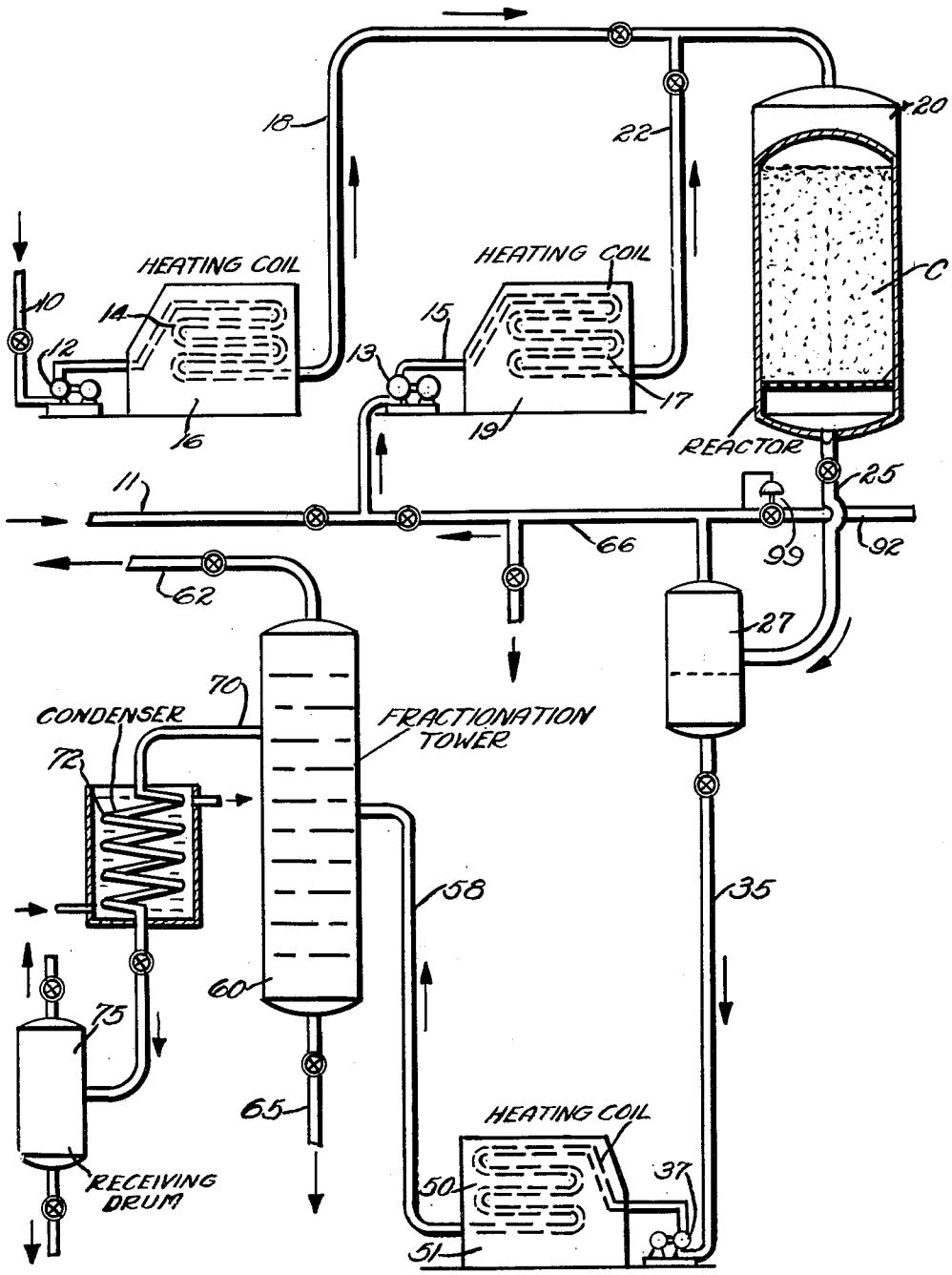
Dec. 6, 1949 A. B. WELTY, JR 2,490,287

UPGRADING OF NAPHTHA

Filed Sept. 19, 1946



Albert B. Welty, Jr. Inventor

By P. J. Whelan Attorney

Patented Dec. 6, 1949 2,490,287

UNITED STATES PATENT OFFICE

2,490,287

UPGRADING OF NAPHTHA

Albert B. Welty, Jr., Mountainside, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

Application September 19, 1946, Serial No. 697,975

5 Claims. (Cl. 196—50)

1

My invention relates to improving the octane rating of virgin naphtha, and I accomplish this result by a two stage treatment; in the first stage I hydroform the naphtha catalytically at rather mild conditions, and in the second stage, I subject the catalytically reformed naphtha to a further thermal reforming treatment.

By hydroforming or dehydrogenation under conditions sufficiently mild that cracking is very slight but severe enough to effect fairly complete dehydrogenation of cyclohexane and its homologs to aromatics, followed by thermal reforming, a product rich in aromatics and olefins having a high octane number, especially by the CFR-Research method, is obtained. Yet the conditions during hydroforming or dehydrogenation are sufficiently mild that little or no coke is formed on the catalyst and only infrequent regeneration, such as once a month or less, if indeed any at all, is required. When hydroforming alone at sufficiently severe conditions to obtain the octane level desired a considerable quantity of coke (1.0–4.0 weight per cent of feed) is laid down on the catalyst and regeneration several times a day is necessary to maintain the catalyst in an active condition.

Reactions other than the formation of aromatics also occur during ordinary severe hydroforming. The principal ones are cracking of the aliphatics and hydrogenation of the olefins formed as a result of this cracking. The result is that in a normal hydroformate a mixture of very high octane number aromatic material and mediocre or poor quality, saturated non-aromatics is obtained. For example, in a certain commercial hydroforming plant located in this country, the product when extracted with liquefied SO_2 under the usual low temperature conditions, produced a raffinate or non-extracted portion boiling approximately in the range of 200 to 250° F., which had an octane number of only 40, (CFR-Research) clearly indicating that there was a substantial quantity of straight-chain paraffinic hydrocarbons present. In the product from the said plant the C_6–200° F. boiling point fraction of the name product had a CFR-Research octane number of about 75, which, when corrected for the amount of benzene estimated to be present, was about 71. East Texas virgin naphtha boiling in the same range has an octane number of about 69 to 70 CFR-Research. In a study made some years ago in connection

2

with the production of aviation gasoline by hydroforming, the hydroformed product boiling in the range of from C_6 to 380° F. was subjected to solvent extraction using liquefied SO_2, the extracted product being a fraction of the product produced by hydroforming a 200 to 290° F. boiling range East Texas virgin naphtha. The blending AFD–3C octane number of the raffinate or unextracted portion was found to be 55, which compares with 71.8 for C_6 to 200° F. East Texas virgin naphtha, 45 for the 200 to 250° F. East Texas fraction and 34 for the 250 to 335° F. fraction. Thus the paraffinic naphthenic raffinate was about the same octane number quality as East Texas virgin naphtha, which is not very good.

It appears that the paraffins in the hydroformate probably are not very highly branched. Therefore they would have a higher CFR-Research rating if they had not been hydrogenated, which, however, is inevitable under hydroforming conditions. Thus, a better yield-octane relationship is obtained by cracking in a second step following a mild hydrofroming—in other words, mild hydroforming followed by thermal reforming.

By hydroforming, I refer to an operation conducted at elevated temperatures and pressure in the presence of a solid catalyst and in the presence of added hydrogen, using a feed stock containing at least 25 to 30 volume per cent of naphthenic hydrocarbons, which process is so operated that there is no net consumption of hydrogen but ordinarily a net production of hydrogen.

The object of my invention, therefore, is to produce high yields of high octane naphtha from virgin naphtha.

Another object of my invention is to increase the octane rating of a virgin naphtha using hydroforming conditions sufficiently mild as to materially reduce the amount of, or eliminate altogether, the coke formed on the catalyst during the hydroforming, thus permitting on-stream operation of the hydroforming process for a greatly extended period of time before it is necessary to regenerate the catalyst or to use the catalyst indefinitely without regenerating the same.

Another object of my invention is to produce a naphtha of high octane rating from a virgin naphtha under conditions such that substantially less mechanical equipment and utilities are required.

Another object of my invention is to convert

virgin naphtha into high octane naphtha, utilizing the older existing thermal equipment which most oil refineries possess to a substantial degree, thus reducing the necessity for replacement by new construction.

Other and further objects of my invention will appear from the following more detailed description and claims.

In the accompanying drawing, I have shown diagrammatically an apparatus layout in which a preferred modification of my invention may be carried into effect.

