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Starks

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[54] **TWO-STAGE HYDROPYROLYSIS-CRACKING PROCESS FOR PRODUCING ETHYLENE**

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[51] **Int. Cl.²**........................ **C07C 3/40;** C10G 13/28

[58] **Field of Search**......... 260/683 R, 673.5; 208/57, 208/58, 61, 89, 107

[56] **References Cited**

UNITED STATES PATENTS

2,089,616	8/1937	McKee	208/107
2,245,819	6/1941	Porter	260/683
3,373,220	3/1968	Hepp	260/683
3,511,771	5/1970	Hamner	208/89
3,839,484	10/1974	Zimmerman et al.	260/683
3,842,138	10/1974	Chahvekilian et al.	260/683

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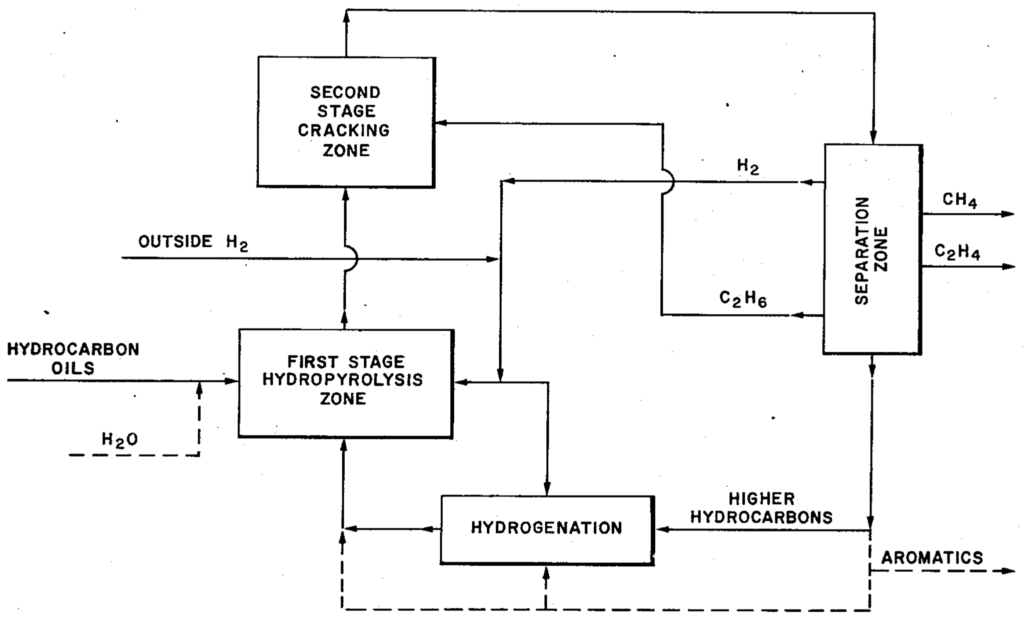
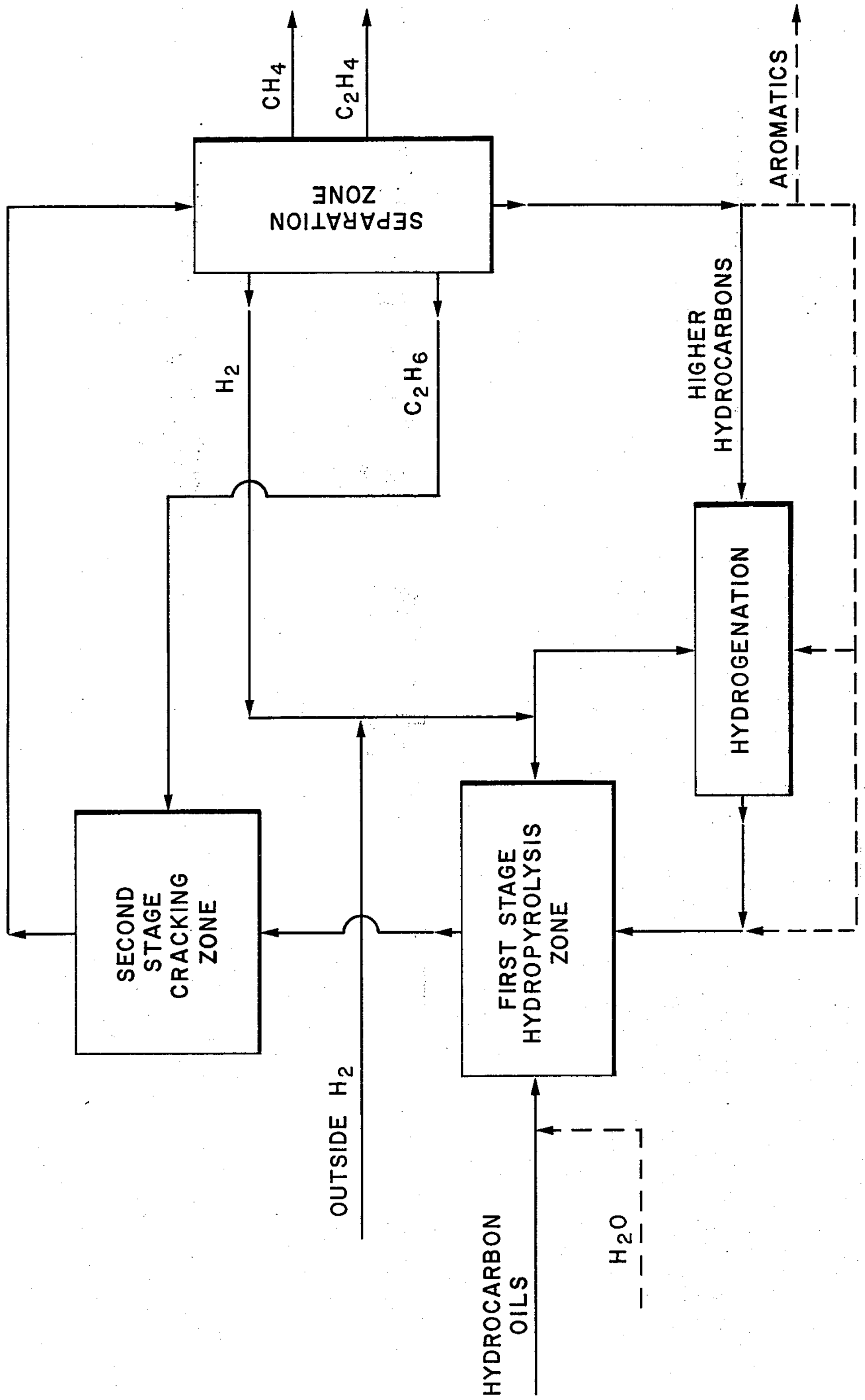
[57] **ABSTRACT**

