United States Patent [19]

Cooper

[11] **3,711,568**

[45] **Jan. 16, 1973**

[54] PYROLYSIS PROCESS

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[52] **U.S. Cl.**.....**260/683 R,** 208/130, 208/132

[51] **Int. Cl.** **C07c 3/30,** C10g 9/36, C10g 9/14

[58] **Field of Search** 260/683; 208/130, 132

[56] **References Cited**

UNITED STATES PATENTS

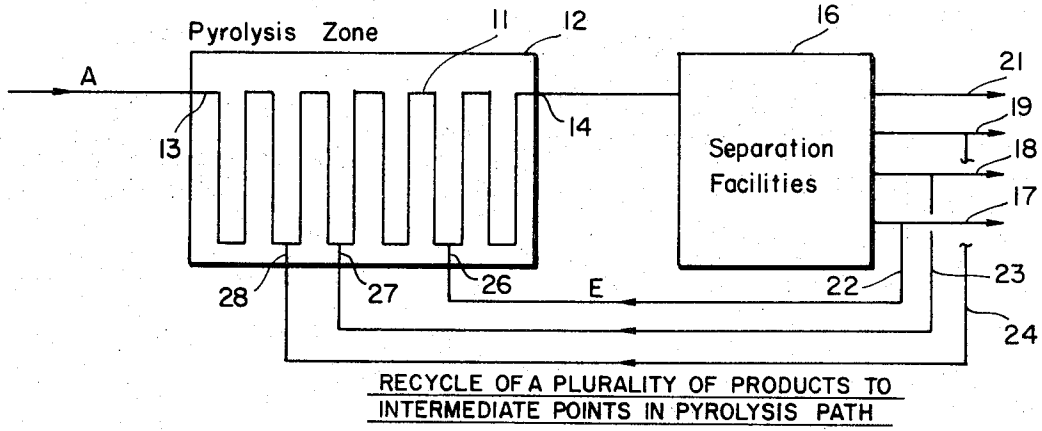
2,668,791	2/1954	Holland	208/130
3,579,601	5/1971	Kivlen	260/683
3,470,263	9/1969	Kitzen	260/683
3,579,438	5/1971	Cruse	208/132
1,924,848	8/1933	Egloff	208/132
2,972,647	2/1961	Fischer et al.	260/683
3,565,970	2/1971	Kelley	260/683

Primary Examiner—Paul M. Coughlan, Jr.
Assistant Examiner—C. E. Spresser
Attorney—Charles E. Baxley, Frank M. Nolan and Thomas E. Tate

[57] **ABSTRACT**

This disclosure teaches a process for pyrolysis of hydrocarbons wherein at least two pyrolysis product are recycled to two different points in the pyrolysis furnace. Three or more pyrolysis products are recycled and introduced into the furnace at a plurality of points on the pyrolysis path.

