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ASPHALTENE HYDROCONVERSION PROCESS

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U.S. Cl. 208—108 11 Claims

ABSTRACT OF THE DISCLOSURE

An asphaltene hydroconversion process for the conversion of asphaltenes to lower boiling hydrocarbons by contacting said asphaltenes with hydrogen in the presence of a solid polymer prepared by interacting an aromatic polycarboxylic acid anhydride or halide producing compound with a polynuclear aromatic compound.

This invention relates to a hydroconversion process for increasing the yield of lower boiling hydrocarbons and more particularly to hydrocracking process wherein an asphaltene containing heavy hydrocarbon charge stock is contacted with hydrogen in the presence of a solid polymer prepared by the interaction of an aromatic polycarboxylic acid, anhydride or halide producing compound with a polynuclear aromatic compound.

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 coke 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 coke.

It has now been found that lower boiling hydrocarbons can be obtained from an asphaltene containing heavy hydrocarbon charge stock by the use of a process which comprises contacting said heavy hydrocarbon charge stock with hydrogen in the presence of a promoting amount of a solid polymer 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 wherein said solid polymer is prepared by the process which comprises interacting an aromatic polycarboxylic compound with a polynuclear aromatic compound. Thus it has been discovered that the hydrogen contact step in the presence of a solid polymer prepared by interacting an aromatic polycarboxylic compound with a polynuclear aromatic compound produces conversion of asphaltenes to lower boiling hydrocarbons without substantial formation of coke. In addition the solid polymer can be continuously used, recovered from the hydrogen contact process, and regenerated for further continued use.

In general the process of this incention is carried out by contacting the asphaltene containing heavy hydrocarbon charge stock with hydrogen in the presence of a promoting amount of solid polymer prepared by interacting an aromatic polycarboxylic compound with a polynuclear aromatic compound, hereinafter referred to as solid polymer. 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 solid polymer. In general a concentration of solid polymer of from about 0.5% to about 20%, more preferably from about 2.0% to about 15% 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.

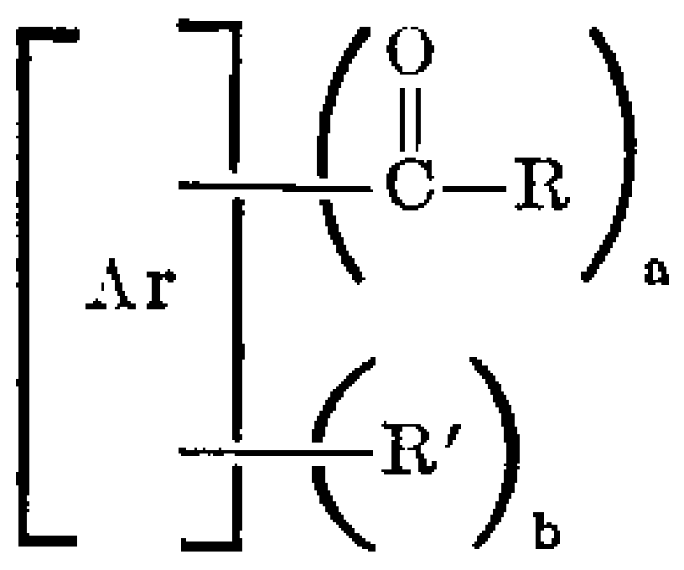
The conditions for hydrogen contact can be varied over a wide range as to liquid hourly space velocity (LHSV, volume of feed to volume of contactor per hour), hydrogen gas rate (volume of hydrogen to volume of heavy hydrocorbon charge stock, s.c.f./bbl.), temperature, pressure and the concentration of solid polymer. These conditions are adjusted in order to produce a hydrogen contact step wherein the hydrogen and solid polymer 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 fraction while minimizing any carbon or coke formation.

It is contemplated within the scope of this invention that the process when practiced on a continuous basis can provide for recycle of non-converted asphaltenes to the charge stock for reprocessing. By the use of the term "without substantial formation of coke" is meant that the process of this invention provides for less than 0.35% by weight coke formation as a function of the total weight of asphaltenes present in the charge stock still more preferably less than 0.06 wt. percent coke formation.

