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(12) Patent:

(54) APPARATUS FOR REACTIONS REQUIRING SHORT CONTACT TIME

(54) APPAREIL POUR REACTIONS EXIGEANT UN CONTACT DE COURTE DUREE

Patent Information

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(74) Agent:

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Patent Cooperation Treaty (PCT): No(30) Application priority data: NoneAvailability of licence: N/ALanguage of filing: Unknown

ABSTRACT:

CLAIMS: Show all claims

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This application is related to Canadian application, Serial Number 496,690, filed October 16, 1942, entitled "CHEMICAL PROCESS".

The present invention relates to improvements in the art of controlling the time or duration of a chemical reaction accurately within narrow limits by quenching the reaction mass with a cooler solid substance.

There are a number of chemical reactions in which the time or duration of the reaction is of the essence. For example, in the catalytic dehydrogenation of hydrocarbons, such as the dehydrogenation of butylene to form butadiene, it is known that the optimum contact time between catalyst and reaction mass at reaction temperatures is of the order of less than one second at subatmospheric pressures. In contact times of the order indicated, the production of butadiene is at a maximum and the formation of undesired decomposition products is at a minimum.

In operating with a fixed bed of catalyst, that is to say, in operating a process in which the reaction gases pass through a body of catalyst in the form of pellets or lumps, it is extremely difficult by any feasible method to limit the contact times to the degree indicated above, namely, to a fraction of a second. In any event, it is difficult to maintain all portions of reaction mixture in contact with the catalyst for such a short period of time because appreciable time is consumed by those molecules of the reactants which diffuse into the aggregates of catalyst particles of the size employed in fixed beds, and are released therefrom. In other words, while those molecules which contact merely the surface of the catalyst pills or pellets may be subjected to the influence of catalyst for a

relatively short period of time, those molecules which actually penetrate into the body of catalyst are in contact with the catalyst for a period of time which is usually sufficient to cause the formation of undesired products with a consequent loss in yield of the desired products.

In order to overcome the foregoing and similar disadvantages, we have devised means for limiting chemical reactions carried out catalytically to short periods of contact time between catalyst and reactant, and we accomplish this end essentially by quenching the reaction mixture with catalyst which is cooler than the said mixture.

The main object of our invention is to control contact time between a gaseous reactant and a catalyst for the reaction by the use of finely divided catalyst and quenching the reaction when the equilibrium is most favorable for the desired product by adding cooled catalyst to the reaction mass.

Another important step in our invention is to feed catalyst to the reaction zone by means of an up-flow standpipe, the details of which will be more fully described hereinafter.

A further object of our invention is to provide a process and suitable means therefor, whereby we may continuously perform vapor phase reaction in the presence of a powdered catalyst, provide means for regenerating the catalyst, and provide other means for returning the regenerated catalyst to the reaction zone to maintain continuity of operation, optimum temperature and pressure conditions and, finally, provide optimum contact times between reactant and catalyst at reaction temperatures.

In order to illustrate our invention and for the purpose of disclosing more fully its nature and purpose, we have shown in the accompanying drawings diagrammatically, a form and arrangement of

apparatus elements in which our invention may be applied to butylene dehydrogenation. Thus, in Fig. I we have shown a complete flow diagram which discloses in connection with the specification a preferred modification of our invention; in Fig. II there is shown an enlarged detail sectional view of our improved reactor; Fig. III is a section taken along the line III-III of Fig. II; Fig. IV is a section taken through the line IV-IV of Fig. II; and Fig. V is a cross-section view taken through the line V-V of Fig. II. Throughout the views similar reference characters refer to similar parts.

Referring in detail to Fig. I, (1) represents generally a reaction vessel. The construction of our improved reactor is shown in detail in Fig. II and will be subsequently described in detail. Catalyst in the form of powder having a particle size of from 200-400 mesh is discharged into the reactor (1) from hopper (10) in a manner as will be presently explained. The hopper (10) contains an active dehydrogenation powdered catalyst preferably in a heated condition and is in communication at its lower end with a standpipe (12) projecting downwardly as shown. This pipe may be of any convenient dimension such as 36 inches in internal diameter, and a vertical length of 40-50 ft. These dimensions are purely illustrative and are governed by the quantity of catalyst to be fed to the reactor (1) in any particular case. The lower end of the pipe is provided with a control valve (14) which is adapted to control the rate of flow by gravity of powder in pipe (12) into the upwardly extending standpipe (18) which projects, as shown, into hopper (1). In other words, the feed of catalyst to the hopper (1) is through a down-flow pipe (12) and an up-flow standpipe (18). This flow may be accomplished by regulating the densities in pipe (12) and (18) respectively, by selecting the proper pipe dimensions, coupled with the introduction of fluidizing gas as follows.

First, to cause catalyst to flow freely in pipe (12) a fluidizing gas is injected therein through pipes (21). By the same token to fluidize the catalyst in pipe (18), gas is injected through pipes (20). It is deemed obvious that by making pipe (18) of smaller internal diameter than pipe (12), the gas velocity in pipe (18) will be greater than that in pipe (12) and hence the density in pipe (18) will be less. Hence, catalyst will flow by the means indicated in the indicated direction. It is to be understood that the amount of gas injected into pipe (12) is much less than that injected into pipe (18), say one-fourth as much or less.

There is also discharged into the reactor a quantity of butylene, this material being supplied through line (5). The catalyst and the butylene are mixed in mixing device (24), and the mixture is then caused to flow upwardly in the hopper reactor. The temperature of the gas in line (5) entering the reactor is about 1000°F., while the catalyst in line (18) is at a temperature of about 1350°F. The gas and catalyst are mixed in proportions such that the temperature of the mixture is about 1250°F., with most catalysts and we prefer to maintain a density of the suspension in the region just above the mixing device (24) of from about 5-15 lbs./cu.ft., which condition is attained by regulating the gas velocities between 2 and 10 ft. per second where the particle catalyst size is from 200-400 mesh. Also a gas pressure of about 190 mm. of mercury is preferred within the reactor in the reaction now in question. Under the conditions stated, the reaction occurs to form ordinarily, butadiene from normal-butylene, and then by means which will be subsequently explained more fully hereinafter, the bulk of catalyst is separated from the reaction mass and gravitates from the bottom of the reactor from which it is withdrawn through standpipe (25), mixed with air in a mixing device (28),

the air entering through line (30), and thence conveyed through pipe (31) into a regenerator (35). The dimensions of regenerator (35) and the gas velocities are such that when the catalyst is mixed with the required amount of air or other free oxygen-containing gas, the density of the mixture is from about 5 to 15 lbs./cu.ft. The catalyst in line (25) is at a temperature of about 1000°F. to 1200°F. and under these conditions when mixed with air at ordinary atmospheric temperature in mixer (28) active combustion takes place in regenerator (35) with the consumption of carbonaceous deposits produced on the catalyst as a result of the reaction taking place in reactor (1). Ordinarily it is preferable to operate regenerator (35) under superatmospheric pressure, say pressures up to 1-5 lbs./sq.in. gauge or higher, as dictated by economic considerations, in order to accelerate the oxidation of the contaminating carbonaceous material. The flue gas and the regenerated catalyst are withdrawn from regenerator through line (40) and discharged into a cyclone separator (41) built into the top of hopper (10). The separator effects separation of the regenerated catalyst from the flue gas, and the latter is withdrawn through line (42) and if desired sent to a second cyclone separator to remove further quantities of catalyst. In some cases, it is desirable to employ three cyclones or even more to insure complete removal and recovery of catalyst from flue gas. The hot flue gases substantially freed of catalyst may then be passed through a waste heat boiler to recover a portion of their energy content. The catalyst separated in cyclone separator (41) gravitates into hopper (10) and is recycled to the reactor in the manner previously described. To promote the flowability of powder from hoppers (10) and (78) a fluidizing gas such as flue gas is discharged into said hoppers through pipes (11) and (79), respectively.

