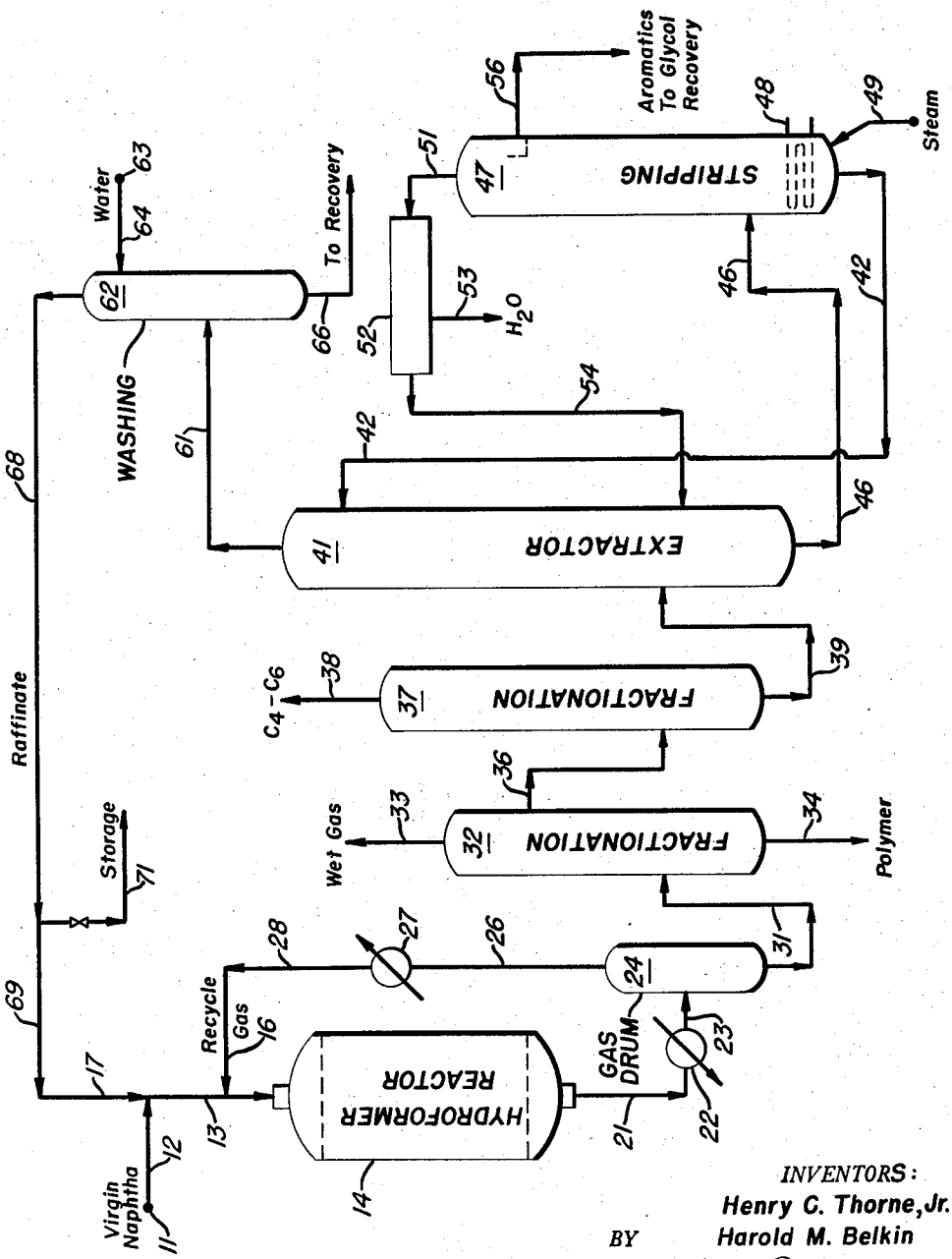
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HYDROFORMING PROCESS

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HYDROFORMING PROCESS

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This invention relates to the production of aromatic hydrocarbons by a combination catalytic reforming and solvent extraction operation. More particularly it relates to improved yields of aromatic hydrocarbons by a combination hydroforming and solvent extraction operation wherein the hydroforming catalyst is molybdenum oxide-alumina.

