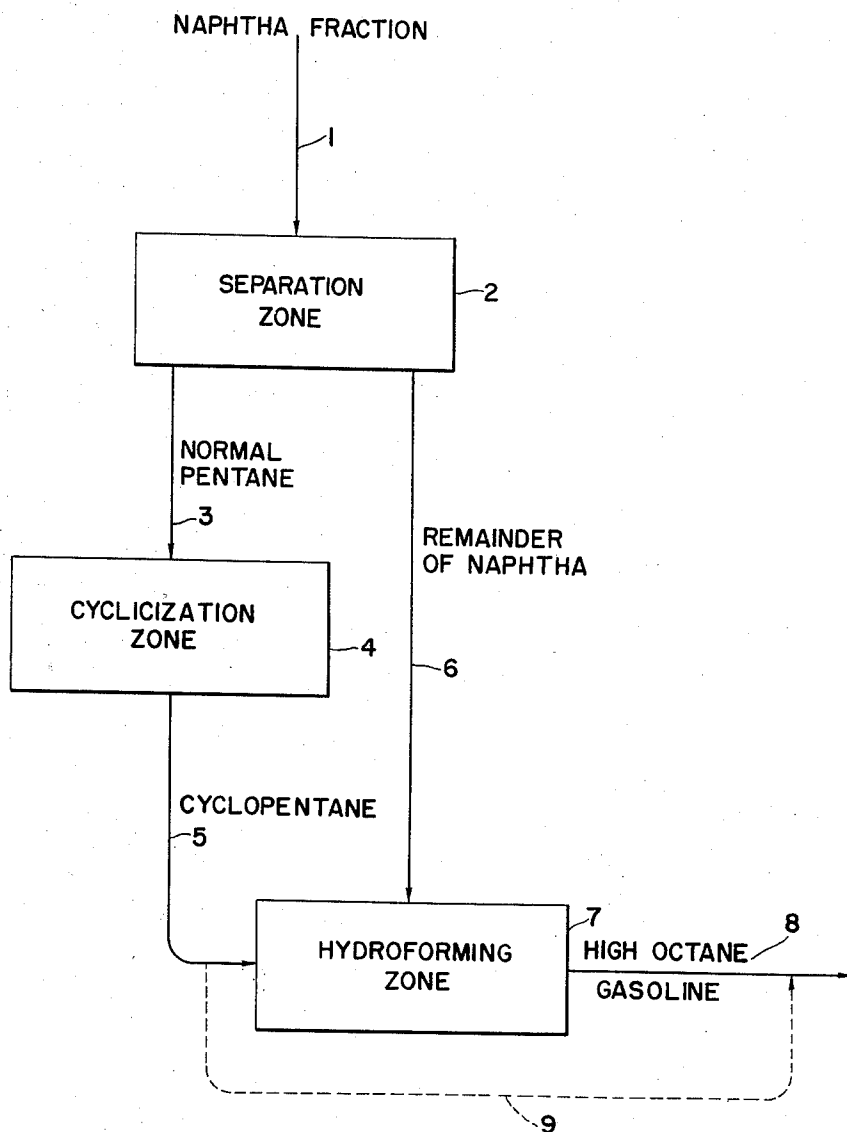
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CYCLIZATION OF ALIPHATIC HYDROCARBONS

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CYCLIZATION OF ALIPHATIC HYDROCARBONS

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19 Claims. (Cl. 260-666)

This invention relates to the cyclization of acyclic hydrocarbons, and more particularly, it pertains to a method of producing cyclopentane and/or substituted cyclopentane from acyclic hydrocarbons.

Cyclopentane and/or alkyl substituted cyclopentane are useful as motor fuels, or in the case of the substituted cyclopentanes, they can be used as starting materials for the production of aromatics. Although these cyclic compounds have particular use in the petroleum field, thus far their exploitation has been limited by virtue of the absence of a satisfactory method of manufacture. By means of this invention, it is proposed preparing these cyclic compounds by a method which is commercially attractive.