Ethylene along with methane may be produced by an integrated process involving a first stage hydropyrolysis of a hydrocarbon oil in the presence of hydrogen followed by cracking of the hydropyrolysis effluent, separating and recycling the hydrogen and ethane and recovering the methane and ethylene.

9 Claims, 1 Drawing Figure




CH4
C2H4
SEPARATION ZONE
AROMATICS
H2
C2H6
HIGHER HYDROCARBONS
HYDROGENATION
SECOND STAGE CRACKING ZONE
FIRST STAGE HYDROPYROLYSIS ZONE
OUTSIDE H2
HYDROCARBON OILS
H2O

TWO-STAGE HYDROPYROLYSIS-CRACKING PROCESS FOR PRODUCING ETHYLENE

This invention relates to an integrated process for producing ethylene. More particularly, the invention relates to an integrated two-stage hydropyrolysis-cracking process for producing ethylene from higher hydrocarbons.

Cracking of various petroleum fractions to produce ethylene is well known in the art. In general, fractions ranging from ethane to heavy gas oil and even whole crude oil have been employed as feedstocks to these cracking operations. The cracking has been carried out in a variety of equipment including fired tubular heaters, pebble-bed heaters, fluidized-bed crackers, and the like. Many processing schemes have also been devised including recycle of various components to increase ethylene yields.