In the drawing, we have shown means for controlling the regeneration temperature of the catalyst in regenerator (35). As shown, catalyst, that is regenerated catalyst, may be withdrawn from hopper (10) through line (62), mixed with air from line (60) in injector (61), thence discharged through cooler (63) and line (65) into regeneration vessel (35). The cooled regenerated catalyst may be at a temperature of say 300-500°F. as it enters the regenerator, and may be in the proportions of say 1/30-2 or more parts by weight of regenerated catalyst per part of unregenerated catalyst. The cooled regenerated catalyst serves to temper the exothermic reaction by adsorbing heat released during regeneration.

Referring again to reactor (1) it will be noted that a second chamber (70) is superimposed at the top of reactor. This chamber contains the reaction products and catalyst added to quench the reaction mixture. The manner of adding the catalyst will be presently described, but first let it be observed that the newly added catalyst plus the remainder of the original catalyst not separated, together with the reaction products, are withdrawn overhead through line (72) and passed into a cyclone separator (75) where the bulk of the quenching catalyst and the catalyst not previously removed are separated from the vapors. The separated catalyst passes into a receiving hopper (78) and in this hopper is at a temperature of about 1000°F. to about 1050°F. One stream of catalyst is withdrawn from hopper (78) through line (80), and carrying pipes (81) for the introduction of fluidizing gas and communicating in its lower end with standpipe (25), as shown. The other stream of catalyst is withdrawn through line (82) carrying a flow control valve (83) at its lower end and inlet pipes (85) for fluidizing gas and thence discharged into bond (84) where it is mixed with a gas such as methane discharged into (84) through pipe (85), and thereafter the catalyst is passed

upwardly through line (90) through a heat exchanger (95) where the catalyst is cooled to a temperature such that when withdrawn through line (100) it is at a temperature of about 600°F., whereupon it is injected into reaction mass in reactor (1) and thereafter carried upwardly in suspension into quenching chamber (70) previously mentioned. The amount of catalyst recycled from hopper (78) to quenching chamber (70) will depend of course entirely on the amount of gas and catalyst flowing into chamber (70) and the temperature thereof. We have found that good results are obtained by recycling to zone (70) from hopper (78) sufficient catalyst so that a temperature of 1000°-1050°F. prevails in chamber (70). In any event, it is usually preferable to add sufficient catalyst to lower the temperature of the reaction mass to about 1000°F. or lower because at this temperature undesired side reactions are prevented and the decomposition of the desired butadiene is substantially nil. The gases freed from catalyst in separator (75) are withdrawn through line (120) and these are preferably passed through a heat exchanger (122) where they are cooled to about 600°F. thence withdrawn through line (125) and passed into Cottrell precipitator (130) where a catalyst is separated and recycled to line (25) through line (132). The gases are drawn overhead from separator (130) through line (133) and pass through a Cottrell precipitator (140) where more catalyst is separated out and the separated catalyst is withdrawn through line (144) carrying flue gas inlets (145) for fluidizing purposes, and recycled through line (31) to regenerator (35). The reaction products now containing only minor amounts of catalyst are withdrawn from Cottrell precipitator through line (150), thence further cooled in cooler (153), thence discharged through line (158) into an oil scrubber (160) where the last traces of catalyst are removed, the scrubbing oil being discharged into the washer through line (162).

The washed gases are withdrawn through line (165), passed through entrainment separator (170) and thence to a pump (180) in which they are compressed and condensed prior to separation in a suitable system. The pressure conditions, i.e., the partial vacuum previously referred to in reactor (1) is maintained through pump (180) and suitable valves, in known manner.

Referring now to Fig. II for a detailed description of our improved reactor and its immediate accessory apparatus, it will be observed that the catalyst and the butylene enter the reaction vessel (1) and pass into the mixing chamber (24) and thence are delivered through a perforate mesh or screen (8) into a reaction space proper (R) limited circumferentially by cylinder (26) where the main reaction takes place, the catalyst and gas being in the form of a dense suspension resembling a liquid in flow characteristics. Disposed about the reaction chamber (R) are a plurality of cyclone separators which operate in the following manner:

A solid crown piece (30), having a base plate (31), forming together a confined space (C) is superimposed above cylinder (28) and the base plate (31) imperforate except for cylinders (29) causes the flow of suspension downwardly into a plurality of cylinders (27), (see Fig. I also) spaced in the form of a circle with their upper ends flush with, or in the plane of a plate (32), imperforate except in the regions of cylinder (28), cylinders (27) and (29). The catalyst in suspension flows through the cylinders (27), carrying vortices (V) which serve to cause turbulence, and the catalyst or the bulk of it gravitates to the space (36) at the bottom of the vessel (1). The gas or vapors, on the other hand, exit from cylinders (27), thence reverse their flow and pass upwardly through cylinders (29) projecting into the space above crown plate (30), and thereafter pass into quenching chamber (70).

Where it is desirable to maintain a short contact time between reactants and the catalyst, the catalyst in space (R) should be shallow and the base plate (31) should be disposed in close proximity to the top of cylinder (28). The actual dimensions of the distance between the plate (31) and the top of cylinder (28) will depend on the particular reaction, the density of the suspension as governed principally by the linear velocity of the gases in the reaction space (R), and the particle size of the catalyst. For instance, in the case of butene dehydrogenation employing a catalyst having a size of from 200-400 mesh and where the contact time is of the order of a second or two, it is obvious that the plate (31) should be disposed merely a few inches above the top of cylinder (28) and that the mass of catalyst above the screen (8) should be no deeper than a few inches, and that the average velocity of the gas through the reaction space should be of the order of about 3-5 ft. per second. Of course, where the catalyst is steam insensitive and the substance may be mixed with reactants to lower the partial pressure of the reactants, the contact times may be somewhat longer since, for example, in the dehydrogenation of butylene to form butadiene there is much less danger of polymerization of the latter where the partial pressure of the latter is greatly reduced by dilution with steam.

The bulk of the catalyst, usually over 90%, is separated from the gases in reactor (1) in the manner indicated and gravitates to the bottom portion (36) of the reaction vessel, while the gases flow upwardly through outlet cylinders (29), thence through pipe (35) into quenching chamber (70). (See Figs. I or II). The catalyst which is separated in the separator (27) collects in the bottom of the reaction vessel as indicated by the catalyst level line (L), and is withdrawn from the said reactor.

