United States Patent

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[54] **HYDROCONVERSION PROCESS**
10 Claims, No Drawings

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[50] **Field of Search** 208/120,
44, 108; 252/455 Z, 426, 430, 438

[56] **References Cited**

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ABSTRACT: An asphaltenes hydroconversion process for the conversion of asphaltenes to lower boiling hydrocarbons by contacting said asphaltenes with hydrogen in the presence of a pyrolyzed polyacrylonitrile polymer or mixtures thereof.

HYDROCONVERSION PROCESS

This invention relates to a hydroconversion process for increasing the yield of lower boiling hydrocarbons and more particularly to a hydrocracking process wherein an asphaltene-containing heavy hydrocarbon charge stock is contacted with hydrogen in the presence of one or more pyrolyzed polyacrylonitrile polymers.

Generally, hydrocracking finds its highest degree of utility in the cracking of hydrocarbons boiling in the heavy naphtha and light gas oil range. It has however met with only limited acceptance in the upgrading of heavy hydrocarbon oils, particularly those containing high-boiling asphaltenes and substantial sulfur and nitrogen contents such as total crude oil, topped crudes and residua, shale oil, coal tars, etc. The various sulfur and nitrogen compounds present in such oils tend to poison the hydrocracking catalyst and to deposit coke during catalytic hydrocracking operation, whereas the conversion of asphaltenes is accompanied by the deposition of carbon and metals. It has been particularly found that the higher boiling petroleum fractions of such oils, i.e. those fractions boiling above about 750° F., and particularly above about 850° F., at atmospheric pressure contain relatively high proportions of the above-mentioned asphaltenes and objectionable contaminating materials. Accordingly, conventional hydrocracking of such fractions, or of oil feeds containing such fractions, has proved to be of very limited effectiveness.

It will be appreciated, therefore, that there is presently a high incentive for discovering a successful means for hydrocracking heavy hydrocarbon stocks containing asphaltenes to valuable lower boiling products.

It is therefore an object of this invention to provide an improved process for hydrocracking such feeds whereby higher yields of lower boiling hydrocarbons are obtained without substantial deposition of carbon.

It has now been found that lower boiling hydrocarbons can be obtained from an asphaltene-containing heavy hydrocarbon charge stock by a process which comprises contacting said heavy hydrocarbon charge stock with hydrogen in the presence of a promoting amount of a promoter selected from the group consisting of a pyrolyzed polyacrylonitrile polymer and mixtures thereof for a time sufficient under hydrogen contact conditions of pressure and temperature to convert at least a portion of the asphaltenes to lower boiling hydrocarbons and recovering lower boiling hydrocarbons. Thus, it has been discovered that the hydrogen contact step in the presence of said promoter produces conversion of asphaltenes to lower boiling hydrocarbons without substantial formation of carbon. In addition the promoter can be continuously used, recovered from the process of this invention and regenerated for further continued use, by the removal of materials which have deposited on the promoter and which adversely affect the effectiveness of the promoter.

In general the process of this invention is carried out by contacting the asphaltene-containing heavy hydrocarbon charge stock with hydrogen in the presence of a promoting amount of the promoter, which term includes pyrolyzed polyacrylonitrile optionally with a support material. The term "promoting amount" is used herein to be that concentration by weight of promoter which during the hydrogen contact step produces a yield of lower boiling hydrocarbons from asphaltenes greater than the yield of lower boiling hydrocarbons from asphaltenes obtained in the absence of the promoter. In general a concentration of promoter of from about 0.5 to about 20 percent, more preferably from about 2.0 to about 15 percent based upon the weight of the heavy hydrocarbon charge stock is utilized during the hydrogen contact step. The lower boiling hydrocarbon fractions are then recovered from the charge stock by conventional means, such as by distillation or vacuum stripping optionally using an inert stripping gas.

