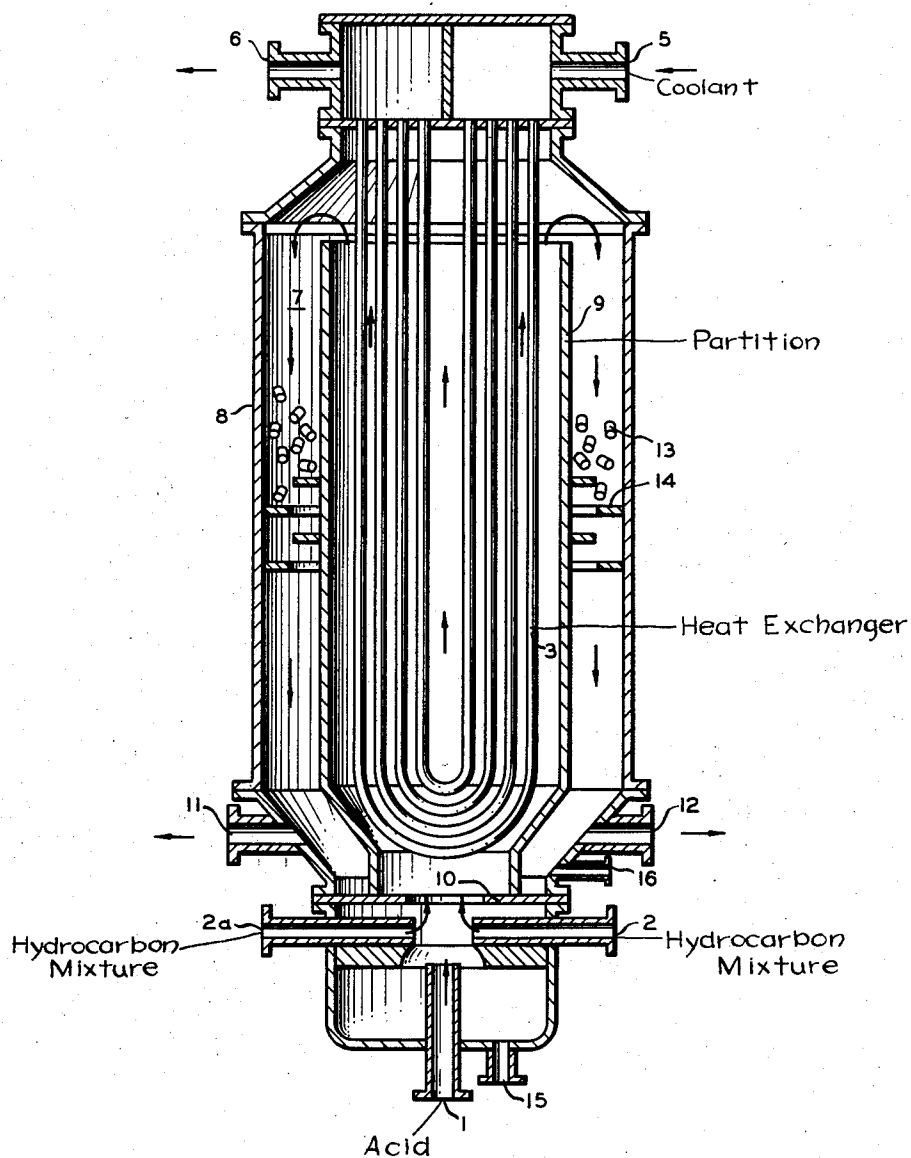


Oct. 7, 1958

C. H. OWEN
METHOD OF AND APPARATUS FOR THE ACID-CATALYZED
ALKYLATION OF HYDROCARBONS
Filed March 12, 1954

2,855,449



INVENTOR.
C. H. OWEN

BY

Hudson & Young
ATTORNEYS

1

2,855,449

METHOD OF AND APPARATUS FOR THE
ACID-CATALYZED ALKYLATION OF
HYDROCARBONSCharley Hillman Owen, Phillips, Tex., assignor to Phillips
Petroleum Company, a corporation of Delaware

Application March 12, 1954, Serial No. 415,797

9 Claims. (Cl. 260—683.58)

This invention relates to a method and to an apparatus for the acid-catalyzed alkylation of hydrocarbons. In one of its aspects the invention relates to the provision of a sufficient time within a contactor, wherein an acid catalyst and hydrocarbons to be alkylated are contacted, by causing the mixture of acid and hydrocarbons to be alkylated to flow substantially axially through the contactor from one end to the other, reversing the direction of flow of the mixture of acid and hydrocarbons and flowing the same through an annular space back to the first-mentioned end of the contactor and then, without further contact of said mixture with additional mixture entering the axial portion of said contactor, withdrawing the thus contacted acid and hydrocarbons from the contactor. In another aspect of the invention, the contacting of acid catalyst and hydrocarbons to be alkylated is accomplished by the flow as described there being provided within the annulus fins, rings, or other alternate materials adapted to provide intimate contact of the acid and hydrocarbons in the said annulus.