As is known by those familiar with this particular art, the types of catalyst which may be employed for dehydrogenations are many and varied. One of these catalysts is metallic nickel. Heretofore, the difficulty with metallic nickel has been that it is so reactive that it is not usable because it not only accelerates the formation of, say, butadiene from butylone but attacks the butadiene to decompose it. In the type of operation which we have described herein, a very active catalyst such as nickel may be successfully employed because the combination of controlled contact time, finely divided catalyst and quenching features enables us to discontinue the reaction and to limit it to a very short period of time of contact between reactants and the nickel at reaction temperatures. In the case of other catalysts such as silica-alumina compositions, alumina-tungsten, alumina-chromium, alumina-molybdenum, the various metallic oxides, and the like, such as copper oxide, nickel oxide, cobalt oxide, or mixtures of the same where the catalyst is less active, our process is also of value not only from the standpoint of quenching the reaction but also from the standpoint of supplying at least a portion of the heat necessary for the reaction by recycling hot regenerated catalyst to the reaction zone.

To recapitulate, our present invention involves the concept of controlling accurately the contact time between a gaseous reactant and a solid catalyst, and while we have described the invention in detail in connection with the specific problem of dehydrogenating an olefin, obviously the inventive concept is applicable to a great number of processes, such as gas oil cracking, desulfurization, aromatization, oxidations, simple and destructive hydrogenations, chlorinations, and numerous other gas phase reactions where contact time is an important consideration from the standpoint of yields or for other reasons. It will be noted that according to our process

we prefer to quench the reaction mass by means of a cooled solid such as a solid catalyst added in sufficient quantity to lower the reaction mass to temperatures substantially below reaction temperatures, and since the process may be operated to quench the catalyst within the reaction zone very short contact times may be effected. On the other hand, if longer contact time between reactant and catalyst is desired, the quenching may be formed in a subsequent stage, say by adding cooled catalyst in line (72). It will be understood that instead of using catalyst to quench the reaction mass, we may use an inert solid such as sand, lime, or refractory material which is added in sufficient quantity and at a sufficiently lower temperature to effect the desired result.

Other features of our invention involve, as heretofore seen, an upflow standpipe arrangement for adjusting pressure differentials between the reaction zone and the regeneration zone; another feature involves furnishing at least a portion of the heat required for endothermic reactions by supplying the proper amount of heated catalyst. Finally, the catalyst flowing in the various means may be fluidized by steam~~s~~ heretofore mentioned, or by the introduction of other gases such as methane, CO₂, CO, air, nitrogen, and the like; that is to say, these gases may be added through lines (60) and (20) and at other points in the system heretofore mentioned, to attain the desired fluidity of catalyst.

The pressure in reactor (1) may vary from about 100 mm. of mercury to above atmospheric pressure, subatmospheric pressure being preferred.

Many modifications of our invention will be obvious to those skilled in this particular art.

What we claim is:

1. In combination a receiver disposed at elevated position adapted to contain powdered catalyst material, an elongated standpipe extending downwardly from said receiver, an upflow standpipe in communication with the first-named standpipe, branch pipes disposed in spaced relationship along the length of both the downflow and upflow standpipes adapted to discharge a gaseous material into said standpipes for the purpose of fluidizing powdered material therein, an enclosed reaction chamber disposed at an elevated position, an extension of said upflow standpipe projecting into said reaction chamber, an inlet conduit adapted to conduct gaseous material into said reactor, a mixing means disposed within said reactor in which the said projection of the said upflow standpipe terminates and in which the conduit means for introducing the said gaseous material terminates, whereby solid material and gaseous material discharged into said reactor may be thoroughly mixed to form a suspension, a plurality of centrifugal separators disposed in the upper portion of said reactor adapted to separate solids from gases, conduit means extending from the upper portion of said reactor whereby gaseous material may be withdrawn, and conduit means extending from the bottom of said reactor whereby solid material may be withdrawn.

2. In combination a receiver for powdered material disposed at an elevated position, a reactor disposed at an elevated position, a downflow elongated standpipe extending from the bottom of said receiver, an upflow standpipe in communication with the downflow standpipe and projecting into said reactor at its upper end, conduit means projecting into said reactor adapted to conduct a gaseous material therein, means disposed within said reactor at the point approximately midvertical of said reactor adapted to thoroughly mix powdered material

and gaseous material fed thereto, a plurality of centrifugal separators disposed above said mixing means within said reactor adapted to separate solid material from gaseous material, a conduit means extending from the upper portion of said reactor adapted to convey gaseous material therefrom, a secondary solid gas separating means adapted to separate solids from the gas issuing from the reactor which solids have not been removed in the primary separators located within the reactor, a regenerator, a bottom draw-off pipe in communication with said reactor adapted to conduct solid material from said reactor, a gas and solid mixing device into which the draw-off pipe from said reactor projects, conduit means for introducing a gaseous material into said last-named mixer to form a suspension therein, conduit means in communication with said last-named mixing device and said regenerator whereby the suspension formed in said last-named mixer may be conducted to said regenerator, means for conducting a regeneration gas to said regenerator, means for withdrawing a suspension from said regenerator containing regenerated catalyst, a centrifugal separator in communication with said last-named conduit means adapted to separate solid from gaseous material, said last-named separator being in direct communication with said receiver whereby solid regenerated catalyst separated from the gaseous material may be returned to said receiver.

3. In combination a reactor disposed at an elevated position, a catalyst receiving hopper disposed at an elevated position, a downflow standpipe projecting from said receiver, an upflow standpipe projecting into said reactor at its upper portion, the said standpipes being in direct communication with each other and forming means for conveying a powdered material from the receiver to the reactor, a plurality of spaced branch pipes disposed in the downflow standpipe and the upflow standpipe adapted to convey the gaseous material thereto.

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to cause the fluidizing of powdered material flowing in said standpipes, conduit means for introducing a gaseous material into said reactor permitting the formation therein of a dense phase suspension, a plurality of centrifugal separators disposed in the upper portion of said reactor adapted to separate solid material from gaseous material, a conduit means disposed at the top of said reactor adapted to withdraw gaseous material therefrom, a secondary centrifugal separating means in communication with said last-named conduit adapted to remove solid material from gaseous material discharged therein and issuing from the reactor, a receiving hopper disposed below said secondary separating means to receive catalyst separated in said secondary separating means, a conduit connecting the last-named receiving hopper with the upper portion of said reactor, a cooling means disposed in said last-named conduit, the said last-named conduit providing means whereby cooled catalyst may be returned to the uppermost portion of the reactor, and means projecting from the lowermost portion of the reactor for withdrawing catalyst.

4. In a device of the character described, including a storage vessel for active catalyst disposed at an elevated position, a reactor also disposed at an elevated position and in communication with said storage means by means of a downflow standpipe and an upflow standpipe, of conduit means for discharging gaseous material at spaced points into said standpipes whereby fluidized material may be continuously fed to the said reactor, and of conduit means for discharging a gaseous reactant into said reactor where it is intermixed with said fluidized catalyst material to form a suspension, the improvement which comprises disposing separation means within the reactor adapted to separate catalyst from gaseous products at the completion of desired contact between reactant and catalyst consisting of a plurality of

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centrifugal separators disposed at the top of said reactor, the centrifugal separators being so disposed and arranged as to force all upwardly moving portions of the gas solid mixture to pass through said cyclone separators whereby the bulk of the catalyst is removed from the reaction products within the said reactor.

