Nov. 25, 1947. D. L. CAMPBELL ET AL 2,431,462

CATALYTIC TREATMENT OF HYDROCARBONS

Filed Nov. 17, 1942 3 Sheets-Sheet 1

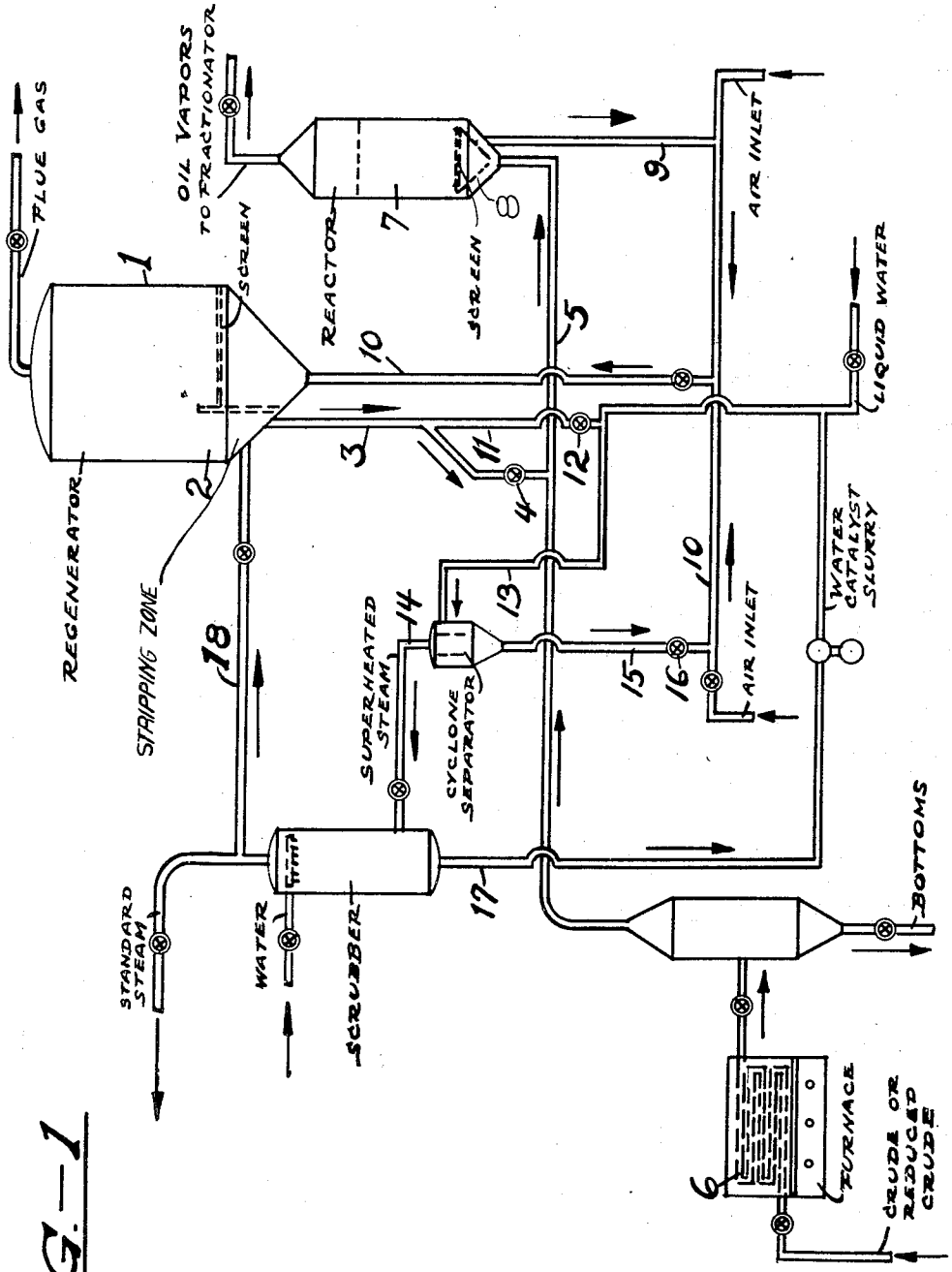

FIG. 1

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Filed Nov. 17, 1942 3 Sheets-Sheet 2