2 Claims, 4 Drawing Figures



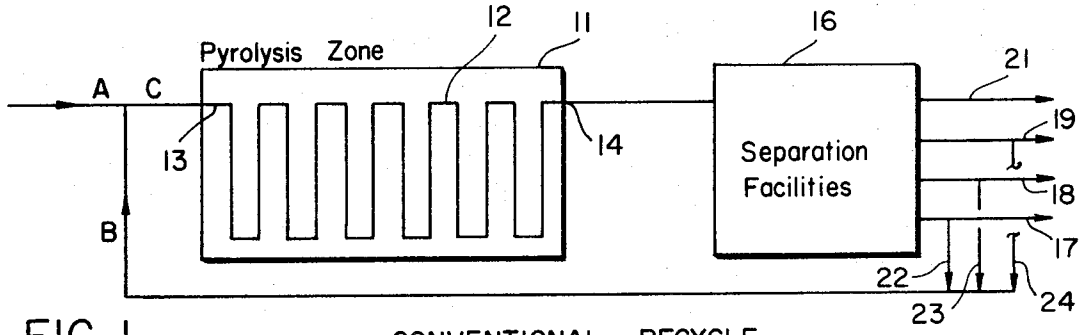


FIG. 1 CONVENTIONAL RECYCLE

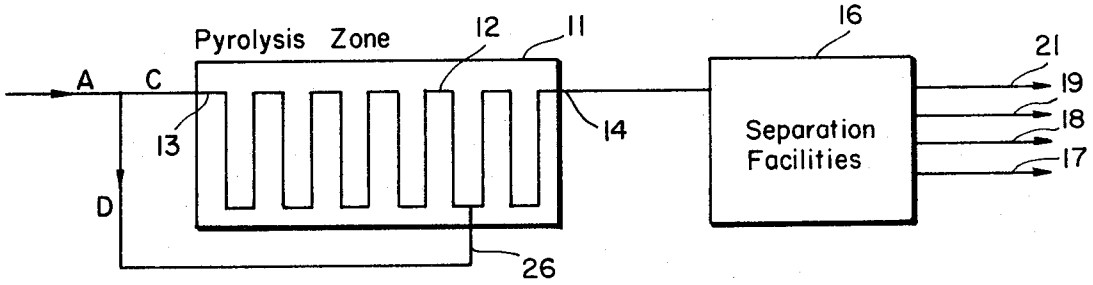


FIG. 2 MULTIPLE FEED POINTS

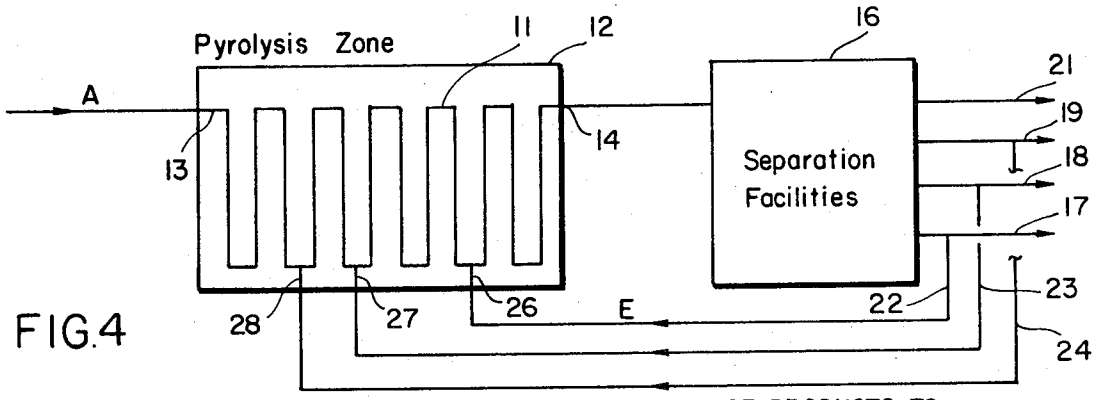


FIG.4 RECYCLE OF A PLURALITY OF PRODUCTS TO INTERMEDIATE POINTS IN PYROLYSIS PATH

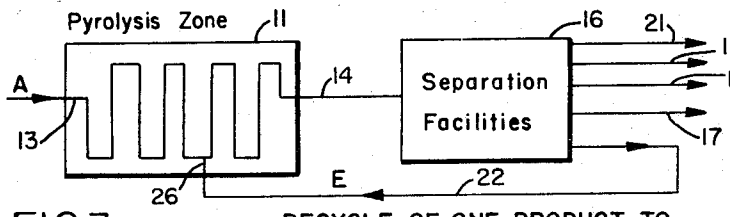


FIG.3 RECYCLE OF ONE PRODUCT TO AN INTERMEDIATE POINT

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PYROLYSIS PROCESS

BACKGROUND OF THE INVENTION

There are two well-known approaches to control of product distributions obtained from pyrolysis furnaces. These approaches form the background of the present disclosure. One of these prior-art approaches contemplates recycling pyrolysis products to the input of the pyrolysis furnace. A second prior-art process contemplates introduction of feed at various points along the pyrolysis path in the furnace. However neither of these prior-art approaches have been able to accommodate a particularly wide variety of feeds while producing a desired product distribution, nor have either of these prior-art approaches been able to control product distribution as accurately as the present invention.

SUMMARY

The present invention copes with disadvantages and limitations of the prior art approaches in a novel and facile way. According to this invention two or more pyrolysis products are recycled to intermediate points on the pyrolysis path in the pyrolysis furnace without addition of feed at those points. Various product streams, each having its own composition, are introduceable at various points along the pyrolysis path in the furnace.

