Patented Sept. 21, 1948

2,449,585

UNITED STATES PATENT OFFICE

2,449,585

SUPPRESSION OF CORROSION IN FERROUS ALLOY VESSELS IN THE TREATMENT OF HYDROCARBONS

Elza Q. Camp, Goose Creek, Tex., assignor, by mesne assignments, to Standard Oil Development Company, Elizabeth, N. J., a corporation of Delaware

No Drawing. Application August 19, 1946, Serial No. 691,655

8 Claims. (Cl. 196—50)

1

The present invention is directed to a method whereby hydrocarbons in contact with a ferrous alloy reaction vessel are thermally reacted under non-catalytic conditions and corrosion of the vessel and the deposition of carbon thereon is suppressed.

It is often commercially desirable to react a hydrocarbon feed stock at elevated temperatures under non-catalytic conditions with the feed stock necessarily in contact with a ferrous metal reaction vessel. When conducting such an operation, it often happens that corrosion of the vessel and the deposition of carbon thereon takes place. An example of such an operation is the thermal vapor phase reaction of a petroleum fraction boiling within the range of 200° to 400° F. for producing butadiene. It will be understood that such a process is usually conducted by passing the feed stock through ferrous alloy tubes arranged in a furnace so that they would be maintained at high temperatures and the carbon deposition and the corrosion heretofore mentioned take place in the tubes of the furnace; this corrosion and carbon deposition may be so rapid that the process is inoperable or at least not commercially attractive. This rapid corrosion may be encountered even though the tubes are constructed of ferrous alloy, such as the nickel and chromium alloyed with iron commonly known as "18—8" alloy which, under many conditions, is very resistant to corresion.

It is an object of the present invention to react thermally a hydrocarbon feed stock under non-catalytic conditions while suppressing corrosion of the reaction vessel and carbon deposition on the walls thereof.

Other objects and advantages of the present invention will be seen from the following detailed description.

In accordance with the present invention, a hydrocarbon feed stock is thermally reacted in the vapor phase under non-catalytic conditions in a reaction vessel with the hydrocarbon in contact with the ferrous alloy forming the interior wall of the vessel and corrosion of the reaction vessel and formation and deposition of carbon on the walls of the reaction vessel is suppressed by maintaining within the reaction zone a small amount of an organic acid. In conducting the operation, it is preferred to employ a petroleum fraction boiling within the range of 200° to 400° F. as the feed stock and maintain the thermal reaction at a temperature within the range of 900° to 1650° F. The organic acid is preferably introduced into the feed stock passed into the reaction vessel but

2

optionally may be separately introduced therein and may be maintained in the reaction zone in amounts extending over a substantial range but usually 5% is the maximum amount employed. Usually it will be found that greater concentrations do not produce improved results over the use of a 4% concentration of said acid.

The organic acid employed for inhibiting the corrosion of the ferrous alloy vessel and the product and deposition of carbon within the reaction zone preferably should have a low boiling range to insure that it remains in the vapor phase with the hydrocarbon feed stock. Preferred examples of low molecular weight organic acid suitable for use in the practice of the present invention are formic acid, acetic acid and propionic acid; however, it may at times be found desirable to employ other acids of greater molecular weight, such as butyric and valeric acids.

The advantages in the practice of the present invention will be further shown by the following examples. In the first example conditions simulating the prior art were employed and in the subsequent examples the method of the present invention was carried out.

Example I

A petroleum fraction boiling within the range of 200° to 400° F. was heated to a temperature of 1450° F. and passed into vapor phase through a reaction vessel constructed of "18—8" chromium-nickel alloy steel for an interval of 20 hours. The reaction was then terminated and the interior of the reaction vessel examined. It was found that the "18—8" alloy had been corroded at a rate of the order of 1 to 2 inches penetration per year and was coated with a copious quantity of carbon.

Example II

A portion of feed stock identical with that used in Example I had added thereto 3% by weight of acetic acid and was subjected to reaction conditions identical to those used in Example I. After the operation was concluded, it was found that the corrosion of the "18—8" alloy and the deposition of carbon on the wall of the reaction vessel was substantially eliminated but neither the corrosion of the alloy nor the deposition of the carbon being of sufficient magnitude to be measurable.

Example III

A portion of the same feed stock used in Example I was employed and to the feed stock 3% by weight of formic acid was added and the mix-

ture subjected to the same reaction conditions employed in Example I. After the reaction had been conducted for 20 hours and the "18—8" alloy examined, it was found that the corrosion of the "18—8" alloy and the deposition of carbon on the alloy were substantially eliminated but neither the corrosion nor deposition of the carbon being substantially great to be measured.

The advantage of the practice of the present invention will be obvious. It will be seen that reactions heretofore impossible or commercially unattractive due to the rapid corrosion of the equipment and deposition of the carbon thereon may be conducted in accordance with the present invention and the corrosion of the reaction vessel suppressed and fouling of the vessel by the deposition of carbon thereon suppressed or eliminated.

Having fully described and illustrated the practice of the present invention, what I desire to claim as new and useful and to secure by Letters Patent is:

1. A method for treating a hydrocarbon feed stock comprising the steps of subjecting the feed stock in a vapor phase in contact with a ferrous alloy reaction vessel to a high temperature to cause non-catalytic reaction thereof and maintaining a carboxylic acid in the feed stock while it is in the reaction zone to suppress corrosion of said vessel.

2. A method in accordance with claim 1 in which the concentration of the carboxylic acid in the feed stock is no greater than 5%.

3. A method for conducting a vapor phase reaction at elevated temperatures including the steps of subjecting a hydrocarbon feed stock to a temperature within the range of 900° to 1650° F. while it is in contact with a ferrous alloy reaction vessel to cause non-catalytic reaction thereof and maintaining a small amount of carboxylic acid in the feed stock in the reaction zone to suppress corrosion of said vessel.

4. A method in accordance with claim 3 in which the concentration of carboxylic acid in the feed stock is no greater than 5%.

5. A method for conducting a vapor phase reaction including the steps of contacting a hydrocarbon feed stock boiling within the range of 200° to 400° F. in the vapor phase and in contact with a ferrous alloy reaction vessel to a temperature within the range of 900° to 1650° F. to cause non-catalytic reaction of the feed stock and maintaining a carboxylic acid in the hydrocarbon feed stock in the reaction zone in a concentration no greater than 5% to suppress corrosion of said vessel.

6. A method in accordance with claim 5 in which the carboxylic acid is acetic acid.

7. A method in accordance with claim 5 in which the carboxylic acid is formic acid.

8. A method in accordance with claim 5 in which the carboxylic acid is propionic acid.

ELZA Q. CAMP.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,605,761	Nielsen	Nov. 2, 1926
1,981,150	Pyzel	Nov. 20, 1934
2,370,533	Gershinowitz	Feb. 27, 1945
2,374,167	Bell et al.	Apr. 24, 1945
2,402,034	Folkins et al.	June 11, 1946

FOREIGN PATENTS

Number	Country	Date
428,749	Great Britain	May 17, 1935
437,613	Germany	Nov. 24, 1926