In the alkylation of hydrocarbons, for example, an isoparaffin with an olefin in the presence of hydrofluoric acid as the catalyst, it has been found that after the initial contacting period is over there are contained in the contacted mixture so-called surviving organic fluorides and that by increasing the residence time of the mixture under intimate contacting conditions it becomes possible to decrease the proportion of such fluorine-containing materials in the hydrocarbon product and in the acid to provide better acid recovery as well as cheaper product purification. See Patent 2,417,106, granted March 11, 1947, to F. E. Frey.

According to this invention, there are provided a novel method and apparatus for the acid-catalyzed alkylation of hydrocarbons. The method of the invention essentially comprises admixing with each other at one end of a contactor the acid and hydrocarbon mixture to be alkylated, flowing the said mixture from said end of the contactor to the other end of the contactor and there turning the flowing mixture through substantially 180°, causing the said turned flowing mixture to flow back toward the first mentioned end of the contactor through an annular portion thereof, which portion can advantageously contain rings, fins or the like to increase intimate contact of the flowing mixture components, and then removing the said thus contacted mixture from said contactor without further contact thereof with incoming acid and hydrocarbons to be contacted. According to the invention, the apparatus comprises an elongated shell with an inlet for acid at one end thereof communicating with the axial portion of the shell, a substantially concentric partition extending substantially from the acid inlet end almost but not completely to the other end of said shell, a partition in a plane transverse to the axis of said shell at the inlet end of said concentric partition in sealing engagement with said concentric partition and said shell, an outlet communicating with the inlet end of the annulus thus formed and at least one inlet for hydrocarbon to be alkyl-

2

ated extending from a point without the acid inlet end of said shell into a point within the axial portion of said shell at the acid inlet end thereof.

In the drawing there is shown an embodiment of an apparatus according to the invention. The embodiment shown contains a hairpin heat exchange bundle for extracting heat which as is known is generated when hydrocarbons are alkylated in the presence of a catalyst.

Referring now to the drawing, there is shown an embodiment of the apparatus according to the invention. The apparatus will now be described in connection with the alkylation of isobutane with butylene. It will be obvious to those skilled in the art that other alkylations can be accomplished within the apparatus of the invention. For example, aromatics can be alkylated with olefins and still other organic compounds can be alkylated with other alkylating agents.

In the drawing, 1 is an inlet pipe through which acid is introduced in an upward direction to be intermingled with a suitable mixture of isoparaffin and olefin introduced through pipes 2 and 2a. The mixture travels upwardly as a turbulent mass into intimate contact throughout its upward travel with the heat exchange surfaces of the hairpin tube bundle 3 through which a coolant is circulated by introducing the same through pipe 5 and withdrawing the same through pipe 6. At the upper end of the axial space containing the hairpin bundle the acid-hydrocarbon mixture is caused to turn through substantially 180° and to pass downwardly in annular space 7 which is provided by shell 8 and substantially concentric partition 9. At the base of the annular space partition 10 blocks off the lower end of the annular space from the lower end of shell 8 and the contacted mixture of acid and hydrocarbons is withdrawn through pipes 11 and 12 to a settler for separation of the acid and alkylated hydrocarbon mixture. The acid and hydrocarbon effluent from the contactor upon separation in the settler are treated in conventional manner.

It will be noted that according to the invention the apparatus is a unitary structure providing in itself not only a place for contacting the acid with the hydrocarbons to be alkylated and for extracting heat during said contacting but also the annular space for extending the residence time within said structure of the contacted mixture to permit the surviving alkyl fluorides or organic fluorides to further react to reduce the fluorine content of the hydrocarbon product and to reduce the hydrocarbon content of the acid. In order to insure intimate contacting, rings 13 and/or fins 14 can be provided within annular space 7, as a particularly advantageous feature of this invention.