The conditions for hydrogen contact can be varied over a wide range as to liquid hourly space velocity (LHSV, volume of feed to volume of contactor per hour), hydrogen gas rate (volume of hydrogen to volume of heavy hydrocarbon charge stock, (s.c.f./bbl.), temperature, pressure, and the concentration of promoter. These conditions are adjusted in order to produce a hydrogen contact step wherein the hydrogen and promoter are present in a concentration sufficient to effect production of lower boiling hydrocarbons and are adjusted in order to maximize the yield of lower boiling hydrocarbons from the heavy hydrocarbon charge stock while minimizing any carbon formation.

It is contemplated within the scope of this invention that the process when practiced on a continuous basis can provide for recycle of nonconverted asphaltenes to the charge stock for reprocessing. By the use of the term "without substantial formation of carbon" is meant that the process of this invention provides for less than 0.35 percent by weight carbon formation based upon the total weight of asphaltenes present in the charge stock, still more preferably less than 0.06 weight percent carbon formation.

The heavy hydrocarbon charge stock is contacted with hydrogen, in the presence of the promoter, in general at a temperature from about 550° F. to about 900° F., preferably from about 725° to about 850° F.; pressures of from about 1,000 to about 6,000 p.s.i.g., preferably from about 2,000 to about 5,000 p.s.i.g.; liquid hourly space velocities of from about 0.1 to about 10, preferably from about 0.5 to about 2.5 volumes of feed per volume of contactor void space per hour; and hydrogen rates of from about 500 to about 20,000 preferably from about 2,500 to about 10,000 standard cubic feet per barrel (s.c.f./bbl.) of feed.

As stated above the process of this invention utilizes one or more pyrolyzed polyacrylonitrile polymers. By the use of the term polyacrylonitrile polymers is meant, a polyacrylonitrile polymer with at least about 80 weight percent of the reoccurring polymerized monomer units being derived from acrylonitrile, more preferably 90 weight percent. The polyacrylonitrile polymer is then subjected to conditions of pyrolysis in the presence of oxygen, herein defined to include oxygen, activated oxygen, an oxygen containing gas such as air, or an oxygen yielding substance. As stated above, it is preferred that the starting polyacrylonitrile polymer have at least 90 weight percent of the polymerized monomer units being derived from acrylonitrile. Thus the remaining 10 percent by weight can be other monomers which polymerize with acrylonitrile. In a still more preferred sense it is preferred that the polyacrylonitrile polymer be derived substantially from acrylonitrile, that is at least 95 weight percent being derived from acrylonitrile. The polyacrylonitrile polymers are for the most part amorphous solids or crystalline solids. It will be understood that for the purposes of this specification that, the term polymer is used in a generic sense to include homopolymers, copolymers, terpolymers, or other inter polymers, which have molecular weights of at least about 25,000, more preferably from about 25,000 to about 1,300,000.

Acrylonitrile is usually polymerized by the free radical polymerization technique (also known as the addition polymerization technique). Such technique consists of contacting the monomer with polymerization initiator either in the absence or presence of a diluent at a temperature usually between 0° and 200° C. The polymerization initiator is a substance capable of liberating a free radical under the conditions of polymerization, e.g., benzoyl peroxide, tert-butyl hydroperoxide, cumyl peroxide, potassium persulfate, acetyl peroxide, hydrogen peroxide, azobisisobutyronitrile, or perbenzoic acid. For reasons of economy, benzoyl peroxide or azobisisobutyronitrile are most commonly used.

Acrylonitrile may also be polymerized or copolymerized using an anionic initiator such as naphthylsodium or butyllithium in tetrahydrofuran solution or sodium metal in liquid ammonia solution.

The polymerization of acrylonitrile may also be effected by other polymerization techniques such as by the use of Ziegler-type catalysts, gamma ray irradiation, or thermal techniques.

The diluent for the polymerization mixture may be either an inert solvent such as benzene, toluene, xylene, cyclohexane, n-

hexane, naphtha, tetrahydrofuran, white oil, or dodecane; or a nonsolvent such as water or liquid ammonia. Thus, the polymerization can be carried out in bulk, solution, emulsion or suspension.