5. A device of the character described comprising means adapted to permit continuous reaction between a powdered material and a gaseous reactant, the combination of an elevated reactor, of an elevated storage hopper for active catalyst, of a downflow standpipe projecting from the storage hopper and terminating in an upflow standpipe projecting into said reactor thus forming a continuous path for powdered material from said storage hopper to said reactor, of a plurality of conduits disposed in spaced relation in the said standpipes adapted to conduct a gas into said standpipes to facilitate the flow of powdered material therein by the addition of a fluidizing gas, of a mixing means disposed within said reactor in communication with the end of the upflow standpipe, of a gaseous reactant conduit means projecting into said reactor and into said mixing means permitting intimate mixing of powdered material and gaseous material, of a plurality of centrifugal separators disposed within the said reactor at a point above said mixing means, said separating means being adapted to separate the bulk of the catalyst from the reactants, of an overhead conduit pipe adapted to withdraw gaseous reactants from said reactor, a bottom draw-off pipe adapted to withdraw catalyst from said reactor, a regenerator conduit means for conducting catalyst from said draw-off pipe to said regenerator, and conduit means for withdrawing regenerated catalyst and returning it to said storage hopper for further use in the process.

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6. In combination, a reaction vessel comprising a vertical cylindrical chamber, conduit means projecting into said chamber for introducing a gaseous medium and a solid catalyst material, a mixing chamber into which said conduit means project adapted to cause intimate mixing of said gas and said solid catalyst material, a reaction space disposed above said mixing chamber adapted to contain the gas and the catalyst during the period of the desired reaction, a plurality of solid gas separating means disposed above said reaction space and within said reaction chamber, said separation means being adapted to separate solid from the gases, a quenching chamber disposed above said separation means, conduit means connecting said separation means with said quenching means, and means for injecting a coolant comprising solid catalyst into a space between the separation means and the quenching chamber.

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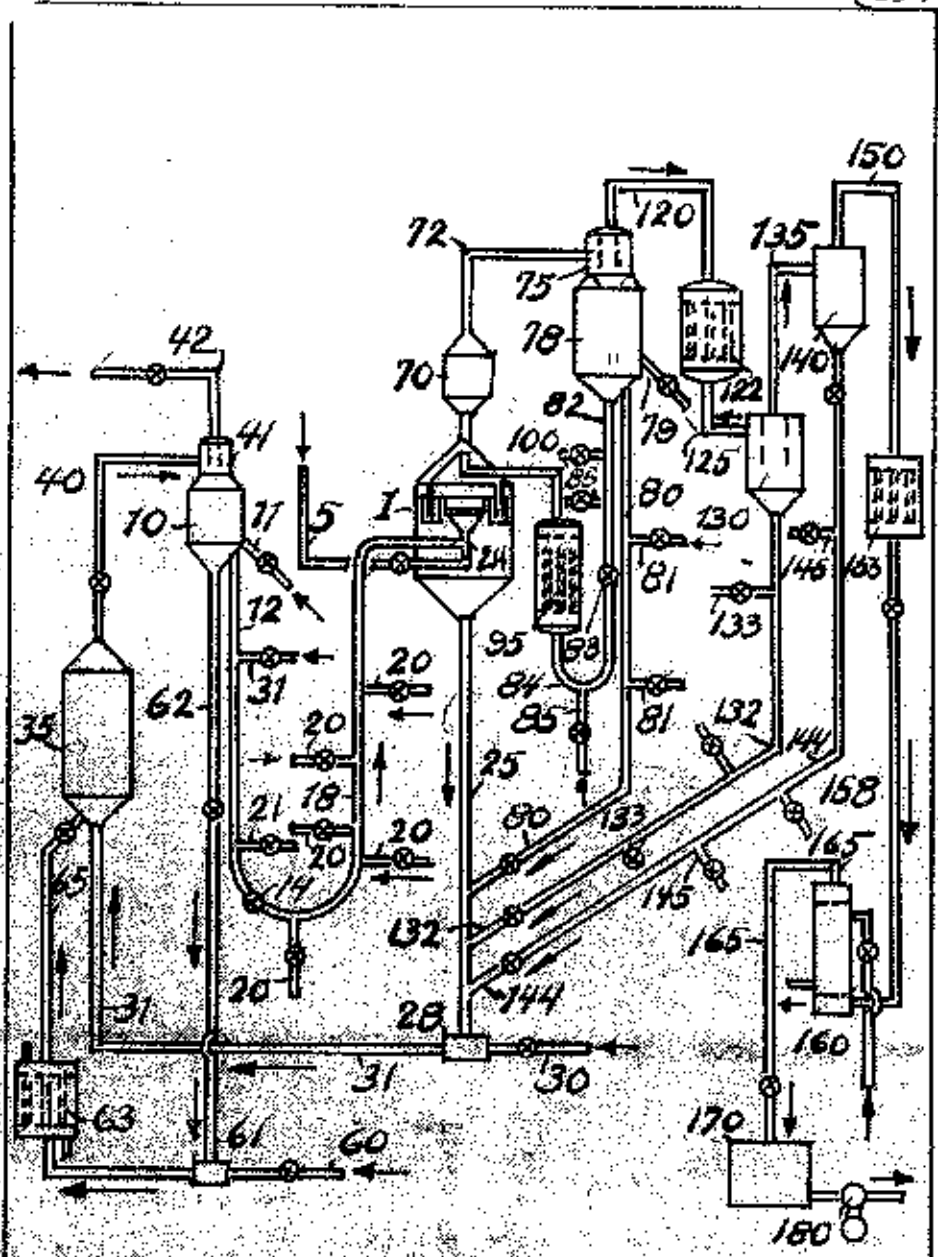


FIG-1

Standard Oil Development
Company
Certified to be the drawings
referred to in the specification
hereunto annexed
Ottawa, Canada, July 18, 1943
Mackay & Co.
Attorneys

