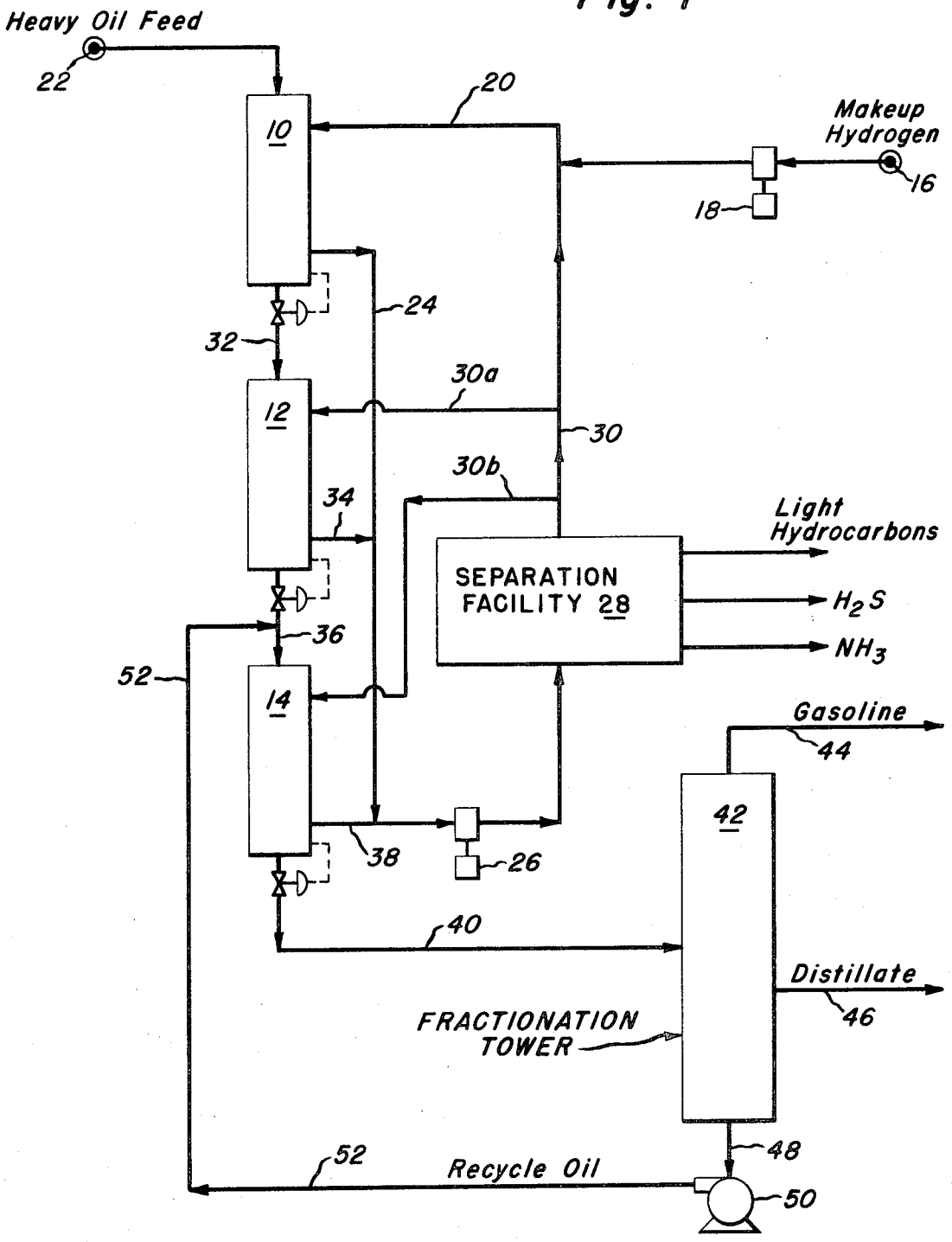
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THREE-STAGE PROCESS FOR HYDROTREATING FEEDS RICH IN POLYNUCLEAR AROMATICS