In accordance with this invention, there is provided a novel integrated two-stage hydropyrolysis-cracking process whereby higher hydrocarbons, including whole crude oil and hydrogenated coal liquids, are pyrolyzed to produce ethylene. The integrated process provides not only for production of ethylene but also methane which can be used in synthetic natural gas. Hydrogen and all other higher organics may be recycled back into the process for eventual conversion to ethylene and methane although it is possible to make further separations on the heavy organic stream to recover aromatics which include benzene, toluene, and xylenes. In the event aromatics are not separated from the heavy organic stream prior to recycle, it is desirable to hydrogenate the stream to convert unsaturates to saturates.

The integrated process of the invention is schematically illustrated in the accompanying drawing together with certain optional features depicted by dotted lines.

The hydrocarbon oils suitable for use in the process of this invention may be defined as those having a density of less than about 0.99, preferably less than about 0.95, and a Conradson carbon content of less than about 20 weight percent, preferably less than about 2 weight percent. Both non-distillate and distillate hydrocarbon oils are suitable such as respectively described in U.S. Pat. No. Re. 27599 and U.S. Pat. No. 3,363,024. For example, crude petroleum or other oils having similar density and volatility characteristics may be used as well as oils derived from coal such as hydrogenated coal oil. Distillate oils boiling in the range of 30°C to 360°C may be used. Similarly, coal tar distillates containing unsubstituted or hydroxy-substituted hydrocarbons can be used. Gases consisting primarily of butane and propane are satisfactory feedstocks. All of the above are intended to be included within the expression "hydrocarbon oils."

The hydrocarbon oils as described above are introduced to a first-stage hydropyrolysis zone along with hydrogen. In the hydropyrolysis zone, the hydrocarbon oils are pyrolytically cracked in the presence of hydrogen to lower hydrocarbons. From an equipment standpoint, a suitable reactor for conducting the hydropyrolysis is described in U.S. Pat. No. 3,363,024, supra. Another suitable device is a conventional tubular furnace used in the usual cracking operations.

The hydropyrolysis is conducted with a mol ratio of hydrogen to hydrocarbon oils of at least 1/1, preferably at least 3/1. The more hydrogen present the less the tendency to form carbon in the zone, other relevant factors remaining constant such as temperature, pressure, etc. Another factor to be considered in determining the amount of hydrogen to employ in a particular operation is that increased hydrogen favors ethane production over ethylene. This factor has significance in connection with the second-stage cracking in that ethane is dehydrogenated to ethylene in that stage. A further consideration is with the amount of excess hydrogen that must be processed and recycled through the integrated process. All factors considered, it is preferable to operate with hydrogen to hydrocarbon oil mol ratios in the range of about 3/1 to 30/1.

The hydrogen for the hydropyrolysis stage is provided by recycling the hydrogen separated in the subsequent separation stage to be described more fully hereinafter, and additionally from any suitable outside source.

The hydrogen and hydrocarbon oil feed may be separately introduced to the hydropyrolysis stage or they may be combined and introduced as a mixture. The hydrocarbon may be introduced through an atomizing nozzle using hydrogen as the atomizing gas. Preferably, the hydrocarbon oil is preheated to a temperature approaching the operating temperature of the hydropyrolysis zone; e.g., 300°C to as high as 550°C.

The hydropyrolysis is carried out at temperatures in the range of 600°C to 900°C, preferably 700°C to 850°C. Higher temperatures favor ethylene over ethane. Pressures of at least 5 atmospheres gauge are employed, usually in the range of 5 to 100 atmospheres gauge and preferably in the range of 15 to 30 atmospheres gauge. Lower pressures favor ethylene to ethane. Residence times in the range of 0.1 second to 60 seconds, preferably 0.5 to 20 seconds, are employed. Shorter residence times favor ethylene over ethane.

Carbon deposition arising from side reactions in the hydropyrolysis zone can be inhibited by providing a small concentration of sulfur compounds in the hydrocarbon oil feed if not already present; e.g., 10 ppm. This is well known in the art and is generally referred to as passification. Usually the addition of sulfur compounds is done on a continuous basis.