A large demand for aromatic hydrocarbons is present today. The major source of aromatic hydrocarbons are from the reformates produced in the catalytic reforming, in the presence of hydrogen, of petroleum naphthas, particularly virgin naphthas. The raffinate produced in the glycolic-solvent extraction of hydroformate, from the catalytic reforming in the presence of hydrogen using catalyst consisting essentially of molybdenum oxide supported by alumina, is of relatively low octane number and, therefore, not of great value as a gasoline component. Appreciable amounts of naphthenes have been found to be present in this raffinate when the solvent extraction process is carried out to produce essentially pure aromatic hydrocarbons. These naphthenes, if converted to aromatic hydrocarbons, are worth considerably more than their value as gasoline components.

An object of this invention is a process for increasing the yield of aromatic hydrocarbons obtainable from petroleum naphthas when said naphtha is catalytically reformed in the presence of hydrogen using a molybdenum oxide-alumina catalyst. Another object is a process for increasing the value of raffinate substantially free of aromatic hydrocarbons produced by solvent extraction of hydroformate from a molybdenum oxide on alumina catalyzed reforming of petroleum naphtha. Other objects will become apparent in the course of the description of the invention.

The annexed figure, which forms a part of this specification, sets out an illustrative embodiment of the invention. Many items of process equipment have been omitted, as these may be readily added thereto by those skilled in the catalytic reforming and solvent extraction arts, which operations are now quite common in the petroleum refining industry.

The main feed to the process is a petroleum naphtha which may boil from about 100° F. to about 425° F. More usually, the feed to the catalytic reforming step is a virgin heavy naphtha which boils between about 200° and 425° F. When it is desired to maximize the recovery of aromatic hydrocarbons from the petroleum naphtha, the naphtha portion of the feed boils between about 130° and 375° F., that is, the initial boiling point is just below the boiling point of benzene. The preferred feed is a virgin naphtha having a high natural naphthene content. Virgin naphtha from source 11 is passed by way of lines 12 and 13 into hydroformer-reactor 14. Recycle gas containing hydrogen is introduced into line 13, from line 16. Raffinate from a source hereinafter described is introduced into line 13 by way of line 17.

Hydroformer-reactor 14 represents a catalytic reforming operation in the presence of hydrogen. Any one of the conventional catalytic reforming processes utilizing the molybdenum oxide-alumina catalyst may be utilized in the process of this invention. The operation may be the conventional fixed bed hydroforming operation or it may be the so-called fluid hydroforming operation. Briefly, in this catalytic reforming operation the naphtha charge and the hydrogen are passed through a catalyst bed at a temperature between about 900° and 1050° F. for a time sufficient to convert naphthenes to aromatic hydrocarbons; usually the time is about that needed to approach an equilibrium condition in the conversion of naphthenes. Many descriptions of hydroforming, both fixed bed and fluidized bed, are available in the art. For example, Intermittent and Fluid Catalytic Reforming of Naphthenes by Henry G. McGrath and Luther R. Hill in Progress in Petroleum Technology, Advances in Chemistry, Series No. 5.

The reactor shown herein is a schematic representation of a fixed bed unit. The conditions of operation may be a naphtha transfer line temperature of 1000° F., a recycle gas transfer line temperature of 1050° F. and the overall temperature in the reactor of 950° F. Pressure in the reactor may be about 250 p. s. i. g. and the space velocity may be about 0.52 volume/hour/volume. The recycle gas rate may be about 2750 s. c. f./bbl. of feed.

The catalyst used in the catalytic reforming operation of this process consists essentially of molybdenum oxide on an alumina support. The catalyst may be either the impregnated alumina type or the gel type. It is preferred to use catalyst prepared by co-precipitation of the alumina gel with a molybdenum salt which is then converted to molybdic oxide. In general, the amount of molybdenum present in the catalyst may be between about 4 and 20 weight percent as molybdic oxide. The preparation of catalyst for hydroformers is set out in some detail in Petroleum Processing 2, 834–842, November 1947. The catalyst in this illustration is a gel type catalyst purchased from the Oronite Chemical Company, and containing about 10 weight percent of molybdic oxide.

The effluent from the reactor is passed by way of line 21, heat exchanger 22 and line 23 into gas drum 24. In gas drum 24, the gaseous conversion products are flashed and are passed by way of line 26, heater 27, lines 28 and 16 back to line 13 for recycle to the reactor. It is to be understood that this flow is greatly simplified from that actually used in the hydroforming operation.