An object of this invention is to provide a method of producing cyclopentane and/or the alkyl substituted derivatives thereof.

Another object of this invention is to cyclicize acyclic hydrocarbons for the production of cyclopentane and/or alkyl substituted cyclopentanes.

Still another object of this invention is to cyclicize a low boiling fraction of petroleum naphtha and subject the resulting cyclic product to hydroforming treatment.

Other objects and advantages of this invention will become apparent from the following description and explanation thereof.

By means of this invention, it is contemplated cyclizing an acyclic hydrocarbon by the method which comprises subjecting said hydrocarbon to treatment with a catalyst containing about 1 to about 50% by weight of platinum, at a temperature of about 250° to about 420° C., preferably, about 300° to about 380° C., a pressure of about 1 atmosphere to about 200 p. s. i. g., a weight space velocity of about 0.001 to about 2 and for a period sufficient to produce a cyclopentane compound. It should be understood for purposes of this specification and the appended claims that the expression "cyclopentane compound" covers generically cyclopentane and alkyl substituted cyclopentane.

The starting material to be used for the preparation of the cyclopentane compound is an acyclic hydrocarbon containing at least five carbon atoms and the starting compound can have up to about fifteen carbon atoms. The cyclopentane compound is readily prepared from acyclic hydrocarbons containing five to about nine carbon atoms. The lower molecular weight hydrocarbons can be obtained as single compounds or as mixtures thereof from petroleum stocks, e. g., naphtha. The higher molecular weight hydrocarbons can also be used as single compounds or as mixtures of varying chain length, and these can be obtained from petroleum stocks. In one aspect of this invention, it is contemplated subjecting a naphtha fraction to a separation treatment whereby a C₅ and/or C₆ fraction is removed therefrom, and this fraction is treated in accordance with the method of this invention prior to being charged to a hydroforming operation for the production of aromatics. Alternatively, the cyclopentane compound can be blended with

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the reformed product to produce a finished material of improved quality. In any event, the starting material for the production of cyclopentane compounds can be a straight chain material, isomers thereof, or mixtures of the foregoing in the same or varying chain lengths. For reasons explained hereinafter, it is preferred to use saturated acyclic hydrocarbons as starting materials, however, mixtures of olefins and saturated hydrocarbons can be used with less satisfactory results.

The invention, as illustrated in the single figure drawing, may be represented by a naphtha fraction which is passed through line 1 into a separation zone 2, wherein normal pentane or some other acyclic hydrocarbon is separated from the remainder of the naphtha and withdrawn through line 3. The normal pentane is passed to a cyclization zone wherein it is contacted with a catalyst containing 1 to 50 percent by weight of platinum at a temperature of about 250° C. to about 420° C., a pressure of about 1 atmosphere to about 200 p. s. i. g., a weight space velocity of about 0.001 to about 2 and for a period of time sufficient to produce a cyclopentane compound. The cyclopentane compound is withdrawn through line 5.

The remainder of the naphtha is passed through line 6 to hydroforming zone 7 wherein it is treated to produce the high octane gasoline which is withdrawn through line 8. The cyclopentane product in line 5 is also usually introduced into the hydroforming zone 7, although if desired it may bypass the hydroforming zone 7 through line 9 and may be blended directly with the high octane gasoline in line 8.

The catalyst employed for this invention comprises about 1 to about 50% by weight of platinum supported on an adsorptive carrier material. Preferably, the platinum compound is about 5 to about 25% by weight of platinum, based on the total weight of the catalyst. The adsorptive carrier material can be, for example, an inorganic metal oxide gel, e. g., alumina, silica, etc., or charcoals derived from animal or vegetable matter. The charcoals are the best suited support material for the catalyst by reason of their high adsorptivity. The charcoals are employed in the activated form and comprise, for example, coconut carbon, norite, etc. It appears that the cyclization reaction is best catalyzed by a support material which possesses high adsorptivity, apparently for the reason that it furnishes better contact between the catalytic metal, platinum, and the acyclic hydrocarbon than is possible with less adsorptive carrier materials. The charcoals appear to have the best carrier material properties from this standpoint, as shown by the yield of cyclopentane. However, it should be understood that this theory is advanced as a possible explanation, and it should not be interpreted as a limitation on the scope of this invention.