One object of this process is to accommodate a wider variety of acceptable feeds than was feasible heretofore while still being able to produce a desired product distribution.

Another object of this process is to obtain readily product distributions that would be extremely difficult to obtain by prior-art approaches.

Still another object of this process is to minimize formation of undesirable by-products such as coke in the pyrolysis furnace.

Still another object of this process is to control more accurately product distribution so that design and/or operation of separating facilities which follow the pyrolysis furnace can be optimized.

Still another object of this process is to make a plant embodying the process compatible with computerized control techniques available for optimizing pyrolysis furnace operations.

BRIEF DESCRIPTION OF DRAWING

The foregoing and other features will become apparent from the following detailed description of a preferred embodiment read in conjunction with the enclosed drawing wherein:

FIG. 1 is a flow diagram illustrating pyrolysis with conventional recycle.

FIG. 2 is a flow diagram illustrating pyrolysis with introduction of a portion of the feed at an intermediate point on the pyrolysis path in the furnace.

FIG. 3 is a flow diagram illustrating pyrolysis with recycle of a single product to a single intermediate point along the pyrolysis path in the furnace.

FIG. 4 is a flow diagram illustrating pyrolysis with recycle of a plurality of products to a plurality of points along the pyrolysis path in the furnace.

DESCRIPTION OF PREFERRED EMBODIMENT

As seen in FIG. 1, according to a conventional recycle approach, feed stream A is introduced to pyrolysis furnace **11** for circulation through coil **12** in non-contact heat exchange relationship with a source of heat. Furnace **11** is provided with inlet **13** and outlet **14** which in turn is connected in series flow relationship with separation facilities **16** wherein the pyrolysis products are separated into streams, for example, **17**, **18**, **19** and **21**. Slip streams **22**, **23** and **24** are taken off streams **17**, **18** and **19** for recycle via line B to join feed stream A as combined stream C for introduction into the pyrolysis furnace **11** via inlet **13**. This approach is discussed in U.S. Pat. No. 2,972,647 to Fisher et al.

The prior-art approach shown in FIG. 2 is comparable to that shown in FIG. 1 except that whether or not recycle is employed, product stream A generally is divided into major portion C and minor portion D. Major portion C is introduced into furnace **11** via inlet **13** in the usual manner but minor portion D is introduced to the pyrolysis furnace at intermediate point **26**. It is also conceivable that D could be the major portion and C the minor portion. Introduction of portion D at several points along the pyrolysis path has been discussed in the prior art; for example in United States patent **3,579,601** to Kivlin and in United States patent **1,924,848** to Egloff.

A variation of convention recycle and multiple feed points is shown in FIG. 3. A single product stream is recycled to a single intermediate point along the pyrolysis path. Examples of this approach are described in U.S. Pat. No. 3,565,970 to Kelley, particularly at column 4, lines 51 to 55; in U.S. Pat. No. 3,579,438 to Cruse, particularly at column 3, lines 31 to 40 and column 4, lines 27 to 57; and in U.S. Pat. No. 3,470,263 to Kitzen, particularly at column 3, lines 27 to 48 and column 10, lines 35 to 36. U.S. Pat. No. 2,668,791 to Holland also discusses addition of a single material at various points along a pyrolysis path to approach a constant temperature operation.

According to the present process (as shown in FIG. 4) feed stream A is conducted in series through pyrolysis furnace **11** from inlet **13** to outlet **14** and in turn through separation facilities **16** in the usual manner. A slip stream **22** is recycled via line E to intermediate point **26** on the pyrolysis path in the furnace. A plurality of slip streams **22**, **23** and **24** can be taken off lines **17**, **18** and **19** respectively for recycle to the pyrolysis furnace at intermediate points **26**, **27** and **28** respectively.

It will be understood that this invention is useful with a wide variety of pyrolysis furnaces and with a wide variety of separation facilities. For example, the furnace illustrated herein could be a plurality of furnaces connected in flow series with intermediate points **26** and/or **27** and/or **28** between successive furnaces. The furnaces may be provided with soaking zones wherein heat is not added. Further the pyrolysis furnace can have a plurality of pyrolysis paths arranged parallel each to the other. Also it should be obvious that an entire product stream could be recycled in lieu of a slip stream and that inert gas or steam may be present in one or more of the streams.

