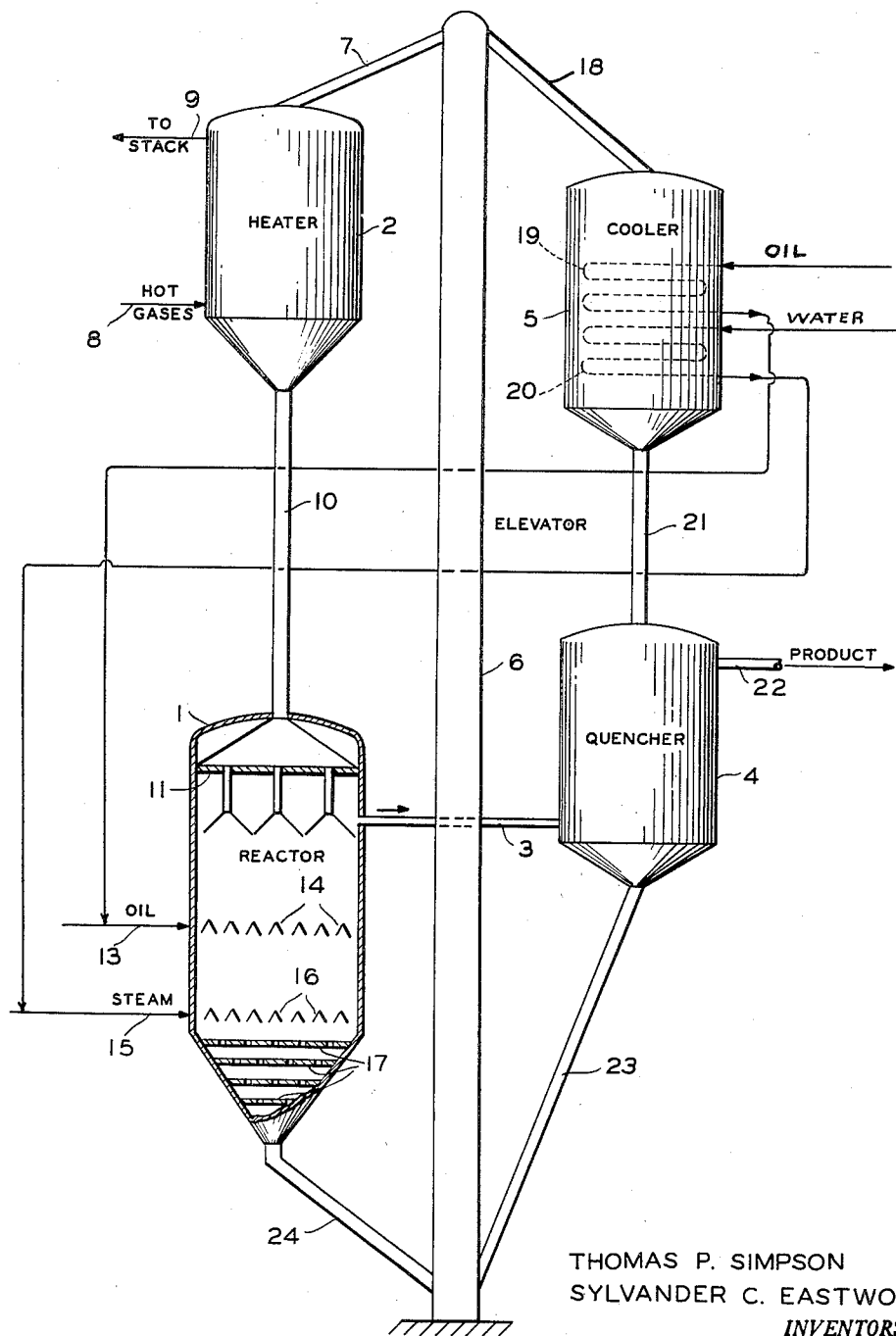


Sept. 7, 1948.

T. P. SIMPSON ET AL
CONTINUOUS CRACKING PROCESS

2,448,922

Filed Jan. 23, 1946



THOMAS P. SIMPSON
SYLVANDER C. EASTWOOD
INVENTORS

BY

Oswald B. Hayes

ATTORNEY

UNITED STATES PATENT OFFICE

2,448,922

CONTINUOUS CRACKING PROCESS

Thomas P. Simpson and Sylvander C. Eastwood,
Woodbury, N. J., assignors to Socony-Vacuum
Oil Company, Incorporated, a corporation of
New York

Application January 23, 1946, Serial No. 642,833

5 Claims. (Cl. 196—55)

1

This invention relates to a process and apparatus for conducting thermal reactions of short duration and is particularly directed to short time, high temperature cracking of hydrocarbon oils to selectively produce a desired product.

A great number of high temperature reactions are extremely complex in nature and may be controlled to a substantial extent by adjustment of time and temperature. The cracking of hydrocarbon oils is typical of this class of process and will be considered herein as exemplary without intending to limit the invention thereto. The hydrocarbon oils begin to undergo various types of reactions in the absence of any catalyst at temperatures on the order of 700° F. and upwards. Although these reactions are generally denominated as "cracking" signifying a splitting of hydrocarbon molecules; a large number of other reactions actually take place including isomerization, polymerization, alkylation, transfer of hydrogen or hydrocarbon radicals and the like.

The charge material is itself complex in nature and after, undergoing reactions of the above types, additional compounds are formed thus further increasing the diversity in chemical composition. The new compounds vary from low molecular weight hydrocarbons and hydrogen through compounds of the same boiling range as the charge stock to heavy "tars" and highly condensed compounds of extremely low hydrogen content generally known as "coke." Some few of the compounds formed may be selectively produced in fairly large yield by careful control of time and temperature, in much the same manner as the conventional cracking process is controlled to give large yields of gasoline.

A typical compound of high commercial value that may be produced in this manner is ethylene. It is well known that thermal reaction of hydrocarbons at elevated temperatures, say greater than about 1200° F., produce large yields of aromatic compounds if the reaction time is fairly long. At these elevated temperatures and short reaction times, the principal product is ethylene. It follows that, if the hydrocarbon charge can be rapidly heated to the desired temperature, held at that temperature for a suitable short period and immediately cooled, ethylene may be produced as the principal product. Preferably the reaction temperature is on the order of 1450° F. to 1600° F. and the reaction time is only a small fraction of a second. Such rapid heating in the conventional coil furnaces can be obtained but large amounts of coke are laid down

2

in the coils thus making necessary frequent shut-downs for cleaning of the coils. Similarly, the temperature may be rapidly reduced by quenching with cold oil, steam or water but this has been found to introduce operating difficulties in that quench oils accumulate tarry and reactive compounds while water tends to emulsify with the oil.

The present invention provides means for overcoming these difficulties by passing the charge in direct contact with a mass of inert refractory material at high temperature and transferring the heated reaction mixture of gases to direct contact with a mass of cold granules of similar nature to those used for heating the charge. By this means it is possible to handle in a relatively simple manner any tars or cokes resulting from the process by conveying granules from both the heater and the quencher to a zone in which such combustible matter is removed by oxidation, thus supplying a portion of the heat required for granules fed to the reactor. In addition, it is thus rendered feasible to use dirty charge stocks and to generate any steam needed from dirty water since contaminants thus introduced are rapidly removed at a later stage in the process.

The invention further provides additional advantages in operation of a simple unit which is essentially self-cleansing, which advantages will appear from consideration of a typical embodiment of the invention as illustrated diagrammatically in the annexed drawings.

As shown in the single figure of the drawings, the invention provides a reactor 1 wherein the charge oil is contacted with highly heated refractory granules supplied thereto from a heater 2. The hot products of reaction are promptly transferred from reactor 1 by line 3 to a quencher 4 wherein the vaporous products of reaction are contacted with cold refractory granules from a cooler 5. The refractory granules move through two cycles, namely, the heater-reactor cycle and the cooler-quencher cycle which follow a common path in part in that the discharge from the reactor and the quencher pass to a common elevator 6 by which they are raised to a high point in the apparatus and divided into two streams for return through the two cycles.

Turning now to the heater-reactor cycle specifically, a suitable portion of refractory granules is fed through a chute 7 to the top of heater 2. In the heater the granules are directly contacted by hot gases, such as products of combustion entering at line 8. The granules are thus heated to an elevated temperature and, are preferably

3

cleansed of any carbonaceous deposits by combustion. Oxygen for this purpose is supplied at line 8 in any suitable manner, such as utilizing an excess of air in the burner supplying hot gases for line 8. The cooled gases are withdrawn from heater 2 by line 9 and passed to the stack, preferably through economizers as known in the art.

The highly heated granules are transferred by a feed leg 10 from heater 2 to reactor 1. The feed leg 10 is of sufficient height that the resistance to flow of gases therethrough obviates necessity for valves in the transfer line from heater to reactor. The highly heated granules from feed leg 10 are discharged onto a tube sheet 11 in the reactor from which they pass through feed pipes 12 to the body of the reactor. Charge stock such as preheated hydrocarbon vapors is admitted by line 13 to any suitable distribution means within the reactor, for example, a plurality of inverted angles 14. As shown herein, the reactor is set up for countercurrent flow of charge vapors through the reactor with respect to flow of refractory granules but it will be understood that the same may be set up for any desired type of flow. The oil vapors move upwardly through the reactor from the distributing angles 14 to a vapor space above the mass of granules from which they are removed by transfer line 3. Alternatively, any other suitable means for vapor withdrawal may be employed.

Many such reactions proceed very favorably in the presence of steam and this material may be introduced at line 15 to distributing angles 16 to be superheated to the desired extent before mixing with oil vapors admitted at angles 14. If desired, the steam may be generated within reactor 1 by admitting water at 15 and similarly the oil vapors may be produced by introducing liquid oil at 13. Generation of oil and water vapor in this manner makes it possible to use dirty charge stock and dirty water for the purpose since contaminants thus introduced to the system are deposited on solid granules which pass eventually to the heater. It may be noted in passing that some of such granules will be diverted through the cooler-quencher cycle but the contaminants can be tolerated in this cycle and the contaminated granules will eventually find their way into the heater and thus be cleansed.

A plurality of drawoff plates 17 are provided in the bottom of the reactor 1 to insure uniform downward flow of granules across the reactor. The plates 17 are pierced at intervals as shown thus avoiding the usual effect of a relatively static mass along the sides of the reactor. The general internal construction of the heater and quencher with respect to means for introducing and withdrawing solids and gases is of the same nature as that specifically shown in connection with reactor 1. Similarly, the solid granules are introduced and withdrawn in cooler 5 in substantially the manner shown for reactor 1.

Cooler 5 may be operated by direct contact of a cooling fluid with the solid granules therein but it is preferred to use heat exchange tubes for this purpose in order to more efficiently recover the heat taken out of the granules in the cooler. Thus, granules fed to the top of the cooler from chute 18 pass over a series of cooling coils 19 and 20 within the cooler 5. A satisfactory arrangement is to supply an oil coolant to the top cooling coil 19 and a water coolant to the lower coil 20. In this manner the upper coil 19 may be used to preheat charge for the system by di-

4

verting the effluent from coil 19 to line 13 supplying charge to the reactor. Effluent from water-cooled coil 20 may be used to generate steam or to supply preheated water to reactor inlet 15.

Cooled granules pass from cooler 5 by way of feed leg 21 to the quencher 4 wherein they are used to chill hot reaction products admitted from transfer line 3. If quencher 4 is operated at a sufficiently high outlet temperature to maintain the product in vapor phase, a countercurrent quenching operation is found desirable. The product is thus withdrawn at outlet 22 and transferred to suitable fractionation and purification equipment for removing the desired product. The effluent of quencher 4 will also contain valuable by-products such as light hydrocarbon gases suitable for use in alkylation, polymerization and gas reforming operations; a highly aromatic gasoline, and a heavy recycle stock which may be returned to the feed or may be used as a source of valuable raw chemicals such as polycyclic aromatics and the like.

It is preferred that the refractory granules removed from quencher 4 by chute 23 and from reactor 1 by chute 24 be conveyed as a composite mass in the elevator 6 to a suitable proportioning means in the top of the elevator.

In a typical operation in the manufacture of ethylene, a Michigan gas oil having an A. P. I. gravity of 33.9 and a boiling range of about 500° F. to 900° F. was preheated to 900° F. and admitted to a bed of Corhart (fused aluminum oxide) granules at a point to give passage through 24 inches of the granules. 44% by weight of steam was mixed with the vaporized gas oil passing through the heated granules. The space velocity employed was 3.19 volumes of liquid oil measured at 60° F. per volume of reactor space per hour. These conditions gave a contact time of 0.30 second at a mean effective temperature of 1538° F. The vaporous reaction products were promptly quenched and upon analysis, 28.7% by weight of ethylene was recovered. Among important by-products were 1.9% by weight of butadiene, 5.9% by weight of propylene and 12.8% by volume gasoline having a lead free octane number of 92.6. The gasoline fraction was found to be highly aromatic and well suited for use as a solvent.