The catalyst is prepared by combining a platinum compound, e. g., chloroplatinic acid, platonic chloride, platinum sulfide, platinum ammine complex, platinum polysulfide, etc., with the carrier material and decomposing the platinum compound to a metallic residue. The decomposition reaction can be effected by calcination or reduction. The calcination treatment involves heating the catalyst mixture to a temperature of at least about 400° F., more usually, about 600° F. to about 1450° F., and for a period of about 1 to 15 hours, more usually, about 2 to 8 hours. The reduction reaction can be effected with citric acid, hydrogen or hydrazine, or other reducing agents in general, particularly those of gaseous form. It is preferred to employ a hydrogen containing gas for the reduction reaction, because this material furnishes an excellent catalyst. Prior to the decomposition reaction, it may be desirable to dry the catalyst mixture in order to remove any water which is present by reason of the

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method of combining the ingredients. The drying step can be conducted at a temperature of about 150° to about 400° F., more usually, about 175° to about 300° F., and for a period of about 3 to about 60 hours.

The temperature at which the cyclization reaction takes place is in the range of about 250° to about 425° F., preferably, about 300° to about 380° F. As the temperature is raised above the preferred upper limit there is a noticeable drop in yield of cyclopentane compound, hence, indicating that the cyclization reaction is definitely favored by lower temperatures than are normally encountered in conventional hydroforming. Within the temperature range described above, the cyclization reaction can be effected at pressures, e. g., about 1 to about 70 p. s. i. a., preferably, about 14 to about 40 p. s. i. a. The quantity of hydrocarbon feed processed relative to the amount of catalyst present in the reaction zone is measured on a weight space velocity, defined as the pounds of liquid feed charged to the reaction zone on an hourly basis per pound of catalyst present therein. The weight space velocity varies from about 0.001 to about 2, preferably, about 0.1 to about 0.5. The conditions given above apply to a fixed bed system or a moving bed system. In the case of a fixed bed system, the reaction period varies from about 0.5 to 100 hours, more usually, about 2 to about 36 hours. A moving bed system involves a catalyst to oil ratio of about 0.001 to about 5. The unreacted acyclic hydrocarbon can be recycled to the cyclization zone in any amount which is desired.

The catalyst may lose activity after processing for a given period of time and the activity can be restored by treatment with a hydrogen containing gas. The regeneration treatment involves pure hydrogen or a gas containing about 40 to 95% by volume of hydrogen, such as the gas produced in a hydroformer. The regeneration treatment is conducted at a temperature of about 250 to 420° C., more usually, about 300° to about 380° C., and for a period of about 0.5 to about 30 hours, more usually, about 1 to about 8 hours. The regeneration pressure can be in the same range as given above for the cyclization reaction. The regeneration gas, on a hydrogen basis, is fed to the catalyst zone at volumetric space velocities ranging from about .5 to about 40 V_0 /hr./ V_c .

The cyclization reaction is conducted preferably with a hydrogen treated catalyst. The catalyst can be treated by one or more of several methods, viz., (1) prior to introducing the hydrocarbon feed to the reactor, the catalyst can be treated with hydrogen; (2) during the reaction phase, the hydrogen can be introduced into the reactor as a separate stream or in combination with the hydrocarbon feed; (3) by the method involving the combination of (1) and (2); etc. It appears that hydrogen prevents the formation of olefinic materials and that these materials adversely influence the cyclization reaction. These conclusions appear to find support in several experiments made in the presence of helium, with and without a helium flush of the catalyst prior to the reaction cycle, as well as an experiment in which an olefin was added to the hydrocarbon feed. In every case where the above were tried, the cyclopentane compound yield decreased significantly. The quantity of hydrogen which is used in general varies from about 1 to about 1000 standard cubic feet of hydrogen (measured at 60° F. and 760 mm.) per barrel of hydrocarbon feed (1 barrel equals 42 gallons), abbreviated as s. c. f. b. In the preferred operation where the hydrocarbon feed is substantially free of olefins, the hydrogen feed can be about 5 to about 50 s. c. f. b. Where olefins are present in the feed, a higher hydrogen rate can be used, viz., about 100 to about 1000 s. c. f. b. in order to hydrogenate olefins and counteract their adverse influence on catalyst activity.