The temperature for the polymerization depends on the catalyst system employed and to some extent the nature of the monomers to be polymerized. Thus, the copolymerization of acrylonitrile with an acrylamide may be catalyzed by an anionic initiator at temperatures from about −100° to 50° C., preferably at −70° to 0° C. On the other hand, the optimum temperature for effecting the free radical catalyzed homopolymerization of acrylonitrile is usually from 0° to 100° C., preferably 30° to 80° C. Similarly, the optimum temperatures for effecting the free radical catalyzed interpolymerization of acrylonitrile with one or more polymerizable comonomers will vary according to the reactivity of these monomers. In most instances such temperatures likewise are within the range from about 0° to 100° C.

A large variety of comonomers can be used to form interpolymers with the acrylamides of this invention. For the most part, the comonomers are polymerizable vinyl monomers. They include, for example (1) esters of unsaturated alcohols, (2) esters of unsaturated acids, (3) vinyl cyclic compounds, (4) unsaturated ethers, (5) unsaturated ketones, (6) unsaturated amides, (7) unsaturated aliphatic hydrocarbons, (8) vinyl halides, (9) esters of unsaturated polyhydric alcohols (e.g., butenediol), (10) unsaturated acids, (11) unsaturated acid anhydrides, (12) unsaturated acid chlorides and (13) unsaturated nitriles other than acrylonitrile.

Specific illustrations of such compounds are:

1. Esters of unsaturated unsaturated alcohols: allyl, methallyl, crotyl, 1-chloroallyl, 2-chloroallyl, cinnamyl, vinyl, methylvinyl, 1-phenally, butenyl, etc., esters of (a) (saturated acids such as for instance, acetic, propionic, butyric, valeric, caproic, stearic, etc.;) (b) unsaturated acids such as acrylic, alpha-substituted acrylic (including alkacrylic, e.g. methacrylic, ethylacrylic, propylacrylic, etc., and arylacrylic such as phenylacrylic, etc.), crotonic, oleic, linoleic, linolenic, etc., (c) (polybasic acids such as oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacie, etc.,) (d) unsaturated polybasic acids such as maleic, fumaric, citraconic, measaconic, itaconic, methylenemalonic, acetylenedicarboxylic aconitic, etc., (e) aromatic acids, e.g., benzoic, phenylacetic, phthalic, terephthalic, benzoylphthalic, etc.

2. The esters of saturated alcohols such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, 2-ethylhexyl, cyclohexyl, behenyl, etc., with unsaturated aliphatic monobasic and polybasic acids, examples of which are illustrated above.

3. Esters of unsaturated polyhydric alcohols, e.g., butenediol, etc., with saturated and unsaturated aliphatic and aromatic, monobasic and polybasic acids, illustrative examples of which appear above.

4. Vinyl cyclic compounds including (a) monovinyl aromatic hydrocarbons, e.g. styrene, o-, m-, p-chlorostyrenes, -bromostyrenes, -fluorostyrenes, -methylstyrenes, -ethylstyrenes, -cyanostyrenes, do-, tri-, and tetra-, etc., -chlorostyrenes, -bromostyrenes, flurostyrenes, -methylstyrenes, -ethylstyrenes, -cyanostyrenes, vinylnaphthalene, vinylcyclohexane, vinylfuran, vinylpyridine, vinylbenzofuran, divinylbenzene, trivinylbenzene, allybenzene, N-vinylcarbazole, N-vinylpyrrolidone, N-vinyloxazolidone, etc.

5. Unsaturated ethers such as, e.g. methyl vinyl ether, ethyl vinyl ether, cyclohexyl vinyl ether; octyl vinyl ether, diallylether, ethyl methallyl ether, allyl ethyl ether, etc.

6. Unsaturated ketones, e.g., methyl vinyl ketone, ethyl vinyl ketone, etc.

7. Unsaturated amides, such as acrylamide, N-methylacrylamide, N-phenylacrylamide, N-allylacrylamide, N-methylolacrylamide, N-allylcaprolactam, etc.

8. Unsaturated aliphatic hydrocarbons, for instance, ethylene, propylene, butenes, butadiene, isoprene, 2-chlorobutadiene, alpha-olefins, etc. 9. Vinyl halides, e.g., vinyl fluoride, vinyl chloride, vinyl bromide, vinyl iodide, vinylidene chloride, vinylidene bromide, allyl chloride, allyl bromide, etc.