The heavy hydrocarbon charge stock is contacted with hydrogen in the presence of the solid polymer in general at a temperature of from about 550° F. to about 900° F. preferably from about 725° F. to about 850° F.; pressures of from about 1000 to about 6000 p.s.i.g. preferably from about 2000 to about 5000 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 2500 to about 10,000 standard cubic feet (s.c.f.) per barrel of feed.

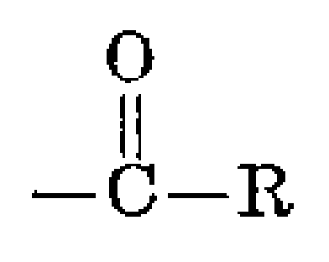
In general the solid polymers which are utilized for the conversion of asphaltenes are prepared by the interaction of an aromatic polycarboxylic compound preferably an aromatic polycarboxylic acid, anhydride and/or halide producing compound with a polynuclear aromatic compound preferably in the presence of a Friedel-Crafts catalyst. Generally, molar ratios of the polynuclear aromatic compound (for compounds having a molecular weight less than about 1000) to the aromatic carboxylic acid, anhydride or halide compound is from about 0.5 to 1 to about 4 to 1 more preferably from about 1 to 1 to about 3 to 1. For polynuclear aromatic compounds having molecular weights of about 1000 or greater such as petroleum cokes and asphaltenes it is preferred to use weight ratios of polynuclear aromatic compounds to the aromatic carboxylic acid anhydride or hydride compound of about 0.1 to 1 to about 3 to 1, more preferably from about 0.5 to 1 to about 2 to 1. In preparing the solid polymers it is preferred to use a Friedel-Crafts catalysts such as zinc chloride, aluminum chloride, aluminum bromide and ferric chloride. In general the catalyst is used at a concentration of from about 0.5 to 4.0 moles of catalyst per mole of aromatic polycarboxylic compound, more preferably from about 0.75 to 2.5 moles of catalyst per mole of aromatic polycarboxylic compound. The reaction conditions as to temperature and time can be varied over a wide range, those conditions being utilized which produce the solid polymer. In general, temperatures of from about 350° F. to about 700° F. more preferably from about 450° F. to about 625° F., for from about 0.5 hours to about 24 hours more preferably from about 1 hour to about 12 hours are utilized. The solid polymers can be recovered from the reaction mixture by conventional means and in addition can be washed with dilute aqueous acid solutions. Typical procedures for preparing the solid polymers are set forth in the articles "Pohl, H. A. and "E. H. Enhelhardt, J. Physical Chemistry 66, 2095 (1962)," and "Pohl, H. A. and D. A. Opp, J. Physical Chemistry 66, 2121 (1962)," which articles are thereby incorporated by reference. It is preferred that the solid polymer when utilized in the process of this invention have a particle size from about 20 microns to about 500 microns more preferably from about 100 microns to about 250 microns, although particle sizes above and below though set forth above can be utilized in the process of this invention.

Typical examples of aromatic polycarboxylic compounds are represented by the structural formula:



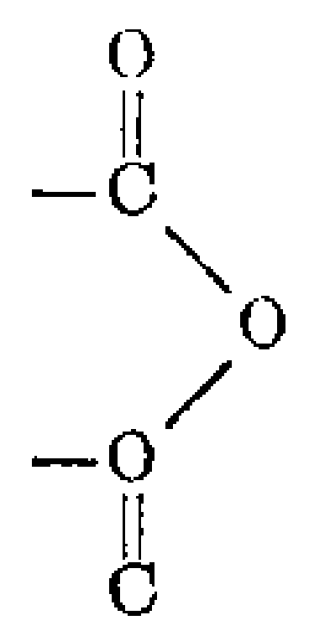
$$\left[\mathrm{Ar}\begin{matrix}\left(-\overset{\displaystyle O}{\overset{\|}{C}}-R\right)_a\\ \left(-R'\right)_b\end{matrix}\right]$$

wherein Ar is an aromatic nucleus, each R is independently selected from the group consisting of —OH, halide, a lower hydrocarbonoxy radical having from about 1 to about 12 carbon atoms and any two groups represented by