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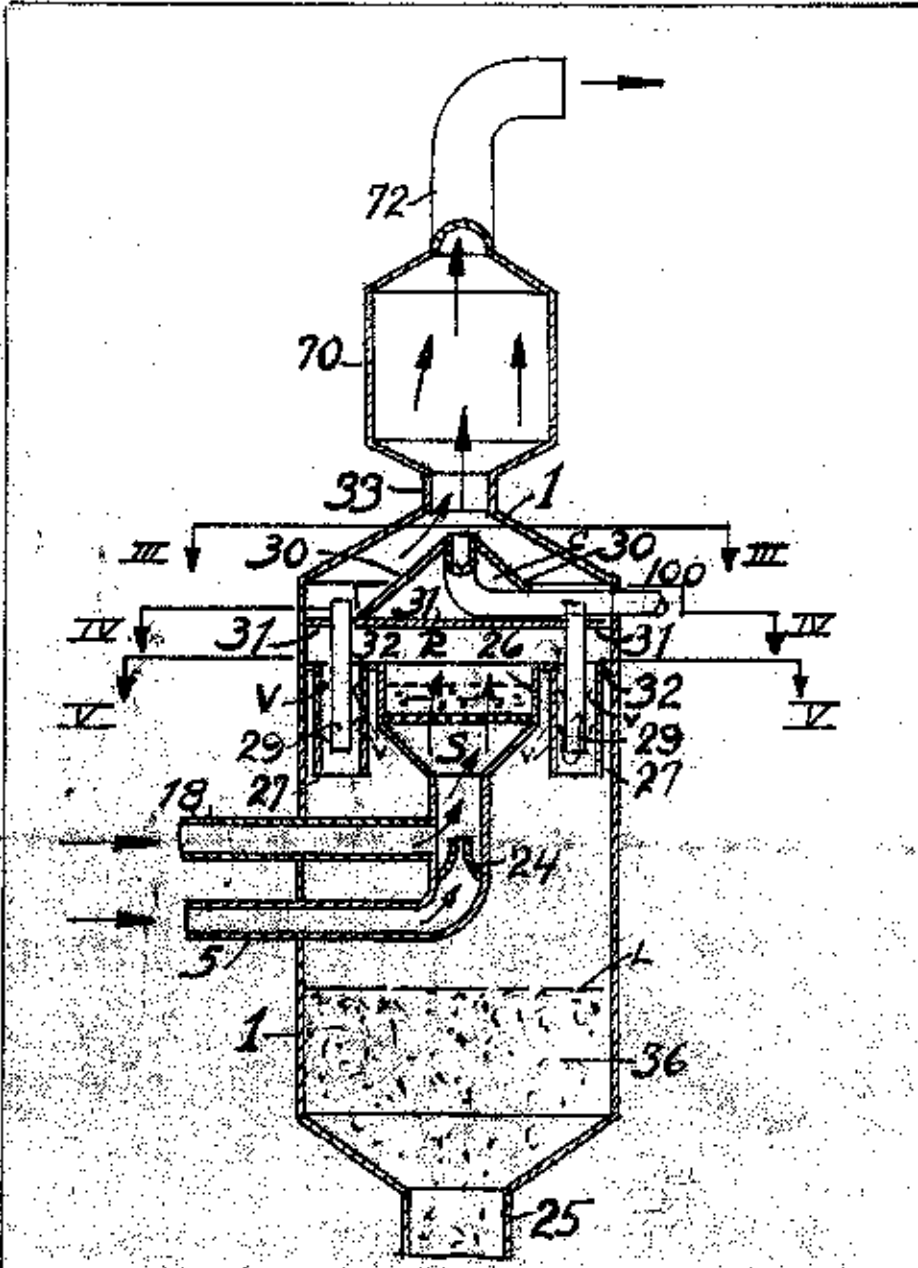


FIG. II

Standard Oil Development Company
Certified to be the drawings referred to in the specification hereunto annexed
Ottawa, Canada, July 18, 1943
Messrs. Clark & Co. Attorneys

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(3)3

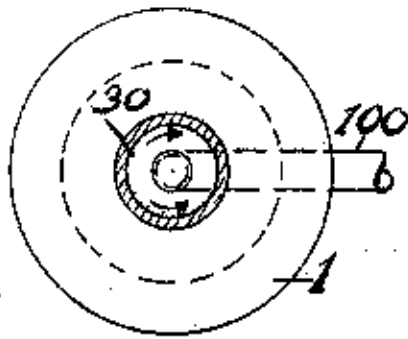


FIG-III

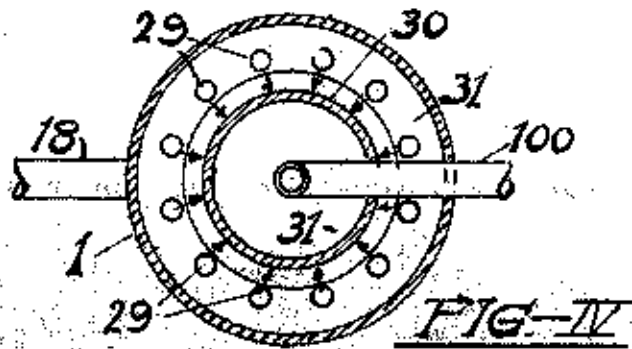


FIG-IV

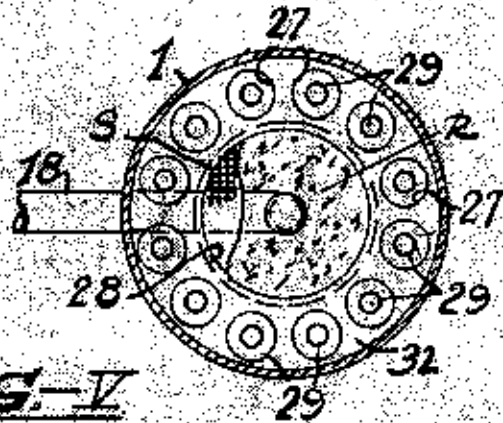


FIG-V

Standard Oil Development
Company
Certified to be the drawings
referred to in the specification
hereunto annexed
Ottawa, Canada, July 16, 1943
Mack & Hildes
Attorneys

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(54) CATALYTIC REACTION PROCESS

(54) PROCEDE POLR REACTIONS CATALYTIQUES

Publication Information(72) Inventors (Country):BRUNO E. ROETHLI (Not Available)
WALTER G. SCHARMANN (Not Available)(73) Owners (Country):

STANDARD OIL DEVELOPMENT COMPANY

(71) Applicants (Country):(74) Agent:(45) Issued on:

Mar. 30, 1948

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23/370

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N/A

Parent Cooperation Treaty (PCT): No(30) Appl. cat. & priority date: NoneAvailability of licence:

N/A

Language of filing:

Unknown

ABSTRACT:CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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It is claimed:

1. In the method of conducting vapor phase reaction in the presence of a powdered catalyst suspended in the vapors during the reaction, the improvement which comprises controlling the time of contact between reactant and catalyst at reaction temperatures by discharging into the reaction mass a quantity of cooled catalyst.

2. In the process of reacting gasiform reactants in the presence of a powdered catalyst suspended in a reactant, the improvement which comprises feeding the catalyst upwardly through a conduit or restricted cross sectional area aided by a fluidizing gas to a reaction zone of reduced pressure mixing the reactants with the fluidized catalyst in a mixing zone, and controlling the time of contact between reactant and catalyst at reaction temperatures by discharging into the reacted mass a quantity of cooled catalyst shortly after the original contact.

3. The process set forth in claim 2 in which the reactant is maintained at reaction temperature in the presence of the catalyst for a period of less than one second.

4. The process set forth in claim 2 in which the reaction is endothermic in nature.

5. The process set forth in claim 2 in which the reaction is endothermic in nature and at least a portion of the superheat necessary for the reaction is supplied by mixing the reactant with hot catalyst in the mixing zone.

The present invention relates to improvements in the art of controlling the time or duration of a chemical reaction accurately within narrow limits by quenching the reaction mass with a cooler solid substance.

There are a number of chemical reactions in which the time or duration of the reaction is of the essence. For example, in the catalytic dehydrogenation of hydrocarbons, such as the dehydrogenation of butylene to form butadiene, it is known that the optimum contact time between catalyst and reaction mass at reaction temperatures is of the order of less than one second at subatmospheric pressures. In contact times of the order indicated, the production of butadiene is at a maximum and the formation of undesired decomposition products is at a minimum.

