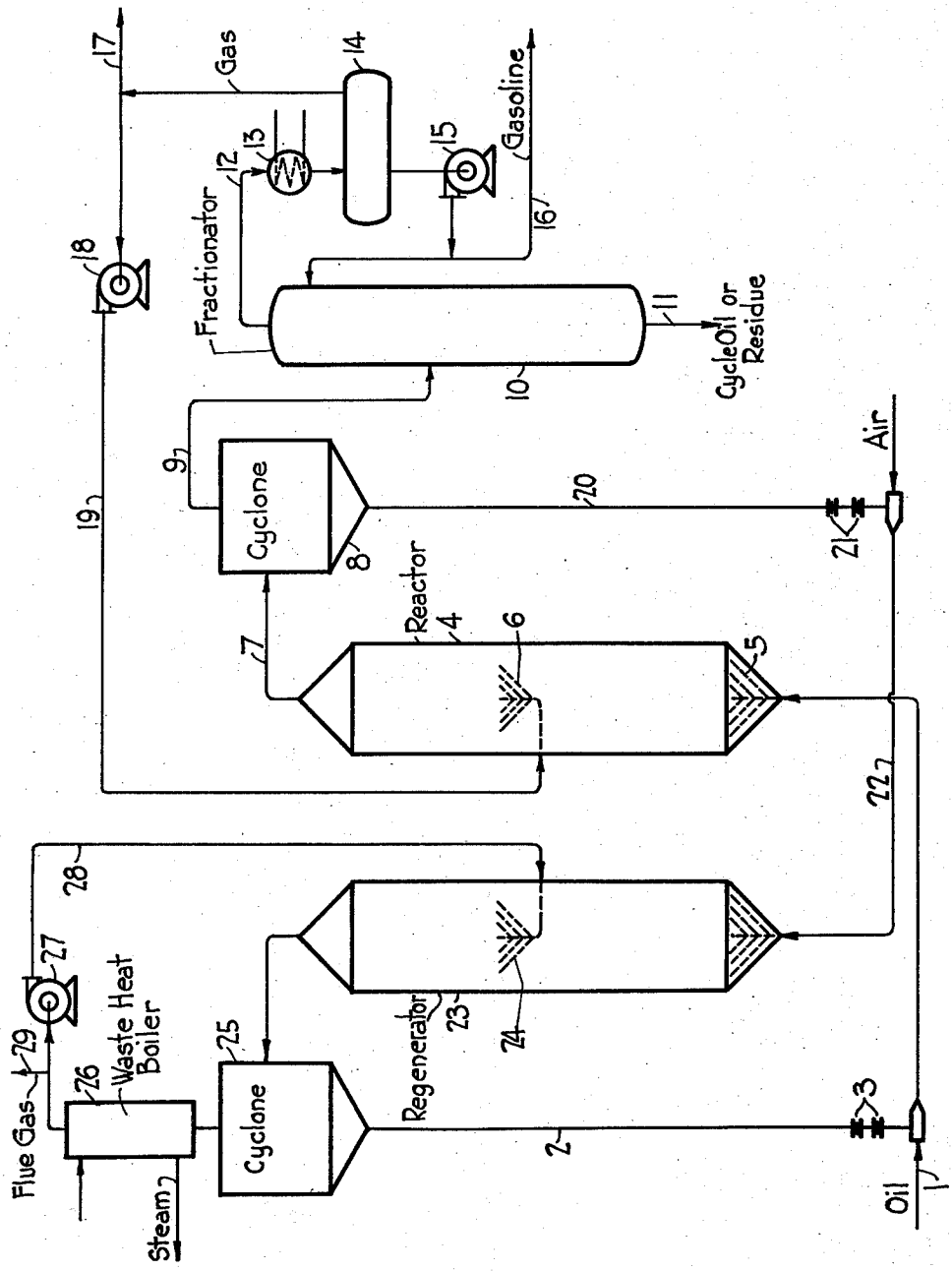
Oct. 2, 1945. N. E. PEERY 2,386,169

METHOD FOR CONTACTING VAPORS OR GASES WITH FINELY DIVIDED CONTACT MATERIALS

Filed Nov. 6, 1944




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Patented Oct. 2, 1945 2,386,169