Filed Oct. 14, 1971 2 Sheets-Sheet 1

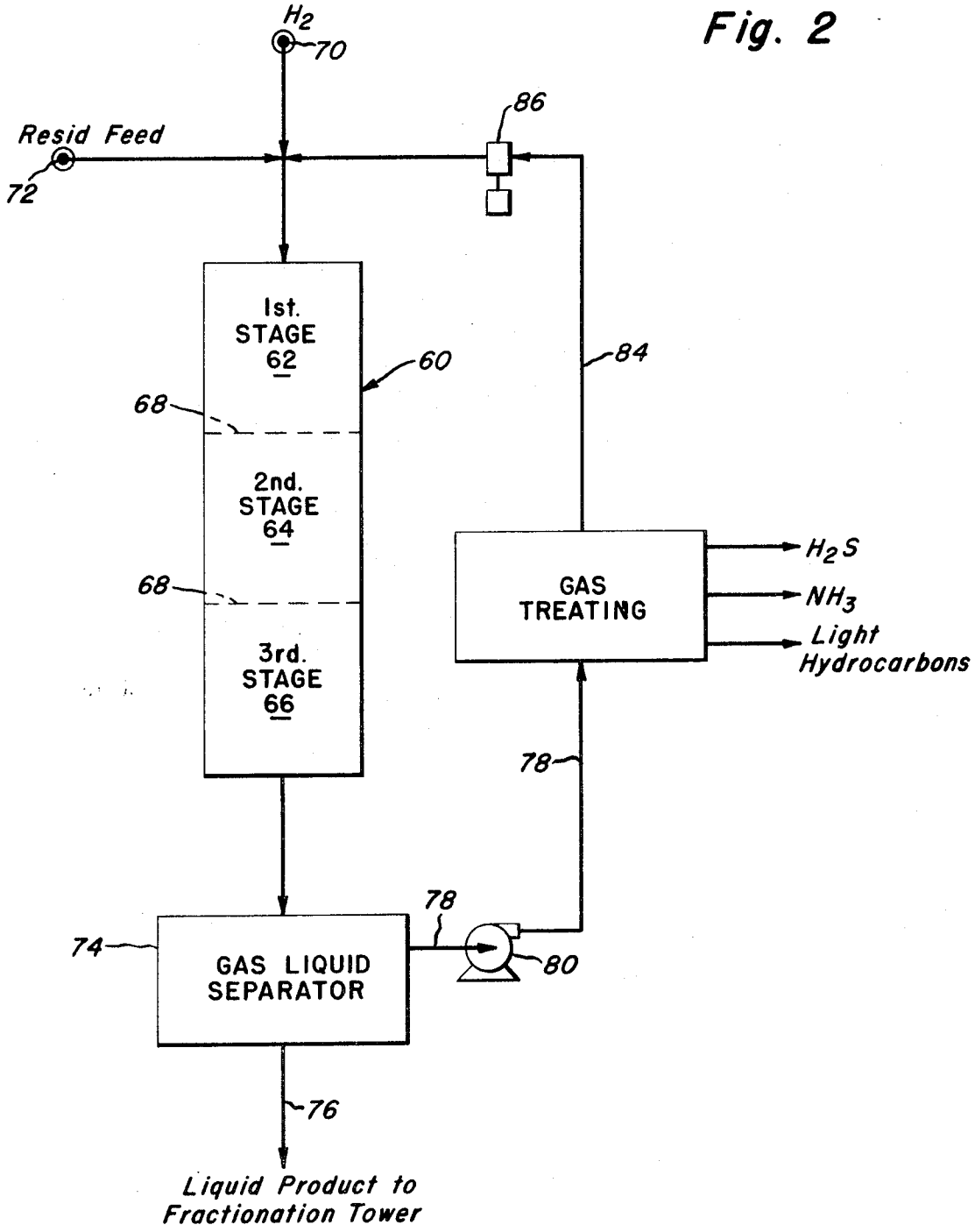
Fig. 1





INVENTORS.
Alvin W. Frazier
Maurice F. Oxenreiter
Arnold N. Wennerberg
BY
ATTORNEY