In operating with a fixed bed of catalyst, that is to say, in operating a process in which the reaction gases pass through a body of catalyst in the form of pellets or lumps, it is extremely difficult by any feasible method to limit the contact times to the degree indicated above, namely, to a fraction of a second. In any event, it is difficult to maintain all portions of reaction mixture in contact with the catalyst for such a short period of time because appreciable time is consumed by those molecules of the reactants which diffuse into the aggregates of catalyst particles of the size employed in fixed beds, and are released therefrom. In other words, while those molecules which contact merely the surface of the catalyst pills

or pellets may be subjected to the influence of catalyst for a relatively short period of time, those molecules which actually penetrate into the body of catalyst are in contact with the catalyst for a period of time which is usually sufficient to cause the formation of undesired products with a consequent loss in yield of the desired products.

In order to overcome the foregoing and similar disadvantages, we have devised means for limiting chemical reactions carried out catalytically to short periods of contact time between catalyst and reactant, and we accomplish this end essentially by quenching the reaction mixture with catalyst which is cooler than the said mixture.

The main object of this invention is to control contact time between a gaseous reactant and a catalyst for the reaction by the use of finely divided catalyst and quenching the reaction when the equilibrium is most favorable for the desired product by adding cooled catalyst to the reaction mass.

Another important step in this invention is to feed catalyst to the reaction zone by means of an up-flow standpipe, the details of which will be more fully described hereinafter.

A further object of this invention is to provide a process and suitable means therefor, whereby we may continuously perform vapor phase reaction in the presence of a powdered catalyst, provide means for regenerating the catalyst, and provide other means for returning the regenerated catalyst to the reaction zone to maintain continuity of operation, optimum temperature and pressure

conditions and, finally, provide optimum contact times between reactant and catalyst at reaction temperatures.

In order to illustrate this invention and for the purpose of disclosing more fully its nature and purpose, there is shown in the accompanying drawings diagrammatically, a form and arrangement of apparatus elements in which the invention may be applied to butylene dehydrogenation. Thus, in Fig. I there is shown a complete flow diagram which discloses in connection with the specification, a preferred modification of the invention; and in Fig. II there is shown an enlarged view of the improved reactor. Throughout the views similar reference characters refer to similar parts.

Referring in detail to the drawings, (1) represents a hopper in which the reaction takes place. The internal construction of the improved reactor is shown in detail in Fig. II and will be subsequently described in detail in discussing that figure of the drawing. Catalyst in the form of powder having a particle size of from 200-400 mesh is also discharged into the reactor from another hopper (10) in a manner as will be presently explained. The hopper (10) contains a dehydrogenation powdered catalyst preferably in a heated and activated condition and is in communication at its lower end with a standpipe (12) projecting downwardly as shown. This pipe may be of any convenient dimension, such as 36 inches in internal diameter, and a vertical length of 40-60 ft. These dimensions are purely illustrative and are governed by the quantity of catalyst to be fed to the hopper in any particular case. The lower end of the pipe is provided with a control valve (14) which is adapted

to control the rate of flow by gravity of powder in pipe (12) into the horizontal bend (16). Horizontal bend (16) is in communication with upwardly extending standpipe (18) which projects, as shown, into hopper (1). In other words, the feed of catalyst to the hopper (1) is through a down-flow pipe (12) and an up-flow standpipe (18). This flow may be accomplished by regulating the densities in pipes (12) and (18) respectively, by selecting the proper pipe dimensions, coupled with the introduction of fluidizing gas as follows: First, to cause catalyst to flow freely in pipe (12) a fluidizing gas is injected therein through pipes (21). By the same token to fluidize the catalyst in pipe (18), gas is injected through pipes (20). It is deemed obvious that by making pipe (18) of smaller internal diameter than pipe (12), the gas velocity in pipe (18) will be greater than that in pipe (12) and hence the density in pipe (18) will be less. Hence, catalyst will flow by the means indicated in the indicated direction. It is to be understood that the amount of gas injected into pipe (12) is much less than that injected into pipe (18), say one-fourth as much or less.

There is also discharged into the reactor a quantity of butylene, this material being supplied through line (5). The catalyst and the butylene are mixed in mixing device (24), and the mixture is then caused to flow upwardly in the hopper reactor. The temperature of the gas in line (5) entering the reactor is about 1000°F., while the catalyst in line (18) is at a temperature of about 1350°F. The gas and catalyst are mixed in proportions such that the temperature

of the mixture is about 1250°F., with most catalysts and it is preferred to maintain a density of the suspension in the region just above the mixing device (24) of from about 15-25 lbs./cu.ft., which condition is attained by regulating the gas velocities between 2 and 10 ft. per second where the particle catalyst size is from 200-400 mesh. Also a gas pressure of about 190 mm. of mercury is preferred within the reactor in the reaction now in question. Under the conditions stated, the reaction occurs to form ordinarily, butadiene from normal-butylene, and then by means which will be subsequently explained more fully hereinafter, the bulk of catalyst is separated from the reaction mass and gravitates from the bottom of the reactor from which it is withdrawn through standpipe (25), mixed with air in a mixing device (28), the air entering through line (30), and thence conveyed through pipe (31) into a regenerator (35). The dimensions of regenerator (35) and the gas velocities are such dimensions that when the catalyst is mixed with the required amount of air or other free oxygen containing gas, the density of the mixture is from about 20 to 25 lbs./cu.ft. The catalyst in line (25) is at a temperature of 1150°F.-1250°F. and under these conditions when mixed with air at ordinary atmospheric temperature in mixer (28) active combustion takes place in regenerator (35) with the consumption of carbonaceous deposits produced on the catalyst as a result of the reaction taking place in reactor (1). Ordinarily it is preferable to operate regenerator (35) under super-atmospheric pressure, say pressures up to 1-5 lbs./sq.in. gauge or higher, as dictated by economic considerations, in

order to accelerate the oxidation of the contaminating carbonaceous material. The flue gas and the regenerated catalyst are withdrawn from regenerator through line (40) and discharged into a cyclone separator (41) built into the top of hopper (10). The separator effects separation of the regenerated catalyst from the flue gas, and the latter is withdrawn through line (42) and, if desired, sent to a second cyclone separator to remove further quantities of catalyst. In some cases, it is desirable to employ three cyclones or even more to insure complete removal and recovery of catalyst from flue gas. The hot flue gases substantially freed of catalyst may then be passed through a waste heat boiler to recover a portion of their energy content. The catalyst separated in cyclone separator (41) gravitates into hopper (10) and is recycled to the reactor in the manner previously described.

In the drawing, we have shown means for controlling the regeneration temperature of the catalyst in regenerator (35). As shown, catalyst, that is regenerated catalyst, may be withdrawn through hopper (10) through line (62), mixed with air from line (60) in injector (61), thence discharged through cooler (63) and line (50) into regeneration vessel (35). The cooled regenerated catalyst may be at a temperature of say 300-500°F. as it enters the regenerator, and may be in the proportions of say 1/30-2 or more parts by weight of regenerated catalyst per part of unregenerated catalyst. The cooler regenerated catalyst serves to increase the heat capacity of the mixture and temper the exothermic reaction by adsorbing heat released during regeneration.