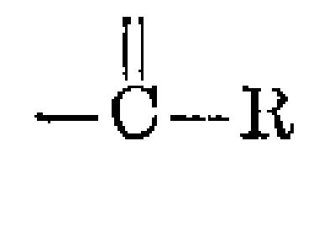


$$-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

which are attached to adjacent carbon atoms on Ar can together form

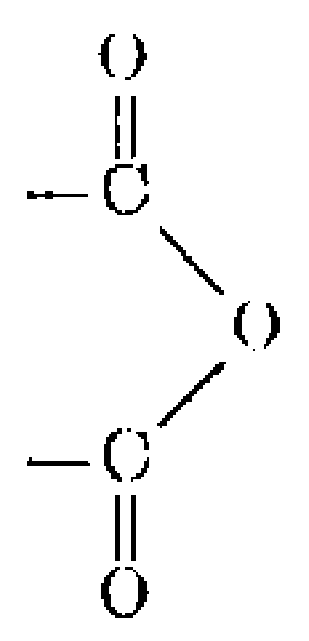


each R′ is a hydrocarbon radical, *a* is an integer having a value of from 2 to 4 and *b* is an integer having a value of from 0 to 4 provided that the sum of $a+b$ is not greater than 6. The particularly preferred aromatic carboxylic acid anhydride and/or halide producing compounds are those compounds represented by the above formula wherein R is selected from alkoxy having from 1 to about 6 carbon atoms, —OH, halide (preferably chloride) and when two groups represented by

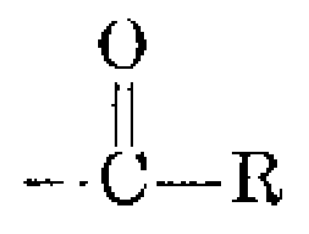


$$-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

together form

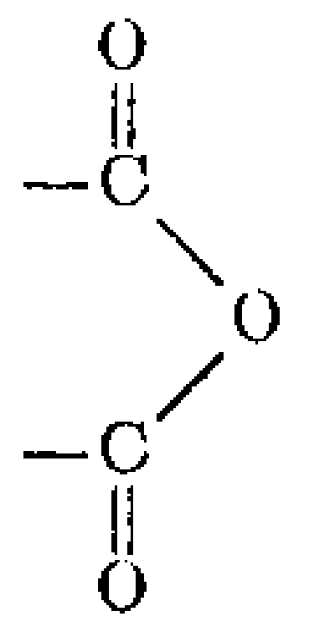


In a still more preferred embodiment of this invention, *b* is from zero to two, more preferably *b* is zero and R is selected from OH, chloride and when two groups represented by



$$-\overset{\displaystyle O}{\overset{\|}{C}}-R$$

together form



When *b* is greater than zero it is preferred that R′ have from 1 to about 16 carbon atoms more preferably from 1 to about 8 carbon atoms and still more preferably from 1 to about 3 carbon atoms. Typical examples of aromatic nucleus are benzene, naphthalene, anthracene, biphenyl and terphenyl. It is preferred that the aromatic nucleus is selected from benzene, naphthalene and biphenyl, more preferably that the aromatic nucleus is benzene.

Typical examples of hydrocarbon radicals which are attached to the oxy radical to form hydrocarbonoxy radicals representing R and hydrocarbon radicals representing R′ are alkyl such as methyl, ethyl, butyl, t-butyl, 3-methyl-1-pentyl, n-octyl and those aliphatic radicals which represent the hydrocarbon portion of a middle distillate or kerosine, cycloalkyl radicals such as cyclopentyl, alkylated cycloalkyl radicals such as mono and polymethylcyclopentyl radicals, aryl and cycloalkyl substituted alkyl radicals such as phenylethyl and cyclohexylpropyl, alkylphenyl substituted alkyl radicals examples of which are benzyl, methylbenzyl, caprylbenzyl, phenylethyl, phenylpropyl, naphthylmethyl, naphthylethyl, aryl radicals such as phenyl, and naphthyl, alkaryl radicals such as xylyl, alkylphenyl, and ethylphenyl. In addition, any groups represented by R that remain in the solid polymers and R′ are defined as hydrocarbon radicals which are noninterfering with respect to the promoting activity of the solid polymer promoter. By non-interfering is meant that the substituents representing R and R′ do not completely nullify the activity of the solid polymer promoter during the hydrogen process step.

Typical examples of aromatic polycarboxylic acid and anhydride producing compounds are phthalic anhydride, m-phthalic acid, terephthalic acid, pyromellitic anhydride, trimellitic anhydride, pyromellitic acid, trimellitic acid, dimethyl terephthalate, diisopropyl terephthalate, dibenzyl terephthalate and dimethylophthalate.

In general the polynuclear aromatic compounds contain a plurality of aromatic rings. A particularly preferred class of polynuclear aromatic compounds are those having a molecular weight below 1000 and in addition polynuclear aromatic compound which contain from 2 to about 9 aromatic rings, preferably fused aromatic rings.

Typical examples of polynuclear aromatic compounds are trans-stilbene, fluoroene, 1,2-benzfluorene, 1,2,3,4-peridinaphthalene fluorene, 9,9′ - bifluorenyl, 9,9′ - bifluorylidene, acenaphthene, acenaphthylene, anthracene, 9,10 - dihydroanthracene, 9,10 - dimethylanthracene, 2-methylphenanthrene, naphthacene, 5,12 - dihydronaphthacene, 1,2-benzanthracene, 7,12 - dimethyl - 1,2 - benzanthracene, 1,2,5,6-dibenzanthracene, chrysene, pyrene, 1,2,6,7 - tetrahydropyrene, 4 - methylpyrene, 3,4 - benzpyrene, 1,2,4,5,8,9 - tribenzpyrene, perylene, 1,12-benzperylene, pentacene, 1,2,8,9 - dibenzpentacene coronene, acridine, 1,5 - dihydroxyanthraquinone, 1,8 - dihydroxyanthraquinone, 1,4 - dihydroxyanthraquinone, 1,2 - dihydroxyanthraquinone, 1 - hydroxyanthraquinone, 1,4,9,10-tetrahydroxyanthracene, 1,4 - dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 2,3 - dihydroxynaphthalene, 6-bromo - 2 - naphthol, 1 - bromo - 2 - naphthol, 7-acenaphthol, 9 - bromophenanthrene, carbazole, phenolphthalein, p - naphtholbenzine, 2 - bromo - e - phenylphenol, dibenzanthrone (violanthrone), p,p' - diphenol, 1,4 - diphenylpiperazine, 1,8 - dihydroxyanthraquinone, 1,5 - dihydroxyanthraquinone, 1,8 - dihydroxyanthraquinone, 1,4 - dihydroxyanthraquinone, 1,2 - dihydroxyanthraquinone, 1 - hydroxyanthraquinone, 1,4,9,10-tetrahydroxyanthracene, 1,4 - dianthraquinonylaminoanthraquinone, 1,4-dihydroxynaphthalene, 1-bromo-2-naphthol.

In addition it is contemplated within the scope of this invention to utilize coke as an aromatic compound, such as asphaltic coke and carboid coke. Thus the coke can be produced by conventional coking means such as by delayed coking processes or fluid coking processes which processes are well known in the art. Various types of cokes which are contemplated within the scope of this invention are described in Carbon and Graphite Handbook by C. L. Mantell, Interscience 1968 which article is incorporated by reference. In addition it is contemplated within the scope of this invention that asphaltenes can be used as the aromatic compound for the preparation of the solid polymer. Such asphaltenes are in general prepared by the extraction of asphalts utilizing aromatic solvents. Asphaltenes are generally classified as those materials which are soluble in aromatic solvents and insoluable in n-paraffins.

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 0.5 to about 10.0 wt. 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 advantageous 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 semi-continuous operating cycles, and in one or more actual or theoretical stages, employing contacting and separation equipment such as has heretofore been employed in hydrocracking of petroleum stocks. In addition a multi-stage 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 non-limiting examples.

EXAMPLE 1

To a glass liner reactor is added 100 grams of pyrene and 108 grams of pyromellitic dianhydride. To this mixture is added with agitation 136 grams of zinc chloride. The reactor is flushed with nitrogen and heated to 500° F. under atmospheric pressure. A temperature of 495° F. is then maintained for a period of 24 hours. The temperature is reduced to ambient temperature and 258.5 grams of a shiny black brittle solid polymer is obtained. The polymer is powdered and extracted three times with 1000 milliliter portions each of a 4 wt. percent hydrochloric acid solution allowing about 24 hours extraction time for each extraction. The product is then filtered and extracted with water for 25 hours, followed by extraction with ethanol for 40 hours and benzene for 24 hours. A solid polymer is then recovered which weighs 165 grams.

EXAMPLE 2

To a glass lined reactor is added 53.5 grams of anthracene and 40.2 grams of phthalic anhydride. To this mixture is added with agitation 81.8 grams of zinc chloride. The reactor is flushed with nitrogen and heated to 500° F. under atmospheric pressure. A temperature of 495° F. is then maintained for a period of 24 hours. The temperature is reduced to ambient temperature and 135.7 grams of a shiny, black, brittle solid polymer is obtained. The polymer is powdered and extracted three times with 500 milliliter portions each of a 4 wt. percent hydrochloric acid solution allowing about 24 hours extraction time for each extraction. The product is then filtered and extracted with water for 25 hours, followed by extraction with ethanol for 40 hours and benzene for 24 hours. A solid polymer is then recovered which weighs 57.2 grams.

EXAMPLE 3

To a glass lined reactor is added 62.5 grams of anthraquinone and 44.4 grams of phthalic anhydride. To this mixture is added with agitation 81.8 grams of zinc chloride. The reactor is flushed with nitrogen and heated to 500° F. under atmospheric pressure. A temperature of 500° F. is then maintained for a period of 24 hours. The temperature is reduced to ambient temperature and a shiny black brittle solid polymer is obtained. The polymer is powdered and extracted with 19–2000 milliliter portions each of a 4 wt. percent hydrochloric acid solution allowing about 24 hours extracting time for each extraction. The product is then filtered and extracted with water until free of chloride ion, followed by extraction with ethanol for 12 hours and benzene for 18 hours. A solid polymer is then recovered which weighs 39.8 grams.

EXAMPLE 4

To a glass lined reactor is added 107 grams of anthracene and 80.4 grams of phthalic anhydride. To this mixture is added with agitation 195 grams of ferric chloride. The reactor is flushed with nitrogen and heated to 500° F. under atmospheric pressure. A temperature of 495° F. is then maintained for a period of 24 hours. The temperature is reduced to ambient temperature and a shiny black brittle solid polymer is obtained. The polymer is powdered and extracted seven times with 2000 milliliter portions each of a 4 wt. percent hydrochloric acid solution allowing about 24 hours extraction time for each extraction. The product is then filtered and extracted with water until free of chloride ion, followed by extraction with ethanol for 12 hours and benzene for 50 hours. A solid polymer is then recovered which weights 70 grams.

EXAMPLE 5

To a glass lined reactor is added 100 grams of a coke from delayed coking mid continent stocks (less than 100 mesh) having the following properties:

Sulfur, wt. percent	1.29
Ash, wt. percent	1.27
Hydrogen, wt. percent	3.9
Nitrogen, wt. percent	1.2
Surface area, m.^{2}/gram	5.0

and 108 grams of pyromellitic dianhydride. To this mixture is added with agitation 136 grams of zinc chloride. The reactor is flushed with nitrogen and heated to 500° F. under atmospheric pressure. A temperature of 500° F. is then maintained for a period of 24 hours. The temperature is reduced to ambient temperature and 248 grams of a shiny black brittle solid polymer is obtained. The polymer is powdered and extracted 10 times with 2000 milliliter portions each of a 10 wt. percent hydrochloric acid solution allowing about 24 hours extraction time for each extraction. The product is then filtered and extracted with water for 24 hours, followed by extraction with ethanol for 24 hours, benzene for 24 hours. A solid polymer is then recovered which was re-extracted with 30,000 ml. of 10 wt. hydrochloric acid solution, extracted with water until free of chloride ion followed by extraction with ethanol. The polymer was dried and 68 grams were recovered.

EXAMPLE 6

960 grams of a mid-continent asphalt (penetration 56 at 77° F.) is put into solution with 920 grams of benzene. The solutioin is mixed with 10,500 ml. of n-pentane and allowed to settle overnight. The pentane layer is decanted from a particulate layer of asphaltenes. This layer is filtered, washed with n-pentane and dried. A product, 171 grams of coffee-brown material that had the following analysis is recovered.

