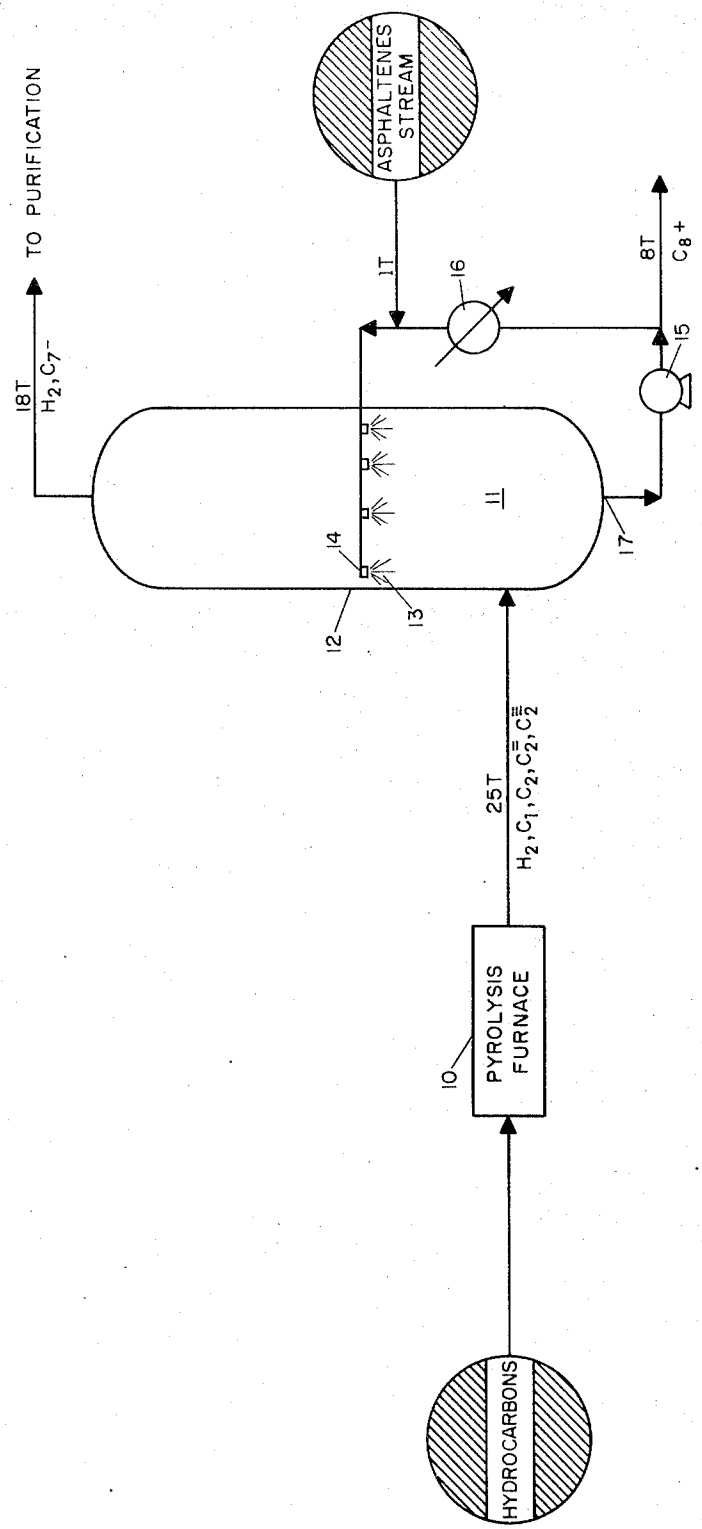
Jan. 15, 1974 T. J. OLESZKO 3,786,110

ASPHALTENES FOR INHIBITING POLYMERIZATION OF PYROLYSIS PRODUCTS

Filed May 19, 1972



United States Patent Office 3,786,110
Patented Jan. 15, 1974

3,786,110

ASPHALTENES FOR INHIBITING POLYMERIZATION OF PYROLYSIS PRODUCTS

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Filed May 19, 1972, Ser. No. 254,956
Int. Cl. C07c 11/24, 3/00
U.S. Cl. 260—679 R 9 Claims

ABSTRACT OF THE DISCLOSURE

Undesired residues from polymers obtained during pyrolysis of petroleum fractions are reduced by incorporating unoxidized or partially oxidized asphaltenes into the pyrolysis product streams. The asphaltenes provide sites for polymer molecules to attach themselves; also asphaltenes are capable of reacting with the highly reactive polyolefins to form low molecular weight polymers—such prevent the forming of high molecular weight polymers.