An advantage of the structure according to the invention resides in the compactness, yet efficiency with which the extended residence time is provided. Thus, although the annulus 7 is filled with contacting material, it is possible by suitable choice of said contacting material and/or said fins to provide additional cooling within annulus 7. This is so because of a flow of heat from annulus 7 in toward the hairpin heat exchange bundle. Thus, it is possible to regulate the temperature within the annulus by regulating the temperature within the axial space in the contactor.

Conduits 15 and 16 are provided in the apparatus to allow removal of fluids from the annular and axial sections, respectively, during shutdown of the unit. These conduits are closed by valves, not shown, during alkylation operation.

Example

In an operation with an HF acid strength of 90% and a contact time in the reactor-contactor of 5 minutes, a residual fluoride content of the hydrocarbon effluent of 0.03% is obtained. By increasing the time, each addi-

3

tional minute of contact time decreases the residual fluorides by 0.002%. By providing a 10 minute total contact time in the reactor-contactor with the design of the invention, the residual fluoride content is reduced to 0.02%.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawing and appended claims to the invention, the essence of which is that there have been provided a method and an apparatus for the contacting of an acid catalyst and compounds to be alkylated by admixing said acid and compounds at one end of a contactor causing the admixture to flow in intimate contact with a cooling heat exchanger throughout substantially the entire length of said contactor axially to its other end, turning said mixture through substantially 180° and then causing it to flow back toward the inlet end of said contactor through an annular contiguous space, said space in a preferred embodiment, containing rings, fins or other alternate material or construction adapted to cause intimate contacting of the components of said mixture and then when said mixture has reached the inlet end of said annulus removing said mixture from the contactor without allowing it to come into contact with freshly introduced acid and compounds to be alkylated.

I claim:

1. A method for the contacting of a liquid hydrofluoric acid catalyst and compounds to be alkylated by admixing said catalyst and said compounds in an axial portion of one end of a substantially vertical contactor zone by causing to impinge at a substantial angle to each other a stream containing said liquid catalyst and a stream containing said compounds, causing the admixture to flow with intimate contact of its components throughout substantially the entire length of said contactor zone axially to its other end, turning said mixture through substantially 180° and then causing it to flow back toward the said one end of said contactor zone through an annular contiguous zone, and then when said mixture has reached the inlet end of said annular zone removing said mixture from said annular zone without allowing it to come into contact with freshly introduced liquid acid catalyst and compounds to be alkylated.

2. A method for the contacting of a liquid hydrofluoric acid catalyst and compounds to be alkylated by admixing said catalyst with said compounds in an axial portion of one end of a substantially vertical contactor zone by passing said acid upwardly into the bottom of said zone into impingement contact with the compounds to be alkylated which are also introduced into the bottom of said zone peripherally to said acid; then causing the admixture to flow with intimate contact of its components throughout substantially the entire length of said contactor zone axially to its other end, turning said mixture through substantially 180° and then causing it to flow downwardly back toward the said one end of said contactor zone through an annular contiguous zone, and then when said mixture has reached the inlet end of said annular zone, removing said mixture peripherally from said annular zone without allowing it to come into contact with freshly introduced liquid acid catalyst and compounds to be alkylated.

3. A method for the contacting of a liquid hydrofluoric acid catalyst and compounds to be alkylated by admixing said catalyst with said compounds in an axial portion of one end of a substantially vertical contactor zone by passing said acid upwardly into the bottom of a restricted mixing zone just below an inlet to the bottom of said contactor zone into impingement contact in said restricted zone with the compounds to be alkylated which are also introduced into said restricted mixing zone peripherally to said acid, then causing the admixture to flow with intimate contact of its components through said inlet to said contactor zone and throughout substantially the entire length of said contactor zone axially to its other end, turn-

4

ing said mixture through substantially 180° and then causing it to flow downwardly back toward the said one end of said contactor zone through an annular contiguous zone, and then when said mixture has reached the inlet end of said annular zone removing said mixture peripherally from said annular zone without allowing it to come into contact with freshly introduced liquid acid catalyst and compounds to be alkylated.

4. A process for the synthesis of hydrocarbons which comprises flowing a liquid hydrofluoric acid alkylation catalyst in an upward direction into one end of a contacting zone; flowing alkylatable reactant fluids into said contacting zone at at least two loci, said reactant fluids flowing toward and at a substantial angle to said catalyst; effecting intimate contact of said catalyst and said reactants at their locus of juncture; passing the mixture resulting from said intimate contact away from said locus of juncture and upwardly through a heat removal zone; removing said mixture from said heat removal zone and passing said mixture first outwardly and then downwardly through an extended residence time zone, said extended residence time zone surrounding in an annular manner, said contacting zone, and wherein in said extended residence time zone the organic fluoride content of said mixture is substantially reduced; and withdrawing from one end of said extended residence time zone the products of said process.

