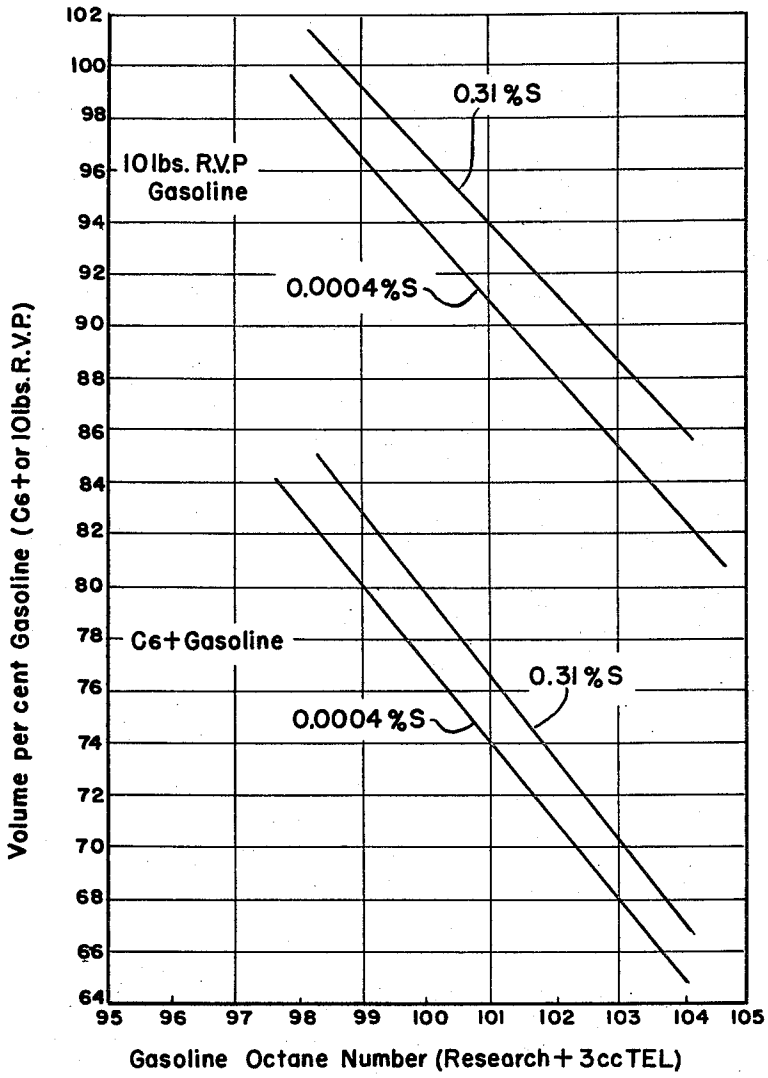
April 6, 1965 W. H. LANG ETAL 3,177,135

REFORMING NAPHTHAS HAVING A HIGH ALKYLCYCLOPENTANE CONTENT

Filed Aug. 24, 1961



INVENTORS.
William H. Lang
Donald M. Nace

by Linn I. Shine

ATTORNEY.

United States Patent Office

3,177,135
Patented Apr. 6, 1965

3,177,135

REFORMING NAPHTHAS HAVING A HIGH ALKYLCYCLOPENTANE CONTENT

William H. Lang, Wenonah, and Donald M. Nace, West Deptford Township, Gloucester County, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

Filed Aug. 24, 1961, Ser. No. 133,622
3 Claims. (Cl. 208—139)

This invention relates to improvements in catalytic reforming. More particularly, the present invention relates to improvements in reforming of naphthas in the presence of controlled amounts of sulfur over supported platinum metal catalysts to produce improved yields of gasolines having high octane ratings.

In catalytic reforming of petroleum naphthas, the following main hydrocarbon reactions occur: dehydrogenation of cyclohexanes to aromatics; dehydroisomerization of alkylcyclopentanes to aromatics; dehydrogenation of paraffins to olefins; dehydrocyclization of paraffins and olefins to aromatics; isomerization of n-paraffins; isomerization of alkylcyclopentanes to cyclohexanes; isomerization of substituted aromatics and hydrocracking of paraffins. Of the above reactions dehydrogenation is generally considered the most important single reaction in the catalytic reforming of petroleum naphthas, with dehydrogenation of naphthenes to aromatics being the chief octane upgrading reaction.

It is well known in the art that supported platinum metal catalysts are utilized in the reforming of various standard naphtha charges to produce high octane gasolines. Commercial platinum reforming catalysts have two distinct types of catalytic sites. Platinum sites alone have the ability to dehydrogenate or hydrogenate hydrocarbons, the extent of which will depend on the thermodynamic equilibrium established by the hydrogen pressure and temperature. Olefins generated at the platinum sites are very reactive and are involved in multi-step reaction sequences which are of great importance in the production of high octane number molecular species. Acidic sites are responsible for intercepting the olefin intermediates. However, platinum sites are involved also in various single step reactions, such as demethylation of paraffins and ring opening of cycloparaffins, which are not as effective in raising the octane number-yield relation of a gasoline as are the dual function catalyzed reactions. Similarly, the acid sites, if too active, can promote excessive degradation reactions which disrupt the desired reaction sequences of the dual function system. A proper balance of platinum function activity and of acid function activity is obviously needed for optimum reforming selectivity. However, this balance of function depends on several factors involved in the reforming process which vary from one specific operation to another. These factors are the composition of the naphtha charge, the operating conditions of the reformer and the quality (octane number and vapor pressure) of the gasoline product desired. It is therefore desirable to utilize a process wherein a platinum reforming catalyst can be used under controllable catalyst function conditions to provide the proper reaction conditions for the various different commercial naphtha charges. This would enable optimum results to be attained in the reforming process without replacing the catalyst for each different type of naphtha feed employed.

It is the object of this invention to provide a one-step process wherein high boiling hydrocarbon naphtha charges containing substantial amounts of alkylcyclopentanes can be reformed under controlled conditions over a supported platinum group metal catalyst to obtain improved gasoline yields having octane ratings (Research+3 cc. TEL) in excess of 98.

It is a further object of this invention to control the activity and selectivity of the platinum metal catalysts utilized in the reforming process by the addition of a sulfur additive to the hydrocarbon naphtha to provide improved maximum yields of high octane gasolines.

These and other objects will become apparent to those skilled in the art by the further consideration of the following disclosure and appended claims.

A reforming process has been discovered which produces improved yields of high octane gasoline by reforming a hydrocarbon naphtha charge having an initial boiling point in excess of 200° F. and an end boiling point of about 400° F. containing at least about 20 mole percent alkylcyclopentanes in the presence of controlled amounts of sulfur-containing compounds over a supported platinum metal catalyst utilizing conventional reforming conditions. Heretofore the presence of sulfur-containing compounds in a crude naphtha was considered a detriment to a catalytic reforming process since the catalyst utilized can be readily poisoned by the sulfur resulting in a significant decrease of the activity and selectivity of the desirable reaction occuring in the upgrading operation of naphthas. The present invention advantageously utilizes controlled concentration of sulfur in the naphtha charge to partially poison active platinum sites of the supported platinum group metal catalyst and effectively increase the selectivity for the chief upgrading reaction of dehydrogenation and isomerization of alkylcyclopentanes to aromatics to obtain improved yields of gasolines having high octane ratings.

The hydrocarbon naphthas used in the process of this invention are those naphthas having an initial boiling point of in excess of 200° F. and an end boiling point of about 400° F. To obtain the improvements in yields of the high octane gasoline, the hydrocarbon naphthas utilized contain at least 20 mole percent of alkylcyclopentanes. The alkylcyclopentanes present in the hydrocarbon naphthas used in the starting materials include those having a boiling point in excess of 200° F. and include the mono-, di-, tri-, tetra- and penta-substituted alkylcyclopentanes, but are substantially free of the lower boiling alkylcyclopentanes such as methylcyclopentane.

A typical naphtha used in this process is a "Wilmington naphtha" which boils in the range of 200° F. to about 400° F. and contains approximately 34 mole percent alkylcyclopentanes. On the other hand a typical "Mid-Continent naphtha" boiling in the range from about 180° F. to about 400° F. containing approximately 18 mole percent alkylcyclopentanes does not show any improvement in the high octane gasoline yields when using the process of this invention. If alkylcyclopentanes concentration of the "Mid-Continent naphtha" is increased so that the mole percentage of alkylcyclopentanes exceeds 20 percent, improvements of gasoline yields are obtained utilizing the process of this invention.

The naphthas which are used in this process as the starting materials are generally pre-treated to lower the nitrogen content and other catalytic poisons to several parts per million or less to prevent poisoning of the supported platinum metal catalyst. The severity of pre-treating necessary to accomplish the reduction of nitrogen derivatives will reduce the sulfur content to a negligible quantity. The naphthas can be pre-treated using conventional known methods, i.e. by passing at elevated temperatures over a cobalt oxide-molybdena-alumina catalyst. If the quantity of catalytic poisons do not exceed the amounts which are detrimental to catalytic reforming, pre-treatment of the naphtha charges are not necessary.

To achieve the improvements demonstrated by the process of this invention, a reducible sulfur compound can be added to the hydrocarbon naphtha charge. The reducible sulfur compound is one susceptible of hydrogenation to

hydrogen sulfide in the reformer. Hydrogen sulfide itself can, if desired, be added to the hydrogen stream or recycle stream of a reformer in amounts sufficient to provide the desired sulfur content. Based on a sulfur weight percent of naphtha charged, sulfur concentrations of about .001 percent to about 0.7 percent, preferably .005 percent to 0.5 percent, will provide the improvements in yields of the high octane gasoline obtained in accordance with the present process.

The use of controlled amounts of sulfur in the reforming process of this invention is exceptional in its behavior since the presence of sulfur will only temporarily poison those sites of the platinum catalysts which produce the undesirable reactions obtained in reforming of naphthas. There are no permanent detrimental effects to the platinum catalysts in using sulfur. For instance, if higher platinum activity is required, the amounts of sulfur can be reduced and the platinum activity of the catalysts increases almost instantaneously. Correspondingly, if less platinum activity is desired, the amounts of sulfur present can be increased to obtain the instantaneous decrease of platinum activity.

Typical reducible sulfur compounds which can be used in this process include, for example, the organic mercaptans, sulfides, disulfides and heterocyclic sulfur compounds, having boiling points within and below the naphtha boiling range such as, tertiary butyl mercaptan, tertiary hexyl mercaptan, ditertiary butyl sulfide, dinormal butyl sulfide, di-tertiary-butyl disulfide, ditertiary octyl disulfide; thiophene; and the like; and as described previously, hydrogen sulfide in the form of a gas. The optimum concentration of sulfur will depend on the composition of the naphtha stock (particularly the concentration of alkylcyclopentanes), the platinum activity of a particular catalyst used and the severity of the reforming operations.

The catalyst which can be used in the process of this invention can be any known type of supported platinum metal catalyst used for reforming. By the term "platinum metal" as used throughout the specification and claims, is meant a metal in the platinum series including platinum, palladium, osmium, iridium, rhodium and ruthenium, as well as alloys or mixtures of these metals. The amount of the platinum group metal on a support can range from about 0.01 percent to about 2 percent by weight based on the total catalyst. The platinum metal portion of the catalyst can be incorporated into the catalyst support by impregnating or co-precipitating the same with a suitable compound of a platinum metal in accordance with procedures well known in the art, using, for example, platinum ammine complex, potassium chloroplatinate, chloroplatinic acid, platinum sulfide, palladium sulfide, rhodium sulfide, platinum polysulfide and the like. The quantity of platinum impregnating compound used in the catalyst preparation will depend on the final concentration of the platinum metal desired. The catalyst support of the platinum metal catalyst can be any suitable carrier material known in the art. These carriers can include such as, for example, alumina, silica, silica-alumina, zirconia, silica-zirconia, pumice, magnesium, alumina-boria, kieselguhr, and the like. The preferred catalysts are those wherein the support or carrier is alumina having platinum deposited thereon and containing small quantities, i.e. 0.1 to 5.0 weight percent of a halide such as chlorine, fluorine or bromine.

The conditions utilized in the process of this invention are those conventional reforming conditions known to the art. The pressure in the reactors is maintained between about 50 and about 1000 p.s.i.g., preferably in the range of about 100 to about 750 p.s.i.g.; the inlet temperature of the reforming reactor ranges from about 880° F. to 1000° F., preferably in the range of 900° F. to 970° F. The liquid hourly space velocity of the naphtha charge can range from about 0.1 to about 10, preferably in the range from 0.5 to 5. The molar ratio of hydrogen to hydrocarbon charge can range from about 2 to about 40, preferably in the range of about 3 to 20.

The process of this invention may be carried out in any equipment suitable for reforming operations. The process may be operated batchwise. It is preferable, however, and generally more feasible to operate continuously. Accordingly, the process is adapted to operations using a fixed bed of catalyst. Also, the process can be operated using a moving bed of catalyst, wherein the hydrocarbon flow may be concurrent or countercurrent to the catalyst flow. A fluid type of operation may also be employed.

The following examples will serve to illustrate the process of the invention without limiting the same:

EXAMPLE 1

A Wilmington naphtha having an initial boiling point in excess of 200° F. and an end boiling point of about 400° F. was pre-treated at 700° F. over a cobalt oxide-molybdena-alumina pre-treating catalyst, at 500 p.s.i.g. and 5 liquid hourly space velocity to remove the nitrogen derivatives. The resulting naphtha having an A.P.I. gravity of 53.9 contained 0.0004 percent sulfur. The composition of the naphtha was 31.0 weight percent paraffins, 52.5 weight percent monocycloparaffins (34 weight percent alkylcyclopentanes), 10.3 weight percent alkylbenzenes, and 6.2 weight percent olefin and dicyclo compounds. The octane number of this naphtha (Research +3 cc. TEL) was 83.8. The above pre-treated naphtha was reformed over a platinum alumina reforming catalyst containing 0.6 weight percent platinum and 0.7 weight percent chlorine. The reforming operation was carried out in a fixed bed unit which used 75 cc. of catalyst under operating conditions of 500 p.s.i.g. pressure, a molar ratio of hydrogen to hydrocarbon charge of 10, a liquid hourly space velocity of 2, and an inlet temperature of the naphtha charge of 900° F. to 960° F. The amount of sulfur added to the naphtha charge is shown in the reforming results described in Table I, below and the accompanying figure.

Table I

SULFUR CONTENT 0.0004% IN NAPHTHA CHARGE

Octane Number (Research+3 cc. TEL)	C_6+Gasoline, Volume Percent	10 lbs. R.V.P. Gasoline, Vol. Percent
97.8	82.5	98.1
100.7	76.2	92.1
103.1	67.8	85.5
103.9	65.4	83.3

SULFUR CONTENT 0.31% IN NAPHTHA CHARGE

98.3	83.8	99.6
100.2	77.7	94.8
103.6	68.2	86.1

The results of Table I, as shown in the figure, indicate overall improvements in gasoline yields having octane numbers greater than 98 when amounts of 0.31 weight percent of sulfur are added to the naphtha charge.

EXAMPLE 2

The pre-treated naphtha charge (0.0004 weight percent sulfur) obtained in Example 1 reformed in the presence of varying amounts of sulfur over a platinum on alumina catalyst containing 0.6 weight percent platinum and 0.7 weight percent chlorine to obtain comparative maximum yield of gasolines of octane numbers of 100 and 104 respectively. The reforming operations were carried out in a fixed bed unit which used 75 cc. of catalyst under operating conditions of 500 p.s.i.g. pressure, a molar ratio of hydrogen to hydrocarbon charge of 10, and a liquid hourly space velocity of 2. The resulting data is tabulated in Table II, below.

Table II

Inlet Temperature, ° F.	Sulfur Content in Naphtha Charge, Wt. Percent	Gasoline Yield of 10 lbs. RVP, Volume Percent	
		Octane Number [1]	
		100	104
920–955	0.0004	93.1	83.0
920–960	0.074	95.8	84.0
920–965	0.31	95.3	85.1

[1] Research+3 cc. TEL.

At sulfur concentrations greater than 0.7 weight percent in the naphtha charge, the activity of the reforming catalyst is reduced significantly and improved yields of high octane gasoline are not obtained.

The results of Example 2 indicate improved gasoline yields having octane numbers in excess of 100 when sulfur is added to the naphtha charge at conventional reforming conditions. This demonstrates that the added sulfur selectively deactivates the catalyst to obtain improved yields over the naphtha charge with negligible quantities of sulfur present.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

What is claimed is:

1. A process for reforming of a hydrocarbon naphtha which comprises passing a hydrocarbon naphtha having an initial boiling point of about 200° F. and an end boiling point of about 400° F. containing at least about 20 mole percent alkylcyclopentanes and sulfur in amounts from about .07 weight percent to about 0.7 weight percent based on the naphtha charge, over a platinum on alumina catalyst containing from about 0.1 to about 2 weight percent platinum and from about 0.1 to about 5.0 weight percent chlorine under reforming conditions.

2. The process of claim 1 wherein the sulfur content ranges from about .005 weight percent to 0.5 weight percent based on the naphtha charge.

3. A process for reforming of a hydrocarbon naphtha which comprises passing a hydrocarbon naphtha having an initial boiling point of about 200° F. and an end boiling point of about 400° F. containing at least about 20 mole percent of alkylcyclopentanes and sulfur in amounts from about .07 weight percent to about 0.7 weight percent based on the naphtha charge, over a platinum on alumina catalyst containing from about 0.1 to about 2 weight percent platinum and from about 0.1 to about 5.0 weight percent chlorine at inlet temperatures of about 900° F. to 970° F., liquid hourly space velocity of between about 0.5 to about 5, pressures of between about 100 and about 750 p.s.i.g., and employing a molar ratio of hydrogen to hydrocarbon charge between about 3 and about 20.

References Cited by the Examiner

UNITED STATES PATENTS

2,508,014	5/50	Davidson	208—141
2,861,944	11/58	Coley et al.	208—138
3,006,841	10/61	Haensel	208—139

ALPHONSO D. SULLIVAN, *Primary Examiner.*

DANIEL E. WYMAN, *Examiner.*