

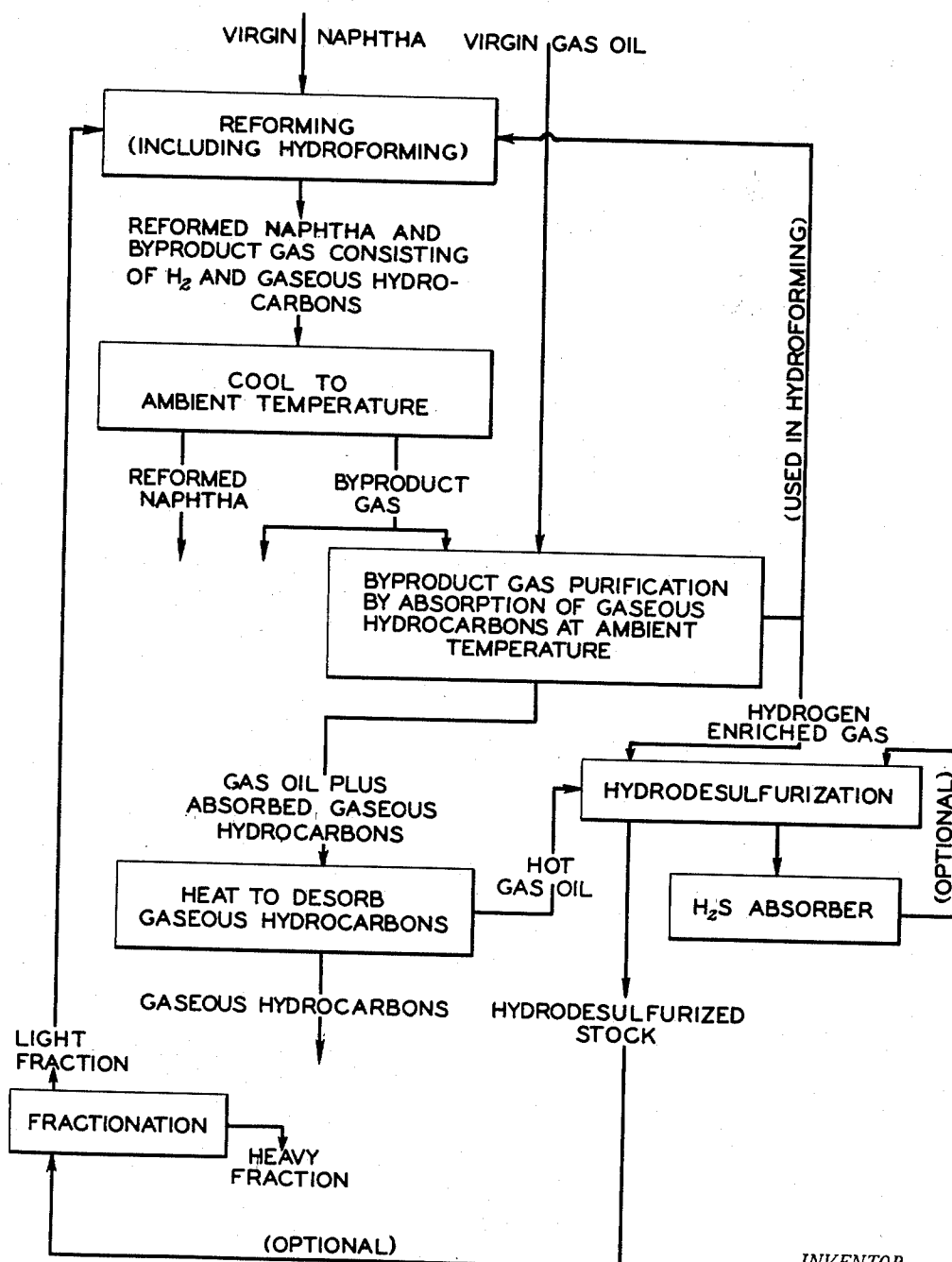
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COMBINATION PROCESS FOR THE CATALYTIC HYDRODESULFURIZATION
AND REFORMING OF HYDROCARBON MIXTURES
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COMBINATION PROCESS FOR THE CATALYTIC HYDRODESULFURIZATION AND REFORMING OF HYDROCARBON MIXTURES

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4 Claims. (Cl. 196—24)

1

This invention relates to a process for the production of gasoline having a higher octane number from virgin naphthas and the like hydrocarbon mixtures by reforming, and for the production of a hydrodesulfurized gas oil wherein a gas oil is used to purify by-product gas from a catalytic reforming or hydroforming step by removing gaseous hydrocarbons from the by-product gas, then separated and heated to drive out the absorbed gaseous hydrocarbons, and then subjected to a hydrodesulfurization treatment in the presence of the scrubbed by-product gas to produce hydrodesulfurized gas oil. If desired, the hydrodesulfurized gas oil may be separated into a heavy fraction and a lighter naphtha fraction, and the naphtha fraction may be subjected to the reforming treatment to produce the improved gasoline and by-product gas which is used in the process.

In catalytic reforming by any of the conventional processes, a by-product gas is obtained which contains hydrogen and also normally gaseous hydrocarbons. This gas may be used as a source of hydrogen for hydrodesulfurization, or in the reforming. However, the gaseous hydrocarbon diluents therein are objectionable, and must be brought to a relatively low proportion. Especially is this so since in a continuous process the hydrogen is used up and the lower hydrocarbons accumulate. Thus it is necessary to separate the hydrocarbons from the hydrogen in a continuous process.

After the reforming treatment, the treated stock is cooled to ambient temperatures such as about 80° F., and the gasoline fraction having the improved octane rating is separated from the by-product hydrogen and gaseous hydrocarbon mixture. In purifying this gas by removing gaseous hydrocarbons and thus raising the percent content of hydrogen therein, it is desirable to carry out the absorption of the gaseous hydrocarbon in a liquid (scrubbing) hydrocarbon at ambient temperatures, such as about 80° F. In order to separate the absorbed gaseous hydrocarbons from the scrubbing liquid, the latter has to be heated to a moderately high temperature to drive off the gaseous hydrocarbons. In a conventional hydrodesulfurizing process, the gas oil or the like charging stock is raised to a relatively high temperature.

2

A marked conservation of energy is achieved in accordance with the invention by combining the two treatments so that the gas oil feed stock to be desulfurized is used as the scrubbing liquid for absorbing the gaseous hydrocarbons from reforming by-product gas and leave a hydrogen enriched gas, and is then heated (1) to drive off the absorbed gaseous hydrocarbons and (2) to raise the gas oil feed stock to a desirable hydrodesulfurization temperature.

The catalytic reforming is carried out in accordance with known procedures. By "reforming" is meant a process of treating a stock at any elevated temperature in the presence of a catalyst to dehydrogenate and/or aromatize the straight chain hydrocarbons and naphthenes in the presence or absence of added hydrogen. When the process is carried out in the presence of added hydrogen, it is commonly called hydroforming. Any reforming catalyst may be used under any reforming conditions. For example, one such catalyst is of the gel type, containing from 18 to 30 mol percent of chromium oxide (calculated as Cr_2O_3) and the remainder aluminum oxide (calculated as Al_2O_3). The pressure may be in the range of 25 to 500 lbs. per square inch gauge, the temperature in the range of 800 to 1200° F., and the flow rate in the range of 0.1 to 10 liquid volumes of hydrocarbon per volume of catalyst per hour. Other catalysts of the class known as aromatizing catalysts may be used; generally these involve an oxide of a metal of the fifth and sixth periodic group, in an amount in the range of 5 to 50 mol percent with the balance being a refractory oxide such as alumina and/or silica or the like.

The hydrodesulfurization treatment is carried out in accordance with known procedures in the presence of a hydrodesulfurizing catalyst. Any hydrodesulfurizing catalyst and any hydrodesulfurizing conditions may be used although these always involve high temperatures. The process is one of reacting added hydrogen to convert the sulfur compound in the stock to gaseous sulfur compounds, generally H_2S . A typical catalyst of this type is cobalt oxide-molybdena-alumina. Another is a chromia-molybdena-alumina catalyst known in the art. Gas oil or the like stocks containing from about 1 to about 6.5% by weight of sulfur in the form of organic sulfur compounds,

3

are treated to reduce the amount of sulfur therein by formation of hydrogen sulfide. The stock may be either in the liquid phase or in the gaseous phase, or mixtures thereof. The treatment may be at a temperature in the range of 500 to 1050° F., and the pressure in the range of 25 to 1000 lbs. per square inch gauge. The feed rate of the hydrocarbon stock to the catalyst may be in the range of 0.5 to 10 liquid volumes per bulk volume of catalyst per hour.

The attached drawing is a schematic flow diagram illustrating the generic aspects of the invention. In order to facilitate a further understanding of the invention, the following specific embodiments are included for illustrative purposes and not necessarily as limitations of the invention.

EXAMPLE 1

About 12,500 barrels per stream day of virgin gas oil containing 2.0% sulfur, is passed downwardly into a gas scrubber at ambient temperature, countercurrent to 3,000,000 cubic feet per stream day of by-product gas, at about 80° F. and at about 350 lbs. per square inch gauge, passed upwardly through the scrubber. The gas oil plus absorbed gaseous hydrocarbons is then separated and passed to a heater at a lower pressure. Any temperature and pressure may be used which will accomplish the desorption. Generally a temperature of 250° up to the hydrodesulfurizing temperature may be used with a low pressure of from 0 to several atmospheres. In the specific example it is brought to a temperature of about 450° F., at a pressure of about one atmosphere, and 600,000 cubic feet per stream day of the gaseous hydrocarbons are driven off. The gas oil is then fed into a hydrodesulfurization unit, containing a cobalt oxide-molybdena-alumina catalyst, at 750° F., 300 p. s. i., 1.0 v./v./hr., together with 2,400,000 cubic feet per stream day of the scrubbed or H₂ enriched gas. The sulfur content of the oil, in the form of organic sulfur, is reduced to 0.25% by weight sulfur.

About 5,000 barrels per stream day of virgin naphtha is fed into a reforming unit, containing a 80 mol percent alumina-20 mol percent chromia catalyst, at 950° F., 25 p. s. i., 1.0 v./v./hr., with 30-minutes on-stream. No hydrogen is fed to the unit. The treated material is then cooled to 80° F. and the liquid phase is drawn off. It consists of 3600 barrels per stream day of 80 ASTM O. N. gasoline. The by-product gas is separated into two parts. 4,000,000 cubic feet per stream day of gas is removed from the system since more is formed in this example than is necessary. The remaining part, 3,000,000 cubic feet per stream day, of the gas is subjected to the above described scrubbing, and the resulting 2,400,000 cubic feet per stream day of hydrogen enriched gas is then used in the above described hydrodesulfurization step.

In the hydrodesulfurization step, the off gas may be recycled. Any H₂S therein may be recycled, or may be removed therefrom by a separate scrubbing treatment, e. g. by aqueous caustic, or by the so-called Girbotol process. If the H₂S is not otherwise removed, it comes out with the gas oil, if the latter is properly cooled, and can be driven off or topped from the gas oil.

If desired, the gas oil may contain the naphtha so that the treated gas oil fraction may be passed to a fractionating column, wherein it is separated into a heavy or higher boiling fraction and a lighter fraction which is fed to the reformer. In

4

such an embodiment the desorption temperature is adjusted downwardly.

The product of this example is of desirable quality and is obtained in good yield.

The following are the material inspections:

Gas oil feed stock

A. P. I., 60° F.	27
Per cent sulfur	2.0
Aniline point	161.5
Avg. mol. wt.	293

Engler distillation range:

5% (volume)	550
10	569
30	610
50	651
70	696
90	751

Virgin naphtha fraction

A. P. I., 60° F.	56
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Engler distillation range:

5% (volume)	194
10	208
30	243
50	270
70	299
90	344

Reformer by-product gas

	Per cent (volume)
H ₂	69
CH ₄	13
C ₂ H ₆	7
C ₃ H ₈	6
C ₄ H ₁₀	3
C ₅ H ₁₂	2

Scrubbed reformer by-product gas

	Per cent (volume)
H ₂	80.5
CH ₄	13.0
C ₂ H ₆	4.5
C ₃ H ₈	2.0
C ₄ H ₁₀	0
C ₅ H ₁₂	0

EXAMPLE 2

In this example the reforming is carried out by the so-called hydroforming, in which the treatment is carried out in the presence of added hydrogen.

About 12,500 barrels per stream day of virgin gas oil having a sulfur content of 2.0%, is passed downwardly into a scrubber unit at ambient temperature, countercurrent to 16,500,000 cubic feet per stream day of by-product gas, at about 80° F. and about 75 p. s. i., passed upwardly through the scrubber. The gas oil containing absorbed gaseous hydrocarbons is then passed to a heater wherein it is brought up to about 400° F., at about one atmosphere, and about 800,000 cubic feet per stream day of the absorbed gaseous hydrocarbons are driven off. The gas oil is then fed into a hydrodesulfurization unit, containing a cobalt oxide-molybdena-alumina catalyst at 750° F., 300 p. s. i., 1.0 v./v./hr., together with 2,500,000 cubic feet per stream day of the scrubbed or H₂ enriched gas. The sulfur content of the oil, in the form of organic sulfur, is reduced to 0.25% by weight sulfur.

5

About 5,000 barrels per stream day of virgin naphtha is fed into a hydroforming unit containing the above described alumina-chromia catalyst, at 980° F., 1.0 v./v./hr. and 75 p. s. i., running 2½ hours on-stream time. The remainder of the scrubbed or H₂ enriched by-product gas, about 13,200,000 cubic feet per stream day, is also fed or recycled into this unit. The hydroformed product is cooled to about 80° F., and the liquid is separated therefrom. It consists of about 4200 barrels per stream day of 78 ASTM O. N. gasoline. The remainder is about 16,500,000 cubic feet per stream day of by-product gas at system pressure, indicating that about 3,300,000 cubic feet per stream day is formed during the hydroforming which is the amount removed in scrubbing and used in hydrodesulfurizing. The products of the example are obtained in good yield and are of good quality as indicated.

The gas oil may contain the naphtha, and if so, the desulfurized gas oil is then passed to a fractionator wherein it is separated into a light or naphtha fraction, e. g., boiling in the range of 200 to 400° F. which is fed to the hydroformer, and a heavy or higher boiling fraction. In such an embodiment the desorption temperature is similarly adjusted downwardly.

Material inspections or characteristics are as follows:

Gas oil

API, 60° F.	27
Per cent sulfur	2.0
Aniline point	161.5
Avg. mol. wt.	293

Engler distillation range:

5% (volume)	550
10	569
30	610
50	651
70	696
90	751

Virgin naphtha fraction

API, 60° F.	56
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Engler distillation range:

5% (volume)	194
10	208
30	243
50	270
70	299
90	344

Hydroformed by-product gas

	Per cent (volume)
H ₂	88
CH ₄	4
C ₂ H ₆	3
C ₃ H ₈	2
C ₄ H ₁₀	2
C ₅ H ₁₂	1

6

Scrubbed hydroformed by-product gas

	Per cent (volume)
H ₂	90
CH ₄	4
C ₂ H ₆	3
C ₃ H ₈	2
C ₄ H ₁₀	1
C ₅ H ₁₂	0

The process of the invention is operative with any hydrodesulfurization process using any of the known suitable catalysts, as well as with any known reforming process and catalyst. The essential requirements are that the reforming produce by-product gas containing hydrogen diluted with hydrocarbon material which can be absorbed by the hydrodesulfurization feed stock.

In view of the foregoing disclosures, variations or modifications thereof will be apparent to those skilled in the art and the invention contemplates all such variations and modifications except as do not come within the scope of the appended claims.

I claim:

1. A process of treating naphtha and gas oil fractions, which comprises reforming naphtha to form gasoline of higher octane number and produce a by-product gas containing hydrogen and gaseous hydrocarbons, scrubbing said reformed by-product gas at an ambient temperature with gas oil feed stock to remove gaseous hydrocarbons from the gas and to provide a hydrogen enriched by-product gas, separating and heating the gas oil feed stock to drive off absorbed gaseous hydrocarbons, and then hydrodesulfurizing the heated gas oil feed stock with said hydrogen enriched by-product gas.

2. The process of claim 1 wherein the reforming is hydroforming and is carried out in the presence of a part of the scrubbed by-product gas.

3. The process of claim 1 in which the naphtha and gas oil is in a single fraction and the desulfurized stock is fractionated and the naphtha fraction is reformed.

4. The process of claim 1 wherein the hydrodesulfurization is carried out with the scrubbed by-product gas and in the presence of cobalt molybdate on aluminum catalyst, at 750° F., a 300 p. s. i., and 1.0 v./v./hr., and the reforming is carried out in the presence of 80 mol per cent alumina-20 mol per cent chromia catalyst at 950° F., 25 p. s. i. and 1.0 v./v./hr.

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