CROSS REFERENCES TO RELATED APPLICATIONS

No related U.S. patent applications are known to the inventor.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates generally to hydrocarbon pyrolysis processes, e.g., to produce acetylene, classified in Class 260, subclass 679 of United States Patent Classification system.

Description of the Prior Art

A search in the U.S. Patent Office disclosed the following prior art: U.S. Pat. 2,864,498 alters the ratio of octane-soluble, magnesia-adsorbable petroleum resins to octane-precipitable, benzene-soluble asphaltenes in an oil to reduce the tendency of such oil to form stable emulsions with water; U.S. Pat. 2,967,818 separates an asphaltic bituminous material into a heavy fraction containing asphaltenes and resins substantially free of asphaltene oils and a lighter solvent fraction containing dissolved residual asphaltic bituminous material including oils; U.S. Pat. 2,970,099 forms an asphalt comprising an alkylated asphaltene fraction having a carbon-to-hydrogen atomic ratio of 0.72–0.84. Alkylating agents include particularly alkyl halides, alkenes and alkanes; U.S. Pat. 3,089,846 forms a well drilling composition by dispersing asphaltene carboxylic acids into a fluid medium consisting of water, oil, and an emulsion of water and oil; U.S. Pat. 3,146,118 prepares an asphalt by blending a telomer of asphaltenes and ester with an asphalt cutter stock. The telomer is formed by precipitating asphaltenes of an asphalt with a C_{5-12} alkane and heating the asphaltenes with C_{6-20} alkyl ester of an acrylic acid in the presence of an organic peroxide; U.S. Pat. 3,366,702 adds oxy-compound inhibitors to pyrolysis products at a point downstream from the quench; U.S. Pat. 3,190,934 separates a hydrocarbon mixture consisting essentially of C_6–C_9 aromatic and aliphatic hydrocarbons into aromatic-rich and aromatic-lean fractions by extracting with bituminous material, e.g., asphaltenes, resins, and asphaltic oils; U.S. Pat. 3,231,488 hydrorefines a hydrocarbon charge stock containing less than about 0.1% by weight of pentane-insoluble asphaltenes by heating at below about 210° C. an asphaltene mixed with a carbonyl, a beta-diketone complex and a heteropoly acid. The resulting colloidal suspension is then reacted with hydrogen at about 225° C. and above 500 p.s.i.g.; U.S. Pat. 3,303,151 polymerizes a vinyl compound with an asphaltic material containing a transition metal and a reducing agent, i.e., metal hydrides, alkyls, aryls, or sesquihalides; and U.S. Pat. 3,317,447 prepares asphaltenes by heating a mixture of asphaltenes and polypropylene with 1–30% by weight of sulfur.

SUMMARY OF THE INVENTION

General Statement of the Invention

According to the invention, in a process for the pyrolysis of hydrocarbons or substituted hydrocarbons in a high temperature zone followed by rapid cooling in a quench zone, the serious problem of formation of hard deposits on the interior of apparatus downstream from the quench zone is solved by the simple expedient of adding asphaltenes to the pyrolysis products in or (less preferably) just after the quench zone. It is an important feature of the invention that the asphaltenes which are readily available in most refineries, e.g. those contained in many whole crudes, may be utilized as the inexpensive polymerization inhibitor for alleviating this problem. Thus the present invention provides the new solution to a previously serious problem without involving the need for purchase of raw materials which are not already available in most refineries. Further, the polymerization inhibitors, which can themselves be hydrocarbons, are not deleterious to the use of the pyrolysis products in any application in which such products are normally used.

Utility of the Invention

The present invention is useful with any of a wide variety of pyrolysis methods including partial oxidation techniques, the well known regenerative "Wulff" process taught in e.g., U.S. Pats. 1,996,185; 2,037,056; 2,236,534; 2,236,535; 2,236,555; 2,319,679; and 2,518,688, and any other process which involves the pyrolysis of hydrocarbons or substituted hydrocarbons in high temperature zones to form unsaturates which tend to polymerize in the downstream equipment.