10. Unsaturated acid anhydrides, e.g. maleic, citraconic, propylacrylic, etc., examples of which appear above.

11. Unsaturated acid anhydrides, e.g., maleic citraconic, itaconic, cis-4-cyclohexene-1,2-dicarboxylic, bicyclo (2.2.1) 5-heptene-2,3 -dicarboxylic, etc.

12. Unsaturated acid halides such as cinnamoyl, acryloyl methacrylyl, crotonyl, oleyl, fumaryl, etc.

13. Unsaturated nitriles other than acrylonitrile, e.g., methacrylonitrile and other substituted acrylonitriles.

The polyacrylonitrile polymer is then subjected to a pyrolysis step. As stated above, the pyrolysis of the polyacrylonitrile polymer is carried out in the presence of oxygen preferably in the presence of air. In general the conditions as to time, temperature, pressure, and oxygen concentration which are utilized are: temperatures of from about 300° to about 500° F., more preferably from about 350° to about 450° F., pressures of from about 0.1 to about 2 atm., preferably of from about 0.5 to about 1 atm., and a contact time in hours of from about 6 to about 96, more preferably from about 12 to about 48. It is preferred in preparing the pyrolyzed polymers to pelletize the polymer prior to pyrolysis. After the pyrolysis step either a tan-to-brown material, or a black carbonaceous material, is recovered which optionally can be, depending upon the pyrolysis conditions, calcined at elevated temperatures such as temperatures of from about 600° to about 800° F. for times of from about 12 hours at the lower temperature to about 0.5 hours at the higher temperature under an inert atmosphere such as nitrogen.

In addition it is contemplated within the scope of this invention that the pyrolyzed polyacrylonitrile polymer or mixtures thereof can be utilized on a support material such as alumina, silica alumina, silica magnesia, activated carbon, and aluminosilicates. In general the pyrolyzed polyacrylonitrile or mixtures thereof is present on a weight percent basis on the support of from about 0.5 to about 50 percent, more preferably from about 1 to about 10 percent.

A wide variety of asphaltene-containing heavy hydrocarbon fractions may be treated, or made suitable for further processing, through the utilization of the method encompassed by the present invention. Such heavy hydrocarbon fractions usually contain from about 0.50 to about 10 weight percent asphaltenes and include full boiling range crude oils, topped or crude oils, vacuum tower bottoms, and visbreaker bottoms product. The present method is particularly well adaptable to the treating of crude oils and topped or reduced crude oils containing large quantities of asphaltenic material, and is especially advantages when applied to the treating of atmospheric or vacuum towers bottoms, e.g., especially 550° F. or higher atmospheric reduced crude oils.

The present invention can be carried out in batch, continuous or semicontinuous operating cycles, and in one or more actual or theoretical states, employing contacting and separation equipment such as has heretofore been employed in hydrocracking of petroleum stocks. In addition a multistage mode of operation that is a repeating of the process several times, can be utilized in carrying out the process of this invention.

The process of this invention can be better appreciated by the following nonlimiting examples.

EXAMPLE 1

To a three-neck 1-liter flask equipped with stirrer thermometer and reflux condenser is added under a nitrogen atmosphere 55 grams (1.0mole) of acrylonitrile, 750 milliliters of water, and 1.0 gram of azo-bis-isobutyronitrile. The mixture is heated with stirring to a temperature of 140° F. which is maintained for a period of 2 hours. After this period, 1 additional gram of azo-bis-isobutyronitrile is added and the mixture stirred at 140° F. for an additional 2 hours. The mixture is reduced to ambient temperature and a solid polymer is

recovered by filtration. The polymer is washed with water, partially air dried and dried for 12 hours at 250° F. A white polymer 36 grams is recovered. The polymer (36 grams) is then pyrolyzed at 300° to 450° F. in an air stream over a period of 12 hours. A brown material (32 grams) is obtained which is then pelleted and calcined at 800° F. for a period of 30 minutes under a nitrogen atmosphere. A yield of 21 grams of black material is then recovered which has 67.2 weight percent carbon, 2.9 weight percent hydrogen, 18.1 percent nitrogen and a surface area of 2 meters ^{2} per gram.

EXAMPLE 2

To a three-neck 1-liter flask equipped with stirrer, thermometer, and reflux condenser is added a nitrogen atmosphere, 55 grams of acrylonitrile, 3.0 grams of methylmethacrylate, 750 milliliters of water, and 1.0 gram of azo-bis-isobutyronitrile. The mixture is heated with stirring to a temperature of 140° F. which is maintained for a period of 2 hours. After this period 1 gram of azo-bis-isobutyronitrile is added and the mixture stirred at 140° F. for an additional 2 hours. The mixture is reduced to ambient temperature and a solid polymer is recovered by filtration. The polymer is washed with water, partially air dried and dried for 12 hours at 250° F. The polymer 25 grams is then pyrolyzed at 300° to 450° F. in an air stream over a period of 12 hours. The material obtained is then pelleted and calcined at 800° F. for a period of 30 minutes under a nitrogen atmosphere. The polymer is then recovered.

EXAMPLE 3

To a three-neck 1-liter flask equipped with a stirrer, thermometer, and reflux condenser is added under a nitrogen atmosphere 55 grams (1.0 mole) of acrylonitrile, 7 grams of N,N'dimethylacrylamide, 750 milliliters of water, and 1.0 gram of azo-bis-isobutyronitrile. The mixture is heated with stirring to a temperature of 140° F. which is maintained for a period of 2 hours. After this period 1 gram of azo-bis-isobutyronitrile is added and the mixture stirred at 140° F. for an additional 2 hours. The mixture is reduced to ambient temperature and a solid polymer is recovered by filtration. The polymer is washed with water, partially air dried and dried for 12 hours at 250° F. The polymer 28 grams is then pyrolyzed at 300° to 450° F. in an air stream over a period of 12 hours. The material obtained is then pelleted and calcined at 800° F. for a period of 30 minutes under a nitrogen atmosphere. The polymer is then recovered.

EXAMPLE 4

To a three-neck 1 flask equipped with a stirrer, thermometer, and reflux condenser is added under a nitrogen atmosphere 60 grams of acrylonitrile, 3 grams of dimethylmaleate, 750 milliliters of water, and 1.0 gram of azo-bis-isobutyronitrile. The mixture is heated with stirring to a temperature of 140° F. which is maintained for a period of 2 hours. The mixture is then reduced to ambient temperature and a solid polymer is recovered by filtration. The polymer is washed with water, partially air dried and dried for 12 hours at 250° F. The polymer 30 grams is then pyrolyzed at 300° to 450° F. in an air stream over a period of 12 hours. The material obtained is then pelleted and calcined at 800° F. for a period of 30 minutes under a nitrogen atmosphere. The polymer is then recovered.

EXAMPLE 5

To a three-neck 1 -liter flask equipped with a stirrer, thermometer and reflux condenser is added a nitrogen atmosphere 55 grams (1.0 mole) of acrylonitrile, 4 grams of vinylacetate, 750 milliliters of water, and 1.0 gram of azo-bis-isobutyronitrile The mixture is heated while stirred to a temperature of 140° F. which is maintained for a period of 2 hours. After this period 1 gram of azo-bis-isobutyronitrile is added and the mixture stirred at 140° F. for an additional 2 hours. The mixture is reduced to ambient temperature and a solid polymer is recovered by filtration. The polymer is washed with water, partially air dried and dried for 12 hours at 250° F. The polymer 40 grams is then pyrolized at 300° to 450° F. in an air stream over a period of 12 hours. The material obtained is then pelleted and calcined at 800° F. for a period of 30 minutes under a nitrogen atmosphere. The polymer is then recovered.

EXAMPLE 6

The pyrolized polyacrylonitrile from example 1 (20 mesh 15 grams) is blended with 500 grams of alumina. The mixture is blended with agitation for a period of 2 minutes followed by pelleting. The mixture is heated to a temperature of 750° F. for a period of 5 hours under a nitrogen atmosphere and 346 grams of pyrolyzed polyacrylonitrile on alumina is recovered.

EXAMPLE 7

The pyrolyzed polyacrylonitrile polymer from example 2 (20 mesh 15 grams) is blended with 500 grams of silica alumina. The mixture is blended with agitation for a period of 2 minutes followed by pelleting. The mixture is heated to a temperature of 750° F. for a period of 5 hours under a nitrogen atmosphere and a pyrolyzed polyacrylonitrile polymer on silica alumina is recovered.

EXAMPLE 8

The pyrolyzed polyacrylonitrile polymer from example 3 (20 mesh 15 grams) is blended with 500 grams of silica magnesia. The mixture is blended with agitation for a period of 2 minutes followed by pelleting. The mixture is heated to a temperature of 750° F. for a period of 5 hours under a nitrogen atmosphere and a pyrolyzed polyacrylonitrile polymer on silica magnesia is recovered.

EXAMPLE 9

The pyrolyzed polyacrylonitrile polymer from example 4 (20 mesh 15 grams) is blended with 500 grams of an aluminosilicate. The mixture is blended with agitation for a period of 2 minutes followed by pelleting. The mixture is heated to a temperature of 750° F. for a period of 5 hours under a nitrogen atmosphere and a pyrolyzed polyacrylonitrile polymer on an aluminosilicate is recovered.

EXAMPLE 10

To a 1,290 milliliter pressure rocking reactor equipped with gas addition means is added 500 grams of a California atmospheric reduced crude oil having the following properties:

Gravity °API	15.2
Carbon Residue, wt. %	8.54
Sulfur, wt. %	1.58
Total Nitrogen, wt. %	0.74
DPI flask dist., wt. %	
IB B—850° F.	38.1
Residue 850° F.+	61.9
wt. % asphaltenes (in 850° F.+) material	9.54

together with 39 grams of the solid polymer (50–150 microns) from example 1. The reactor is flushed with hydrogen and the temperature is increased to 750° F. under a hydrogen atmosphere. A total pressure of 4,000 p.s.i.g. is maintained at 750° F. for a period of 42 hours. After this time the temperature is reduced to ambient temperature. It is determined that the hydrogen consumption based on the pressure drop is 1,150 standard cubic foot per barrel of charge. The oil is recovered from the pressure reactor and filtered to recover the solid polymer catalyst. It is determined that there is no carbon deposit formation.

EXAMPLE 11

To a 1,290 milliliter pressure rocking reactor equipped with gas addition means is added 502 grams of a California atmospheric reduced crude oil the properties of which are set forth in example 10 together with 50 grams of the polymer on alumina from example 6. The reactor is flushed with hydrogen and the temperature is increased to 750° F. under a hydrogen atmosphere. A total pressure of 4,000 p.s.i.g. is maintained at 750° F. for a period of 42 hours. After this time the temperature is reduced to ambient temperature. It is determined that the hydrogen consumption based on the pressure drop is 810 standard cubic foot per barrel of charge. The oil is recovered from the pressure reactor and filtered to recover the solid polymer catalyst. It is determined that there is no carbon deposit formation.

EXAMPLE 12

Example 10 is repeated except that the solid polymer is omitted from the process. After a period of 44 hours and a temperature of 750° F. and a hydrogen pressure of 4,000 p.s.i.g. it is determined that a carbon deposit is formed.

The test results on the oil product obtained from examples 10 through 12 are set forth below in table I.

The autoclave appearance at the end of the run was obtained through visual inspection. The percent disappearance of asphaltenes was determined by a modified procedure for deasphalting and deresinizing a crude oil described in Analytical Edition, Industrial and Engineering Chemistry, Vol. 13, 1941, p. 314. This procedure for determining asphaltene concentration comprises heating a sample (5 grams) together with 100 milliliters of mixed hexanes. The liquid is filtered into a Gooch crucible (asbestos lined) leaving behind that material which settled from the mixed hexane. The settled material is treated with warm mixed hexanes until a substantially water white filtrate is obtained. The solid which remains is then filtered into the Gooch crucible which is rewashed until the color is water white. The Gooch crucible containing asphaltenes is then air dried in an oven at 210° F. The difference in weight between the Gooch crucible before and after the hexane extraction is determined as the weight of asphaltenes from which the percent of asphaltenes is calculated.

The weight percent disappearance of asphaltenes is obtained by dividing the difference between the weight percent asphaltenes in the charge and the weight percent asphaltenes present after the process by the weight percent asphaltenes present in the charge times 100.

TABLE I

Recovered Oil Product from Example	10	11	12
Product Analysis	75	78	+108[a]
wt. % disappearance of asphaltenes			
Autoclave appearance at end of run	Clean	Clean	Heavy

(a) A 108 wt. percent gain in calculated asphaltenes.

The results in table I demonstrate the outstanding effectiveness of the process of this invention for converting asphaltenes which are present in a hydrocarbon charge stock to lower boiling hydrocarbons. More particularly, the process of this invention provides for the conversion of asphaltenes without the formation to any substantial degree of carbon or coke deposits. Thus, the results obtained in examples 10 and 11 demonstrate that the solid polymer produces asphaltene conversion while eliminating carbon deposits. These results are in sharp contrast to the heavy carbon deposits and +108 weight percent increase in asphaltenes from example 12. Thus the process of this invention produces conversion of asphaltenes to lower boiling hydrocarbons while minimizing carbon and coke formation during the process.

While this invention has been described with respect to various specific examples and embodiments it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

We claim:

1. An asphaltene hydroconversion process which comprises contacting an asphaltene-containing hydrocarbon charge stock with hydrogen at a temperature between about 550° and 900° F. in the presence of from about 0.5 to about 20 percent by weight based on said hydrocarbon charge of a promoter comprising a calcined pyrolized acrylonitrile polymer to convert at least a portion of the asphaltenes to lower boiling hydrocarbons and recovering the lower boiling hydrocarbons, said calcined pyrolized acrylonitrile polymer having been prepared by pyrolyzing an acrylonitrile polymer in the presence of oxygen at a temperature between about 300° and 500° F. and calcining the pyrolysis product in an inert atmosphere at a temperature between about 600° and 800° F.

2. A process of claim 1 where the acrylonitrile polymer contains at least 90 percent by weight of acrylonitrile monomer units.

3. A process of claim 2 wherein the acrylonitrile polymer contains at least 95 percent by weight acrylonitrile monomer units.

4. A process of claim 1 wherein the acrylonitrile polymer has a molecular weight of from about 25,000 to about 1,300,000.

5. A process of claim 3 wherein the acrylonitrile polymer has a molecular weight of from about 25,000 to about 1,300,000.

6. A process of claim 1 wherein the promoter polymer comprises a pyrolyzed acrylonitrile polymer on a support material selected from the group consisting of alumina, silica-alumina, silica-magnesia, and alumino-silicate and mixtures thereof.

7. A process of claim 6 wherein the support material is selected from the group consisting of silica alumina, an alumino-silicate and mixtures thereof.

8. A process of claim 6 wherein the pyrolyzed acrylonitrile polymer is present under the support material on a weight percent basis of from about 0.5 to about 50 percent.

9. A process of claim 7 wherein the pyrolyzed acrylonitrile polymer is present under the support material on a weight percent basis of from about 0.5 to about 50 percent.

10. A process of claim 9 wherein the acrylonitrile polymer contains at least about 95 percent by weight of acrylonitrile monomer units.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,617,506 Dated November 2, 1971

Inventor(s) EDWARD L. COLE and IRVING G. SCHWAGER

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 32, delete "unsaturated" second occurrence

Column 4, line 51, "advantages" should read --advantageous--

Column 5, line 51, after "1" insert --liter--

Column 5, line 58, after "hours." insert --After this period 1 gram of azobisisobutyronitrile is added and the mixture stirred at 140°F. for an additional two hours.--

Column 5, line 73, "while" should read --with--

Claim 6, line 1, cancel "polymer"

Signed and sealed this 19th day of September 1972.

(SEAL)
Attest;

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents