

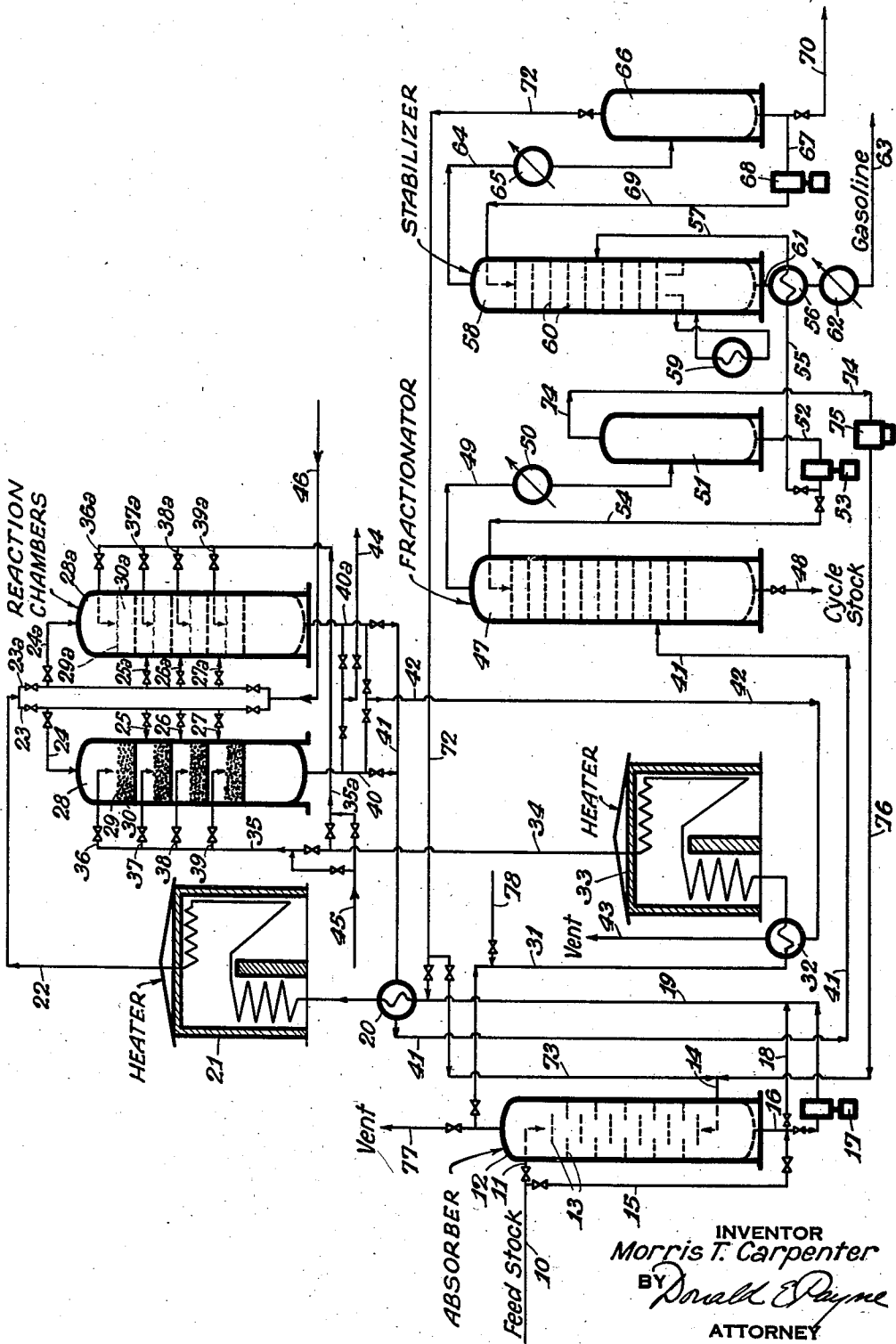
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CATALYTIC CONVERSION APPARATUS

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CATALYTIC CONVERSION APPARATUS

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This invention relates to catalytic conversion apparatus and it pertains more particularly to the catalytic conversion of hydrocarbons of various kinds and boiling ranges into high quality motor fuel.

An object of my invention is to provide improved means for supplying the heat required for catalytic cracking. A further object is to provide a means for using simple catalyst chambers for catalytic cracking, thereby avoiding the expensive, complex cumbersome chambers that have heretofore been deemed essential. A further object is to utilize more effectively the normally liquid and normally gaseous portions of feed stock to obtain maximum yields of highest quality motor fuel therefrom. A further object is to improve the thermal efficiency of a catalytic cracking system, to utilize available heat in all parts of the system to the fullest extent, and at the same time to avoid the necessity of using an extraneous heat transfer fluid system.

It has long been known that catalytic cracking will yield high quality motor fuels. Economically, however, such processes have not been able to compete successfully with thermal processes because of: (1) the expensive construction, repair and operating costs of complicated catalytic chambers, (2) the expense and difficulty of catalyst regeneration, and (3) the poor heat economy of prior catalytic systems. An object of my invention is to overcome these difficulties and to place catalytic cracking on a sound economic basis.

In practicing my invention I proceed directly contrary to the current notion that heat exchange tubes, fins, etc., must be closely spaced throughout the catalyst mass. Instead of simultaneously contacting the catalyst throughout the system with hot feed stock to effect instantaneous and simultaneous cracking in all parts of the system, I effect the cracking in a gradually advancing hot zone or wave front which starts at one end of the chamber and gradually moves to the other end thereof.

To supply the heat for the cracking reaction I superheat the incoming stock to a certain extent and supply the rest of the necessary heat by the introduction of super-heated gases at that point of the system at which the cracking is occurring. As the catalyst in the top of the chamber becomes spent (due to carbon deposition or to other causes), the reaction at that point practically ceases, and the reaction zone moves along the chamber to the next adjacent

portion of the catalyst. To avoid too long a time of contact with the hot catalyst, and to avoid excess coke deposits, both the feed and the hot gases may be by-passed around the spent catalyst and introduced directly into the current reaction zone. The hot cracked products do pre-heat the catalyst beyond the reaction zone, but the necessary heat to effect substantial cracking is supplied only to the zone where it is desired for cracking to take place. Thus there is no danger of over-cracking due to too long time of contact.

Revivification is also effected in a gradually moving zone or wave front, the temperature and oxygen content of regeneration gases being regulated to prevent over-heating. In regeneration cool gases may be used to remove the exothermic heat of combustion, just as in the case of catalytic cracking hot gases are used to supply the necessary endothermic heat. The hot spent regeneration gases give up their heat to gases entering the catalytic cracking system.

A feature of the invention is the utilization of hot gases rich in hydrogen, both for maintaining the desired temperature at any given reaction zone and to prolong the life of the catalyst. The hydrogen tends to keep the catalyst clean and to improve the quality and yield of the finished products.

Another feature is the saving in compressor costs and the increase in gasoline yields effected by the use of an absorber to pick up, in the incoming stock, condensable hydrocarbons separated from the reaction products or obtained from other sources. Gases from a high pressure stabilizer may be either returned to this absorber at relatively high pressure or introduced with the feed stock to effect what is commonly termed gas reversion, i. e., a chemical combination of gases with liquids to form high quality motor fuels of intermediate boiling range.

The invention will be more clearly understood from the following detailed description read in connection with the accompanying drawing which forms a part of this specification, and which shows simply a flow diagram with the furnaces, catalyst chambers, towers, etc., diagrammatically represented in vertical section.

The invention will be described as applied to the conversion of Mid-Continent gas oil into high quality, high octane number gasoline. It should be understood, however, that the invention is equally applicable to all cracking stocks, particularly stocks of the naphtha through gas

oil boiling range. Heavier stocks, including residual stocks, may be catalytically cracked and normally gaseous hydrocarbons may be caused to react in the cracking process to effect what is called gas reversion.

The gas oil feed stock is introduced through line 10 and branched line 11 to the top of absorber tower 12 which is provided with suitable baffle or bubble plates 13, and into which hydrocarbon gases are introduced at the base through line 14. If desired, some or all of the feed stock may be by-passed through line 15 to line 16 through which the enriched feed stock is withdrawn from the absorber. The charging stock is then pumped by pump 17 or passed through line 18 to line 19, heat exchanger 20 and pipe still or equivalent heater 21. This still is preferably operated at approximately atmospheric pressure and at a temperature of about 800 to 925° F., preferably about 850° F. It should be understood, however, that temperatures as high as 1050° F. may be used, particularly if higher pressures are employed, and the pressures may range from atmospheric to 1500 pounds per square inch. The hot gases and vapors from the pipe still are passed from the heater through line 22 to headers 23 or 23a, which have branch lines 24, 25, 26, 27 and 24a, 25a, 26a and 27a, respectively. These branch lines lead to reaction chambers 28 and 28a at points above the various catalyst beds 29 and 29a, which are supported on conventional screen supports 30 and 30a. These reaction chambers may be from about 20 to 50 feet high and about 5 to 10 feet in diameter. The trays may be spaced at intervals ranging from about 1 to 2 feet and the catalyst on each tray may vary in thickness from 4 or 5 inches to about a foot or more. It will thus be seen that I have provided a series of contiguous catalyst beds, each separated from adjacent beds by an open space, and I have provided means for introducing hot feed gases above the catalyst on each tray.

As a catalyst I prefer to employ small cylindrical pellets about $\frac{1}{8}$ to $\frac{1}{4}$ of an inch in height and diameter, which pellets are made by admixing acid treated Death Valley clay with about 25% of water to form a slurry, forcing this slurry through an orifice under about 1000 pounds pressure to give a "spaghetti," and baking this spaghetti for several hours at about 1050° F. It should be understood, however, that I may use any activated hydrosilicate of alumina catalyst; other natural clays or acid-treated natural clays may be substituted for Death Valley clay, and synthetic clays may be prepared by precipitating alumina on silica gel. I prefer to employ about 15 to 40 mol. % of alumina in the composition, about 25% to 30% usually being the optimum. This optimum percentage of alumina may be obtained in natural clays such as Olmstead, Atapulgus, Floridin earth, montmorillonite, Filtrol, diatomaceous earth, fuller's earth, etc., by acid or other chemical treatment. Activated clays may be used as such or they may be impregnated with from about 1 to 10% of oxides of nickel, copper, manganese or other catalytic materials which have the known properties of promoting hydrogenation and desulfurization and/or which may promote catalyst regeneration. It should also be understood that instead of the clay type catalysts I may employ magnesium chromite, boron silicate or any other known catalytic cracking catalyst of proven effectiveness.

The particular catalyst per se forms no part of my present invention.

Gases rich in hydrogen and containing substantial quantities of methane, ethane, ethylene, etc., are withdrawn from the top of absorber 12 through line 31 and passed through heat exchanger 32, pipe still or equivalent heater 33, and thence through line 34 to manifolds 35 and 35a. These manifolds are provided with valved side lines 36, 37, 38 and 39, 36a, 37a, 38a and 39a, respectively, which communicate with the open spaces above each catalyst bed in the same way that valved branch lines 24 to 27 and 24a to 27a, respectively, communicate therewith.

Fluids from the reaction chambers may be selectively withdrawn through lines 40 and 40a through line 41 which leads through exchanger 20 to fractionator 47. They may likewise be selectively withdrawn through line 42 which leads through heat exchanger 32 to vent line 43. They may also be selectively withdrawn through line 44.

Hot gases, preferably flue gas containing the desired amounts of oxygen, may be introduced through line 45 selectively into manifold 35 or manifold 35a. A purging fluid such as steam may be introduced through the same lines. Cold regeneration gases may be introduced through line 46 selectively into manifold 23 or 23a. It should be understood, of course, that gases of any composition and at any desired temperatures may be introduced at desired points in the reaction chambers, either through line 45 or line 46.

It should be understood that while I have disclosed only two reaction chambers, I contemplate the use of any number of such chambers as may be required for a given installation, due consideration being given to the time necessary for catalyst regeneration. While one chamber is "on stream," one or more of the chambers are being revived. This is familiar practice and needs no further detailed description.

As hereinabove stated, I introduce the hot charging stock gases at about 850° F. through branch line 24 into the top of reaction chamber 28, the valves in lines 25, 26 and 27 being closed and catalyst chamber 28a being cut off for re-vivification. Since the contained heat of the charging stock may not be sufficient to supply the endothermic heat of cracking, I introduce through branch line 36 superheated gases from pipe still 33, these gases being of a temperature of about 1000 to 1500° F. With the heat thus imparted in the top catalyst bed, the gas oil will crack to form the desired gasoline compounds, together with certain radicals which may chemically combine with the introduced gases to form additional amounts of high quality gasoline. The cracked gasoline and gases from the top catalyst zone passes down through the other zones of the tower, thus preheating them and bringing them up to reaction temperature. Since the lower catalyst beds are at a lower temperature than that required for cracking, there will be no appreciable decomposition of the reaction products formed in the upper bed, and, in fact, there may be a partial hydrogenation of the cracked gasoline as the components move downwardly through the tower.

When the upper catalyst bed becomes substantially de-activated, because of coke deposits, etc., I open valve 25 to by-pass part or all of the incoming hot stock around the spent catalyst zone. I may at the same time open valve 37 to

supply super-heated fixed gases for supplying the endo-thermic heat of cracking; I prefer, however, to have these gases and unreacted vapors pass through the top catalyst layer until that layer is substantially spent. Similarly, I progress from zone to zone throughout the entire length of the column and I regulate the reaction temperature in each zone by the relative amounts of charging stock and super-heated fixed gases which are introduced into that zone. I may, of course, effect cracking substantially simultaneously throughout the length of the column, but this renders temperature control difficult to obtain, and it also makes it necessary for the cracked products from the top of the tower to have too long a time of contact with the catalyst at reaction temperature. My invention relates primarily to the catalytic conversion of the hydrocarbons in a particular zone which gradually moves from the top of the tower to the bottom thereof. By effecting the reaction in this manner the tower can be operated for a long period of time before regeneration is necessary, and accurate temperature control can be obtained all along the line.

While reaction chamber 28 is "on stream," chamber 28a is purged, revived and again purged preparatory to once more going "on stream." The purging may be effected by steam or by vacuum. Regeneration is effected by burning the carbon from the catalyst at a temperature of not higher than about 1000 to 1050° F. This temperature may be accurately controlled by regulating the amount of oxygen in the hot flue gases which are preferably introduced through line 45, header 35a and branch lines 36a, etc. It should be understood, however, that the exothermic heat of combustion can be dissipated in part by the use of cold gases from line 46, header 23a and branch lines 24a, etc. Here, again, I use the parallel systems for introducing fluids of different temperatures in regulated amounts to maintain the desired temperatures at each and every point of the catalyst chamber. If any catalyst bed tends to become overheated the hot gases are immediately shut off and cold gases introduced at that point. The valves in the side lines may be automatically operated in accordance with temperature conditions in the catalyst bed. Such automatically operated valves are well-known to those skilled in the art and they will therefore not be described in further detail.

The hot gases which leave the reaction chambers at about 1050° F. are passed through line 42 to heat exchanger 32 wherein they give up their heat to the gases entering the system through line 31. This effectively utilizes the heat of regeneration for supplying the endothermic heat of cracking. Sometimes, to produce better heat transfer coefficients, it may be desirable to use the hot spent regeneration gases for generating steam.

After regeneration, the catalyst chamber is purged, the purged gases being removed through vent line 44. Catalyst chamber 28a is then ready to go "on stream" as soon as all of the catalyst beds in chamber 28 have become spent.

Just as exchanger 32 picks up the heat from the spent regeneration gases, so that the heat may be utilized for further catalytic cracking, heat exchanger 20 provides for the transfer of heat from cracked products to the feed stock entering pipe still 21. I have found that the above arrangement of heat exchangers is very effective and efficient—playing an important part

in placing the catalytic process on an economically sound basis. The reaction products which have been cooled in exchanger 20 are then passed through line 41 to fractionator 47 which may consist of a column with from 10 to 40 trays or bubble plates. Material above the gasoline boiling range is withdrawn from the base of the fractionator through line 48. This material, called "cycle stock," may be stored for subsequent catalytic cracking in the same system, it may be passed to another catalytic or thermal cracking unit, or may be recycled with the incoming feed stock.

Gasoline and gases from the top of fractionator 47 are conducted through line 49 to water condenser 50 which liquefies most of the gasoline, a large part of the butanes and some propane and lighter hydrocarbons. These liquids are separated in separator 51, a part of them being recycled through line 52, pump 53 and line 54 as reflux to the top of the fractionator tower. The major part of the liquefied products are passed through line 55, exchanger 56 and line 57 to an intermediate point of stabilizer tower 58. This tower is preferably operated at about 200 to 400 pounds pressure per square inch and is provided with a suitable reboiler 59 at its base. Here again we may employ from about 10 to 40 bubble plates 60. Stabilized gasoline is withdrawn from the base of the tower through line 61, heat exchanger 56, water cooler 62 and line 63 to a suitable storage tank. This gasoline is characterized by an extremely low sulfur content, a stability against oxidation and gum formation, and an extraordinarily high octane number which may range from 75 to 95.

Vapors from the top of the stabilizer are withdrawn through line 64 to the water condenser 65, wherein they are partially liquefied, the liquids being separated from the gases in pressure separator 66. A portion of these liquids are recycled through line 67, pump 68 and line 69 for reflux in the stabilizer tower. The remaining liquids are withdrawn through line 70; these liquids may be used or sold as liquefied gas since they contain chiefly propane, propylene and butanes, or they may be recycled to the system either with the incoming feed stock or with liquids in line 19 entering heat exchanger 20.