Referring again to reactor (1), it will be noted that a second chamber (70) is superimposed at the top of reactor. This chamber contains the reaction products and catalyst added to quench the reaction mixture. The manner of adding the catalyst will be presently described, but first let it be observed that the newly added catalyst plus the remainder of the original catalyst not separated, together with the reaction mass, are withdrawn overhead through line (72) and passed into a cyclone separator (75) where the bulk of the quenching catalyst and the catalyst not previously removed are separated from the vapors. The separated catalyst passes into a receiving hopper (78) and in this hopper is at a temperature of about 1050°F. One stream of catalyst is withdrawn from hopper (78) through line (80), communicating in its lower end with standpipe (25), as shown. The other stream of catalyst is withdrawn through line (82) carrying a flow control valve (83) at its lower end and thence discharged into bend (84) where it is mixed with a gas such as methane discharged into (84) through pipe (85), and thereafter the catalyst is passed upwardly through line (90) through a heat exchanger (95) where the catalyst is cooled to a temperature such that when withdrawn through line (100) it is at a temperature of about 600°F., whereupon it is injected into reaction mass in reactor (1) and thereafter carried upwardly in suspension into quenching chamber (70) previously mentioned. The amount of catalyst recycled from hopper (78) to quenching chamber (70) will depend of course entirely on the amount of gas and catalyst flowing into chamber (70) and the temperature thereof. It has been

found that good results are obtained by recycling to zone (70) from hopper (73) sufficient catalyst so that a temperature of 1000°-1050°F. prevails in chamber (70). In any event, it is usually preferable to add sufficient catalyst to lower the temperature of the reaction mass to about 1000°F. or lower because at this temperature undesired side reactions are prevented and the decomposition of the desired butadiene is substantially par. The gases freed from catalyst in separator (75) are withdrawn through line (120) and these are preferably passed through a heat exchanger (122) where they are cooled to about 600°F., thence withdrawn through line (125) and passed into Cottrell precipitator (130) where a catalyst is separated and recycled to line (25) through line (132). The gases are drawn overhead from separator (130) through line (135) and pass through a Cottrell precipitator (140) where more catalyst is separated out and the separated catalyst is withdrawn through line (144) and recycled through line (31) to regenerator (35). The reaction products now containing only minor amounts of catalyst are withdrawn from Cottrell precipitator through line (150), thence further cooled in cooler (155), thence discharged through line (158) into an oil washer (160) where the last traces of catalyst are removed, the scrubbing oil being discharged into the washer through line (162). The washed gases are withdrawn through line (165), passed through entrainment separator (170) and thence to a pump in which they are compressed and condensed prior to separation in a suitable system. The pressure conditions, i.e. the partial vacuum previously referred to in reactor (1) is maintained through pump (180) and suitable valves, in known manner.

Referring now to Fig. II for a detailed description of the improved reactor and its immediate accessory apparatus, it will be observed that the catalyst and the butylene enter the reaction vessel (1) and pass into the mixing chamber (24) and thence are delivered into the reaction chamber (25) where the main reaction takes place, the catalyst being in the form of a dense mass or phase thoroughly intermixed with the reactant. Disposed about the reaction chamber (25) are a plurality of cyclone separators (28). These separators are arranged contiguously in the form of a ring or circle about the reaction vessel, and in escaping from reaction vessel (25) the fluidized mass and reactant gas are forced into the separators (28). The bulk of the catalyst, usually over 90%, is separated from the gases and gravitates to the bottom portion (36) of the reaction vessel, while the gases flow upwardly through outlet pipes (29), thence through pipe (32) into quenching chamber (70). The catalyst which is separated in the separators (27) collects in the bottom of the reaction vessel, as indicated by the catalyst level line (L), and is withdrawn from the said reactor and arranged such as to maintain the heated catalyst continuously in the said reaction vessel.

As is known by those familiar with this particular art, the types of catalyst which may be employed for dehydrogenations are many and varied. One of these catalysts is metallic nickel. Heretofore the difficulty with metallic nickel has been that it is so reactive that it is not usable because it not only accelerates the formation of, say, butadiene from butylene but attacks the butadiene to decompose it.

In the type of operation which we have described herein, a very active catalyst such as nickel may be successfully employed because the combination of controlled contact time, finely divided catalyst and quenching features enables us to discontinue the reaction and to limit it to a very short period of time of contact between reactants and the nickel at reaction temperatures. In the case of other catalysts such as silica-alumina compositions, alumina-tungsten, alumina-chromium, alumina-molybdenum, the various metallic oxides, and the like, such as copper oxide, nickel oxide, cobalt oxide or mixtures of the same where the catalyst is less active, this process is also of value not only from the standpoint of quenching the reaction but also from the standpoint of supplying at least a portion of the heat necessary for the reaction by recycling hot regenerated catalyst to the reaction zone.

To recapitulate, the present invention involves the concept of controlling accurately the contact time between a gaseous reactant and a solid catalyst, and while the invention has been described in detail in connection with the specific problem of dehydrogenating an olefin, obviously the inventive concept is applicable to a great number of processes, such as gas oil cracking, desulfurization, aromatization, oxidations, simple and destructive hydrogenations, chlorinations, and numerous other gas phase reactions where contact time is an important consideration from the standpoint of yields or for other reasons. It will be noted that according to this process, it is preferred to quench the reaction mass by means of a cooled solid, such