# UNITED STATES PATENT OFFICE

2,386,169

## METHOD FOR CONTACTING VAPORS OR GASES WITH FINELY DIVIDED CONTACT MATERIALS

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Application November 6, 1944, Serial No. 562,164

8 Claims. (Cl. 196—52)

This invention relates to an improved method for the contacting of gases or vapors with finely divided solid catalysts or other contact agents. A particular embodiment of the invention relates to an improved method for effecting various catalytic conversions or treatments of gases or vapors with finely divided solid contact materials wherein the finely divided contact agent is continuously cycled through a conversion or treating zone and a separate regeneration zone. Still more particular embodiments of the invention relate to the catalytic cracking of hydrocarbon oils and the regeneration of finely divided solid contact agents.

As is known, there are a great many catalytic conversions and treatments which are accelerated by contacting the material to be converted or treated in the vapor state with solid catalysts or other contact agents under suitable conditions. In many cases the solid contact agent is employed in the form of pellets or other relatively large lumps of pieces and remains in a relatively fixed position with respect to the material contacted therewith. It is generally recognized, however, that in most cases, by the use of a suitable system, the treatment or conversion can be carried out with the contact agent in a finely divided state, and that, in general, several distinct advantages can be gained in so doing. With these advantages in mind, considerable attention has been given, particularly in the past several years, to the development of various systems for the application of finely divided contact agents. As a result, a considerable number of systems and modifications have been suggested. The various sytems proposed may be classified into a few distinct types according to whether the treatment is carried out in tubes or chambers, whether the contact agent is transported with the reactant vapors or falls countercurrent thereto, and whether the contact agent is employed in a dense or freely suspended state. The type of system found to be best for most general application and adopted by the industry is that type in which the finely divided contact agent is employed in a pseudo-liquid or fluidized state. The process of the invention is of this type.

Dry, non-sticky solids, when in a suitable state of subdivision, may be made to exist in three distinct states. (1) If allowed to settle in bulk, they form a hard micro-porous solid mass which may be friable, but is usually difficult to return to the original finely divided state except by grinding. (2) If mixed with a sufficient quantity of agitated gas or vapor, the individual particles are uniformly dispersed and suspended in the gas or vapor. In this state the mixture may be compressed or expanded and the solid may be considered as being in a pseudo gaseous state. (3) If aerated with a limited amount of gas or vapor they exist in a pseudo-liquid or fluidized state. When in the fluidized state they behave in most respects as a liquid. Thus they flow freely; they may be pumped like a liquid; like a liquid they form an interface between the pseudo-liquid and pseudo-gas phase; gases may be "bubbled" up through the fluidized phase much as with a true liquid. Thus, if a quantity of a finely divided solid contact agent, for instance a powder passing a 100 mesh screen, is allowed to stand in a reactor or other vessel with no injection of gas it will settle into a dense relatively hard mass. If, on the other hand, a controlled amount of gas is injected into the bottom of the vessel the finely divided solid will be maintained in the pseudo-liquid state. If the quantity of gas injected is gradually increased, it is found that the density of the pseudo-liquid or fluidized solid gradually decreases while the density of the gas phase above the pseudo-liquid gradually increases until a point is reached at which a small increase in the amount of gas added causes a great increase in the density of the upper gas phase and the whole or a good portion of the solid becomes freely suspended in the gas. This behavior is analogous to the behavior of a liquid in equilibrium with its vapors under constant pressure when the temperature is increased, the gas velocity corresponding to the temperature and the critical gas velocity corresponding approximately to the critical temperature. The gas velocity at this point, hereinafter called the critical velocity, depends upon the physical properties of the particular solid and the viscosity of the gas. In the case of the finely divided synthetic silica-alumina catalysts for example, the critical velocity is in the order of 1.5 to 3 feet per second calculated for the same conditions but with the catalyst absent. The density of the fluidized catalyst corresponding to the critical gas velocity as hereinbefore defined, is hereinafter referred to as the critical density.