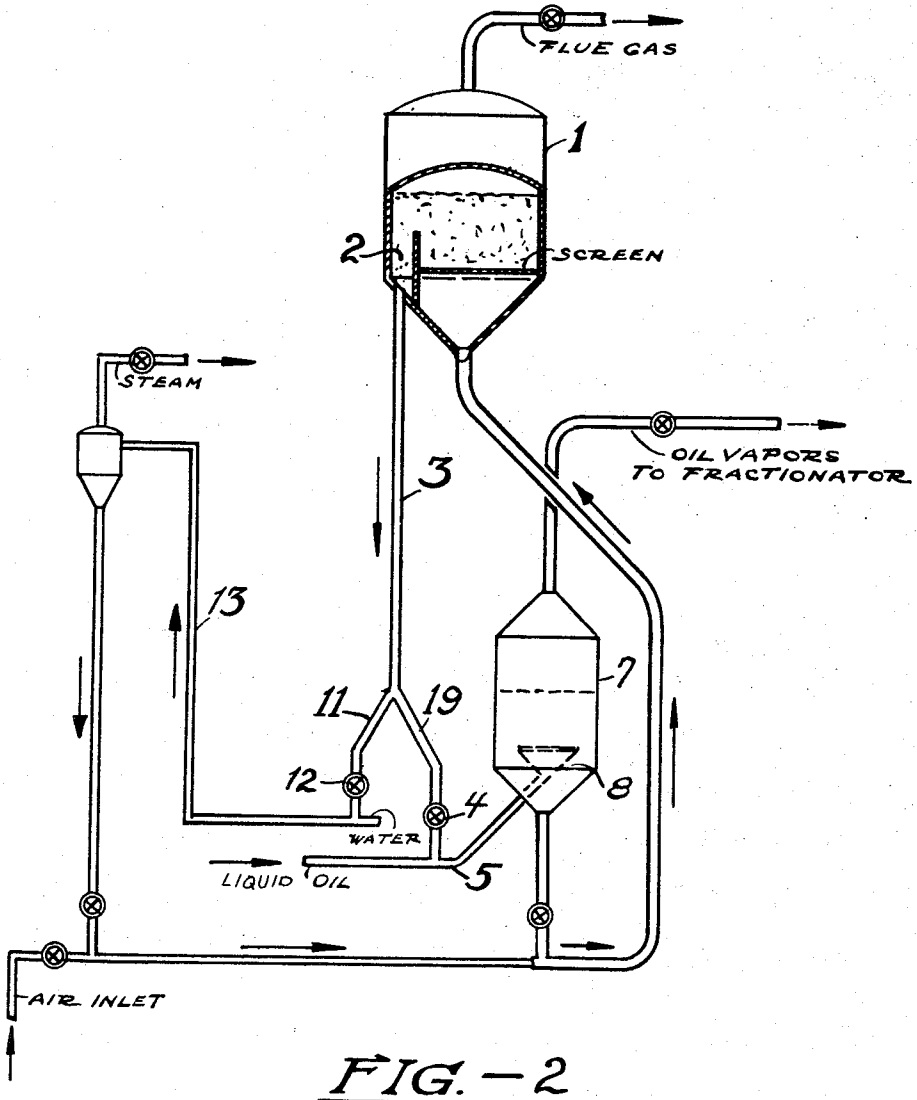

FIG. — 2

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CATALYTIC TREATMENT OF HYDROCARBONS

Filed Nov. 17, 1942 3 Sheets-Sheet 3

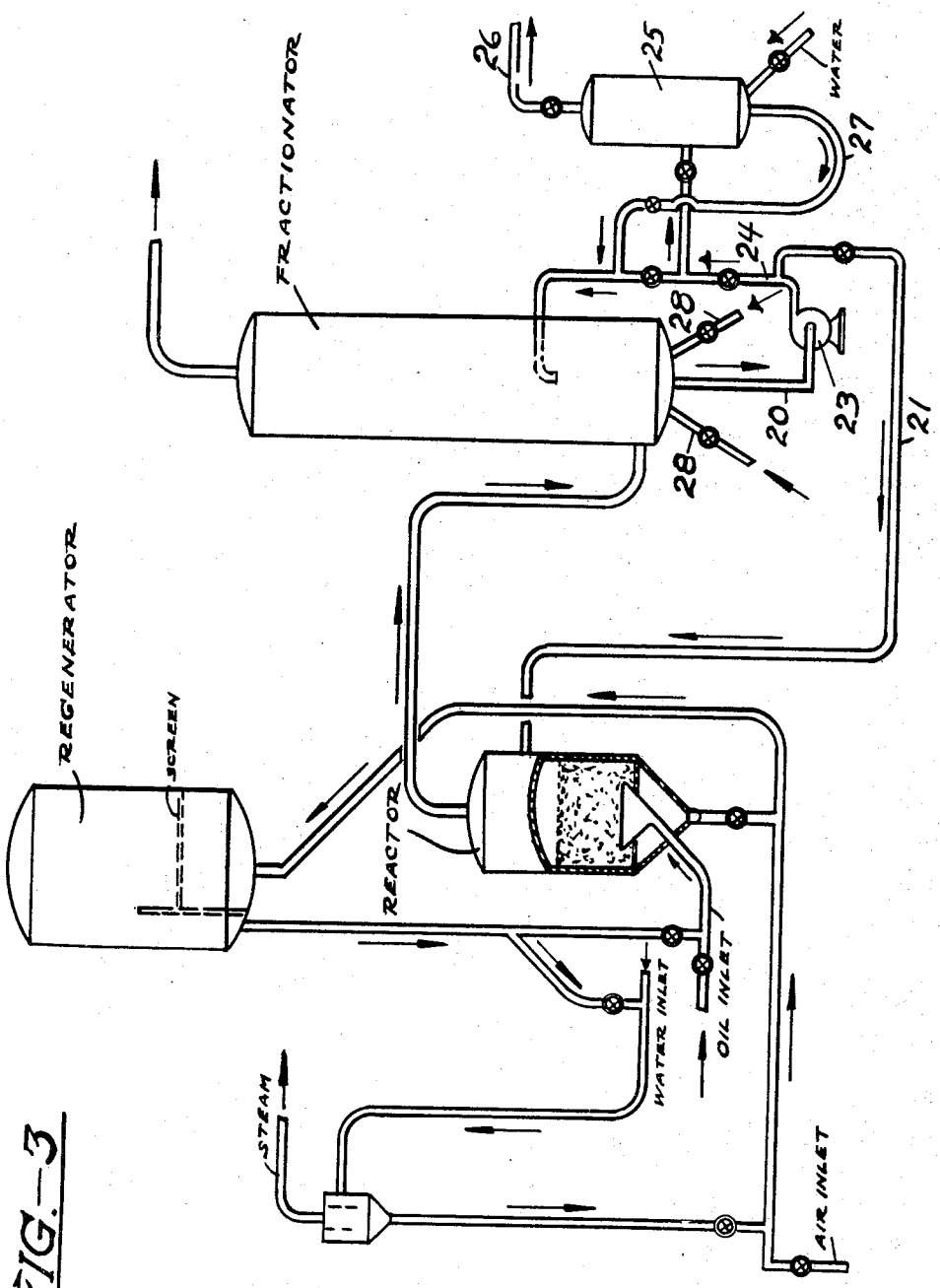

FIG. 3

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UNITED STATES PATENT OFFICE

2,431,462

CATALYTIC TREATMENT OF HYDROCARBONS

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Application November 17, 1942, Serial No. 465,832

1 Claim. (Cl. 196—52)

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The present invention relates to the art of treating hydrocarbon oils catalytically and in particular to the method of controlling catalyst temperature and removing heat by means of injecting water directly into various streams without the use of ordinary heat exchangers, etc. The catalytic treatment of hydrocarbon oils in such processes as catalytic cracking, hydroforming, etc., has been described previously. Several methods are known in which these processes are carried out in what is known as the moving catalyst type of operation. In this type of operation two principal phases are involved; first the treating reaction proper where, for example, a relatively heavy oil is contacted with a catalytic material at a treating temperature of 700–1000° F.; and a second phase in which the catalytic material is exposed to oxygen-containing gas for the purpose of regeneration at say 1000°–1200° F. These two steps are carried out in separate vessels, the catalyst being moved from one to the other by means of such devices as screw conveyors, standpipes, etc. It will be understood that the present invention is not to be limited by the type of conveying system used.

Another hydrocarbon oil treating process to which this invention may be applied is hydroforming, a process in which natural or cracked naphthas are contacted with an alumina base catalyst containing molybdenum oxide or chromia at 800°–1000° F. and 50–500 lbs. per sq. in. pressure with a resulting increase in octane number.

Several heat transfer problems are encountered in processes of this type. One of the principal ones is that of the removal of the heat of regeneration. In earlier designs this problem was solved by circulating a stream of the hot catalytic material through a heat exchanger in which it was cooled, transferring heat to some cooling medium such as boiling water or feed stock to be preheated. Another very excellent solution to the problem is to inject the liquid feed stock preheated to a greater or lesser extent into a stream of hot regenerated catalytic material, the mixture then passing into the reaction zone. In this way, the heat of regeneration was used to preheat the feed stock and to supply the heat of reaction, if any. This second method is, of course, limited to cases where the coke formation in the process is low enough so that the heat to be removed from the regenerator does not exceed the heat which can be removed in preheating the feed stock from room temperature to the desired reaction temperature. The

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present invention, as will be shown below, is a method by which even greater quantities of heat can be removed from the regenerator and may be used to supplement the feed stock preheating scheme.

Another problem encountered in the design of these plants is the removal of heat from the products of the reaction. This is ordinarily done by some type of indirect heat exchange. It will be seen that the methods of this application can be made to offer a considerable simplification in this problem as well.

In accordance with our invention, we have devised a plane which may be operated to crack hydrocarbon oils in the presence of catalyst and to regenerate the spent or fouled catalyst continuously, the temperature of the catalyst undergoing regeneration being accurately controlled without the use of coolers and heat exchangers. We have found that we may inject water at atmospheric or slightly elevated temperature if desired into a stream of hot catalytic solids, thereby generating steam and at the same time cooling the solid material. The solid material is separated from the steam so that the latter may be used while the solid material is returned to the regenerator. In lieu of water other heat exchange fluids such as Dowthern, mercury or hydrocarbon oils may be used.

Figure 1 of the drawings is a diagrammatic illustration of suitable apparatus for removing the heat of regeneration by generating steam in accordance with the present invention.

Figure 2 is a diagrammatic illustration of a modified form of apparatus which permits the elimination of a heating furnace for bringing the charging stock up to reaction temperature.

Figure 3 is a diagrammatic illustration of a suitable combination of apparatus for removing the heat of regeneration as well as the heat from the overhead products leaving the reactor.

In Figure 1, character 1 represents a regeneration vessel in which catalytic material containing a carbonaceous deposit is revivified by contact with air at temperatures in the ranges 1000 to 1100° F. and of 1000 to 1200° F. The catalytic material is in the form of a rather fine powder containing as high as 30% of material smaller than 20 microns in size, although our invention applies when coarser catalyst is used. The regenerated solids are withdrawn through well 2 into standpipe 3, in which the pressure is raised sufficiently so that the catalytic material may be discharged through slide valve 4 and mixed with oil vapors in line 5. The oil vapors

may, for example, be produced by vaporizing part of a reduced crude in furnace 6 and the mixture of catalytic solids and oil vapors are passed into the cracking reactor 7. In this vessel, the desired cracking reaction takes place, the oil vapor products passing overhead to fractionating equipment not shown, while the catalytic material containing a deposit of coke is removed through well 8 and returned to the regenerator through standpipe 9 and return line 10. The catalytic solids are conveyed back to the regenerator by means of a stream of air.

In order to remove heat from the regenerator a portion of the hot catalytic solids withdrawn from the regenerator is transferred by means of standpipe 11 through slide valve 12 into line 13 and the flow through standpipe 11 may be regulated by a restriction at the bottom of the standpipe, such that the pressure above said restriction is higher than that below the restriction. In line 13, the hot solids are contacted with a stream of liquid water. Due to the small size of the solid particles and by means of injecting the water in a number of high velocity jets, the heat transfer from the catalyst to the water is very rapid and it has been demonstrated that the water will be completely converted into superheated steam in a very short length of time and the catalyst will be cooled to a temperature from 400° to 900° F. This mixture of steam and catalyst particles is then passed through a cyclone separator or other separating means. The steam may be withdrawn as a useful by-product of the cracking operation, for example, through line 14. The catalytic solids cooled to a temperature of about 800–900° F. flow through standpipe 15 through valve 16 and are conveyed by means of air through line 10 back to the regenerator. In this way, the heat of the regeneration step is used to generate superheated steam without the use of an indirect heat exchanger.

It may be desirable to install a screw pump or a restriction at the bottom of the standpipe whereby the pressure above the restriction is higher than that below the restriction other means of raising the pressure of the catalyst in line 11 so that the steam may be generated at a higher pressure than would otherwise be the case, thus enhancing its value. Another refinement is the removal of the last traces of catalytic material in the steam leaving the cyclone or other type of separator by means of scrubbing, for example, with liquid water. By spraying the steam containing a trace of catalytic solids with a stream of water, its temperature will be lowered to the saturation point very rapidly, and by condensing a small amount (much less than 1%) of the steam the last traces of powdered material in the gas stream will be transferred to the liquid stream and may be recycled as illustrated in line 17.

A further refinement in this method of generating steam is to strip of flue gas the solid materials being withdrawn from well 2 by recirculating a small amount of the steam production as shown through line 18.

In Figure 2 the invention is applied to a plant in which the furnace is eliminated by using part of the hot regenerated solids for preheating and vaporizing the feed to be cracked. In cases where more than about 5½ to 6% of carbon on feed is produced in the cracking step, the heat to be removed from the regenerator is greater than that needed in the preheating and vaporizing of the oil feed. These high percentages of coke formation are encountered in the cracking of the heavier feed stocks such as reduced crudes, etc. The present invention finds ready application in the removal of the remainder of this heat of regeneration. In Figure 2 the stream of catalytic solids removed from the regenerator through standpipe 3 is divided into two parts, one stream passes through standpipe 19 and slide valve 4, where it is subsequently mixed with the liquid oil to be cracked. The oil is vaporized in line 5 and passed into reactor 7 as in the case of Figure 1. The other portion of the solid material is passed through standpipe 11 and slide valve 12, where it is mixed with liquid water. Steam is produced in line 13 as in the previous case. The cooled solids are transferred by means of air back to the regenerator. This plan is quite inexpensive inasmuch as both the furnace for vaporizing the feed stock and the coolers for removing heat of regeneration are eliminated.

Another phase of the present invention has to do with the removal of heat from the overhead products leaving the reaction vessel. The products of reaction in these plants are generally passed through one or more stages of cyclone separators for the removal of the bulk of the catalytic solids, but even after this they still contain a small amount of catalyst. These oil vapors containing traces of catalyst are then passed through the bottom of a fractionating tower for separation into the various commercial products. These oil vapors enter the tower at substantially a reaction temperature, say 800 to 1000° F. It is a function of the bottom part of the fractionator to remove much of this superheat so that the vapors passing into the main part of the fractionator will be at, say 500 to 600° F., and it is also necessary that the last traces of catalyst be removed from the vapors. Generally, this has been done by installing contacting means such as disc and doughnut plates and contacting the incoming gases in this apparatus with a recirculated stream of heavy bottoms. This recirculation stream is passed through a heat exchanger of some kind, generally a waste heat boiler, for the removal of excess heat. The catalytic solids are removed in the scrubbing operation and a small stream of slurry is returned to the reaction vessel so that, by this means, the catalytic solids may be returned to the cracking system.

Figure 3 shows the usual reactor-regenerator-fractionator system. The hot slurry stream is withdrawn from the bottom of the fractionator through line 20 and pump 23. A small portion of this stream then flows through line 21 and is returned to the reactor bearing the recovered catalytic solids. The remainder of this slurry stream is passed through line 24 into the contacting tower 25. Liquid water is introduced into the bottom of this tower through a number of small openings and at a carefully controlled rate. The water is very rapidly vaporized and the oil stream cooled thereby so that a stream of steam may be withdrawn through line 26 while the cooled liquid oil is removed through 27 and returned to the fractionator for recontacting with the incoming hot reaction products.

One of the important features of this invention is that contacting tower 25 may be operated at any desired pressure up to the condensing pressure of the steam. For example, although the fractionating tower may be operating at say 5 lbs./sq. in. gauge the oil stream may be pumped by means of pump 23 to 200 lbs./sq. in. gauge.