The deposits prevented or alleviated by the present invention previously required very heavy amounts of maintenance in equipment downstream from the pyrolysis zone. For example, in one major Wulff pyrolysis installation, quench towers previously became nearly filled with deposits which were sufficiently hard that they had to be removed by air-operated jack hammers (such as are used to break up concrete roads or concrete blocks). The addition of relatively small amounts of asphalt-containing topped whole crude, according to the present invention, reduced the deposits to relatively thin coatings of a buttery consistency which were readily scraped from the tower. The tower had previously required cleaning approximately every four to six weeks, and after the application of the invention, required cleaning only about every 12 months. The plant is no longer shut down for cleaning of the quench tower but operates between normal turnarounds. Cleaning is only incidental to the turnaround and is negligible.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic representation of a typical Wulff pyrolysis installation showing the point of injection of the asphaltenes according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Starting materials.—Pyrolysis feedstocks: The pyrolysis feedstocks for the present invention can be any of a wide variety of hydrocarbons including any hydrocarbons from C_2 to about C_{30+}, more preferably aliphatic hydrocarbons in the range of from about C_2 to about C_{12}, and most

preferably alkanes either straight or branch chain in the range of from about C_4 to about C_8. These may be substituted hydrocarbons if desired, e.g., by halogens (e.g., fluoro carbon feedstocks such as trichloromonofluoroethane, etc.) or by sulfonates, nitrates, substituted aromatics and ethers. Suitable feedstocks include ethylene dichloride, nitroethane, chlorohexane, benzyl nitrate, butane, propane, light and heavy naphthas, refinery off gases, ethyl benzene and methane. It should be understood that treatment with asphaltenes is applicable to all manner of hydrocarbons subjected to pyrolyzing because even methane, when pyrolyzed, yields ethylene and a variety of heavier hydrocarbons which can cause deposits of the type alleviated or eliminated by application of the present invention.

Asphalts: The asphalts for use with the present invention are preferably residues from a distillation which removes materials lighter than about 650° C. Suitable sources of asphalts are crude oil, tar sands, and asphalt lakes. In general, the asphalts may be any of the heavy ends derived from crude oils, especially preferably asphaltic crudes.

Useful sources of asphalts are whole crudes, particularly asphaltic crudes, crude residues which contain asphalts, topped crudes, reduced crudes (crude tower bottoms), and especially preferred, vacuum tower bottoms. Gas oils and other lighter materials are generally undesirable for this purpose.

Preferably from about 0.10 to about 25, more preferably from 0.5 to 15, and most preferably from 2.0 to about 10 percent by volume of asphalts will be added to the liquid pyrolysis products. In a large measure, the quantity of asphalt to be added depends upon the nature and quantity of free or unstable, easily polymerizable hydrocarbons present.

Pyrolysis products: The cracked gases produced in the pyrolysis of the above hydrocarbon and other feeds will generally be benzene, xylenes, toluene, and olefins, as well as ethylene and acetylene. The bottoms from the pyrolysis process are generally heavy aromatics such as naphthalenes and alkyl-substituted naphthalenes. Of course, where substituted products are utilized as feed, the products will themselves generally be substituted, e.g., with nitrates, sulfates, halo groups, etc.

Pyrolysis process: While the invention is particularly useful with the Wulff pyrolysis process in which regenerative furnaces rapidly heat the feed and in which quench oils rapidly cool the pyrolysis products, the invention can also be used with other conventional pyrolysis techniques, e.g., steam crackers for ethylene production or production of other olefins, partial oxidation processes for production of unsaturates, thermal dehalogenation, etc.