EXAMPLES

This process will here be exemplified with regard to pyrolysis of normal butane (n-butane) and recycle of propylene, ethane and propylene, as well as propylene and hydrogen. However it should be understood that these examples are merely illustrative and that the inventive concept there advanced has a far wider scope of application than the examples herein contain.

Controlling conditions which prevail throughout the following examples are as follows:

Feed is introduced at 950°F.

Inlet pressure is 150 psia.

Tubes are all 60 feet long, 3 inch I.D., 4 inch O.D.

Heat transfer rate is 30,000 BTU/hr sq. ft.

The total amount of each feed material is constant.

The furnace coil length (total) is the same within each example.

The steam/hydrocarbon ratio is 0.5 moles/mole.

EXAMPLE I

Illustrates the effect of recycling propylene to various locations of a pyrolysis furnace having **18** tubes.

Case I (no recycle per FIG. **1**)

Pyrolysis furnace feed is 100 moles/hr n-butane and 50 moles/hr of steam.

Case II (conventional recycle per FIG. **1**)

Pyrolysis furnace feed is 16 moles/hr of propylene, 100 moles/hr of n-butane, and 58 moles/hr of steam.

Case III (multiple feed points per FIG. **2**)

Feed from Case II is split. 80 percent goes to furnace inlet; 20 percent goes to a location where the temperature is approximately 1,565°F and the stream contains 14.9 moles/hr of propylene and 14.9 moles/hr of n-butane together with various reaction products (Tube **16**).

Case IV (Invention per FIG. **4**)

Pyrolysis furnace feed is 100 moles/hr of n-butane and 50 moles/hr of steam. At a location where the temperature is approximately 1,420°F and the stream contains 50.6 moles/hr of n-butane together with various reaction products a new stream is introduced consisting only of 16 moles/hr of propylene and 8 moles/hr of steam (Tube **16**).

Major Products (moles per 100 moles of n-butane reacted)

	Case			
Product	I	II	III	IV
Propylene	12.5	12.3	0.6	28.4
Ethylene	51.0	60.5	65.5	54.1
Butylenes	14.0	15.0	12.5	15.1
Butadienne	3.0	5.4	6.5	4.0
Hydrogen	20.2	23.1	22.9	20.9
Methane	70.1	86.5	108.1	72.9
Ethane	20.2	15.3	8.1	20.6

EXAMPLE II

Illustrates the effect of recycling ethane and propylene to various locations of a pyrolysis furnace having 16 tubes.

Case I (conventional recycles per FIG. **1**)

Feed to pyrolysis furnace is 10 mole/hr of ethane, 16 moles/hr of propylene, 100 moles/hr of n-butane, and 63 moles/hr of steam.

Case II (multiple feed points per FIG. **2**)

Feed from Case I is split. 50 percent goes to furnace inlet. 25 percent goes to a location at which the temperature is approximately 1,450° and the stream contains 8.3 moles/hr of ethane, 12.6 moles/hr of propylene, and 23.3 moles/hr of n-butane together with various products (Tube **9**). The remaining 25 percent goes to a location at which the temperature is approximately 1,455°F and the stream contains approximately 11.9 moles/hr of ethane, 18.3 moles/hr of propylene, and 33.3 moles/hr of n-butane (Tube **13**).

Case III - A (Invention per FIG. **4**)

Feed to pyrolysis furnace is 100 moles/hr of n-butane and 50 moles/hr of steam. At the location where the temperature is approximately 1,355°F and the stream contains 86.9 moles/hr of n-butane together with various products, a new stream consisting only of 10 moles/hr of ethane and **5** moles/hr of steam is introduced (Tube **9**). At a later location where the temperature is approximately 1,385°F and the stream contains 17.4 moles/hr of ethane and 69.5 moles/hr of n-butane, together with various products, a new stream is introduced consisting only of 16 moles/hr of propylene and 8 moles/hr of steam (Tube **13**).

Case III - B (Invention per FIG. **4**)

Feed to the pyrolysis furnace is 100 moles/hr of n-butane and 50 moles/hr of steam. At the location where the temperature is approximately 1,355°F and the stream contains 86.9 moles/hr of n-butane together with various products, a new stream consisting only of 16 moles/hr of propylene and 8 moles/hr of steam is introduced (Tube **9**). At a later location where the temperature is approximately 1,410°F and the stream contains 24.2 moles/hr of propylene and 63.1 moles/hr of n-butane together with various reaction products a new stream consisting only of 10 moles/hr of ethane and 5 moles/hr of steam is introduced (Tube **13**).

