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PYROLYZING HYDROCRACKED NAPHTHAS TO PRODUCE UNSATURATED HYDROCARBONS

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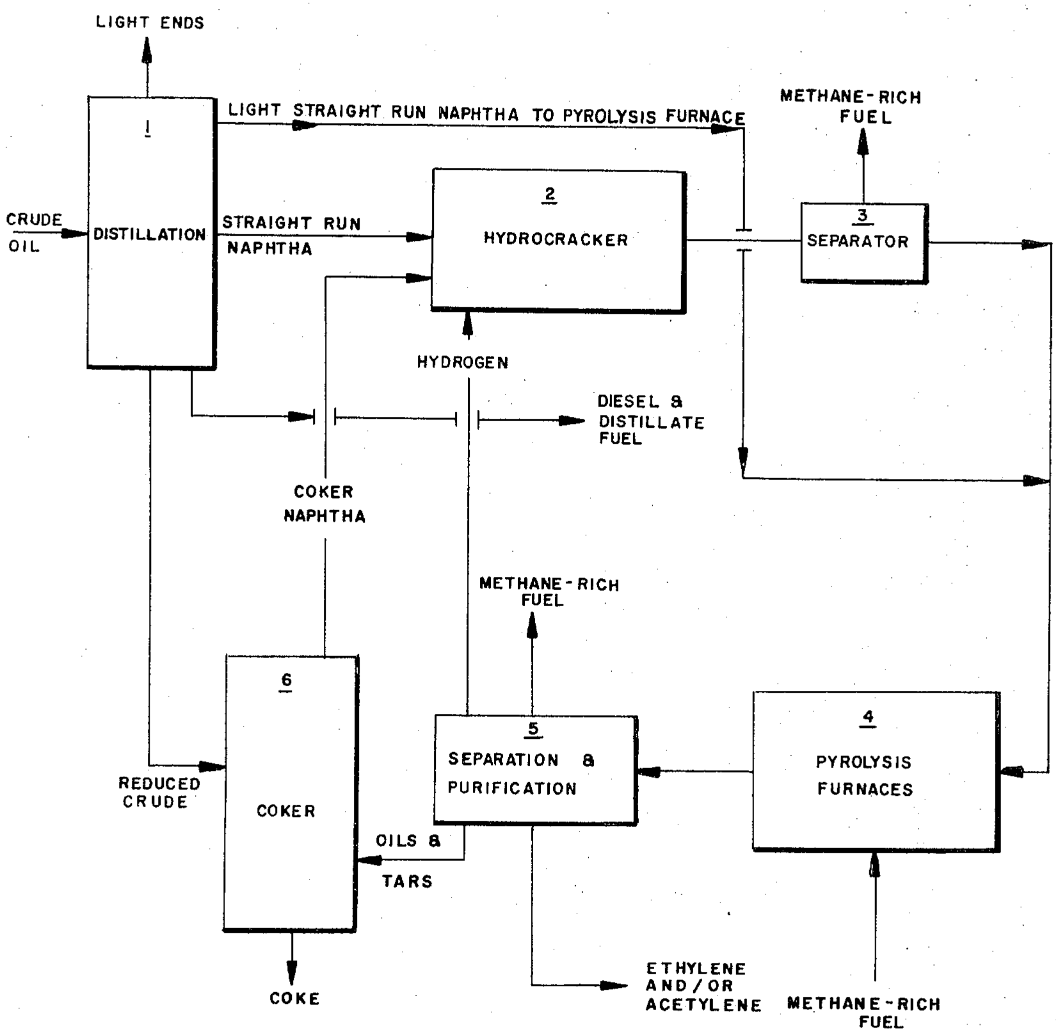

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PYROLYZING HYDROCRACKED NAPHTHAS TO PRODUCE UNSATURATED HYDROCARBONS

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ABSTRACT OF THE DISCLOSURE

Yields of unsaturated hydrocarbons, e.g. ethylene and acetylene, from pyrolysis furnaces are improved by first hydrocracking naphthas, e.g. straight-run naphthas or coker naphthas, and charging the resulting mixture or paraffins and isoparaffins to the furnace. Hydrogen from the pyrolysis products can be recycled to the hydrocracker. Fuel from the pyrolysis products can be utilized to heat the pyrolysis furnace. Oils from the pyrolysis products can be recycled to a coker which produces coker naphthas for use in the process.