Fig. 2


H2
70
Resid Feed
72
86
1st. STAGE 62
60
84
68
2nd. STAGE 64
68
3rd. STAGE 66
GAS TREATING
H2S
NH3
Light Hydrocarbons
78
78
74
GAS LIQUID SEPARATOR
80
76
Liquid Product to Fractionation Tower

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3,726,787

# THREE-STAGE PROCESS FOR HYDROTREATING FEEDS RICH IN POLYNUCLEAR AROMATICS

Alvin W. Frazier, Chicago Heights, Ill., Maurice E. Oxenreiter, Dyer, Ind., and Arnold N. Wennerberg, Chicago, Ill., assignors to Standard Oil Company, Chicago, Ill.

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U.S. Cl. 208—59 7 Claims

## ABSTRACT OF THE DISCLOSURE

Disclosed is a three-stage process for converting into gasoline and distillate fuels a hydrocarbon feed rich in polynuclear aromatics. The first stage employs a catalyst comprising an alkali metal component or an alkaline earth metal component or both, supported on activated carbon. The second and third stages employ a catalyst comprising metallic components from Group VI and Group VIII of the Periodic Table, supported on a refractory, inorganic cracking matrix.

## BACKGROUND

Hydrocarbons including polynuclear aromatics, especially the resid fraction from crude oil, are frequently low value fuels available in large volumes. Present processes have been developed to coke such resids, crack them, deasphalt them and/or hydrocrack them and distill out a feed suitable for a fluidized cracking unit. Each of these processes leads to loss of the starting material to coke or a lower value fuel. It is the objective of our invention to convert essentially all of the hydrocarbon feed high in polynuclear aromatics to a valuable high octane gasoline or distillate fuel. Upon studying the accompanying description of our invention, it will be evident that our process not only has the advantage that the low value resids can be converted to the more valuable gasoline and distillate fuels, but such conversion can also be done in an economic manner, employing a single hydrogen supply source, the same recycle compressor and an integral, single refinery unit, thus conserving on equipment and hydrogen.

## THE INVENTION

We have invented a three-stage hydrocracking process for converting into gasoline and distillate fuels hydrocarbons including polynuclear aromatics. The boiling range, at normal pressure ranges, of gasoline and distillate fuels is between about 100 and about 650° F. as compared to a typical boiling range of about 650+° F. and higher for the hydrocarbon feed. Suitable feeds would preferably be resid hydrocarbons but bottoms from reformer units, shale oil, tar sands oil, or coal-derived liquids could also be used, either solely or combined with the resid hydrocarbons. Usually the feed contains polynuclear aromatics ranging from about 0.1 to about 30 wt. percent of the feed, and the feed may also include organic nitrogen and sulfur compounds. The organic nitrogen compounds typically comprise from about 0.0 to about 1.0 wt. percent of the feed and the organic sulfur compounds typically comprise from about 0.0 to about 6.0 wt. percent of the feed.

The key to the successful operation of our process is the first stage or reaction zone, where the polynuclear aromatics in the feed are hydrocracked. In this first reaction zone the feed contacts, at elevated temperatures and pressures and in the presence of hydrogen, a catalyst comprising activated carbon and an alkali metal component or an alkaline earth metal component or both. The amount of metal component is sufficient to promote cracking of



polynuclear aromatics. In some instances it may also be desirable to include metallic components from Groups VI and VIII of the Periodic Table such as, for example, nickel, tungsten, cobalt, molybdenum, iron, or their oxides or their sulfides.

Feeds including polynuclear aromatics having a number average molecular weight of about 400 or greater can most advantageously be treated according to our process. For example, resids include such polynuclear aromatics called asphaltenes and resins. The asphaltene concentration in, for example, a vacuum resid ranges between about 0.1 and about 30 wt. percent depending on its crude oil source, and the resin concentration ranges between about 25 and 70 wt. percent. The resins and asphaltees are structurally similar materials; however, resins are generally of lower molecular weight, heptane soluble, and are adsorbed on the surface of silica gel when a heptane solution of resins and oils is passed over a column of silica gel. The asphaltenes have high molecular weights such as, for example, from about 1,000 to about 15,000 and are insoluble in hot heptane.