In this way the steam produced by this process is just as valuable as that which would be produced in an expensive heat exchanger and is somewhat more valuable due to the fact that it is superheated as well. Saturated or only slightly superheated steam can be produced by proper choice of water and oil flow or by adjusting the contacting tower pressure.

In order to prevent or at least to greatly reduce the quantity of oil vapors passing into the steam phase in contacting tower **25**, it is desirable to add stripping steam as shown in line **28** into the bottom of the fractionating tower. This steam removes the lighter constituents of the recycled oil into the fractionating tower itself.

By combination of the concepts of Figure 2 with those in Figure 3, it will be seen that the ideas of this invention permit the elimination of the three main heat exchangers; (1) the oil vaporizer, (2) the catalyst coolers for removing regeneration heat; and (3) the exchanger used to remove heat from the reactor overhead stream.

To recapitulate, the present invention relates broadly to transferring heat from the regeneration side of a continuous catalytic cracking operation to the cracking side through the medium of a directly applied liquid such as water. Where water is used and where pressure is employed superheated and high pressure steam may be obtained which is an important utility in an oil refinery. By managing the heat balance in the manner previously indicated, a plant may be operated with a minimum of equipment and utility, thus of course effecting important economies in the operation of a plant of the character hereinbefore described.

It will be understood that in a large plant the various temperature controls which must be maintained will depend on a number of factors including the nature of the oil. It will be apparent, therefore, that the amount of water or other liquid which must be used for cooling the catalyst will depend on how much coke is burned during the regeneration, for the critical fact in heat generation during regeneration of the catalyst obviously depends on the amount of carbonaceous materials burned. Consequently, it will require calculations to apply the principles of this invention to a given cracking operation using a given feed stock and a given catalyst, but these details may be readily solved by a competent engineer and he will be enabled to put into operation the proper heat balances by applying sufficient cooling medium to the hot regenerated catalyst to abstract the desired amount of heat, by first observing the amount of such heat available as a result of regenerating the catalyst and, consequently, it is deemed desirable to simplify the present explanation by eliminating numerical data on a few runs since the number of possible variables in a system such as the present one is so great that such data would not be too helpful. As a general guide, however, we have set forth hereinbefore the fact that a certain amount of coke should be laid down on the catalyst during cracking and, in general, the catalyst should be used in cracking until it contains that amount of coke necessary to supply sufficient heat to support the cracking reaction or a substantial portion thereof. We have also pointed out that where the stock is one which produces 5½ to 6% by weight of carbon based on the feed stock, the heat removed from the regenerator is greater than that needed in the preheating and vaporization of the oil. This, for example, is the situation

where heavy crudes are cracked, and it will be realized that in cracking gas oil the coke formation based on feed is much less and, therefore, the heat available is much less. However, as a guide it may be stated that where the catalyst to oil ratio by weight in the reaction zone is from 2 to 20 parts of catalyst per part of oil, the amount of coke deposited on the catalyst as it enters the regenerator may vary from 0.1 to 2% by weight based on the catalyst. It will be further understood, of course, that in cracking operations the temperatures vary; thus, for producing aviation base stock, the temperatures are in the neighborhood of 800° F. to 825° F.; for producing motor gasoline they may vary from 800° F. to 950° F., and for cracking to form butylenes the temperatures may be as high as 1000° F. Hence it can be seen that for any particular cracking operation, the principles of this invention must be adapted responsive to the conditions of operations necessary.

Many modifications of our invention falling within the scope thereof may be made by those who are familiar with this art without departing from the spirit thereof.

What we claim is:

In a method of causing a chemical reaction to take place in vapor phase in the presence of a finely divided catalyst in which the vapors pass through said reaction zone in the presence of said finely divided catalyst suspended in said vapors, and in which the catalyst is regenerated with the production of heat in a regeneration zone, the improvement which comprises removing at least a portion of the heat evolved in the regeneration zone by withdrawing catalyst from the regeneration zone through a vertical standpipe through which the catalyst flows in a downward direction and through which the catalyst flow is regulated by a restriction at the bottom of a standpipe such that the pressure above the restriction is higher than in a cooling zone below the restriction, the catalyst in the vertical standpipe being out of vapor contact with the catalyst in the cooling zone, forcing liquid water into the cooling zone where it is converted into high-pressure steam, separating the catalyst from the steam and returning the separated, cooled catalyst to the regeneration zone.

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