One of the first commercial applications of finely divided contact agents in a fluidized state was in the catalytic cracking of hydrocarbon oils with synthetic silica-alumina cracking catalysts. In the earlier plants the oil vapors to be cracked and the air for regeneration were contacted with the fresh and partially spent catalyst respectively in an upflow hindered settling reactor and re-

generator respectively. The up-flow hindered settling reactor consists essentially of a vertically disposed cylindrical vessel of carefully chosen cross section and provided with a suitable inlet at the bottom and a suitable outlet at the top. In operation the vapors carrying a quantity of the finely divided catalyst in suspension enter at the bottom and a suspension of like composition is withdrawn at the top. Due to the lowered velocity in the reaction chamber a condition of hindered settling is established. Since a relatively large amount of catalyst must be carried overhead (usually from 1 to 20 pounds of catalyst per pound of oil) the density of the exit suspension must be relatively high (compared to bottom-draw-off systems) and the density of the main catalyst mass is fixed at a relatively low value. This condition is difficult to maintain constant. Thus if the velocity is allowed to decrease slightly the density of the effluent decreases markedly, the density of the main catalyst mass increases and remains in a fluidized state, and little or no catalyst is withdrawn until the reactor overflows; if the velocity is allowed to increase slightly the rate of catalyst carry-over is greatly increased, the density of the main catalyst mass decreases, and the reactor is largely depleted of catalyst. Another disadvantage of this system is that it allows catalyst segregation to take place. Thus, there is a considerable tendency for the smaller catalyst particles (fines) to pass through the reactor quickly leaving the coarser particles to remain in the reactor for considerable periods of time.

More recent plants are provided with so-called bottom-draw-off reactors and regenerators. The bottom-draw-off reactor has several advantages over the up-flow hindered settling reactor and is considered to be a substantial improvement. In the bottom-draw-off reactor the vapors carrying finely divided catalyst in suspension are introduced at or near the bottom as before. The partially spent catalyst is continuously removed from the bottom of the reactor through a standpipe (catastat). Since the catalyst is removed from the bottom instead of the top the vapor velocity in the reactor is not critical and may be adjusted at a safe rate well below the critical velocity. This allows a much greater flexibility and ease of control. Likewise the difficulty due to segregation is entirely eliminated. A most important advantage, however, is that it allows a more dense fluidized bed of catalyst to be used. Since the activity or eeffctiveness of the catalyst is proportional to the amount of available catalytic surface in the reactor and this in turn is proportional to weight of catalyst in the reactor, it is evident that by doubling the density of the catalyst bed the efficiency of the process may be doubled. This direct ratio of improvement is not obtained however with bottom draw-off reactors because of certain other defects or disadvantages inherent in the bottom draw-off system. A primary disadvantage of the bottom draw-off reactors is that, the inlet for fresh catalyst and the outlet for spent catalyst being both at or near the bottom, a considerable amount of the fresh catalyst introduced is immediately withdrawn without being properly used. This is referred to as "by-passing." Another disadvantage is that the free space above the level of the fluidized catalyst (disengaging space) is relatively free of catalyst (density less than about 0.5 pound per cubic foot).

In catalytic cracking this allows a certain amount of undesired thermal reaction to take place in the disengaging space. In catalyst regeneration it makes the very undesirable phenomena known as "after-burning" difficult to prevent or control.

In the method of the present invention the gas or vapor is contacted with the finely divided contact material in such a manner that the respective advantages of both the up-flow hindered settling reactor and the bottom draw-off fluid catalyst reactor are realized without their attendant disadvantages. This is accomplished by contacting the finely divided contact agent at two separate and distinct vapor velocities and catalyst densities as hereinafter described. The principles of the invention may most conveniently be explained in connection with a typical operation. To assist in the description reference is had to the attached drawing wherein there is shown by means of diagrammatic figures, not drawn to scale, the more important apparatus and flows in a typical system adapted for the continuous operation and continuous regeneration of the finely divided catalyst according to the method of the invention. The system illustrated is adapted for carrying out various catalytic conversions and/or treatments with various finely divided solid contact agents. However, for the purpose of the description the catalytic cracking of a hydrocarbon oil with a finely divided clay-type cracking catalyst will be used as a typical example.