Hydrogen, wt. percent	7.6
Nitrogen, wt. percent	1.0
Sulfur, wt. percent	6.2
Ash, wt. percent	1.1

100 grams of the above material is powdered and mixed with 108 grams pyromellitic dianhydride. To this mixture is added with agitation 136 grams of zinc chloride. The reactor is flushed with nitrogen and heated to 500° F. under atmospheric pressure, a temperature of 500° F. is then maintained for a period of 24 hours. The temperature is reduced to ambient temperature and 298 grams of a solid polymer is obtained. The polymer is powdered and extracted 12 times with 2700 milliliter portions each of a 4 wt. percent hydrochloric acid solution allowing about 24 hours extraction time for each extraction. The product is then filtered and extracted with water for 25 hours, followed by extraction with ethanol for 40 hours, and benzene for 24 hours. A solid polymer is then recovered.

EXAMPLE 7

To a 1290 milliliter pressure rocking reactor equipped with gas addition means is added 502 grams of a California atmospheric reduced crude oil having the following properties:

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

together with 50 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 775 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 coke deposit formation.

EXAMPLE 8

To a 1290 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 7 together with 50 grams of the solid polymer (50 to 150 microns) from Example 2. 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 in 1070 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 coke deposit formation.

EXAMPLE 9

To a 1290 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 7 together with 50 grams of the solid polymer (50 to 150 microns) from Example 3. 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 29 hours. After this time the temperature is reduced to ambient temperature. It is determined that the hydrogen consumption based on the pressure drop is 720 standard cubic foot per barrel of charge. The oil is removed from the pressure reactor and filtered to recover the solid polymer catalyst. It is determined that there is no coke deposit formation.

EXAMPLE 10

To a 1290 milliliter pressure rocking reactor equipped with gas addition means is added 501 grams of a California atmospheric reduced crude oil the properties of which are set forth in Example 7 together with 50 grams of the solid polymer (50–150 microns) from Example 4. 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 42.5 hours. After this time the temperature is reduced to ambient temperature. It is determined that the hydrogen consumption based on the pressure drop is 930 standard cubic foot per barrel of charge. The oil is removed from the pressure reactor and filtered to recover the solid polymer catalyst. It is determined that there is no coke deposit formation.

EXAMPLE 11

To a 1290 milliliter pressure rocking reactor equipped with gas addition means is added 500 grams of a California atmospheric reduced crude oil the properties of which are set in Example 7 together with 50 grams of the solid polymer (50–150 microns) from Example 5. 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 between 750 to 765° F. for a period of 30 hours. After this time the temperature is reduced to ambient temperature. It is determined that the hydrogen consumption based on the pressure drop is 760 standard cubic foot per barrel of charge. The oil is removed from the pressure reactor and filtered to recover the solid polymer catalyst. It is determined that there is no coke deposit formation.

EXAMPLE 12

To a 1290 milliliter pressure rocking reactor equipped with gas addition means is added 500 grams of a California atmospheric reduced crude oil the properties of which are set forth in Example 7 together with 50 grams of the solid polymer (50–150 microns) 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 680 standard cubic foot per barrel of charge. The oil is removed from the pressure reactor and filtered to recover the solid polymer catalyst. It is determined that there is no coke deposit formation.

EXAMPLE 13

Example 11 is repeated using the same amount of California atmospheric reduced crude and 50 grams of

(50–150 micron) coke from delayed coking Mid-continent stocks, the properties of which are set forth in Example 5. After a period of 46 hours at a temperature of 750° F. and a hydrogen pressure of 4,000 p.s.i.g. It is determined that a heavy carbon deposit is formed.

EXAMPLE 14

Example 7 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 heavy carbon deposit is formed.

The test results on the oil product obtained from Examples 7 through 14 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, page 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 Gouch crucible (asbestos lined) leaving behind that material which settled from the mixed hexanes. The settled material is copiously treated with warm mixed hexanes until a substantially water white filtrate is obtained. The solids which remain are then filtered into the Gouch crucible which is rewashed until the color is water white. The Gouch crucible containing asphaltenes is then air dried in an oven at 210° F. The difference in weight between the Gouch 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	7	8	9	10	11	12	13	14
Product analysis, wt. percent disappearance of asphaltenes	94	80	62.4	64	71	86.5	20.4	[1] +108
Autoclave appearance at end of run	(2)	(2)	(2)	(2)	(2)	(2)	(3)	(3)

[1] A 108 wt. percent gain in calculated asphaltenes.
[2] Clean.
[3] Heavy carbon.

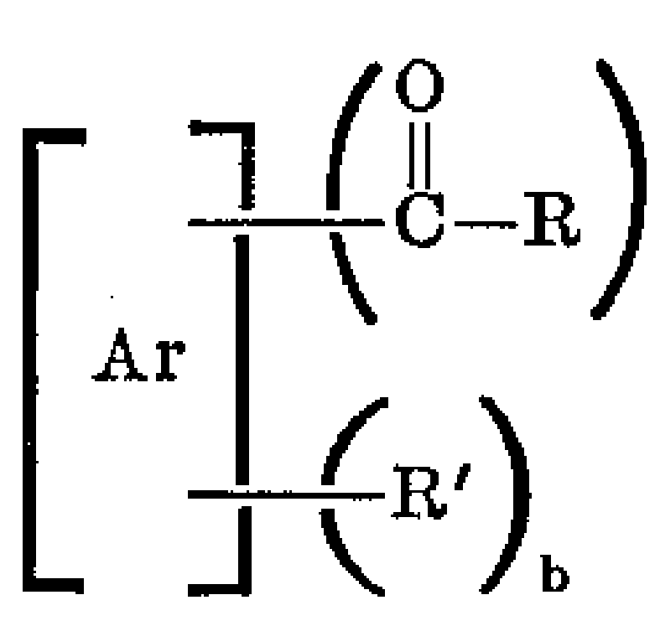
The results in Table I demonstrate the outstanding effectiveness of the process of this invention for converting asphaltenes which are present in a hydrocarbon charge stock. More particularly, the process of this invention provides for the conversion of asphaltenes without the formation to any substantial degree of carbon or coke deposits. Thus the results obtained in Examples 7 through 12 demonstrate that the solid polymer produces asphaltene conversion while eliminating carbon deposits. These results are in sharp contrast to the low conversion and heavy carbon deposits utilizing a coke from delayed coking mid-continent stocks (Example 13) or Example 14 wherein a +108 weight percent increase in asphaltenes occurred together with carbon deposits when the polymer was omitted.

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:

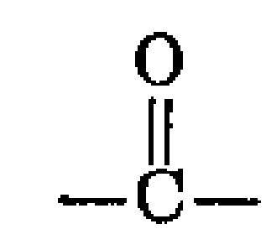
1. A process for the conversion of an asphaltene containing heavy hydrocarbon charge stock which comprises contacting said heavy hydrocarbon charge stock with hydrogen in the presence of about 0.5% to about 20% by weight based on the hydrocarbon charge stock of a solid polymer for a time sufficient under hydrogen contact conditions of about 1000–6000 p.s.i.g. pressure and 550–900° F. temperature to convert at least a portion of the asphaltenes to lower boiling hydrocarbons and recovering lower boiling hydrocarbons wherein said solid polymer is prepared by the process which comprises interacting an aromatic polycarboxylic compound with a polynuclear aromatic compound.

2. A process of claim **1** wherein the polycarboxylic compound is represented by the structural formula



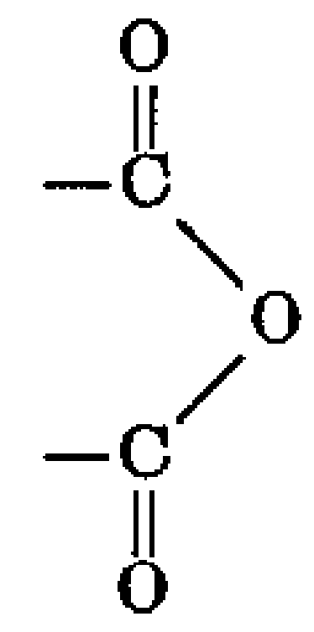
$$\left[\mathrm{Ar}\begin{matrix}-\left(\overset{\overset{O}{\|}}{C}-R\right)_a\\ -\left(R'\right)_b\end{matrix}\right]$$

wherein Ar is an aromatic nucleus, each R is independently selected from the group consisting of —OH, halide, a lower hydrocarbonoxy radical having from about 1 to about 12 carbon atoms and any two groups represented by



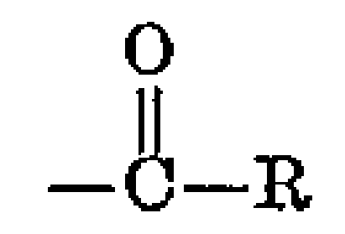
$$-\overset{\overset{O}{\|}}{C}-R$$

which are attached to adjacent carbon atoms on Ar can together form



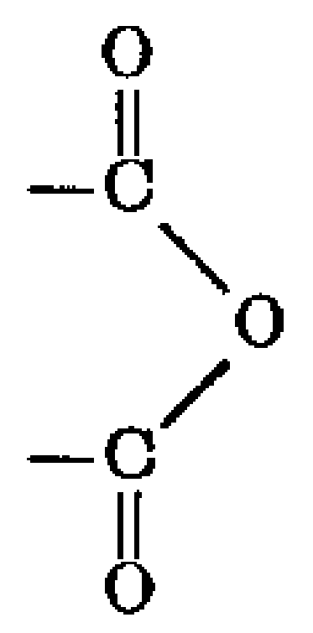
each R′ is a hydrocarbon radical, *a* is an integer having a value of from 2 to 4 and *b* is an integer having a value of from 0 to 4 provided that the sum of $a+b$ is not greater than 6.

3. A process of claim **2** wherein *b* has a value of zero, R is selected from the group consisting of alkoxy having from 1 to about 6 carbon atoms, OH, chloride and when two groups representing

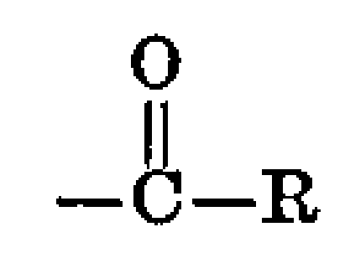


$$-\overset{\overset{O}{\|}}{C}-R$$

together form

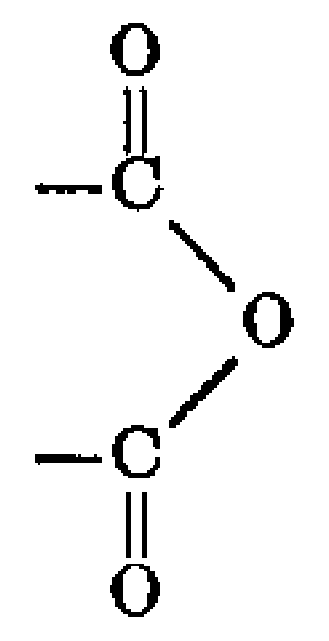


4. A process of claim **3** wherein R is selected from the group consisting of hydroxyl, chloride and any two groups representing



$$-\overset{\overset{O}{\|}}{C}-R$$

together form



5. A process of claim **4** wherein the aromatic carboxylic compound is selected from the group consisting of phthalic anhydride, pyromellitic anhydride, trimellitic anhydride and mixtures thereof.

6. A process of claim **2** wherein the polynuclear aromatic compound contains from 2 to about 9 fused aromatic rings.

7. A process of claim **2** wherein the polynuclear aromatic compound is selected from the group consisting of coke, asphaltenes, and mixtures thereof.

8. The process of claim **1** wherein the solid polymer is prepared in the presence of a Friedel-Crafts catalyst.

9. The process of claim **8** wherein the Friedel-Crafts catalyst is selected from the group consisting of zinc chloride, ferric chloride, aluminum chloride and mixtures thereof.

10. The process of claim **2** wherein the solid polymer is prepared in the presence of a Friedel-Crafts catalyst.

11. The process of claim **10** wherein the Friedel-Crafts catalyst is selected form the group consisting of zinc chloride, ferric chloride, aluminum chloride and mixtures thereof.

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