The liquid from gas drum 24 is passed by way of line 31 into fractionation zone 32. In this zone, wet gas comprising methane, ethane, propane, and some butane is taken overhead and is passed to refinery usage by way of line 33. A bottoms product, commonly known as polymer, is withdrawn by way of line 34. This material comprises polycyclic aromatics and other hydrocarbons; this material has an ASTM distillation initial temperature of about 300° F.

The intermediate liquid product from zone 32 is passed by way of line 36 into fractionation zone 37. In this zone, there is taken overhead a butane-pentane-hexane fraction labeled as C_4–C_6. This overhead fraction is sent to refining operations by way of line 38. In order to decrease the load on the subsequent solvent extraction step and also decrease the recycle load on the hydroformer-reactor, all material boiling below about 155° F. (true boiling point) is taken overhead in this fractionation operation. The bottoms product, which is hereinafter designated as hydroformate, usually boils over the range of about 130° F. and 300° F.

The hydroformate from zone 37 is passed by way of line 39 into extractor 41. Extractor 41 is a vessel adapted for the liquid-liquid contacting of the hydroformate and

a solvent essentially immiscible therein. The solvent utilized in this process is a glycolic solvent. Particularly suitable are the polyglycols, i. e., polymeric glycols containing ether linkages. Examples of these solvents are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, propylene glycol, and dipropylene glycol. The selectivity of the solvents are improved by the presence of small amounts of water, for example, from about 4 to 10 volume percent. The preferred glycolic solvents are diethylene glycol, dipropylene glycol, or mixtures of these along with water. The glycol content is between about 88 and 96 volume percent and the water between about 4 and 12 volume percent. In this embodiment, the solvent consists of about 57% diethylene glycol, 34% of dipropylene glycol, and 9% of water. The solvent is introduced near the top of extractor **41** by way of line **42**.

The amount of solvent used is dependent upon the type of feed, the type of solvent, and the temperature conditions in extractor **41**. The solvent-feed volume ratio may be between about 5 and 15. In this illustration, the solvent to feed ratio is about 6.5.

In order to increase the capacity of the solvent, extractor **41** is operated at a temperature between about 200° and 300° F.; in some cases, the temperature may be either lower or higher than these. In this embodiment, extractor **41** is operated at a substantially constant temperature of about 295° F.

A raffinate phase and an extract phase are formed in extractor **41**. The extract phase is withdrawn from the bottom of extractor **41** by way of line **46** and is introduced into stripping zone **47**. Stripping zone **47** is provided with an internal heater **48** and a conduit **49** for the introduction of stripping steam. Stripping zone **47** is provided with fractionation means not shown. There is taken overhead a vapor stream by way of line **51** which contains steam, essentially all of the remaining non-aromatic hydrocarbons and some of the aromatic hydrocarbons. This stream is condensed in zone **52** and liquid water removed by way of line **53**. The hydrocarbons are passed by way of line **54** and introduced into extractor **41** as reflux. The point of introduction of these hydrocarbons by way of line **53** is below the point of entry of the hydroformate and somewhat above the exit point of the extract phase.

Essentially pure aromatic hydrocarbons are withdrawn as a side stream from stripping zone **47** by way of line **56**. This side stream contains some glycol and water and must be further treated before it is suitable for use. These aromatics may be water-washed and clay treated to produce nitration grade benzene, toluene, and C_8 aromatic hydrocarbons. These procedures are conventional and are not discussed at any length herein.

The raffinate phase is withdrawn from the top of extractor **41** and is passed by way of line **61** into washing zone **62**. Washing zone **62** is adapted for the intimate contacting countercurrently of hydrocarbons and water. Water from source **63** is passed by way of line **64** into an upper point of zone **62**. The water dissolves the glycol from the raffinate phase and is withdrawn by way of line **66** and passed to means for recovering the glycol agent. The washed raffinate, which is substantially free of aromatic hydrocarbons, is passed by way of lines **68**, **69** and **17** to line **13** for introduction into the hydroformer-reactor.