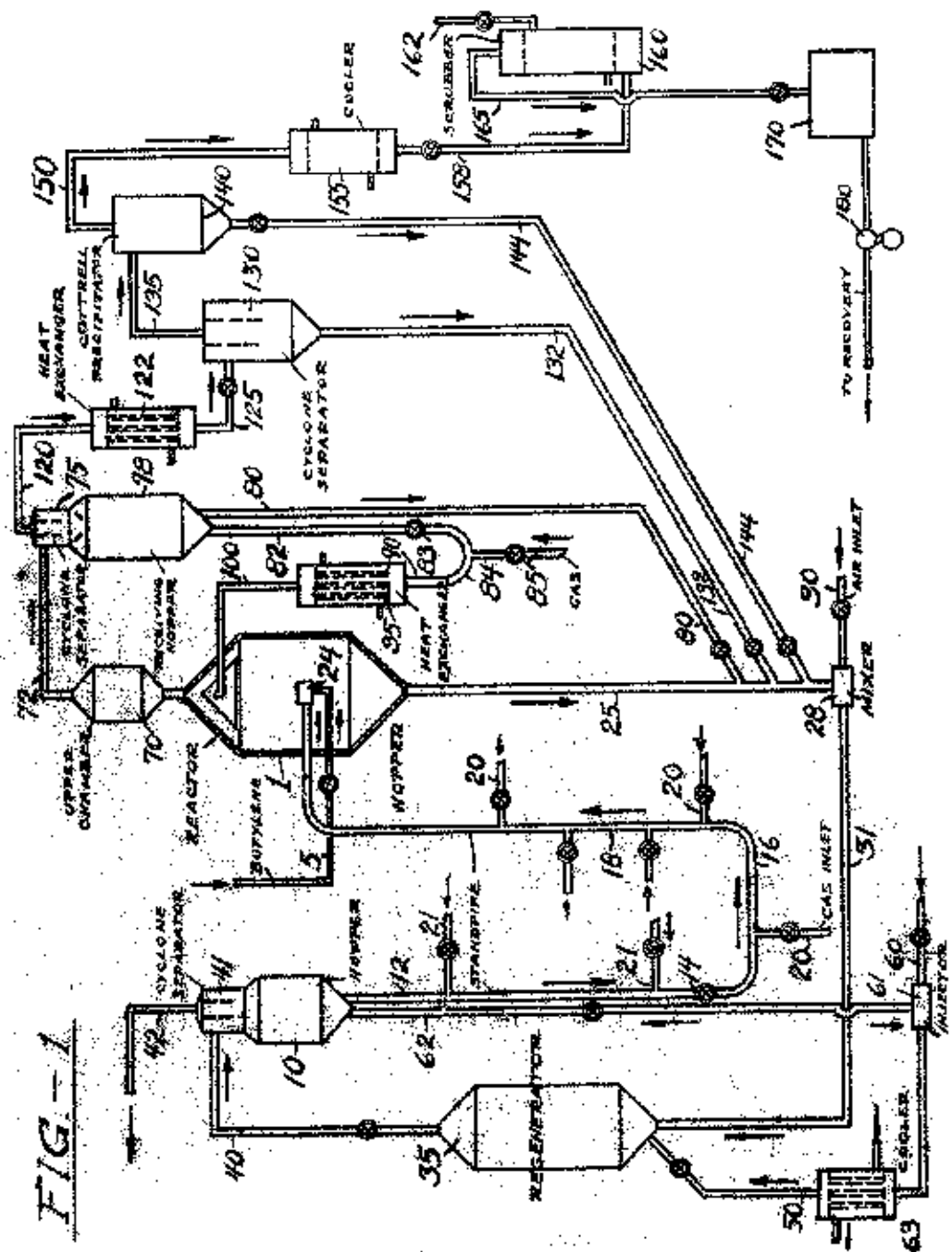
as a solid catalyst added in sufficient quantity to lower the reaction mass to temperatures substantially below reaction temperatures, and since the process may be operated to quench the catalyst within the reaction zone very short contact times may be effected. On the other hand, if longer contact time between reactant and catalyst is desired, the quenching may be formed in a subsequent stage, say by adding cooled catalyst in line (72). It will be understood that instead of using catalyst to quench the reaction mass, an inert solid may be used such as sand, lime, or refractory material which is added in sufficient quantity and at a sufficiently lower temperature to effect the desired result.

Other features of the invention involve, as heretofore set forth, an up-flow standpipe arrangement for adjusting pressure differentials between the reaction zone and the regeneration zone; another feature involves furnishing at least a portion of the heat required for endothermic reactions by supplying the proper amount of heated catalyst. Finally, the catalyst flowing in the various means may be fluidized by steam as heretofore mentioned, or by the introduction of other gases such as methane, CO₂, CO, nitrogen, and the like; that is to say, these gases may be added through lines (60) and (20) and at other points in the system heretofore mentioned, to attain the desired fluidity of catalyst.

The pressure in reactor (1) may vary from about 100 mm. of mercury to above atmospheric pressure, sub-atmospheric pressure being preferred.

Many modification of the invention will be obvious to those skilled in this particular art.

FIG-1



Standard Oil Development Company

Certified to be the drawings referred to in the specification hereunto annexed.
 Ottawa, Oct. 16, 1942

Marko Holick
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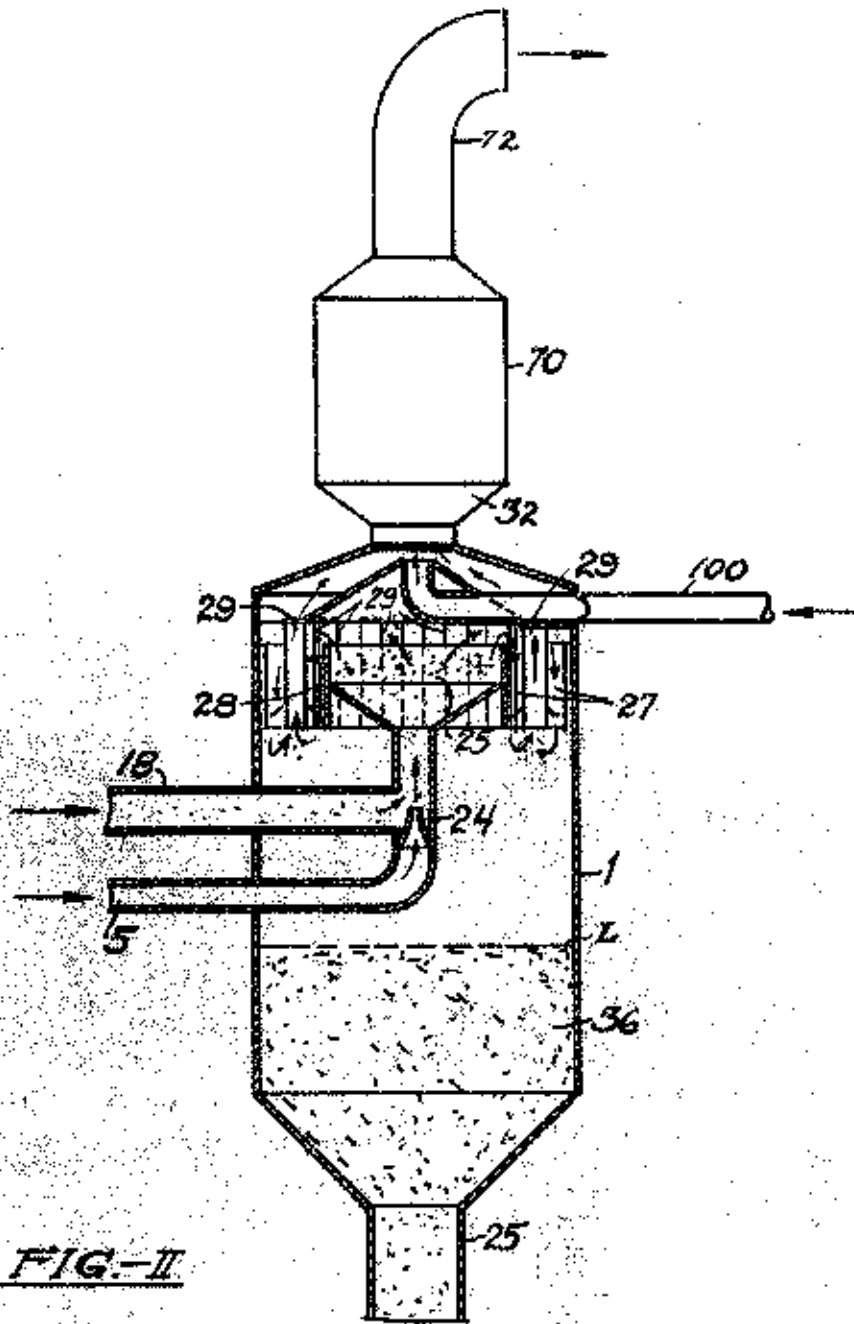


FIG.-II

*Standard Oil Development
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