Major Products (moles per 100 moles of n-butane reacted)

	Case			
Product	I	II	III-A	III-B
Propylene	32.7	25.7	44.0	32.8
Ethylene	57.5	60.2	52.7	55.5
Butylenes	14.2	12.3	14.0	15.3
Butadienne	4.4	5.1	3.3	4.1
Hydrogen	23.1	22.5	21.1	22.0
Methane	78.2	90.3	70.6	73.6
Ethane	22.4	16.9	27.4	26.2

EXAMPLE III

Illustrates the effect of recycling propylene and hydrogen to various locations of a pyrolysis furnace having 16 tubes.

Case I (conventional recycle per FIG. **1**)

Pyrolysis furnace feed is 100 moles/hr n-butane, 16 moles/hr of propylene, 8 moles/hr of hydrogen, and 58 moles/hr of steam, all to inlet of first tube.

Case II (multiple feed points per FIG. **2**)

Feed from Case I is split: 50 percent goes to pyrolysis furnace inlet, 25 percent goes to the location at which the stream is at approximately

1,480°F, and contains 19.4 moles/hr of n-butane and 11.2 moles/hr of propylene, together with various products (tube **9**). The remaining 25 percent goes to the location at which the feed is at approximately 1,485°F, and contains 26.4 mole/hr of n-butane, and 16.0 mole/hr of propylene, together with various products (tube **13**).

Case III - A (Invention per FIG. **4**)

Feed to pyrolysis furnace is 100 mole/hr of n-butane and 50 mole/hr of steam. At the location where the temperature is approximately 1,355°F and the stream contains 87 mole/hr of n-butane together with various products a new stream consisting only of **8** mole/hr of hydrogen is added (tube **9**). At a later location where the temperature is approximately 1,395°F and the stream contains 66.9 mole/hr of n-butane together with various products a new stream consisting only of 16 mole/hr of propylene and 8 mole/hr of steam is added (tube **13**).

Case III - B (Invention per FIG. **4**)

Feed to pyrolysis furnace is 100 mole/hr of n-butane and 50 mole/hr of steam. At the location where the temperature is approximately 1,355°F and the stream contains 87 mole/hr of n-butane together with various products, a new stream consisting only of 16 mole/hr of propylene and 8 mole/hr of steam is introduced (tube **9**). At a later location where the temperature is approximately 1,410°F and the stream contains 23.7 mole/hr of propylene and 67.9 mole/hr of n-butane together with various products a new stream consisting only of 8 mole/hr of hydrogen is introduced.

Major Products (moles per 100 moles of n-butane reacted)

	Case			
Product	I	II	III-A	III-B
Propylene	22.2	14.2	34.0	25.2
Ethylene	55.5	57.9	51.2	54.6
Butylenes	16.8	14.2	16.2	16.6
Butadienne	4.6	5.4	3.6	4.3
Hydrogen	23.8	21.0	23.9	24.2
Methane	74.1	91.0	67.1	71.9
Ethane	22.8	17.4	25.5	23.4

It will be understood by those skilled in pyrolysis that wide deviations can be made from the foregoing examples without departing from the spirit of invention as set forth in the following claims.

I claim:

1. A process for pyrolysis of a hydrocarbon feed and comprising steps as follows:

providing an elongated pyrolysis zone beginning with an inlet end and terminating with an outlet end and subjected along its length to noncontact heating,

passing the feed through the pyrolysis zone from the inlet end to the outlet end to produce at least a first and a second pyrolysis product each different from the other and from the feed,

separating the first and second pyrolysis products from each other,

recycling a portion of the first pyrolysis products to the pyrolysis zone at a first point between the inlet end and the outlet end,

and recycling a portion of the second pyrolysis product to the pyrolysis zone at a second point between the inlet end and the outlet end.

2. The process according to claim **1** wherein:

at least three pyrolysis products are produced each different from the other and from the feed,

and a portion of each of these pyrolysis products are recycled each to a different point along the pyrolysis zone between the inlet end and the outlet end.

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