Since the raffinate contains a higher proportion of paraffinic hydrocarbons than does the virgin naphtha portion of the feed, it may not be desirable to recycle all of the raffinate in order to avoid a build-up of paraffins. In such case, a portion of the raffinate stream is passed to storage by way of valved line **71**. Normally, a major proportion of the raffinate produced will be recycled to hydroformer-reactor **14**.

Example

The results obtainable by the process of the invention are illustrated by the following example. A virgin naphtha having a CFR-R octane number of 59.2 and an ASTM distillation: Initial, 160° F., 50%, 210° F., and maximum, 288° F., was catalytically reformed in a commercial fixed bed unit using gel-type molybdenum oxide-alumina catalyst containing 10 weight percent of molybdic oxide. The liquid hydroformate, including all of the pentanes, had a CFR research clear octane of 88.7.

The hydroformate was distilled to obtain a fraction having a boiling range: Initial, 176° F., 50%, 214° F., and maximum, 303° F. The fractionated hydroformate was contacted with 7 volumes of a solvent consisting of about 57% diethylene glycol, 34% of dipropylene glycol, and 9% of water at a temperature of about 295° F. The extract phase was steam stripped to remove overhead all the non-aromatic hydrocarbons. This overhead was condensed and introduced into the extraction zone as reflux.

Essentially pure aromatic hydrocarbons were then removed from the glycol solvent. The raffinate phase was washed with water to remove glycol solvent entrained therein.

This raffinate had an octane number CFR-research clear of 47.4. The ASTM distillation was: Initial, 169° F., 50%, 197° F., and maximum, 297° F. An analysis for hydrocarbon type indicated that it consisted of paraffins, 73.0%, olefins, 2.5%, naphthenes, 21.5%, and aromatics, 3.0%.

The raffinate was charged to the miniature fixed bed hydroforming unit under conditions essentially identical with those described for the reforming of the virgin naphtha. The yield of liquid material boiling above butane, i. e., C_5+ was 65% as compared with 70% for the wider boiling range virgin naphtha. The CFR-research clear octane of the C_5+ liquid was 85.6. The ASTM distillation of the C_5+ liquid was: Initial, 112° F., 50%, 177° F., and maximum, 332° F. Analysis of the material for hydrocarbon types showed it to consist of paraffins, 64.0%, olefins, 1.0%, naphthenes, 2.5% and aromatics, 32.5%. Thus it is indicated that essentially all the naphthenes present in the virgin naphtha can be converted to aromatic hydrocarbons by the process of this invention.

Thus having described the invention, what is claimed is:

1. A process which comprises (1) reforming a naphthene-containing petroleum naphtha in the presence of hydrogen and a catalyst consisting essentially of molybdenum oxide on an alumina support, (2) distilling the liquid product to obtain a reformate containing aromatics and unconverted naphthenes, (3) solvent extracting said reformate with a glycolic solvent under conditions to produce an essentially pure aromatic extract and a substantially aromatic-free raffinate, and (4) cycling raffinate to the reforming operation for reforming along with said naphtha.

2. The process of claim 1 wherein said reformate boils over the range between about 130° F. and 300° F.

3. The process of claim 1 wherein said solvent is diethylene glycol, 88–96%, and water, 4–12%.

4. The process of claim 1 wherein said solvent is dipropylene glycol, about 35%, water, about 10%, and diethylene glycol, about 55%.

5. The process of claim 1 wherein said solvent is triethylene glycol.

6. A process which comprises (1) hydroforming, using a molybdenum oxide alumina catalyst, a feed containing a virgin petroleum naphtha boiling between about 130° F. and 375° F. and containing naphthenes and a raffinate, (2) distilling the liquid product of said reforming to obtain a reformate boiling over the range of about 130° F. and 300° F. which reformate contains aromatics and

unconverted naphthenes, (3) solvent extracting said reformate using a glycolic solvent at a temperature between about 200° F. and 300° F. to produce a substantially aromatic-free raffinate phase and an extract phase, (4) steam stripping said extract phase in a fractionator to produce an overhead consisting of aromatic and non-aromatic hydrocarbons, a sidestream of essentially pure aromatic hydrocarbon, and a bottoms stream of glycol, (5) cycling said overhead to said extraction zone at a point below the point of reformate entry, (6) water washing said raffinate phase to remove glycol and (7) passing

at least a major proportion of said raffinate to said hydroforming operation.

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