The gases from the top of pressure separator 66 may be recycled through line 72 to line 19 (since the gases are under sufficient pressure to avoid the necessity of compression), or they may be introduced through line 72 and line 73 through line 14 in absorber 12. The bulk of the gases introduced through line 14, however, will usually come from low pressure separator 51, the gases being withdrawn therefrom through line 74, compressed by compressor 75 and introduced through line 76 to line 14 at the base of the absorber. These gases may contain upwards of 20% of hydrogen. By passing them through the absorber, all of the condensables are removed therefrom before they are heated to the high temperatures which might be destructive of propanes and butanes. If methane or other fixed gases tend to accumulate in the system they may be vented therefrom through line 77 at the top of absorber 12. On the other hand, if the nature of the charging stocks makes possible the consumption of more gases than are produced, additional hydrogen or gaseous hydrocarbons may be introduced into the system through line 78.

While I prefer to operate the absorber at a pressure of about 50 to 100 pounds per square

inch, it should be understood that higher pressures may be used, particularly when it is desired to incorporate large amounts of gaseous hydrocarbons into the liquid feed stock to effect what is commonly referred to as gas reversion. The catalysts and operating conditions for catalytic cracking seem to effect to a considerable extent the combination of normally gaseous hydrocarbons with normally liquid hydrocarbons to form high quality motor fuels of intermediate boiling range. Likewise, the hydrogen content of the gases introduced through headers 35 and 35a not only has a noticeable effect in keeping the catalyst clean for a relatively long period of time, but it appears to effect a certain degree of hydrogenation of the reaction products.

While I have described in detail a preferred embodiment of my invention, it should be understood that I do not limit myself to any of the details hereinabove set forth except as defined by the following claims, which should be construed as broadly as the prior art will permit.

I claim:

1. In a catalytic cracking system wherein one catalyst chamber is "on stream" while another catalyst chamber is undergoing regeneration, means for pre-heating normally liquid charging stock by exchanging it with cracked products from the chamber "on stream," means for pre-heating normally gaseous charging stock by heat exchange with hot regeneration gases from the chamber undergoing regeneration, means for further heating a normally liquid charging stock to a temperature of about 800 to 925° F., means for further heating the normally gaseous charging stock to a temperature of about 1000 to 1500° F., and means for introducing in regulated amounts both the normally liquid charging stock and the normally gaseous charging stock into the catalyst chamber which is "on stream."

2. A catalytic hydrocarbon conversion system which comprises a plurality of catalyst chambers, a plurality of catalyst beds in each chamber, a first manifold for each chamber with means communicating with the top of each catalyst bed therein, a second manifold for each chamber with means communicating with the top of each catalyst bed therein, a fluid exit line at the base of each chamber, a pipe still coil for heating oil to a temperature of at least about 800 to 925° F., a transfer line from the pipe still

coil to said first manifolds, a second pipe still coil for heating a hydrogen-containing gas to a temperature of about 1000 to 1500° F., a transfer line connecting said second heating coil to the second manifolds, a fractionation system, means for discharging reaction fluids from the fluid exit line of each chamber to said fractionation system, an absorber, means for introducing an oil at the upper part of said absorber, means for passing a gas from said fractionation system to the lower part of said absorber, means for passing liquids from the base of said absorber to said first named pipe still coil, means for passing gas from the top of said absorber to said second pipe still coil, a valve between each transfer line and each manifold connected thereto whereby fluids from said pipe still coils may be selectively passed through one catalyst chamber while another catalyst chamber is undergoing regeneration, valves for closing the connection between the fluid exit lines and the fractionation system whereby a catalyst chamber undergoing regeneration can be disconnected from the fractionation system, means for introducing a regeneration gas through one of said manifolds which has been disconnected from a pipe still coil transfer line, and means for withdrawing regeneration gases through the fluid exit line.

3. A catalytic hydrocarbon conversion system which includes a plurality of catalyst chambers, means including a first heat exchanger and a first pipe still heating coil for heating a hydrocarbon charging stock to reaction temperatures, means for selectively introducing said heated charging stock into one of said catalyst chambers, means including a second heat exchanger and a second pipe still heating coil for superheating a gas to a temperature of about 1000 to 1500° F., means for selectively introducing said gas into the same catalyst chamber into which the preheated charging stock is introduced, means for regenerating catalyst in the catalyst chamber in which the charging stock is not being introduced whereby hot regeneration gases are produced, means for passing said hot regeneration gases through said second heat exchanger, and means for passing hot reaction products from the other reactor through said first heat exchanger.

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