Patented May 16, 1950 2,508,014

UNITED STATES PATENT OFFICE

2,508,014

CATALYTIC REFORMING OF GASOLINE

Donald D. Davidson, Long Beach, Calif., assignor to Shell Development Company, San Francisco, Calif., a corporation of Delaware

No Drawing. Application May 16, 1947, Serial No. 748,653

6 Claims. (Cl. 196—50)

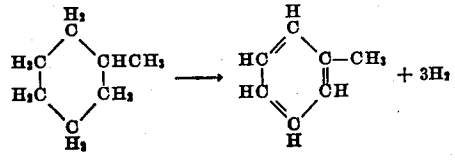
1

The present invention relates to a process for the catalytic treatment of motor fuel with hydrogen at elevated temperatures to produce motor fuel having superior anti-knock properties. More specifically the invention relates to a process wherein gasoline having poor anti-knock properties is treated with a special catalyst under specific conditions of temperature, pressure and time of reaction to afford a better improvement or upgrading of the gasoline in a more economic and practicable manner.

Numerous processes have been proposed for the upgrading of motor fuel and fractions thereof by catalytic treatment with hydrogen. These processes may be divided into two distinct categories. The first category consists of those processes carried out at temperatures generally below about 800° F. wherein the motor fuel is refined by hydrogenation of impurities or undesirable constituents. The second category consists of those processes carried out under dehydrogenation conditions to improve the anti-knock properties of the fuel. The present process is of this latter type.

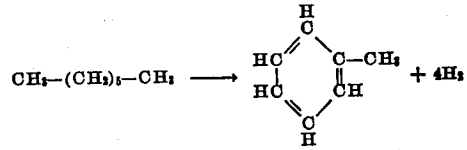
In the upgrading of motor fuel by catalytic treatment with hydrogen under dehydrogenation conditions, various reactions or hydrocarbon conversions take place which are little understood. The most notable characteristic of such processes is, however, the conversion of non-aromatic hydrocarbons to aromatic hydrocarbons. The aromatic hydrocarbons as a class have much better anti-knock properties than the non-aromatic constituents of the motor fuel and by converting the non-aromatic constituents to aromatic hydrocarbons a considerable improvement in the anti-knock properties of the fuel is possible. The production of aromatic hydrocarbons is now known to take place (using a molybdenum oxide catalyst) by three main reactions:

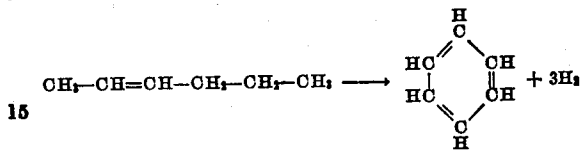
The first and more important of these reactions is the dehydrogenation of hydroaromatic naphthenes according to the typical equation:



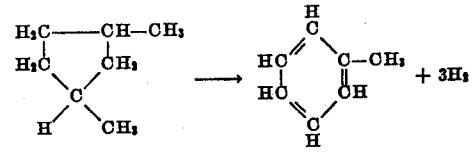
2

The second is the dehydrocyclization of paraffins and olefins to aromatics according to the typical equations:





The third, which is of lesser importance, is the dehydroisomerization of non-hydroaromatic naphthenes according to the typical equation:



All of these reactions, it will be noted, involve dehydrogenation.

Aside from these reactions, a variety of other reactions also take place. While some of these reactions, such as cracking, polymerization, and condensation are recognized, they are generally minor reactions in the process. As a consequence, processes of these types have been considered primarily as specific dehydrogenation processes to increase the aromaticity of the motor fuel. The development and improvement of processes of this type for the upgrading of motor fuel has largely centered on an empirical search for improved dehydrogenation catalysts, and in testing the various catalysts the aromatic content of the product has been used as a measure of the catalyst activity.

The formation of aromatic hydrocarbons in the product is, however, an insufficient criterion upon which to evaluate catalysts for use in improving motor fuels. In the first place it is found that different catalysts and conditions giving the same aromatic formation give products of

appreciably different octane numbers. Although the aromatic hydrocarbons have excellent octane numbers they have low heat contents, low lead susceptibilities, and high densities. With a motor fuel of any given octane number it is therefore desirable that the concentration of aromatics be as low as possible and the best process is one which gives the desired improvement in anti-knock properties with the least formation of aromatic hydrocarbons. Also with catalysts and process conditions affording suitable upgrading of the motor fuel an appreciable amount of cracking or degradation takes place. This not only results in decreased yields of the upgraded product, but also results in the deposition of carbonaceous deposits on the catalyst, which in turn causes the catalyst to lose its activity in a relatively short time and thus makes more frequent regeneration of the catalyst necessary. Thus, while the formation of aromatic hydrocarbons is important it is necessary to consider the octane number of the product and also to take into account the selectivity of the catalytic action in evaluating a catalyst for this purpose.

It is an object of the present invention to provide an improved process for upgrading motor fuel or substantial fractions thereof. More particular objects are to provide a process whereby motor fuels may be substantially improved in anti-knock properties to a higher degree than would be indicated by the production of aromatic hydrocarbons and with an increased yield of upgraded product. Another object of the invention is to provide a process whereby motor fuels may be upgraded to a high degree while operating in a substantially continuous manner.

The above objects, as well as other lesser objects which will be apparent from the following description, are achieved according to the process of the invention by treating motor fuels under specific conditions of operation with regard to temperature, pressure, recycle gas, and time of reaction with a specially promoted catalyst.

The process of the invention is applicable for the upgrading of straight-run stocks, as well as cracked stocks. However, cracked stocks are preferably employed only in conjunction with straight-run stocks in mixtures in which the straight-run stock predominates. The straight-run stock to be treated is preferably one having a low octane number, as, for example, a clear motor octane number below about 48, the straight-run stock to be treated preferably should not contain any appreciable amount of material boiling below about 180° F., or above about 500° F. The most preferred stock is that portion of straight-run gasoline boiling between about 200° F. and about 425° F. In the case of cracked stocks, although stocks of the same boiling range may be employed, it is preferred to treat low-octane stocks (having a clear motor octane number below 65) boiling predominantly between 300° F. and 400° F. Particularly suitable mixtures of straight-run stock and cracked stock are, for example, from two to ten parts of 200° F. to 400° F. straight-run naphtha to one part of 300° F. to 400° F. cracked naphtha. The cracked naphtha may be mixed with the straight-run stock prior to being contacted with the catalyst in the reaction zone, or it may be introduced separately into the reaction zone.

The described feed stocks are treated in the process of the invention under special conditions with a special catalyst. The catalyst used consists of a major amount of an activated alumina carrier or base promoted by minor specific amounts of silica, zinc oxide, and molybdenum oxide. The alumina base material is preferably an activated alumina gel. However, activated crystalline aluminas may also be employed. It is considered that the alumina base should have a microporous structure, affording an available surface of at least 100 square meters per gram and preferably at least 150 square meters per gram. Most of the available activated aluminas have specific surfaces well above 100 square meters per gram. The alumina base material should preferably be treated to remove substantially all of the alkali metal impurities normally present. Thus, it is preferred that the alumina base material contain not more than 0.1% alkali metal. The alumina itself exerts a certain catalytic activity for the desired treatment, but its function in the present catalyst is primarily as a carrier and promoter for the supported oxides.

The catalyst is promoted by a small amount of silica. The inclusion of silica in a catalyst of this general type generally tends to sharply increase the cracking tendency of the catalyst, and for this reason it is generally substantially absent from catalysts used for upgrading motor fuels where cracking is undesired. The concentration of silica is preferably between .6% and about 6% by weight, based on the alumina. Because of the tendency of the silica to promote cracking, the concentration should not exceed about 8%. The effect of silica in catalysts of this type is illustrated in the following Table I, wherein there is shown pertinent data from a series of comparable experiments with a molybdena-alumina catalyst promoted with various amounts of silica:

Table I

	Silica		
	0.67%	3.3%	0%
Yield of debutanized product, per cent b.v. of feed	75.9	74.3	72.3
Clear F-2 engine rating	74.2	73.4	72.3
Butane and lighter gas production, Cu. ft. per bbl. of feed	520	640	760
Average aromatic in fresh product, per cent b.v.	58.8	59.5	62.4

From the data it will be seen that silica exerts a detrimental effect. Thus, not only is the cracking increased (as indicated by the increased yield of gaseous products and lower yield of debutanized product), with increasing silica content, but the anti-knock properties of the product declines. The aromatic content shows an increase, but this is due primarily to concentration by cracking out of certain non-aromatic constituents.

The silica should be incorporated in the catalyst prior to the incorporation of the zinc and molybdenum oxide. The preferred method is to incorporate the silica at the time of preparing the alumina base, as by impregnating the alumina gel with sodium silicate, or ethyl silicate, or by mixing sodium silicate with the sodium aluminate used to make the alumina gel.

The detrimental effects of silica noted above are largely overcome in the present catalysts by the simultaneous inclusion of specific minor amounts of zinc oxide. The zinc oxide is incorporated on the surface of the pre-dried alumina base by impregnation after incorporation of the silica. Thus, the alumina base promoted by the silica may be dried and then soaked in a solu-

tion of zinc nitrate, zinc acetate, or any other suitable zinc salt which is easily convertible to the oxide. As will be pointed out, it is usually necessary to employ two or more impregnation treatments to incorporate the desired amount of molybdenum. According to a preferred method, the zinc and part of the molybdenum are incorporated by one impregnation and then the remainder of the molybdenum is incorporated by one or more subsequent impregnations. The amount of zinx oxide incorporated should be between 2.5% and 12% by weight, based on the alumina. The exact concentration within this range does not appear to be particularly important. However, concentrations in the higher end of this range are somewhat preferred with the higher applicable concentrations of molybdenum and the concentrations in the lower end of this range are preferred with the lower applicable concentrations of molybdenum. In these cases there is somewhat more molybdenum than zinc in the catalyst. In all cases there is a great excess of alumina over zinc oxide, and usually an excess of zinc oxide over silica.

The molybdenum oxide is incorporated on the surface of the alumina base material by impregnation. Any of the conventional methods for impregnating alumina bases with molybdenum oxide may be used. A preferred method is to saturate the activated base material with an aqueous solution of ammonium molybdate, or molybdic acid, followed by a mild calcination to produce molybdenum oxide. The molybdenum content of the catalyst used in the process of the present invention may be in the range of 4% to 6%, but is preferably higher than in most conventional molybdena-alumina catalysts, or at least 8% by weight. On the other hand, excessive concentrations of molybdenum are harmful, and for this reason the concentration is not increased above about 25% by weight. The preferred concentration of molybdenum varies somewhat with the alumina base used, but is usually between 10% and 18%. In order to incorporate these amounts of molybdenum on the surface of the catalyst by impregnation, it is usually necessary to impregnate the material two or more times.

The process of the invention is carried out at temperatures above about 825° F. and preferably above 875° F. The temperature should not, however, exceed about 1050° F. and is preferably maintained below about 1025° F. Preferred temperatures within the applicable range are between about 900° F. and 1000° F.

The process is carried out in the vapor phase under a positive pressure of at least 500 p. s. i. g. It is important that at least this minimum pressure be maintained. The preferred range of pressure is between 700 p. s. i. g. and 1000 p. s. i. g. Pressures above 1,000 p. s. i. g. may be employed but are unnecessary and require more costly equipment.

The process is carried out in the presence of a large excess of added hydrogen. While hydrogen from an exterior source may be used it is more economical to recycle the gaseous products of the process. This gas consists predominantly of hydrogen from the dehydrogenation reactions and hydrocarbon gases produced by the minor amount of cracking which invariably takes place. It may also contain small amounts of hydrogen sulfide. The exact composition of this gas will vary with the particular feed treated. A sufficient amount of this gas is recycled so that at least 2,500 cubic feet of hydrogen is recycled per barrel of feed and preferably at least 3,000 cubic feet per barrel. Larger amounts up to about 10,000 cubic feet per barrel may be used but the recirculation of hydrogen in amounts greater than about 8,000 cubic feet per barrel affords little additional advantage and increases the cost of operation.

The recycled product gas, when this is used to supply the hydrogen, is preferably treated by one of the known methods to remove hydrogen sulfide.

Under the specified conditions a through-put rate of charge stock corresponding to a liquid hourly space velocity of about 1 will yield a satisfactory product. However, liquid hourly space velocities from about 0.5 up to about 3 may often be advantageously employed.

When treating a feed stock as specified with the described catalyst under the specified conditions, the process is carried out in a substantially continuous manner. Thus, the process may be carried out continuously for several hundred hours without the necessity of subjecting the catalyst to a reactivation treatment. When, after a long period it becomes necessary to reactivate the catalyst, this may be done by any of the conventional reactivation treatments commonly used with molybdena-alumina catalysts. For the purpose of the present specification and claims, a substantially continuous operation is considered to be one in which the onstream period is at least 10 times the period required for reactivation. Thus, if it requires one day to reactivate the catalyst the process is carried out continuously for at least ten days.

The described process is endothermic. When the catalyst is disposed in an unheated reactor or catalyst case (adiabatic reactor) and the feed preheated to the reaction temperature is passed there through, there is a gradual temperature drop along the length of the catalyst bed. This type of operation allows the use of relatively inexpensive adiabatic type of reactors and is preferred especially when treating feed stocks containing cracked gasoline and when operating at low octane levels. When treating straight-run stocks at high octane levels the process may be carried out with better results in a reactor in which at least a part of the required heat is supplied directly to the catalyst. In this type of operation the catalyst is preferably disposed in heated catalyst tubes or in a catalyst case provided with heating coils or the like. The best octane number-yield relationship is obtained when sufficient heat is supplied to produce an increasing temperature gradient in the catalyst bed in the direction of flow, for example, the outlet temperature being up to 50° F. higher than the inlet temperature. Except when operating at very high octane levels it is generally uneconomical to supply more heat than required to provide isothermal reaction conditions and in most cases a compromise between adiabatic and isothermal reaction conditions gives the most satisfactory and economical results.

By way of example one suitable application of the process is as follows: The feed is a straight-run naphtha of 200 to 400° F., boiling range containing about 0.1% sulfur. The feed is pumped to a charge pressure of about 800 p. s. i. g., mixed with 5,000 cubic feet of recycle gas per barrel of feed at 800 p. s. i. g., and then passed through a feed preheater wherein it is preheated to about 950° F. During the initial three hours of opera-

tion sufficient high sulfur extract is added to the feed to bring the concentration of sulfur up to about 0.3%. For a plant of 2500 barrels per day capacity, two reactors are used. Each reactor contains 72 vertical 4,6-Cr, Mo steel tubes of 5¾ inches internal diameter and holding 25 feet of catalyst. The catalyst is in the form of granules of 8–14 mesh. The pressure drop across the catalyst bed is about 100 p. s. i. g. The reactor tubes are placed in a circular heater of conventional design which supplies sufficient heat that the exit temperature is maintained at about 980° F. The product from the reaction zone is heat-exchanged with the oil feed stream and is then cooled to a temperature of about 110° F. and passed to a high pressure accumulator-separator. The gases are passed through a phosphate treater to remove hydrogen sulfide and are then recycled. The liquid product is passed through a low pressure separator wherein a further quantity of gas separates. This latter gas is passed to an absorber. The liquid is passed to a conventional stabilizer. The stabilized product may be washed with caustic to remove remaining traces of hydrogen sulfide.

When after a long period of use the catalyst finely declines in activity to a point where the desired improvement cannot be maintained under conditions within the specified range, the catalyst may be reactivated in situ. After first purging the catalyst with steam at 125 p. s. i. g. and 1,000° F., steam at a vapor space velocity per minute of 12 and air at a vapor space velocity per minute of 0.9 (inlet oxygen concentration of 1.5%) is passed through the catalyst bed. The catalyst bed should be at a temperature of about 850° F. at the start of the reactivation and the temperature should not be allowed to exceed about 1,200° F. at any time.

Example I.—An alumina gel was promoted with silica, zinc oxide and molybdenum oxide. The zinc and molybdenum were incorporated simultaneously by impregnating with an aqueous solution of zinc nitrate and molybdic acid. The finished catalyst contained the following concentration of promoter elements (per cent by weight on the dry basis):

	Per Cent
Si	About 2.8
Zn	About 8.1
Mo	About 11.9

This catalyst was used to treat a 300–460° F. straight-run naphtha having the following inspection data:

Gravity, °A. P. I.	45.5
Refractive index, N_D^{20}	1.4418
Sulfur, per cent by weight	0.14
Bromine No.	1.4
Aromatics, per cent by volume	13.2
Octane No. (F–2 clear)	39.9

The following conditions of treatment were employed:

Maximum catalyst temperature	°F.	975
Average catalyst temperature	°F.	960
Pressure	p. s. i. g.	700
Feed rate	LHSV	1
Hydrogen	cu. ft. per bbl.	5000

The process was carried out continuously under isothermal conditions. The average aromatic content of the flash product over the first 100 hours was 61.3% by volume. The product taken over a test period of from 114 to 159 hours showed a yield of 74.0% by volume of debutanized product containing 60.1% by volume aromatics and having clear motor octane number of 75.0 (F–2).

Example II.—A catalyst promoted by silica, zinc oxide and molybdenum oxide and containing the following concentrations of promoter elements (per cent by weight on the dry basis)

	Per cent
Si	About 2.8
Zn	About 5
Mo	About 10

was prepared using the same alumina. In this case the zinc was incorporated by soaking in a solution of zinc nitrate, and after drying at about 100–110° C., the molybdenum was separately incorporated by soaking in a solution of molybdic acid in aqueous ammonium hydroxide. The catalyst had a specific surface of about 332 square meters per gram.

The above-described feed stock was treated with this catalyst under the above-described conditions. The average aromatic content of the flash product over the first 100 hours was 59.7% by volume. The clear motor octane number of the debutanized product obtained over a test period of from 79 to 116 hours was 75.1 (F–2) and the yield was 75.5% by volume.

The described process involving the particular combination of feed stock, catalyst and process conditions not only allows operation in a more economical manner, but also produces better yields of motor fuel of superior quality. Thus, the gasoline when treated by the described process has an octane number which is usually 2 to 5 points higher than that produced by treating the same feed stock by conventional methods. In other words a given desired octane number may be obtained with a lesser formation of aromatic hydrocarbons. Although it is possible to produce a product of equivalent octane rating by prior known methods, this can only be done at a greater cost with short cycle, intermittent type of operation, and with lower yields of a more aromatic product. While the present process offers distinct economical advantages when operating to produce a product of quality competitive with that produced by reforming, conventional hydroforming and the like, it is most advantageous and preferably employed to produce a debutanized product having a clear F–2 octane number of about 72 or higher.

The expression "F–2" in the foregoing specification and in the appended claims refers to the F–2 octane number, also known as the A. S. T. M. octane number or motor method octane number.

I claim as my invention:

1. The process for the substantially continuous upgrading of motor fuels by catalytic treatment with hydrogen which comprises substantially continuously vaporizing a straight-run gasoline fraction boiling predominately within the range of 185° F. and 500° F. and having a clear F–2 octane number below 48, substantially continuously contacting the vaporized gasoline in the presence of at least 2500 cu. ft. per barrel of hydrogen at a liquid hourly space velocity between 0.5 and 3, a temperature between 825° F. and 1025° F., and a pressure of at least 500 p. s. i. g., with an impregnated molybdenum oxide-alumina catalyst promoted with between 0.6% and 8% of silica and between 2.5% and 12% of zinc oxide, the amount of molybdenum being in excess of the zinc in the catalyst.

2. The process for the substantially continuous upgrading of motor fuels by catalytic treatments with hydrogen which comprises substantially continuously vaporizing a straight-run gasoline fraction boiling predominately within a range of 200° F. and 400° F. and having a clear F–2 octane number below 48, substantially continuously contacting the vaporized gasoline in the presence of at least 2500 cu. ft. per barrel of hydrogen at a liquid hourly space velocity between 0.5 and 3, a temperature between 825° F. and 1025° F., and a pressure of at least 500 p. s. i. g. with an impregnated molybenum oxide-alumina catalyst promoted with between 0.6% and 8% of silica and between 2.5% and 12% of zinc oxide, the amount of molybdenum being in excess of the zinc in the catalyst.

3. The process for the substantially continuous upgrading of motor fuels by catalytic treatment with hydrogen which comprises substantially continuously vaporizing from 2 to 10 parts of a straight-run gasoline fraction boiling predominately within 200° F. and 400° F. and one part cracked naphtha boiling predominately within 300° F. and 400° F., substantially continuously contacting the vaporized mixture of gasolines in the presence of at least 2500 cu. ft. per barrel of hydrogen at a liquid hourly space velocity between 0.5 and 3, a temperature between 825° F. and 1025° F., and a pressure of at least 500 p. s. i. g., with an impregnated molybenum oxide-alumina catalyst promoted with between 0.6% and 8% of silica and between 2.5% and 12% of zinc oxide, the amount of molybdenum being in excess of the zinc in the catalyst.

4. The process for the substantially continuous upgrading of motor fuels by catalytic treatment with hydrogen as specified in claim 1 in which the concentration molybdenum in the catalyst is between 8% and 25%.

5. The process for the substantially continuous upgrading of motor fuels by catalytic treatment with hydrogen which comprises substantially continuously vaporizing a straight-run gasoline fraction boiling predominately within the range of 185° F. and 500° F. and having a clear F–2 octane number below 48, substantially continuously contacting the vaporized gasoline in the presence of at least 2500 cu. ft. per barrel of hydrogen at a liquid hourly space velocity between 0.5 and 3, a temperature between 825° F. and 1025° F., and a pressure of at least 500 p. s. i. g., with an impregnated molybdenum oxide-alumina catalyst promoted with between 0.6% and 8% of silica and between 2.5% and 12% of zinc oxide, said zinc oxide being incorporated by impregnation on top of the silica, the amount of molybdenum being in excess of the zinc in the catalyst.

6. The process for the substantially continuous upgrading of motor fuels by catalytic treatment with hydrogen which comprises substantially continuously vaporizing a straight-run gasoline fraction boiling predominantly within the range of 185° F. and 500° F. and having a clear F–2 octane number below 48, substantially continuously contacting the vaporized gasoline in the presence of at least 2500 cu. ft. of hydrogen per barrel of feed at a liquid hourly space velocity between 0.5 and 3, a temperature between 825° F. and 1025° F. and a pressure of at least 500 p. s. i. g. with a catalyst consisting essentially of an alumina base containing from 0.6 to 8% of silica having on its surface from 2.5 to 12% of zinc oxide based on the alumina and containing from 8 to 25% molybdenum incorporated on the surface of the zinc oxide as molybdenum oxide, the amount of molybdenum being in excess of the zinc in the catalyst.

DONALD D. DAVIDSON.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,249,595	Benedict	July 15, 1941
2,344,330	Sturgeon	Mar. 14, 1944
2,395,836	Bates	Mar. 5, 1946
2,406,646	Webb et al.	Aug. 27, 1946
2,408,996	Parker et al.	Oct. 8, 1946
2,410,891	Meinert et al.	Nov. 12, 1946
2,427,800	Mattox	Sept. 23, 1947
2,437,531	Huffman	Mar. 9, 1948

FOREIGN PATENTS

Number	Country	Date
570,072	Great Britain	June 21, 1945