Referring to the drawing, the hydrocarbon oil to be cracked, for instance a gas oil, is preheated and vaporized by means not shown and the vapors are charged to the system via line 1. The vapor picks up a desired amount of hot freshly regenerated catalyst from the standpipe 2. The amount of catalyst added is usually within the range of from about 3 pounds to about 25 pounds per pound of oil and is controlled by suitable slide valves 3. The oil vapors carrying the suspended catalyst enter the bottom of the reactor 4 and are distributed by a suitable distributing manifold 5. The reactor 4 is essentially an elongated chambear of such cross section that the desired plant capacity may be obtained without exceeding the critical vapor velocity. In operation a substantial bed of the finely divided catalyst is maintained in the lower half of the reactor. The height of the catalyst bed is adjusted to afford the desired space velocity and normally extends up to at least the height of the manifold 6. The bed of finely divided catalyst is maintained in a pseudo liquid state by the vapors introduced at the bottom. The density of the fluidized bed is relatively high and is above the critical density.

In order to maintain a desired depth of catalyst bed and to effect withdrawal of the partially spent catalyst the vapor velocity in the upper section of the reactor is increased to exceed the critical velocity. The increase in the vapor velocity is obtained by the injection into the reactor of a second portion of gas or vapor via manifold 6. In the system illustrated, the gas added is a recycled portion of the product gases. The mixture of product vapors, partially spent catalyst and added gas leaves the reactor at the top via line 7 and passes to a suitable cyclone separator 8 wherein the partially spent finely divided catalyst is separated. The mixture of product vapors and recycled gas passes via line 9 to a fractionator 10. Cycle oil or heavy residue is removed from the bottom of the fractionator via line 11. The gasoline and gaseous products are removed from the fractionator via line 12 and after being cooled in a condenser 13 are passed to a separator 14. Gas-

oline is withdrawn from the separator 14 via pump 15 and line 16. The gaseous product from the separator consists largely of hydrocarbon gases having 4 or less carbon atoms. A portion of this gas is withdrawn via line 17 and another portion is recycled to manifold 6 via pump 18 and line 19.

The partially spent catalyst withdrawn from the separator 8 via standpipe 20 and slide valve arrangement 21 may be regenerated in a conventional up-flow hindered settling regenerator or a conventional bottom draw-off fluid catalyst regenerator or by any other means. It is however preferably regenerated using the principles just described. Thus the partially spent catalyst is picked up and carried by a stream of air via line 22 to the bottom of the regenerator 23 where it is injected into the bottom of a fluidized bed of the catalyst undergoing regeneration. As before, the fluidized bed is maintained at a relatively high density above the critical density by control of the air flow. An additional quantity of gas, which in the case illustrated is recycled flue gas, is introduced at about midway in the regenerator by the manifold 24. The amount of gas added, as before, is adjusted to give a gas velocity in the upper section of the regenerator above the critical velocity. The regenerated catalyst is carried with the mixed gas stream out from the top of the regenerator to a suitable cyclone separator 25. The regenerated catalyst is recycled to the reactor as described via standpipe 2. The hot spent regeneration gas is passed through a waste heat boiler 26. A portion of the partially cooled gas is recycled to the regenerator 23 via pump 27, line 28 and manifold 24. The remainder is withdrawn from the system via line 29.

It will be apparent that the above-described typical operation may be modified in certain respects while still retaining the principles of the invention. For instance, the process may be applied for other conversions than catalytic cracking; various other finely divided solid catalysts may be used in place of the clay-type catalysts and the gas or vapor injected via manifolds 6 and/or 24 may be any suitable material other than the particular products shown. On the other hand essential features of the invention are: (1) that the finely divided contact agent enters the reactor or regenerator at or near the bottom and is withdrawn with the gas or vapor from the top, (2) that the amounts of gas or vapor introduced with the catalyst at the bottom are insufficient to exceed the critical velocity, thereby maintaining a definite bed of relatively dense fluidized catalyst in the lower section of the contactor, and, (3) that a second portion of gas or vapor is introduced between the bottom and the top of the contactor in such an amount that the velocity of the combined vapors or gases exceeds the critical velocity.

I claim as my invention:

1. Method for continuously contacting a gas or vapor with a recycled finely divided contact agent which comprises injecting near the bottom of a bed of said finely divided contact agent a mixture of said gas or vapor and said finely divided contact agent, the rate of flow of said gas or vapor being adjusted to maintain said bed of finely divided contact agent in a relatively dense pseudo-liquid state, and injecting at a point substantially at the top of said bed a gas or vapor at such a rate that the velocity of the combined gas or vapor exceeds the critical velocity corresponding to said pseudo-liquid state, thereby to produce and maintain a free suspension or gaseous phase above said point of injection and to remove in suspension from the top of said bed a quantity of said finely divided contact agent substantially equivalent to the amount of said finely divided contact agent injected near the bottom.