CROSS REFERENCES TO RELATED APPLICATIONS

U.S. Pat. application Ser. No. 821,164 filed Apr. 25, 1969 now U.S. Pat. 3,617,495 and Ser. No. 819,171, filed Apr. 25, 1969 now U.S. Pat 3,556,987 relate to the general field of the present invention

BACKGROUND OF THE INVENTION

(1) Field of the Invention

The present invention relates generally to the field of hydrocarbon conversion processes. More specifically the invention relates to the field of chemistry of carbon compounds, hydrocarbons, acyclic, olefins from hydrocarbons by dehydrogenation, usually classed in United States Patent Office Class 260–683.3.

(2) Description of the Prior Art

U.S. 3,143,490 produces more branched-chain paraffins by dehydrogenating normal paraffins, then hydrogenating them to cause branching. U.S. 2,750,420 cracks hydrocarbons, producing ethylene and acetylene. Acetylene may be selectively hydrogenated to ethylene or ethane. Other patents of substantially less pertinance are: U.S. 1,460,545 (producing ethylene from pure ethane); U.S. 2,045,255 (producing ethylene under subatmospheric pressure); U.S. 2,274,204 (oxydehydrogenating hydrocarbons); U.S. 2,354,892 (dehydrogenating hydrocarbons with activated alumina-tungsten oxide catalyst); U.S. 2,399,540 (oil soluble metal-organic catalyst for hydrocarbon conversion); U.S. 2,514,294 (specialized fractionation of mixed hydrocarbon products); U.S. 2,549,240 (catalytic dehydrogenation of ethylene to acetylene); U.S. 2,629,753 (catalytic pyrolysis of ethane to ethylene); U.S. 2,653,903 (sequential cracking of petroleum fractions); U.S. 2,877,279 (cracking apparatus); U.S. 2,924,632 (catalyst regeneration); and U.S. 3,437,585 (extraction process in combination with dehydrogenation).

SUMMARY

(1) General Statement of the Invention

Naphthas, e.g. straight-run naphthas or coker naphthas or mixtures thereof are hydrocracked, and the resulting mixture of paraffins and isoparaffins low in naphthenes and aromatics is charged to a pyrolysis furnace for the production of ethylene and/or acetylene and other unsaturated hydrocarbons. Hydrogen separated from product gas can be recycled to the hydrocracker, methane-rich fuels from the product gas can be used to heat the pyrolysis furnaces, and tars and oils from the pyrolysis gas can be sent to a coker which produces coker naphtha for use in the product. The pyrolysis furnaces may be of the steam cracker type or of the Wulff type or of other conventional design.

The invention improves yields of ethylene and acetylene from pyrolysis furnaces. Tars, coke, and by-product diolefins and aromatics are reduced. Fouling the process equipment is substantially reduced. On-stream time between shut-downs for decoking of equipment is increased. Furnace life and ease of operation are increased.

(2) Utility of the Invention

The present invention produces unsaturated hydrocarbons, e.g. acetylene, which can be hydrochlorinated to produce vinyl chloride for production of vinyl chloride polymers according to well-known techniques and ethylene which can be polymerized according to well-known techniques to produce polyethylene.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a schematic representation of a preferred embodiment of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

(1) Starting Materials

The starting materials for the present invention are hydrogen produced by any conventional technique and utilized in the hydrocracking step; and naphthas, e.g. coker naphthas and straight-run naphthas. By naphtha is meant any hydrocarbon having a boiling range within the general range of from about 80° F. to about 450° F., more preferably from about 80° F. to about 400° F. By "coker naphtha" is meant a naphtha produced as a by-product from the coking of hydrocarbon residua, e.g. delayed petroleum coking. By "straight-run naphtha" is meant a naphtha produced by the distillation of crude oil. The preferred starting materials are hydrocarbons containing from 1 to about 7, more preferably from about 2 to about 6, and most preferably from 2 to about 5 carbon atoms per molecule. In general, normal and isoparaffins containing 2–5 carbon atoms have been found to be the best feeds for pyrolysis furnaces. Olefins are less desirable feed stocks. All feed stocks of 6 or more carbon atoms (particularly normal C_8 and above) are less desirable than those of the 2–5 carbon number. The heavier feed stocks are less desirable because the yields of acetylene and ethylene are lower and the corresponding yields of coke, tars, and oils are greater. For carbon numbers of 6 or greater, normal and isoparaffins are the most desirable, olefins and naphthenes are less desirable, aromatic hydrocarbons are the least desirable. Feeds of 6 or more carbon atoms are susceptible to a side reaction of cyclization and aromatization. Aromatic formation is much less with feeds of 2–5 carbon atoms because it requires sequential bi-molecular reactions. Two-body reactions have a much lower probability of occurrence than uni-molecular reactions. The present invention permits the production of a feed stock consisting primarily of paraffins and isoparaffins in the 2–5 carbon number range. This feed stock is therefore particularly well suited for use in pyrolysis furnaces.

(2) Hydrocracking

Hydrocracking is accomplished in the range of from 500 to about 1000, more preferably 600 to about 900, and most preferably 700 to about 850° F. and 600 to about 3000, more preferably 800 to about 2000, and most preferably 1000 to about 1800 p.s.i.g. Liquid hourly space velocities in the range of from 0.5 to about 10, more preferably 0.5 to about 5, and most preferably 1 to about 3, feeding from 2000 to about 5000, more preferably 2500 to about 4500, and most preferably 3000 to about 4000 Standard cubic feet (SCF) of hydrogen per barrel of naphtha feed to the hydrocracker. Hydrocracking is more generally discussed in *Hydrocracking Handbook;* Reprinted from Hydrocarbon Processing. Gulf Publishing Company (1969) and Scott, J. W., Robbers, J. A., Mason, H. F., Patterson, N. J. and Kozlowski, R. H., *"Isomax Gives Gasoline or Distillate"* Hydrocarbon Processing & Petroleum Refiner, *42,* 131–136 (July 1963) and in the references cited therein.

(3) Pyrolysis

Pyrolysis in Wulff furnaces is generally accomplished at temperatures of from 800 to about 1200° C., with residence times at the peak furnace temperatures of 0.008 to about 0.02 secs. followed by extremely rapid quenching. Normally 1.5–3 lbs. of steam are fed to the furnace per lb. of naphtha charge. The Wulff Process pyrolysis is more fully described at page 384 of Miller, Acetylene, Its Property Manufacture and Uses. Steam cracking is accomplished at about 800–900° F. at a residence time of 0.2–1.0 sec. using about 0.2–1.0 lbs. of steam per lb. of feed. No catalyst is used and the cracking is done inside alloy tubes hung in a direct fired furnace. Steam cracking furnaces are more fully described at p. 125, of Miller, "Ethylene and Its Industrial Derivatives."

(4) Examples

The invention can be more fully understood by reference to the specific embodiment shown in the drawing. Crude oils fractionated in the distillation column **1** give five primary products: (1) light ends (mostly methane and ethane which can be sent to the plant fuel system), (2) light straight-run naphtha (C_3–C_5 hydrocarbons which can be sent directly to the pyrolysis furnace), (3) straight-run naphtha (approximate boiling range 80–430° F., which provides feed to the hydrocracker in accordance with the invention), (4) diesel fuel and distillate fuels (boiling in the range of 400–650° F. and suitable for direct sale), and (5) reduced crude (boiling at 650° F. or above which can be sent to the coker).

The straight-run naphtha containing mostly paraffins and naphthenes is sent to the hydrocracker **2** along with the naphtha produced by the coker. Only one stage is required in the hydrocracker. The hydrocracker operates at approximately 800° F., 1500 p.s.i.g., 2.5 liquid hourly space velocity, 4000 SCF hydrogen per barrel of naphtha feed and utilizes a nickel-molybdenum catalyst on a silica alumina support. The hydrocracker effluent is sent to a flash drum **3** where hydrogen and methane are separated from the other products. The hydrogen can be recycled to the hydrocracker and the methane-rich fuel can be used as fuel for the pyrolysis furnaces or fed to the plant fuel system. The liquid effluent, a mixture of propane, butane, isobutane and light gasoline fractions containing over 90% paraffins and less than 10% aromatics and naphthenes, can be sent to the pyrolysis furnace **4**. In addition, substantial sulfur and nitrogen removal has been accomplished in the hydrocracking.

The pyrolysis furnace **4** is a Wulff-type furnace operating at a center temperature of approximately 1200° C. with a residence time at peak furnace temperature of approximately 0.008 secs. and includes a rapid oil quench.

Feed to the pyrolysis furnace consists of a mixture of light straight-run naphtha from the distillation tower **1** and liquid products from the separator **3**. 1.6 Lbs. of steam are mixed with each lb. of feed as it enters the furnace. This feed stock contains only small amounts of naphthenes or aromatics and is essentially olefin-free. In addition, the carbon range of the feed stock is substantially in the 2–5 carbon atom range with some 6-carbon atom molecules, but is essentially free of components having more than 6 carbon atoms.

In the pyrolysis furnace **4**, the feed stock is cracked to a mixture of acetylene, ethylene, methane and hydrogen. Only a small amount of propylene, aromatic oils, and tars are produced. Separation and purification section **5** consists of distillation and scrubbing of products. The products produced by the total components of the invention are: acetylene and ethylene for sale; hydrogen for recycle to the hydrocracker furnace; methane-rich fuel gas used as fuel for the pyrolysis furnace; and a small stream of oils and tars sent to the coker **6**.