The catalyst used in the first reaction zone is somewhat selective. Present data indicate that the polynuclear aromatics, when treated according to this process, are converted to lower molecular weight aromatics including with some feeds substituent alkyl groups. It is desirable to maintain a high concentration of resins in the reaction mixture, since resins help maintain the asphaltenes in solution. Thus the asphaltenes will not precipitate and clog the reactor or form coke deposits on the catalyst. Present data indicate that this carbon catalyst promotes cracking of the polynuclear aromatics without the catalyst bed plugging for periods in excess of 720 hours. These data also indicate that our process can reduce the molecular weight of asphaltenes by a factor of about 10, and the molecular weight of resins by a factor of about 3. Consequently, resin concentration in the reaction mixture of our process is always relatively high, minimizing loss of asphaltene solubility. The tendency toward reactor plugging is thus greatly reduced. And, surprisingly, our catalyst cracks or otherwise modifies the metal-containing compounds in the resid, and the metals are deposited on our catalyst without any noticeable adverse effects during the time of our experiments. High molecular weight sulfur-containing compounds are also cracked in our process. Our catalyst, however, appears to have little effect on low molecular weight sulfur compounds commonly found in resids such as benzothiophene and dibenzthiophene. Hence, there can be virtually complete demetallization and partial desulfurization of the resid using our catalyst.

Specifically, the catalyst used in the first zone comprises activated carbon having a surface area in the range of from about 200 to about 2,500 square meters per gram of carbon. This catalyst can be in either powder or granular form. In the granular form the preferred surface area ranges fom about 800 to about 2,000 square meter per gram of carbon. This activated carbon is impregnated with the metal component which is preferably in the form of a hydroxide, sulfide or oxide. Preferred alkali metals are potassium, sodium, lithium, rubidium and cesium. Preferred alkaline earth metals are magnesium, calcium, strontium and barium. The concentration of metal typically varies from about 0.1 to about 50 wt. percent based on the weight of carbon.

In preparing the catalyst, a metal salt can be used as a starting ingredient. It is dissolved in water and then the aqueous solution can be mixed with the activated carbon. The water is then removed to deposit the salt on the carbon. Also, decomposable salt forms such as acetates or formates can be used as starting ingredients. These can be mixed with the carbon and heated so that the salts will

decompose and the metals be deposited on the carbon surface. We have found the most preferred method of preparation to be dissolving a metal hydroxide in an alcoholic solution such as methanol, ethanol or propanol, mixing carbon with the solution and then removing the alcohol. The most preferred metal hydroxide is potassium hydroxide.

In the second and third stages or reaction zones the catalyst employed comprises metallic components from Groups VI and VIII of the Periodic Table supported on a refractory, inorganic cracking matrix. The metallic components may be in the metal, metal oxide, or metal sulfide form. The amount of metallic component ranges between about 1.0 and about 30 wt. percent based on the weight of the support material. Preferred support materials are silica-alumina, alumina, magnesia, zirconium and other such inorganic oxide metals. Zeolitic materials may also be used in the support, and it is especially desirable to include such materials in the catalyst used in the third reaction zone. Such catalysts are generally well known in the petroleum processing art.

The product withdrawn from the first zone is fed at elevated temperatures and pressures into the second zone where the catalyst is particularly adapted to promote the cracking of essentially all inorganic nitrogen and sulfur compounds remaining in the withdrawn product. The most preferred catalyst comprises tungsten and nickel components (sulfide form) supported on silica-alumina. The amount of nickel sulfide ranges between about 1.0 and about 10 wt. percent based on the weight of the support material, and the amount of tungsten sulfide ranges between about 1.0 and about 20 wt. percent based on the weight of the support material.

The product from the second zone is withdrawn and is fed into the third reaction zone, at elevated temperatures and pressures, where it contacts the catalyst that promotes the cracking of this withdrawn product into a low boiling fuel. The most preferred catalyst for this purpose comprises cobalt and molybdenum components (oxide form) on silica-alumina. The amount of cobalt ranges between about 1.0 and about 10 wt. percent based on the weight of the support material, and the amount of molybdenum ranges between about 1.0 and about 20 wt. percent based on the weight of the support.