2. Method for continuously contacting a gas or vapor with a cycled finely divided clay-type catalyst which comprises injecting near the bottom of a bed of said finely divided clay-type catalyst a mixture of said gas or vapor and said finely divided catalyst, the rate of flow of said gas or vapor being adjusted to maintain said bed of finely divided catalyst in a relatively dense pseudo-liquid state, and injecting at a point substantially at the top of said bed a gas or vapor at such a rate that the velocity of the combined gas or vapor exceeds the critical velocity corresponding to said pseudo-liquid state, thereby to produce and maintain a free suspension or gaseous phase above said point of injection and to remove in suspension from the top of said bed a quantity of said finely divided catalyst substantially equivalent to the amount of said finely divided catalyst injected near the bottom.

3. Method for the treatment of a hydrocarbon oil with a cycled finely divided clay-type catalyst which comprises injecting near the bottom of a bed of said finely divided catalyst a mixture of vapors of hydrocarbon oil to be treated and said finely divided catalyst, the rate of flow of said vapors being adjusted to maintain said bed of finely divided catalyst in a relatively dense pseudo-liquid state, and injecting at a point substantially at the top of said bed a gas or vapor at such a rate that the velocity of the combined gas or vapor exceeds the critical velocity corresponding to said pseudo-liquid state, thereby to produce and maintain a free suspension or gaseous phase above said point of injection and to remove in suspension from the top of said bed a quantity of said finely divided catalyst substantially equivalent to the amount of said finely divided catalyst injected near the bottom.

4. Process according to claim 3 in which the gas or vapor injected near the top of the bed is a normally gaseous hydrocarbon fraction.

5. Process according to claim 3 in which the gas or vapor injected near the top of the bed is a recycled gaseous fraction of the product of the process.

6. Method for continuously contacting a gas or vapor with a recycled finely divided contact agent which comprises injecting near the bottom of a bed of said finely divided contact agent a mixture of said gas or vapor and said finely divided contact agent, the rate of flow of said gas or vapor being adjusted to maintain said bed of finely divided contact agent in a relatively dense pseudo-liquid state, and injecting at a point substantially at the top of said bed a recycled portion of previously contacted gas or vapor at such a rate that the velocity of the combined gas or vapor exceeds the critical velocity corresponding to said pseudo-liquid state, thereby to produce and maintain a free suspension or gaseous phase above said point of injection and to remove in suspension from the top of said bed a quantity of said finely divided contact agent substantially equivalent to the amount of said finely divided contact agent injected near the bottom.

7. Method for the catalytic cracking of a hydrocarbon oil with a clay-type cracking catalyst which comprises injecting near the bottom of a bed of said finely divided catalyst a mixture of vapors of hydrocarbon oil to be cracked and said

finely divided catalyst, the rate of flow of said vapors being adjusted to maintain said bed of finely divided catalyst in a relatively dense fluidized state, injecting at a point substantially at the top of said bed a recycled gas obtained as hereinafter specified at such a rate that the velocity of the combined gas and vapor exceeds the critical velocity corresponding to said fluidized state, thereby to produce and maintain a free suspension or gaseous phase above said point of injection and to remove in suspension from the top of said bed a quantity of said finely divided catalyst substantially equivalent to the amount of said finely divided catalyst continuously supplied to said bed, separating finely divided catalyst from the suspension, separating a gaseous fraction from the product, and recycling at least a portion of said separated gaseous fraction as hereinbefore specified.

8. Method for the regeneration of a partially spent finely divided contact agent with air which comprises injecting near the bottom of a bed of said finely divided contact agent maintained under regeneration conditions a mixture of air and said partially spent finely divided contact agent, the rate of flow of air being adjusted to maintain said bed of finely divided contact agent in a relatively dense fluidized state, and injecting at a point substantially at the top of said bed a recycled portion of spent regeneration gas at such a rate that the velocity of the combined gases exceeds the critical velocity corresponding to said fluidized state, thereby to produce and maintain a free suspension or gaseous phase above said point of injection and to remove in suspension from the top of said bed a quantity of regenerated finely divided contact agent substantially equivalent to the amount of said finely divided contact agent continuously supplied to said bed.

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