If the hydrogen produced by the Wulff or other pyrolysis operation is not sufficient for the operation of the hydrocracker, additional hydrogen can be obtained by reforming a portion of the methane-rich gases recovered from the separations plant **5**. This can easily be accomplished because the methane-rich gas is sulfur-free when it leaves the separations plant.

(5) Modifications of the Invention

It should be understood that the invention is capable of a variety of modifications and variations which will be made apparent to those skilled in the art by a reading of the specification and which are to be included within the spirit of the claims appended hereto.

For example, while the above specific embodiment utilizes a Wulff-type pyrolysis furnace, a stream cracker of the type commonly used to produce ethylene can readily be substituted for use with the invention.

What is claimed is:

1. In a process for the preparation of unsaturated hydrocarbons by pyrolysis of naphthas boiling in the range of about 80 to 450° F. in a pyrolysis furnace, the improvement comprising hydrocracking said naphthas at from about 500 to about 1000° F. and about 600 to about 3000 pounds per square inch gauge while feeding about 2000 to about 5000 standard cubic feet of hydrogen per barrel of naphtha fed, to form a mixture of paraffins and isoparaffins said mixture consisting essentially of hydrocarbons containing from 1 to about 7 carbon atoms per molecule and pyrolyzing the resulting mixture of paraffins and isoparaffins in said pyrolysis furnace, at from about 800 to about 1200° C.

2. The process of Claim **1** wherein the unsaturated hydrocarbons comprise ethylene.

3. The process of Claim **1** wherein the unsaturated hydrocarbons comprise acetylene.

4. The process of Claim **1** wherein the naphthas are selected from the group consisting of straight-run naphthas and coker naphthas.

5. The process of Claim **1** wherein hydrogen is produced as a coproduct with said unsaturated hydrocarbons and said hydrogen is recycled to said hydrocracking step.

6. The process of Claim **1** wherein there is also produced as a co-product to said unsaturated hydrocarbons a methane-rich fuel gas which is used as at least a portion of the fuel for heating said pyrolysis furnace.

7. The process of Claim **1** wherein there is produced as co-products to said unsaturated hydrocarbons a stream of oils and tar which are sent to a coker which in turn produces coker naphtha for hydrocracking and thereafter charging to said pyrolysis step.

8. The process of Claim **1** wherein said pyrolysis furnace is a Wulff pyrolysis furnace.

9. The process of Claim **1** wherein the pyrolysis furnace is a steam cracker.

10. In a process for the preparation of ethylene and acetylene by pyrolysis of straight-run or coker naphthas boiling in the range of about 80 to 450° F. in a pyrolysis furnace, the improvement comprising hydrocracking said straight-run naphtha or said coker naphtha at from about 500 to about 1000° F. and about 600 to about 3000 pounds per square inch gauge while feeding about 2000 to about 5000 standard cubic feet of hydrogen per barrel of naphtha fed, to form a mixture of paraffins and isoparaffins, said mixture containing from 1 to about 7 carbon atoms per molecule charging the resulting mixture of paraffins and isoparaffins to said pyrolysis furnace operating at from about 800 to about 1200° C., producing hydrogen, methane-rich fuel gas, a stream of oils and tar, ethylene, and acetylene in said pyrolysis furnace, recycling said hydrogen for use in the hydrocracking step, recycling said methane-rich fuel gas for use in heating said pyrolysis furnace, and coking said stream of oils and tar to produce coker naphtha for charging to said pyrolysis step.

References Cited

UNITED STATES PATENTS

1,917,324	7/1933	Pier et al.	208—61
3,184,402	5/1965	Kozlowski et al.	208—59
3,556,987	1/1971	Zimmerman Jr. et al.	260—683 R
2,245,819	6/1941	Porter	23—285
3,456,032	7/1969	Kniel	260—683
3,470,263	9/1969	Kitzen	260—683 R
2,236,555	4/1941	Wulff	260—679
2,899,475	8/1959	Davison	260—683

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U.S. Cl. X.R.

260—679; 208—61

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,839,484 Dated October 1, 1974

Inventor(s) Carle C. Zimmerman et al

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

Col. 1, line 16:	Delete "or" and insert --of--.
Col. 2, line 14:	After "fouling" insert --of--.
Col. 3, line 33:	Delete "800-900°F." and insert therefor --800-900°C.--.

Signed and Sealed this

Twentieth **Day of** *September 1977*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

LUTRELLE F. PARKER
Acting Commissioner of Patents and Trademarks