As previously indicated, the present invention can be used for the production of single cyclopentane compounds, e. g., cyclopentane, or mixtures of such compounds. An excellent application of this invention

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involves it being used with a commercial hydroformer. In this case, the naphtha feed to the hydroformer is subjected to a separation treatment whereby the C_5 and/or C_6 hydrocarbons are removed therefrom. The higher boiling fraction is passed to the hydroformer; whereas the C_5 and/or C_6 hydrocarbons are charged to a cyclization reactor which is operated in accordance with the present invention. The reaction product from the cyclization reactor is treated for the separation of cyclopentane compounds, and the remaining unreacted C_5 and/or C_6 hydrocarbons are recycled for further cyclization treatment. The cyclopentane compounds are charged to the hydroformer. Recycling of unreacted acyclic hydrocarbon can be used whether the cyclized product is passed to a hydroformer or not. The net hydrogen produced in the hydroformer can be used for treatment of the catalyst in the cyclization reactor. The hydroformer to which the cyclopentane compounds are charged can be one involving the use of a reforming catalyst possessing dehydrogenation-hydrogenation properties or aromatization characteristics, e. g., a group V or VI metal oxide or sulfide, e. g., MoO_3 , chromia, etc.; a heteropoly acid in which the outer acid forming element is, for example, molybdenum; or a platinum or palladium catalyst. The catalytic element is supported on a carrier material, e. g., alumina, silica, pumice, zinc spinel, etc., and it comprises about 0.05 to about 30% by weight of the total catalyst. The reaction is conducted at a temperature of about 80° to about 1025° F., a pressure of about 25 to about 1000 p. s. i. g., a weight space velocity of about 0.1 to about 15, a catalyst to oil ratio (where appropriate) of about 0.1 to about 10, and a hydrogen rate of about 1000 to about 10,000 s. c. f. b. The naphtha feed is one which contains C_5 or C_6 acyclic saturated hydrocarbons or both, and the naphtha was an end point of about 320° to about 460° F.

Having thus described generally the present invention, reference will be had to specific examples for a fuller understanding thereof.

The catalyst employed in the following examples were prepared as follows:

CATALYST I

45 grams of 6-14 mesh activated coconut charcoal were combined with an aqueous solution containing 21 grams of $H_2PtCl_6 \cdot 6H_2O$. The mixture was heated by means of a steam bath until substantially all the water was removed. The dried solids contained about 15% by weight of platinum metal (present in the compound). The dried catalyst mass was then placed in a test unit reactor and flushed with hydrogen. Following the flushing step, the catalyst was activated by raising the temperature to 300° C. over a period of 9 hours with hydrogen flushed through the reactor. The finished catalyst was maintained in an active state by a hydrogen atmosphere at a temperature of 290° C.

CATALYST II

50 grams of a catalyst containing 0.3% by weight of platinum supported on alumina were combined with an aqueous solution containing 26.1 grams of $H_2PtCl_6 \cdot 6H_2O$. The mixture was dried in an oven at 240° F. until substantially all of the water was removed. On a platinum basis, the catalyst contained 15% by weight of platinum. The dried catalyst was placed in a suitable reactor and then flushed with hydrogen. The catalyst was activated by maintaining a flow of hydrogen thereover and controlling the temperature at 300° C. for a 9 hour period. Thereafter, the catalyst was maintained in a hydrogen atmosphere at 290° C. prior to actual use.