(1) Example of catalyst preparation for first reaction zone

To prepare a catalyst which includes 30 wt. percent potassium hydroxide based on the weight of carbon, first prepare, at 70° F. 100 grams of a methanol solution including 20 grams of potassium hydroxide dissolved in 80 grams of methanol. Seventy grams of activated carbon is then mixed with this solution and the methanol is evaporated. A preferred carbon is manufactured by Pittsburgh Carbon and Chemical Company, designated as SGL active granular carbon, mesh size 20–30, and having a surface area of about 800 square meters.

(2) Example of catalyst preparation for second reaction zone

Eighty-two grams of silica-alumina powder were impregnated with 14.8 grams nickelous nitrate,

$$NiNo_3 \cdot 6H_2O$$

and 20.6 grams ammonium metatungstate,

$$(NH_4)_6H_2W_{12}O_{40}$$

dissolved in 85 ml. of warm water. The sample is dried at 250° F. and pelleted or extruded. The pellets or extrudates are calcined in air for 3 hours at 1000° F.

(3) Example of catalyst preparation for third reaction zone

Eighty-two grams of silica-alumina powder were impregnated with 14.8 gram of cobaltous nitrate,

$$Co(NO_3)_2 \cdot 6H_2O$$

and 27.6 grams of ammonium paramolybdate dissolved in 85 ml. of warm water. The sample is dried at 250° F. and pelleted or extruded. The pellets or extrudates are calcined in air for 3 hours at 1000° F.

The following table illustrates the operating conditions within the three reaction zones:

TABLE

| | First zone | | Second zone | | Third zone | |
|---|---|---|---|---|---|---|
| | Broad range | Typical | Broad range | Typical | Broad range | Typical |
| Temperature, ° F | 750–850 | 810 | 600–800 | 700 | 650–800 | 25 |
| Pressure, p.s.i.g. | 500–4,000 | 2,000 | 600–3,500 | 1,800 | 800–3,000 | 1,600 |
| Feed rate, vols. of hydrocarbons/vol. of catalyst per hour | 0.1–3.0 | 0.4 | 0.5–5.0 | 2.0 | 0.5–2.0 | 1.0 |
| Hydrogen feed rate, s.c.f. of hydrogen/barrel of feed | 2,000–20,000 | 5,000 | 500–5,000 | 1,500 | 2,000–20,000 | 10,000 |

## DESCRIPTION OF PREFERRED EMBODIMENTS

FIG. 1 schematically depicts one embodiment of the process of our invention. In this embodiment three reactors **10**, **12** and **14** are connected in series. Hydrogen from source **16** is fed through compressor **18** and line **20** to the top of reactor **10** where it is mixed with feed from source **22**. The feed may be any hydrocarbon including polynuclear aromatics and preferably is a resid hydrocarbon, bottoms from reformer units, shale oil, or mixtures thereof.

Reactor **10** includes the carbon supported catalyst, as described, which is particularly adapted to crack the polynuclear components of the feed. The catalyst is preferably in a fixed bed and the feed and hydrogen flow downwardly through the bed. The feed also normally includes some organic nitrogen and sulfur compounds and the catalyst does promote some cracking of these materials. Thus hydrogen sulfide, ammonia and light hydrocarbons ($C_2$ or less) are formed in reactor **10** and withdrawn from the bottom of this reactor via line **24**. These gases and hydrogen flow via line **24** into compressor **26** which feeds them to separation facilities **28** where the light hydrocarbons, hydrogen sulfide and ammonia are withdrawn from the system. The hydrogen is recycled via lines **30** and **20** to the top of reactor **10**. A liquid hydrocarbon is also withdrawn from reactor **10** via valved line **32**. This material is the first intermediate product which is essentially free of polynuclear aromatics but contains some organic nitrogen and sulfur compounds. In this first intermediate product the percent nitrogen typically is about 0.2 wt. percent or less, and the sulfur is typically 1.5 wt. percent or less.

The liquid product from reactor **10** flows into the top of reactor **12**. Hydrogen from line **30***a* also flows into the top of reactor **12** and is mixed with the liquid product from reactor **10**. Reactor **12** contains the catalyst, as described, which is particularly adapted to crack the organic nitrogen and sulfur compounds in the liquid product from reactor **10**. This catalyst is preferably in a fixed bed and the products flow downwardly into this bed, with the organic nitrogen and sulfur compounds and some hydrocarbons being cracked to form ammonia, hydrogen sulfide and hydrocarbon gases. These gaseous materials are withdrawn via line **34** which feeds them into line **24** where they are forwarded via compressor **26** to separation facilities **28**. A second intermediate product, essentially free of nitrogen and sulfur compounds, is withdrawn from reactor **12** via valved line **36**.

This second intermediate product and some hydrogen from line **30***b* flow into the top of reactor **14**. Reactor **14**

holds a fixed bed of catalyst, as described, which is particularly adapted to promote cracking of the second intermediate product into low boiling fuel. The second intermediate product and hydrogen flow downwardly through reactor **14**. Hydrocracking occurs within the reactor to consume some of the hydrogen. Unused hydrogen is withdrawn via line **38** and forwarded to compressor **26** for recycling. An effluent leaves reactor **14** via valved line **40** which is rich in low boiling fuel components. This effluent is forwarded to fractionation tower **42** where it is distilled, with gasoline being withdrawn from line **44**, distillate fuel being withdrawn from line **46**, and heavier materials being withdrawn via line **48** and recycled through pump **50** and line **52** to valved line **36** for reprocessing.

FIG. 2 schematically depicts a second embodiment of the process of our invention wherein a single reactor **60** is utilized. This reactor includes three contiguous, fixed beds of catalyst **62**, **64** and **66**. Beds **62** and **66** are separated from bed **64** by screens **68**. Bed **62** includes the carbon catalyst adapted to hydrocrack polynuclear aromatics, bed **64** includes the catalyst which promotes desulfurization and denitrification of hydrocarbons, and bed **66** includes the catalyst which promotes hydrocracking of hydrocarbons to low molecular weight components suitable for gasoline and distillate fuels. Hydrogen from source **70** is mixed with resid feed from source **72**. This hydrogen-resid mix flows downwardly through the three fixed beds of catalyst. In bed **62** the polynuclear components are hydrocracked, in bed **64** the organic nitrogen and sulfur compounds are hydrocracked to form ammonia and hydrogen sulfide, and in bed **66** the hydrocarbons are converted to hydrocarbon materials suitable for blending in gasoline or distillate fuels. Effluent from the bottom of reactor **60** flows into a gas liquid separator **74**. Liquid product is withdrawn via line **76** and forwarded to a fractionation tower, and gases are withdrawn via line **78** and pumped by pump **80** into gas treating facilities **82** where hydrogen sulfide, ammonia and hydrocarbon gases are separated from hydrogen. Hydrogen is recycled via line **84** through compressor **86** to the top of reactor **60** where it is mixed with make-up hydrogen from source **70** and resid feed.

We claim:

**1.** A process for converting into low boiling material hydrocarbons including organic nitrogen and sulfur compounds and polynuclear aromatics, comprising the steps of:

(a) contacting, at elevated temperatures and pressures, said hydrocarbons in a first reaction zone with hydrogen and a catalyst comprising activated carbon and an alkali metal component or an alkaline earth metal component or both, said metal component being present in an amount sufficient to promote cracking of said polynuclear aromatics, whereby a first intermediate product is formed,

(b) contacting, at elevated temperatures and pressures, said first intermediate product in a second reaction zone with hydrogen and a catalyst that promotes cracking of essentially all organic nitrogen and sulfur compounds in said first product, whereby a second intermediate product is formed, and

(c) contacting, at elevated temperatures and pressures, said second intermediate product in a third reaction zone with hydrogen and a catalyst that promotes cracking of said second intermediate product into said low boiling materials.

**2.** A process for converting into low boiling material hydrocarbons including organic nitrogen and sulfur compounds ranging from about 0.0 to about 6.0 wt. percent of the feed, and polynuclear aromatics ranging from about 0.1 to about 30 wt. percent of the feed, comprising the steps of:

(a) contacting said hydrocarbons in a first reaction zone with hydrogen and a catalyst comprising an activated carbon having a surface area in the range of from about 200 to about 2,500 square meters per volume of catalyst and from about 0.1 to about 50 wt. percent of an alkali metal component or an alkaline earth metal component or both, based on the weight of the carbon, conditions within said first reaction zone being: a temperature of from about 750 to about 850° F., a pressure of from about 500 to about 4000 p.s.i.g., and a feed rate of from about 0.1 to about 3.0 volumes of hydrocarbons per volume of catalyst per hour;

(b) withdrawing product from said first zone and contacting said withdrawn product in a second reaction zone with hydrogen and a catalyst comprising a refractory, inorganic cracking matrix supporting from about 1.0 to about 30 wt. percent, based on the weight of the matrix, of a metallic component from Group VI or Group VIII of the Periodic Table, said conditions within the second zone being: a temperature of about 600 to about 800° F., a pressure of from about 600 to about 3500 p.s.i.g., and a feed rate of from about 0.5 to about 5.0 volumes of hydrocarbons per volume of catalyst per hour;

(c) withdrawing product from said second zone and contacting said withdrawn product in a third reaction zone with hydrogen and a catalyst comprising a refractory, inorganic cracking matrix supporting from about 1.0 to about 30 wt. percent, based on the weight of the matrix, of a metallic component from Group VI or Group VIII of the Periodic Table, said conditions within said third reaction zone being: a temperature of from about 650 to about 800° F., a pressure of from about 800 to about 3000 p.s.i.g., and a feed rate of from about 0.5 to about 2.0 volumes of hydrocarbons per volume of catalyst per hour; and

(d) withdrawing from said third reaction zone a product rich in hydrocarbons boiling in the range of from about 100 to about 650° F. at normal pressures.

**3.** The process of claim **1** wherein the catalyst in said second and third reaction zones comprises a Group VI or Group VIII metal component supported on a refractory, inorganic cracking matrix.

**4.** The process of claim **1** wherein the reaction conditions are:

first zone:
- Temperature of about 750 to about 850° F.
- Pressure from about 500 to about 4000 p.s.i.g.
- Feed rate of about 0.1 to about 3.0 volumes of hydrocarbons per volume of catalyst per hour
- Hydrogen feed rate of about 2000 to about 20,000 standard cubic feet of hydrogen per barrel of feed.

second zone:
- Temperature of about 600 to about 800° F.
- Pressure from about 600 to about 3500 p.s.i.g.
- Feed rate of about 0.5 to about 5.0 volumes of hydrocarbons per volume of catalyst per hour
- Hydrogen feed rate of about 500 to about 5000 standard cubic feet of hydrogen per barrel of feed.

third zone:
- Temperature of about 650 to about 800° F.
- Pressure from about 800 to about 3000 p.s.i.g.
- Feed rate of about 0.5 to about 2.0 volumes of hydrocarbons per volume of catalyst per hour
- Hydrogen feed rate of about 2000 to about 20,000 standard cubic feet of hydrogen per barrel of feed.

**5.** The process of claim **4** wherein the catalyst in said first zone comprises an activated carbon having a surface area in the range of about 200 to about 2,500 square meters per gram of carbon and from about 0.01 to about 50 wt. percent of an alkali metal component or an alkaline earth metal component or both, based on the weight of the carbon.

6. The process of claim 5 wherein the catalyst in the second zone comprises nickel and tungsten components on silica-alumina, and the catalyst in the third zone comprises cobalt and molybdenum components on silica-alumina.

7. The process of claim 5 wherein the alkali metal component or alkaline earth metal component in the catalyst in the first reaction zone is in the form of a hydroxide, sulfide or oxide.


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DELBERT E. GANTZ, Primary Examiner

G. E. SCHMITKONS, Assistant Examiner

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