EXAMPLE

Hydrocarbons are fed to pyrolysis furnace **10** which is, in this example, a Wulff regenerative pyrolysis furnace which is alternately heated by combustion of fuel gas (not shown) and then used to crack hydrocarbons by contact with the hot furnace refractories. The hydrocarbons fed are naphthas produced from Libyan crude together with minor hydrocarbon fraction streams obtained from other points in the refinery. The pyrolysis furnace operates at approximately 1200° C. and the products are about 25 tons per hour of hydrogen, ethane, methane, ethylene, acetylene, and minor amounts of carbon and other products. The hot pyrolysis products are fed to a lower stage **11** of quench tower **12** where they contact quench oil **13** sprayed from nozzles **14** fed by a pump **15** via cooler **16**. The quench oil is collected at the bottom outlet **17** of the quench tower **12** and is recycled through cooler **16** back into the spray heads **14**. About eight tons per hour of a stream of octane and heavier hydrocarbons is withdrawn for further purification or for burning. About 18 tons of hydrogen and C_7-lower hydrocarbons is withdrawn from the quench tower as overheads and is sent for further purification, particularly to recover ethane and acetylene.

The above description of this example is substantially conventional operation of a Wuff unit. Over a period of time, the downstream purification equipment as well as the upper portions of the quench tower will become caked with polymerized deposits which will be mechanically strong and difficult to remove.

According to the present invention, one ton per hour of an asphaltene-containing stream (in this case atmospheric tower bottoms obtained from the distillation of Libyan crude in a conventional tower operating at approximately 2.5 absolute), is fed to the stream of quench oil being circulated to the nozzles **14**. This feed is continued over a period of months of operation and it is found that the deposits on the downstream equipment are greatly reduced in quantity and that their consistency is similar to that of warm butter or a soft grease. The deposits are readily removed by low pressure water stream or hand scraping performed during routine maintenance at 12 month intervals, the normal turnaround interval.

MODIFICATIONS OF THE INVENTION

A variety of modifications and variations in the invention will be apparent to those skilled in the art upon a reading of the present specification and it should be understood that all such modifications and variations are to be included within the spirit of the claims appended hereto.

What is claimed is:

1. In a process for the manufacture of unsaturated hydrocarbons or unsaturated substituted hydrocarbons by the pyrolysis of hydrocarbons or substituted hydrocarbons by first pyrolyzing at elevated temperature and thereafter quenching the products of said pyrolysis, comprising adding to said pyrolysis products during said quenching step a quantity of polymerization inhibitor to inhibit the formation of high molecular weight deposits on equipment used in said quenching step and on downstream equipment, the improvement wherein said inhibitor consists essentially of asphalt-containing hydrocarbons boiling above about 650° C.

2. A process according to claim **1** wherein said hydrocarbons or substituted hydrocarbons comprise whole or topped crude oil.

3. A process according to claim **1** wherein said hydrocarbons are selected from the group consisting of refinery off gases, hydrogen, methane, ethane, ethylene, propane, propylene, C_{4s} and C_{5s}, light and heavy straight-run naphthas, and naphtha from thermal cracking processes and mixtures thereof.

4. A process according to claim **1** wherein said asphalt-containing hydrocarbons are selected from the group consisting of crude oil, reduced crude, vacuum-reduced crude and mixtures thereof.

5. In a process for the manufacture of unsaturated hydrocarbons or unsaturated substituted hydrocarbons for the pyrolysis of hydrocarbons or substituted hydrocarbons by first pyrolyzing at elevated temperature and thereafter cooling the products of said pyrolysis, comprising adding to said pyrolysis products during said cooling step a quantity of a polymerization inhibitor to reduce the formation of high molecular weight deposits on equipment contacted by said pyrolysis products during or after said cooling step the improvement wherein said inhibitor comprises asphalts boiling above about 650° C.

6. A process according to claim **5** wherein said hydrocarbons or substituted hydrocarbons comprise whole or topped crude oil.

7. A process according to claim **5** wherein said hydrocarbons are selected from the group consisting of saturated and unsaturated hydrocarbons from C_1 to C_{20}.

8. A process according to claim **5** wherein said asphalt-containing hydrocarbons are selected from the group consisting of crude oil, topped crude and/or vacuum-reduced crude.

9. A process according to claim 8 wherein said asphalt-containing hydrocarbon is vacuum-reduced crude containing minimum quantity of distillable gas oils.

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DELBERT E. GANTZ, Primary Examiner

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U.S. Cl. X.R.

208—48 Q; 260—683 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,786,110 Dated January 15, 1974

Inventor(s) Thaddeus J. Oleszko

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

Col. 4, line 12:	After "2.5" insert --atmospheres--.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.