In order to determine the effect of hydrogen on the cyclization reactor, two experiments were performed, namely, one in which helium was employed for treating the catalyst and the other in which hydrogen was substituted for helium. The results of these tests are given in Table I.

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Table I

Run No.	1	2
Catalyst	I.	I.
Hydrocarbon	2,2,4-trimethylpentane.	2,2,4-trimethylpentane.
Temperature, ° C.	325.	325.
Pressure, p. s. i. g.	14.7.	14.7.
Space velocity, $V_0/\text{hr.}/V_c$	0.063.	0.063.
H ₂ feed, mols.	0.016.	None.
H ₂ flush, mols.	0.193.	Do.
He feed, mols.	None.	0.067.
He flush, mols.	do.	0.020.
Product, mol percent (1) C ₅ H ₁₀	22.0.	4.9.

¹ Output basis.² 1,1,3-trimethylcyclopentane.

It can be seen from the data in Table I above that a significant decrease in yield of cyclopentane compound was obtained by using helium in place of hydrogen for the treatment of the catalyst.

In another series of experiments, a comparison was made between a catalyst in which activated charcoal was employed as a support material and another catalyst in which alumina was the carrier material. The results of these experiments are given in Table II below.

Table II

Run No.	1	2	3
Catalyst	I.	I.	II.
Feed	n-Pentane.	2,4-dimethylpentane.	2,4-dimethylpentane.
Temperature, ° C.	325.	327.	325.
Pressure, p. s. i. g.	14.7.	14.7.	14.7.
Space vel., $W_0/\text{hr.}/W_c$	0.13.	0.13.	0.13.
H ₂ flush, mols.	0.06.	0.05.	.04.
Product (mols per mol of feed reacted):			
Cyclopentane	0.404.		
1,3-dimethylcyclopentane.		0.327.	.093.

In Table II above, it is noted that the platinum catalyst containing charcoal as the support material was very active in cyclizing n-pentane to cyclopentane. Further, runs 2 and 3 furnish a comparison between catalysts containing the two different support materials. It is apparent that the catalyst containing activated charcoal as the support material was significantly more active than the catalyst containing alumina as a support material.

Additional experiments were performed in order to determine the effectiveness of the present invention with respect to higher straight chain saturated hydrocarbons. The results of these experiments are given in Table III below.

Table III

Run No.	1	2	3
Catalyst	I.	I.	I.
Feed	n-Hexane.	n-Heptane.	n-Octane.
Temperature, ° C.	325.	325.	325.
Pressure, p. s. i. g.	14.7.	14.7.	14.7.
Space Vel., $W_0/\text{hr.}/W_c$	0.13.	0.13.	0.13.
H ₂ flush, mols.	0.06.	0.05.	0.01.
Product (mols per mol of reacted feed):			
Methylcyclopentane	.079.	.03.	
C ₇ -cyclopentane		.186.	
C ₈ -cyclopentane			0.207.

It is apparent from the data given in Table III above that the present invention is effective for the cyclization of various types of straight chain saturated hydrocarbons to produce significant quantities of cyclopentane compounds.

Having thus provided a general description of the present invention with specific examples thereof, it should be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the scope of the present invention is defined by the appended claims.

We claim:

1. A process which comprises subjecting a naphtha

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fraction containing a straight chain hydrocarbon selected from the group consisting of a C₅ hydrocarbon, a C₆ hydrocarbon and mixtures thereof to a separation treatment whereby a straight chain hydrocarbon is removed therefrom, contacting at least the remainder of the naphtha fraction with a platinum catalyst under suitable reforming conditions in a reforming zone to produce a high octane quality gasoline material, treating a catalyst comprising about 5 to about 25% by weight of platinum with a hydrogen containing gas, contacting the straight chain saturated hydrocarbon with the treated platinum catalyst at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a., and a weight space velocity of about 0.001 to about 2 thereby producing a cyclopentane compound, and combining the cyclopentane compound with the remainder of the naphtha fraction.

2. A process which comprises contacting an acyclic hydrocarbon containing 5 to about 15 carbon atoms with a catalyst comprising about 1 to about 50% by weight of platinum supported on activated charcoal, at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a. and a weight space velocity of about 0.002 to about 2, thereby producing a cyclopentane compound.

3. A process which comprises contacting an acyclic hydrocarbon containing about 5 to 9 carbon atoms with a catalyst comprising about 5 to about 20% platinum supported on activated charcoal, at a temperature of about 300° to about 380° C., a pressure of about 1 to about 70 p. s. i. a. and a weight space velocity of about 0.1 to about 0.5 thereby producing a cyclopentane compound.

4. A process which comprises contacting a straight chain saturated hydrocarbon containing 5 to 15 carbon atoms with a catalyst comprising about 1 to about 50% by weight of platinum supported on activated charcoal, at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a. and a weight space velocity of about 0.1 to about 0.5 thereby producing a cyclopentane compound.

5. A process which comprises contacting a straight chain saturated hydrocarbon containing 5 to about 9 carbon atoms with a catalyst comprising about 5 to about 25% by weight of platinum supported on activated charcoal, at a temperature of about 300° to about 380° C., a pressure of about 14 to about 40 p. s. i. a., a weight space velocity of about 0.1 to about 0.5 thereby producing a cyclopentane compound.

6. A process which comprises treating a catalyst comprising about 1 to about 50% by weight of platinum supported on activated charcoal with a hydrogen containing gas, contacting the treated catalyst with an acyclic hydrocarbon containing 5 to about 15 carbon atoms at a temperature of about 250° to about 420° C., a pressure of about 1 to 70 and weight space velocity of about 0.1 to about 0.5 thereby producing a cyclopentane compound.

7. A process which comprises treating a catalyst comprising about 5 to about 25% by weight of platinum supported on activated charcoal with a hydrogen containing gas, contacting the treated catalyst with an acyclic hydrocarbon containing 5 to about 15 carbon atoms at a temperature of about 300° to about 380° C., a pressure of about 14 to about 40 p. s. i. a., and a weight space velocity of about 0.1 to about 0.5 thereby producing a cyclopentane compound.

8. A process which comprises treating a catalyst comprising about 1 to about 50% by weight of platinum supported on activated charcoal with about 1 to about 1000 s. c. f. b. of hydrogen, contacting the treated catalyst with an acyclic hydrocarbon containing about 5 to about 9 carbon atoms, at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a., a weight space velocity of about 0.001 to about 2 and thereby producing a cyclopentane compound.

9. A process which comprises contacting normal pentane with fixed catalyst comprising about 1 to about 50%

by weight of platinum supported on activated charcoal at a temperature of about 250° to about 420° C. for a reaction period from about 0.5 to about 100 hours thereby producing cyclopentane.

10. A process which comprises contacting normal pentane with a fixed catalyst comprising about 5 to about 20% by weight of platinum supported on activated charcoal at a temperature of about 300° to about 380° C. for a reaction period from about 0.5 to about 100 hours thereby producing cyclopentane.

11. A process which comprises contacting normal pentane with a catalyst comprising about 5 to about 20% by weight of platinum supported on activated charcoal at a temperature of about 300° to about 380° C., a pressure of about 14 to about 40 p. s. i. a. and a weight space velocity of about 0.1 to about 0.5 thereby producing cyclopentane.

12. A process which comprises contacting normal pentane with a fixed catalyst comprising about 1 to about 50% by weight of platinum supported on activated charcoal at a temperature of about 250° to about 420° C. for a reaction period from about 0.5 to about 100 hours thereby producing cyclopentane.

13. A process which comprises treating a catalyst comprising about 1 to about 50% by weight of platinum supported on activated charcoal with about 1 to about 1000 s. c. f. b. of hydrogen, contacting the treated catalyst with normal pentane at a temperature of about 250° to about 450° C., a pressure of about 1 to about 70 p. s. i. a. and a volumetric space velocity of about 0.001 to about 2 thereby producing cyclopentane.

14. A process which comprises subjecting a naphtha fraction containing a straight chain hydrocarbon selected from the group consisting of a C₅ hydrocarbon, a C₆ hydrocarbon and mixtures thereof to a separation treatment whereby a straight chain hydrocarbon is removed therefrom, contacting the remainder of the naphtha fraction with a platinum catalyst under suitable reforming conditions in a reforming zone to produce a high octane quality gasoline material, treating a catalyst comprising about 5 to about 25% by weight of platinum with a hydrogen containing gas, contacting the straight chain saturated hydrocarbon with the treated platinum catalyst at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a., and a weight space velocity of about 0.0001 to about 2 thereby producing a cyclopentane compound, and passing the cyclopentane compound to the reforming zone.

15. The process of claim 14 wherein the platinum catalyst containing about 5 to about 25% by weight of platinum is supported on activated charcoal.

16. A process which comprises subjecting a naphtha fraction containing a straight chain hydrocarbon selected from the group consisting of a C₅ hydrocarbon, a C₆ hydrocarbon and mixtures thereof to a separation treatment whereby a straight chain hydrocarbon is removed therefrom, contacting the remainder of the naphtha fraction with a platinum catalyst under suitable reforming conditions in a reforming zone to produce a high octane quality gasoline material, treating a catalyst comprising about 5 to about 25% by weight of platinum with a hydrogen

containing gas, contacting the straight chain saturated hydrocarbon with the treated platinum catalyst at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a., and a weight space velocity of about 0.001 to about 2 thereby producing a cyclopentane compound, and combining the cyclopentane compound with the high quality gasoline material.

17. A process which comprises subjecting a naphtha fraction containing an acyclic hydrocarbon selected from the group consisting of those having 6 or more carbon atoms to a separation treatment whereby the acyclic hydrocarbon is removed therefrom, contacting the acyclic hydrocarbon with a catalyst containing about 1 to about 50% by weight of platinum at a temperature of about 250° to about 420° C., a pressure of about 1 to about 70 p. s. i. a. and a weight space velocity of about 0.1 to about 0.5, thereby producing a cyclopentane compound, charging the remainder of the naphtha fraction and the cyclopentane compound to a reforming zone wherein it is contacted with a reforming catalyst under conditions such that a high octane gasoline material is produced.

18. A process which comprises subjecting a naphtha fraction containing normal pentane to a separation treatment whereby normal pentane is removed therefrom, contacting the remainder of the naphtha fraction with a platinum catalyst under suitable reforming conditions in a reforming zone to produce a high octane quality gasoline material, treating a catalyst comprising about 5 to about 25% by weight of platinum with a hydrogen containing gas, contacting the normal pentane with the treated platinum catalyst at a temperature of about 250° to about 420° C. and a pressure of about 1 to about 70 p. s. i. a. thereby producing cyclopentane and passing the cyclopentane to the reforming zone.

19. A process which comprises subjecting a naphtha fraction containing normal pentane to a separation treatment whereby the normal pentane is removed therefrom, contacting the remainder of the naphtha fraction with a platinum catalyst under suitable reforming conditions in a reforming zone to produce a high octane quality gasoline material, treating a catalyst comprising about 5 to about 25% by weight of platinum with a hydrogen containing gas contacting the normal pentane with the treated platinum catalyst at a temperature of about 250° to about 420° C. and a pressure of about 1 to about 70 p. s. i. a. thereby producing cyclopentane and combining the cyclopentane with the high quality gasoline material.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,849,504

August 26, 1958

Chia-chen C. Kang et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 28, for "80°" read -- 800° --; column 6, line 23, for "0.002" read -- 0.001 --; column 7, line 46, for "0.0001" read -- 0.001 --; column 8, line 43, for "25°" read -- 25% --.

Signed and sealed this 3rd day of February 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents