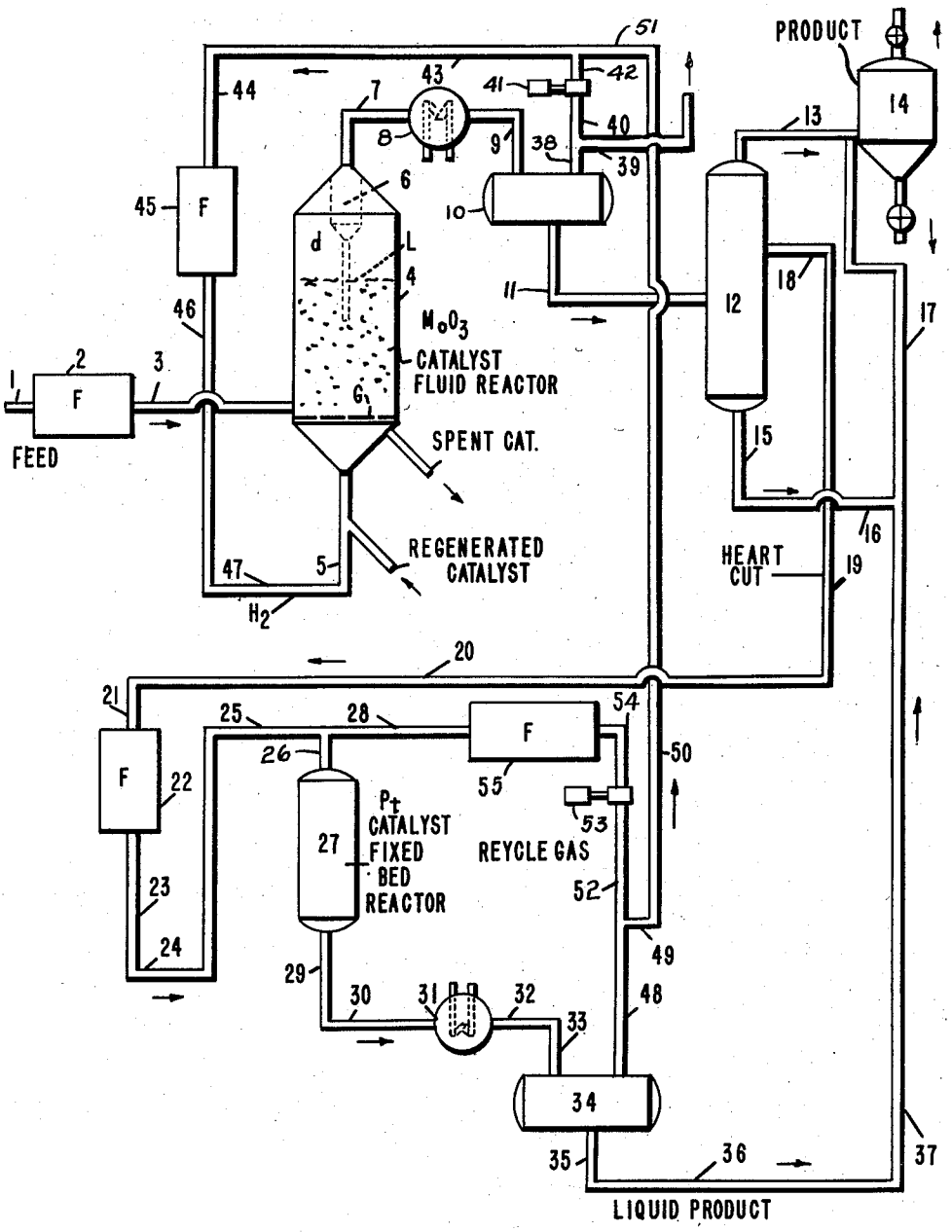
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HYDROFORMING IN TWO STAGES

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CHARLES E. HEMMINGER INVENTOR

BY J. Cashman ATTORNEY

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HYDROFORMING IN TWO STAGES

Charles E. Hemminger, Westfield, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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The present invention relates to improvements in the hydroforming of naphthas and more particularly relates to improvements in hydroforming naphthas containing substantial amounts of sulfur.

Hydroforming is defined as an operation in which naphthas, usually virgin naphthas containing a substantial amount of naphthenes, are contacted at elevated temperatures and pressures in the presence of a solid catalytic material and hydrogen, and under conditions in which there is no net consumption of hydrogen, to produce a hydroformed product of improved octane rating.

Heretofore, and prior to this invention, it was a matter of record and commercial practice to employ platinum suitably supported as a hydroforming catalyst. Other catalysts such as group 6 metal oxides suitably supported have also been used as catalysts in the hydroforming operation.

In the case where the catalyst is platinum and the feed stock contains substantial quantities of sulfur material, precautions must be taken to protect the expensive catalyst from injury or deactivation by these sulfur materials. In the case of cracked naphtha which is to be reformed, the said naphtha may contain substantial quantities of olefinic material which also tends to deactivate the catalyst by the formation of gummy deposits thereon.

Furthermore, whether the naphtha be virgin stock or a cracked stock, it may—and often does—contain metallic poisons such as arsenic, iron and vanadium, etc. which also tend to poison the catalyst.

The present invention provides means for pretreating the naphtha feed to remove sulfur and other poisons therefrom before it contacts a platinum catalyst. In brief compass, the present invention provides a two-stage operation in which the naphtha is first treated in the presence of a sixth group metal oxide, such as molybdenum oxide, under conditions such that sulfur and other poisons are removed from the feed. During this initial or pretreating stage some hydroforming of the product occurs. The product from this first stage is then cooled to condense the normally liquid constituents thereof. The condensate from this first-stage is then subjected to fractional distillation, and a fraction boiling from 0 to about 250° F. is recovered for a product. A bottoms fraction boiling above about 350° F. is recovered and also recovered for product. A heart cut, namely, a product boiling from about 250° F. to 300° F., is recovered from the said fractional distillation step, and this material which is substantially free from sulfur or other poisons is subjected to hydroforming in the presence of a platinum catalyst.

The object of the present invention, therefore, is to provide a process in which naphthas, which may be a virgin, a cracked, or a Fischer naphtha, may be hydroformed to produce a product of improved octane quality in a manner which is cheap and efficient.

A more specific object of the present invention is to provide a process for efficiently and economically hydroforming naphthas containing sulfur and other poisons.

Another object of the present invention is to hydroform naphthas utilizing a platinum catalyst under conditions such that the platinum catalyst is protected from the influence of poisons contained in the original feed.

Another object of the present invention is to provide a process for hydroforming naphthas utilizing a platinum catalyst under conditions such that the amount of platinum catalyst for a given plant size is substantially reduced.

Another object of the present invention is to hydroform a naphtha under conditions such that a product of greater middle volatility (increased amount of product distilling at 212° F.) is obtained than is normally obtained utilizing a platinum catalyst.

The accompanying drawing illustrates diagrammatically a flow plan in which a preferred modification of the present invention may be carried into effect.

Referring in detail to the drawing, a naphtha feed enters the present system through line **1**, is heated in furnace **2** and thence charged via line **3** to a reactor **4**. Reactor **4** contains a fluidized bed of molybdenum oxide catalyst extending from a grid or screen G to upper dense phase level L. A hydrogen-containing gas is charged into the bottom of reactor **4** through line **5**, passes upwardly through the grid G, and comingles with the vaporized naphtha and catalyst C in reactor **4**. Under conditions of operation more fully set forth hereinafter, the desired conversion occurs, and the product vapors emerge from the dense phase and pass through a dilute phase suspension of catalyst and gasiform material extending from L to the top of the reactor. The major portion of the catalyst is separated from the effluent product in this catalyst disengaging space. However, before the product is withdrawn from reactor **4** it is forced through one or more "cyclones" **6** wherein entrained fines are removed and returned to the dense bed C of catalyst through one or more dip pipes *d*. The effluent from the reactor is withdrawn through line **7** and cooled to a temperature of about 100° in cooler **8** and thence charged via line **9** to a receiving drum **10**. From receiving drum **10** liquid condensate is withdrawn through line **11** and charged to a fractionating distillation column **12** which is provided with the conventional reboiler and refluxing equipment (not shown). A fraction boiling from about 100° to about 250° F. is taken overhead from column **12** through line **13**. This material is then charged to a product receiving drum **14**. A bottoms fraction is withdrawn from column **12** through line **15**, thence passed via line **16** to line **17** and eventually to line **13** for delivery to product storage drum **14**.

An intermediate fraction boiling from about 250° to 350° F. is withdrawn from column **12** through line **18** and delivered via lines **19**, **20** and **21** to a reheat furnace **22** wherein it is vaporized and heated and thence withdrawn through line **23** and charged via lines **24**, **25** and **26** to a second reactor **27** containing a fixed bed of platinum catalyst. Simultaneously, a hydrogen-containing gas in line **28** is passed to line **26** and thence passed with the oil feed into the top of reactor **27**. In reactor **27** the desired conversion occurs, and the product is withdrawn therefrom through line **29**, thence passed via line **30** to a cooler **31** wherein the normally liquid material is condensed. The product passes via lines **32** and **33** into a receiving drum **34**. The hydroformed product is withdrawn from **34** through line **35** and thence passed by lines **36**, **37**, **17** and **13** to product receiving drum **14**.

Referring again to receiving drum **10**, the normally gaseous constituents are withdrawn therefrom through line **38**. This gasiformed material contains essentially hydrogen and C_1 to C_6 hydrocarbons. A portion of this material may be rejected from the system into line **39**. Another portion of this material is passed via line

40 to a compressor 41, thence withdrawn from compressor 41 through line 42, thence charged through lines 43 and 44 to furnace 45, and thence passed via lines 46 and 47 to line 5 for reuse in reactor 4.

Now referring to receiving drum 34 which contains the hydroformed product produced in the platinum-containing reactor 27, the overhead material which consists mainly of hydrogen and normally gaseous hydrocarbons is withdrawn therefrom through line 48. A portion of this gasiform material may be passed via lines 49, 50 and 51 into line 43 where it is mixed with the recycle gas from receiving drum 10 and passed through line 44 into furnace 45 where it is heated and thence passes through lines 46 and 47 to line 5 for reuse in reactor 4. It is pointed out that the recycled gas in line 48 contains from about 85 to 95% hydrogen whereas the gas recovered from the receiving drum 10 in line 38 would contain from 65 to 85% hydrogen were it not blended with the recycle gas in line 48 or from the receiving drum 34. The other portion of the gas in line 48 is passed via line 52 to a compressor 53, thence passed via line 54, to a reheat furnace 55 from which it is withdrawn through line 28 into line 26 for recycling to reactor 27.

In order to more fully explain and describe the present invention, the following operating conditions are set forth:

Reactor 4

	Range	Preferred
Catalyst composition, wt. percent MoO_3 on alumina	5–20	8–12
Particle size range, microns	10–150	20–100
Temperature, ° F., average	800–950	850–925
Pressure, p. s. i.	50–500	100–300
Space velocity, lbs. oil per hour per lb. feed	0.3–10	1–3
Recycle gas rate, in standard cubic ft. per bbl. of oil	500–7,000	1,500–4,000
Concentration of H_2, in recycle gas, vol. percent	50–90	60–80

Reactor 27

	Range	Preferred
Catalyst composition, wt. percent Pt on alumina	0.02–1.0	0.1–0.5
Temperature, ° F., average	800–975	875–925
Pressure, p. s. i.	50–500	200–400
Space velocity, lbs. oil per hour per lb. feed	0.5–10	2–5
Recycle gas rate, in standard cubic ft. per bbl. of oil	1,000–7,000	2,000–5,000
Concentration of H_2, in recycle gas, vol. percent	60–95	80–90

It will be understood that the catalysts in reactors 4 and 27 will require at least periodic regeneration to maintain their activity. The catalyst in reactor 4 may be withdrawn continuously or periodically and treated under known conditions with an oxygen-containing gas in a regenerator (not shown) in order to burn off and remove the sulfur, carbonaceous and other contaminating deposits. It is to be noted that most all of the sulfur in the feed deposits on the molybdena catalyst in the reactor and is removed during regeneration as SO_2.

In like manner the catalyst in reactor 27 must be treated intermittently with diluted air according to known procedure to restore its activity. However, since the feed to reactor 27 is a clean stock it may be operated for a period up to six months continuously without requiring regeneration of the said catalyst. During the period, however, when it is necessary to regenerate the platinum catalyst in reactor 27, the feed thereto may be stored temporarily while the catalyst is undergoing regeneration, thus requiring only a single platinum reactor vessel. However, if desired, a second reactor may be provided so that when one reactor is off-stream for regeneration of the catalyst, the other may be placed onstream.

An important advantage of the system previously described is that in hydroforming naphtha 50–75% of the hydroforming is carried out in the first stage, thus leaving about 25–50% to be carried out in the second platinum stage. This means that the process may be operated with a single platinum catalyst-containing reactor, thus reducing the cost of the plant of a given capacity.

It will be understood that cobalt molybdate may be used in place of a sixth group metal oxide carried on active alumina in the first stage of the above described process, and that palladium on active alumina may be used in the second stage in place of the platinum on active alumina. It is advisable, however, to use about three times as much palladium as platinum when compounding the former catalyst composition. Also, it is desirable in the interest of heat stability to incorporate in either or both catalysts, used in the first and second stages of the above described process, from 0.6 to 5% of silica, based on the total weight of the catalyst composition.

With respect to the heart cut which is subjected to hydroforming in the second stage of the presently described process, a naphtha fraction boiling in the range of from about 150° to 375° F. may be recycled to the hydroforming zone.

What is claimed is:

1. The method of hydroforming a naphtha containing sulfur which comprises contacting said naphtha with a fluidized bed of a desulfurizing catalyst selected from the class consisting of molybdenum oxide carried on activated alumina and cobalt molybdate, in the presence of added hydrogen, at elevated temperatures and pressures for a sufficient period of time to convert the sulfur contained in the said naphtha to volatile sulfur compounds and to accomplish 50–75% of the hydroforming operation, withdrawing the treated naphtha from contact with the fluidized bed of molybdenum oxide catalyst, cooling and condensing the product, recovering a fraction boiling substantially within the range above about 250°–350° F., contacting this fraction, in the presence of added hydrogen, under hydroforming conditions of temperature, pressure and contact time with a platinum group metal catalyst to complete the hydroforming process, recovering from the latter step the product, mixing said product with the material boiling below 250° F. and above 350° F. recovered from the first step to obtain a naphtha which is substantially sulfur-free and of improved octane number.

2. The method set forth in claim 1 in which the light and heavy ends of the product from the first stage are combined with the product of the second stage.

3. The method set forth in claim 1 in which the catalyst in the second stage is palladium.

4. The method set forth in claim 1 in which cobalt molybdate is used in the first stage.

5. The method set forth in claim 1 in which the catalyst bases contain from 1 to 5% silica based on the alumina support.

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