An alternative to the use of sulfur compounds is water or steam although for a given degree of effectiveness in inhibiting carbonization, greater quantities of water are required compared to sulfur compounds. Usually, up to about 3 mol of water per mol of hydrocarbon oil will be effective although greater quantities can be employed. Water not only inhibits carbonization but it has also been found that water affects hydropyrolysis by tending to favor ethylene over ethane.

The effluent from the first-stage hydropyrolysis zone is then introduced to the second-stage cracking zone. In the second-stage cracking zone, the effluent is subjected to low pressure cracking. Temperatures in the range of 750° to 900°C, preferably 800°–850°C, are employed. Pressures usually not above about 2 atmospheres gauge, and preferably not above 1 atmosphere gauge, are used. The residence time may be in the range of about 0.01 second to 10 seconds with 0.1 second to 1 second being preferred.

Since the conditions in the second-stage cracking zone are also ideal for dehydrogenating ethane to ethylene, ethane from the separation zone is recycled to the second-stage cracking zone. Thus, the second-stage zone not only serves to crack higher hydrocarbons in the effluent from the first stage hydropyrolysis zone but also serves to dehydrogenate ethane which is produced both in the first and second stages as well as that recycled.

The effluent product mixture from the second stage cracking zone is then processed for recovery of methane and ethylene in the separation zone. Conventional techniques for separating hydrogen, methane, ethylene, ethane and higher hydrocarbons may be employed. A convenient separation and recovery system involves rapidly cooling or quenching the product mixture immediately on exiting from the second-stage cracking zone and then processing the cooled mixture through a series of low-temperature fractional distillation columns as are known in the art. Hydrogen is first separated and recycled to the first-stage hydropyrolysis zone as earlier discussed. Methane is then separated and recovered and may be conveniently utilized as a synthetic natural gas component. Ethylene is next to be separated and may be sent to storage or transport as an item of commerce. Ethane is next separated and recycled to the second-stage cracking zone as earlier described. The remaining higher hydrocarbons are then hydrogenated in a conventional manner to remove any unsaturation and recycled to the first-stage hydropyrolysis zone to again be processed and converted to lower hydrocarbons and eventually to ethylene and methane.

While the above technique for separation is essentially a selective step-wise distillation, it should also be mentioned that the reverse may also be employed, that is, a selective step-wise condensation.

Since the higher hydrocarbons will contain varying amounts of aromatics, principally benzene, toluene, and xylenes, a further separation step may be performed prior to hydrogenation and recycle. Such separation may be accomplished in any known manner to separate essentially all aromatics or only those components desired. If essentially all aromatics are separated, the remaining higher hydrocarbon stream may be recycled as is to the first-stage hydropyrolysis zone without hydrogenation. It is preferred, however, to hydrogenate the higher hydrocarbon stream prior to recycle even though the aromatics or some of the aromatics have been removed.

The following examples will serve to further illustrate the invention.

EXAMPLE 1

A mixture of 2.3 liquid vol/min kerosene (boiling point range of 190°C to 270°C and a specific gravity of 0.82), 2.65 liquid vol/min water and 161 gas vol/min hydrogen (mol ratio of H_2 to hydrocarbon is about 18.0) are introduced to the first-stage hydropyrolysis zone of a type described in U.S. Pat. No. 3,363,024. Recycle hydrogen and recycle higher hydrocarbon inlets are also provided. The hydropyrolysis is conducted at temperatures ranging from 750°–800°C, a pressure of 20.4 atmospheres gauge and a residence time of 7–10 seconds.

The effluent from the first-stage hydropyrolysis zone is then depressured into the second-stage cracking zone of a tubular furnace type. An ethane recycle inlet is also provided to this zone. The second-stage cracking is carried out at temperatures of 850°–900°C, pressures of 0.7–1.7 atmospheres gauge and a residence time ranging from 0.1–0.5 second.

The product mixture from the second-stage hydropyrolysis zone is rapidly cooled or quenched and conducted into a series of fractional distillation columns. Hydrogen is separated and recycled to the first-stage hydropyrolysis zone. Methane is separated and sent to storage. Ethylene is separated and sent to storage. Ethane is separated and recycled to the second-stage cracking zone. The remaining higher hydrocarbon stream is hydrogenated and recycled to the first-stage hydropyrolysis zone.