We claim:

1. A process for conducting a high temperature vapor-phase cracking of hydrocarbons in the presence of steam during a short interval of time which comprises contacting said hydrocarbons in liquid phase with a mass of highly heated granular refractory material in a reaction zone to vaporize and rapidly raise the temperature of said reactants to reaction temperature, contacting water with said granular material in said reaction zone to produce steam and mix the same with said vaporized hydrocarbons, removing vapors from said reaction zone and passing such heated vapors into contact with a mass of cold granular refractory material in a quenching zone to thereby quench the vapors and halt said reaction, continuously removing granular material from said reaction zone and said quenching zone, transferring a portion of granular material so removed to a heating zone, transferring another portion thereof to a cooling zone, heating refractory material in said heating zone to an elevated temperature and transferring refractory material so heated to said reaction zone, cooling refractory material in said cooling zone by indirect heat exchange with liquid hydrocarbons

5

and with water and transferring the cooled refractory material to said quenching zone, transferring liquid hydrocarbons heated by indirect heat exchange with hot granules in said cooling zone to said reaction zone for contact with granular material therein as aforesaid and transferring water heated by indirect heat exchange with hot granules in said cooling zone to said reaction zone for contact with granular material therein as aforesaid.

2. In apparatus for conducting a high temperature reaction of short duration; an elevator, a heating chamber, means to transfer solids from the top of said elevator to said heating chamber, means to pass heating medium in contact with solids in said heating chamber, a reaction chamber, means to transfer heated solids from said heating chamber to said reaction chamber, means to admit reactants to said reaction chamber, means to transfer solids from said reaction chamber to the bottom of said elevator, a cooling chamber, means to transfer solids from the top of said elevator to said cooling chamber, a quenching chamber, means to transfer solids from said cooling chamber to said quenching chamber, means to transfer solids from said quenching chamber to the bottom of said elevator, means to transfer gaseous reaction products from said reaction chamber to said quenching chamber and means to remove said reaction products from said quenching chamber.

3. In apparatus for conducting a high temperature reaction of short duration; an elevator, a heating chamber, means to transfer solids from the top of said elevator to said heating chamber, means to pass heating medium in contact with solids in said heating chamber, a reaction chamber, means to transfer heated solids from said heating chamber to said reaction chamber, means to admit reactants to said reaction chamber, means to transfer solids from said reaction chamber to the bottom of said elevator, a cooling chamber, indirect heat transfer means in said cooling chamber, means to transfer solids from the top of said elevator to said cooling chamber, a quenching chamber, means to transfer solids from said cooling chamber to said quenching chamber, means to transfer solids from said quenching chamber to the bottom of said elevator, means to transfer gaseous reaction products from said reaction chamber to said quenching chamber and means to remove said reaction products from said quenching chamber.

4. In apparatus for conducting a high temperature reaction of short duration; an elevator, a heating chamber, means to transfer solids from

6

the top of said elevator to said heating chamber, means to pass heating medium in contact with solids in said heating chamber, a reaction chamber, means to transfer heated solids from said heating chamber to said reaction chamber, means to admit reactants to said reaction chamber, means to transfer solids from said reaction chamber to the bottom of said elevator, a cooling chamber, indirect heat transfer coils in said cooling chamber, means to transfer solids from the top of said elevator to said cooling chamber, a quenching chamber, means to transfer solids from said cooling chamber to said quenching chamber, means to transfer solids from said quenching chamber to the bottom of said elevator, means to transfer gaseous reaction products from said reaction chamber to said quenching chamber and means to remove said reaction products from said quenching chamber.

5. In apparatus for conducting a high temperature reaction of short duration; an elevator, a heating chamber, means to transfer solids from the top of said elevator to said heating chamber, means to pass heating medium in contact with solids in said heating chamber, a reaction chamber, means to transfer heated solids from said heating chamber to said reaction chamber, means to admit reactants to said reaction chamber, means to transfer solids from said reaction chamber to the bottom of said elevator, a cooling chamber, indirect heat transfer coils in said cooling chamber, means to transfer effluent from said coils to the reactant inlet of said reaction chamber, means to transfer solids from the top of said elevator to said cooling chamber, a quenching chamber, means to transfer solids from said cooling chamber to said quenching chamber, means to transfer solids from said quenching chamber to the bottom of said elevator, means to transfer gaseous reaction products from said reaction chamber to said quenching chamber and means to remove said reaction products from said quenching chamber.

THOMAS P. SIMPSON.
SYLVANDER C. EASTWOOD.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,376,190	Roetheli et al.	May 15, 1945
2,389,636	Ramseyer	Nov. 27, 1945
2,403,375	Kassel	July 2, 1946
2,405,395	Bahlke et al.	Aug. 6, 1946