5. An apparatus comprising in combination a shell; in said shell a concentrically disposed substantially cylindrical partition forming an unobstructed concentric portion within said shell and an annulus extending from one end of said shell almost but not completely to the other end of said shell; a heat exchanger element in said unobstructed concentric portion extending substantially throughout the entire length of said portion; at said one end of said shell, contiguous therewith, an intermingling section; at least one substantially axially disposed inlet conduit to said section; a conduit substantially axially disposed between said one end of said shell and said section, establishing communication between said section and said one end of said shell within said concentrically disposed partition; at least one other inlet conduit to said section disposed at a substantial angle to said axially disposed inlet; and at least one outlet conduit from said annulus to without said shell near the end of said shell at which said section is provided.

6. An apparatus comprising a shell, in said shell an unobstructed concentric partition forming an annulus extending from one end of said shell almost but not completely to the other end of said shell, at least one substantially axially disposed inlet at the end of said shell from which said concentric partition extends, communicating directly at said one end of said shell with the axial space within said concentric partition and at least one other inlet also communicating directly with the axial space within said concentric partition and disposed substantially at right angles to said first-mentioned inlet and a plurality of circumferentially placed outlets from said annulus to without said shell near the end of said shell at which said inlets are provided.

7. An apparatus comprising in combination a shell; in said shell a concentrically disposed substantially cylindrical partition forming an unobstructed concentric portion within said shell and an annulus extending from one end of said shell almost but not completely to the other end of said shell; heat exchanger element in said unobstructed concentric portion extending substantially throughout the entire length of said portion; at said one end of said shell, contiguous therewith, an intermingling section; at least one substantially axially disposed inlet conduit to said section; a conduit substantially axially disposed between said one end of said shell and said section, establishing communication between said section and said one end of said shell within said concentrically disposed partition; said substantially axially disposed inlet conduit

5

to said section terminating just ahead of said conduit substantially axially disposed between said one end of said shell and said section; a plurality of inlet conduits disposed circumferentially around the end of said substantially axially disposed inlet conduit to said section; said plurality of inlet conduits disposed circumferentially around the end of said substantially axially disposed inlet conduit being also disposed at a substantial angle to said axially disposed inlet conduit; and at least one outlet conduit from said annulus to without said shell near the end of said shell at which said section is provided.

8. An apparatus according to claim 7 in which there are a plurality of outlet conduits from said annulus to without said shell near the end of said shell at which said section is provided, the said plurality of outlet conduits being circumferentially disposed near the end of said shell at which said section is provided.

9. An apparatus comprising an outer vessel substantially vertically disposed, means disposed within said vessel extending substantially the entire length of said vessel for dividing said vessel into an inner vertically disposed compartment and an outer vertically disposed annular compartment, a vertically disposed catalyst inlet means located in the lower section of said vessel for introducing said catalyst into said inner vertically disposed compartment, horizontally disposed means located in the lower section of said vessel for introducing fluid reactants horizontally into the upwardly flowing stream of said catalyst

6

to effect intimate mixing thereof, indirect cooling means extending substantially the entire length of said inner compartment, means for circulating a refrigerant through said cooling means, and upper end means of said cooling means opposite said catalyst inlet means to effect substantially 180 degree turn of the acid-hydrocarbon mixture to effect flow of said mixture downwardly through said vertically disposed angular compartment, contacting material disposed in said annular compartment to effect heat exchange and extended surface for intimate contacting and additional residence time of the reactants, and a fluid outlet in direct communication with the lower section of said annular compartment.

References Cited in the file of this patent

UNITED STATES PATENTS

2,212,932	Fairlie	Aug. 27, 1940
2,381,256	Callaway	Aug. 7, 1945
2,385,200	Friedel	Sept. 18, 1945
2,417,106	Frey	Mar. 11, 1947
2,454,869	Goldsby	Nov. 30, 1948
2,491,618	Luetzelschwab	Dec. 20, 1949
2,594,329	Mayhew	Apr. 29, 1952
2,594,330	Mayhew	Apr. 29, 1952
2,701,184	Rupp	Feb. 1, 1955
2,720,447	Jones et al.	Oct. 11, 1955