EXAMPLE 2

A light naphtha (BP 85°–150°C) at a rate of 0.034 ml/min and hydrogen at a rate of 100 cc/min (mol ratio of hydrogen to hydrocarbon to about 16.2) were introduced to a hydropyrolysis zone formed by a ⅜-inch stainless steel tubular reactor one foot in length of which a volume of about 16 cc in the central area constituted the hot zone. The hydropyrolysis was carried out at a temperature of 750°C (hot point), a pressure of 6.8 atmospheres gauge and an average residence time of 2.5 sec.

The effluent from the hydropyrolysis zone was analyzed by GLC as 12.4 weight percent H_2, 36.3 weight percent methane, 1.1 weight percent ethylene, 41.4 weight percent ethane, and 9.0 weight percent higher hydrocarbons.

The effluent from the hydropyrolysis is then introduced to second-stage cracking operated under atmospheric pressure and 800°–850°C. Calculations based on thermodynamic equilibrium at 850°C indicate a product containing a hydrocarbon distribution as follows: 41 weight percent methane, 23.4 weight percent ethylene, 26.6 weight percent ethane, 4.9 weight percent benzene, and 4.1 weight percent higher hydrocarbons.

The methane, ethylene, and benzene are recovered, the hydrogen and higher hydrocarbons are recycled to the hydropyrolysis zone and the ethane is recycled to the second-stage cracking zone.

Thus, having described the invention in detail, it will be understood by those skilled in the art that certain variations and modifications may be made without departing from the spirit and scope of the invention as described herein and defined in the appended claims.

I claim:

1. A process for producing ethylene from higher hydrocarbons comprising

a. introducing a hydrocarbon oil and hydrogen to a first-stage hydropyrolysis zone, the mol ratio of hydrogen to hydrocarbon oil being at least 1/1;

b. hydropyrolyzing the hydrocarbon oil in the presence of the hydrogen in said zone under conditions of temperatures in the range of about 600°C to 900°C, pressures of at least about 5 atmospheres gauge and residence times in the range of about 0.1 to 60 seconds, to produce a hydropyrolysis effluent;

c. introducing substantially all of the hydropyrolysis effluent to a second-stage cracking zone and subjecting said effluent to cracking conditions of temperatures in the range of about 750°C to 900°C, pressures not in excess of about 2 atmospheres gauge and residence times in the range of about 0.01 to 10 seconds, to produce a cracking zone effluent;

d. separating said cracking zone effluent into a hydrogen stream, a methane stream, an ethylene stream, an ethane stream, and a higher hydrocarbon stream;

e. recycling the hydrogen stream to the first stage hydropyrolysis zone and recycling the ethane stream to the second-stage cracking zone;

f. and recovering the methane stream and ethylene stream.

2. A process according to claim **1** wherein the hydrocarbon oil has a density of less than about 0.99 and a Conradson carbon content of less than about 20 weight percent.

3. A process according to claim **1** wherein the conditions of hydropyrolysis are temperatures in the range of about 700°C to 850°C, pressures in the range of about 5 to 100 atmospheres gauge and residence times in the range of 0.5 to 20 seconds.

4. A process according to claim **3** wherein the hydrogen to hydrocarbon oil mol ratio is in the range of about 3/1 to 30/**1**.

5. A process according to claim **3** wherein water is also introduced to the first-stage hydropyrolysis zone.

6. A process according to claim **3** wherein the second-stage cracking zone conditions are temperatures in the range of about 800°C to 850°C, pressures not in excess of about 1 atmosphere gauge and residence times in the range of 0.1 to 1 second.

7. A process according to claim **1** wherein the higher hydrocarbon stream is hydrogenated and recycled to the first-stage hydropyrolysis zone.

8. A process according to claim **1** wherein the higher hydrocarbon stream is separated into an aromatics stream and a remaining stream, recovering the aromatics stream and recycling the remaining stream to the first-stage hydropyrolysis zone.

9. A process according to claim **8** wherein the remaining stream is hydrogenated prior to recycling.

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