Referring in detail to the drawing, a naphtha feed, such as for example, West Texas virgin naphtha containing 40 to 50 per cent of naphthenes is introduced into the present system through line 10 and then pumped by a pump 12 through a fired coil 14, disposed in a suitable furnace 16 (other suitable heating means could have been used) at a low enough temperature to avoid substantial cracking thence withdrawn through line 18 and fed with hydrogen into a hydroforming case 20 containing a bed of catalyst C supported on a perforated plate or grid F. The hydrogen used in the process is pumped from line 11 by pump 13 via line 15 into a fired coil 17 in a furnace 19 (other suitable heating means could have been employed here, also) wherein the hydrogen is heated to a temperature of 900 to 1050° F. and thence conducted via line 22 into line 18, where it flows with the oil vapors into the hydroforming case 20. The catalyst in the case was 10% molybdenum oxide on 90% activated alumina by weight and was in the form of pills. Other catalysts such as cobalt oxide-molybdenum oxide on alumina or molybdenum oxide on zinc-alumina spinel or cobalt molybdate on zinc-alumina spinel may also be used successfully. Hereinafter I shall set forth by way of a specific example, the operating conditions prevailing in reactor case 20. The hydroformed product is withdrawn from reactor case 20 through line 25 and discharged into a separator 27 wherein it was separated into a gaseous fraction, which is taken off overhead. The product gas is released through line 92 by means of pressure regulator 99 which maintains the desired pressure on the hydroformer. Recycle gas is conducted via line 66 to the hydrogen furnace 19. Liquid bottoms from the separator 27 are withdrawn through line 35, passed through a pump 37 and forced through a fired coil 50, disposed in furnace 51, (here, again, other suitable heating means may be employed) where they are heated to a temperature of 980° to 1080° F. which effects the desired cracking. The product withdrawn through line 58 is subjected to fractional distillation in column 60. From column 60 unsaturated normally gaseous hydrocarbons are recovered overhead through line 62, while a heavy product containing polymer is withdrawn through line 65. The main product, namely the motor gasoline is recovered through line 70, cooled in condenser 72 and collected in a receiving drum 75.

In order to further describe my invention, I set forth below a specific example illustrating a preferred modification of my invention, with the understanding that the specific details recited therein are purely illustrative and do not impose any limitations thereon.

Example I

I subjected a West Texas virgin naphtha containing 40 to 50 volume per cent naphthenes and boiling within the range of from 300 to 400° F. to

hydroforming in case 20 using a catalyst consisting of 10% molybdenum oxide on zinc-alumina spinel ($ZnO.Al_2O_3$), a temperature of 892 to 919° F. prevailing in the case 20 while maintaining a pressure of 750 to 800 pounds per square inch gauge therein. The feed rate of oil was 0.5 volume of oil per volume of catalyst per hour. 2000 cubic feet of hydrogen per barrel of oil were fed to the reactor. The hydroformed product obtained from separator 27 had the following inspection:

Aromatics	volume per cent	49.8
Aniline Pt.	°F.	55
Gravity	°A. P. I.	43.4
Distillation:		
5%	°F.	216
20%	°F.	298
50%	°F.	333
80%	°F.	358
95%	°F.	399
Refractive index (N_D^{20})		1.45770
Specific dispersion		142

The hydroformate was then subjected to thermal reforming under the following conditions: A coil outlet temperature of 1030° F. was maintained in heater coil 50, with a pressure of 750 pounds per square inch gauge, and a feed rate of 10.3 volumes of oil per volume of reactor per hour. The motor gasoline fraction has the following inspection:

Gravity	°A. P. I.	43.8
Distillation:		
5% at	°F.	142
20%	°F.	245
50%	°F.	326
80%	°F.	357
95%	°F.	404
Reid vapor press.–lbs. per sq. in		7.1
Sulfur wt. percent		0.020
Aniline Pt., °F		25
Bromine No. centigrams/gram		26
Octane Numbers:		
ASTM clear		81.0
CFRR clear		92.7
CFRR+1.5 ccTEL[1]/gal		96.9

[1]TEL=tetraethyl lead.

The yield of this product based on original 300/400° F. West Texas virgin naphtha was 87.5 volume per cent It will be noted from the above characteristics of the hydroformate and the effluent from the thermal reforming stage that the boiling points corresponding to the distillation percentages of the higher boiling fractions are substantially unchanged.

To summarize briefly, ordinary hydroforming of naphtha to improve the octane number thereof is undesirable for many reasons. In the first place, as it has been performed heretofore in many commercial installations a great deal of the time is consumed in regenerating and purging the catalyst due to the fact that substantial quantities of coke are formed on the catalyst. In other words, in a typical commercial hydroforming plant, the procedure is to operate the on-stream operation for four hours, whereupon it becomes necessary to discontinue the on-stream operation to regenerate and recondition the catalyst. This regeneration and purging of the catalyst required about four hours so that in any given calendar day the unit is operating only approximately one-half of the time to produce a hydroformed gasoline or naphtha. Of course, by employing two reactors, the process may be operated continuously but this requires not only

an additional reactor but also additional accessory equipment, such as conduits, valves, electrical timing devices for opening and closing valves, compressors, pumps, etc. One advantage of my present invention is that in my operation, wherein I hydroform under mild temperatures conditions in the first stage of my process, I may operate the hydroforming unit continuously and without interruption for regenerating the catalyst from five to ten weeks and, another advantage is that I produce less normally gaseous hydrocarbons, since the hydroforming operation is almost exclusively one of dehydrogenation of naphthenes without any substantial cracking of hydrocarbons with its attendant gas and coke formation. By mild hydroforming conditions I refer to operations in which the temperature is from about 40 to 100 degrees lower than in the usual hydroforming process. In other words, when hydroforming was carried out commercially during the war to produce toluene, the feed entered the reactors at around 1020 to 1050° F. and the products were withdrawn from the reactor at 850 to 870° F. so that the average temperature was around 950° to 975° F. According to my process the same is operated at, say, from 875 to 920° F. average catalyst temperature in the reaction zone. Furthermore, I prefer to use substantially higher pressures in the hydroforming step. Whereas in the commercial operation the pressure of around 250 pounds per square inch, and certainly not over 400 pounds per square inch, was employed, I prefer to operate at pressures of the order of 500 to 750 pounds per square inch in the said hydroforming stage.

In the second stage of my process, I effect a certain degree of cracking, which produces olefins, but, unlike the ordinary hydroforming process, these are not hydrogenated to the lower octane number paraffins to any substantial degree since there is not an excess of free hydrogen nor a catalyst present in the thermal reforming zone. In the thermal reforming stage of my process I operate at high temperatures, say, up to 950 to 1150° F. and a pressure of 500 to 800 pounds per square inch and a relatively high feed rate; in other words, a feed rate of from 5 to 15 volumes of oil per volume of reactor per hour.

A further advantage of my process is that the hydrogen produced is of greater purity, that is to say, the hydrogen recovered from the hydroformed product is over 80 volume per cent pure, whereas in the ordinary hydroforming process it is about 50 per cent hydrogen. The hydrogen I obtain is of sufficient purity to be used to saturate unsaturated hydrocarbons commercially.

Numerous modifications of my invention may be made by those familiar with the art without departing from the spirit thereof.

Having described my invention in the best manner in which it may be performed, what I claim is:

1. The method of producing high octane naphtha which comprises first subjecting a naphthenic naphtha to hydroforming in the presence of a hydroforming catalyst selected from the group consisting of molybdenum oxide, cobalt oxide-molybdenum oxide and cobalt molybdate and added hydrogen in a reaction zone maintained under a temperature of from about 875° to 920° F. and a pressure of from about 500 to 750 pounds per square inch and under conditions whereby a very limited amount of carbon is produced to permit hydroforming operations for extended periods of time without catalyst regeneration, allowing the naphtha to remain resident in the reaction zone for a sufficient period of time to effect substantial dehydrogenation of naphthenes, withdrawing the product from the reaction zone, separating hydrogen therefrom and subjecting the substantially hydrogen free naphtha to thermal reforming under a temperature of from about 980° to 1080° F. and a pressure of from about 500 to 800 pounds per square inch and at a feed rate of from about 5 to 15 volumes of oil per volume of reactor per hour to form a high octane naphtha in which the components in the high boiling fractions of the naphtha from the hydroforming step are substantially unchanged in boiling point.

2. The method of claim 1 in which the hydroforming catalyst consists essentially of 10 weight per cent molybdenum oxide on 90 weight per cent zinc aluminate.

3. The method set forth in claim 1 in which the virgin naphtha contains from 40 to 50 volume per cent naphthenes.

4. The method of claim 1 in which the hydroforming catalyst is supported on alumina.

5. The method of claim 1 in which the hydroforming catalyst consists essentially in cobalt molybdate on zinc aluminate.

ALBERT B. WELTY, JR.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
2,143,472	Boultbee	Jan. 10, 1939
2,321,006	Burk et al.	June 8, 1943
2,344,330	Sturgeon	Mar. 14, 1944
2,410,891	Meinert et al.	Nov. 12, 1946

FOREIGN PATENTS

Number	Country	Date
418,926	Great Britain	Nov. 2, 1934
488,651	Great Britain	July 7, 1938