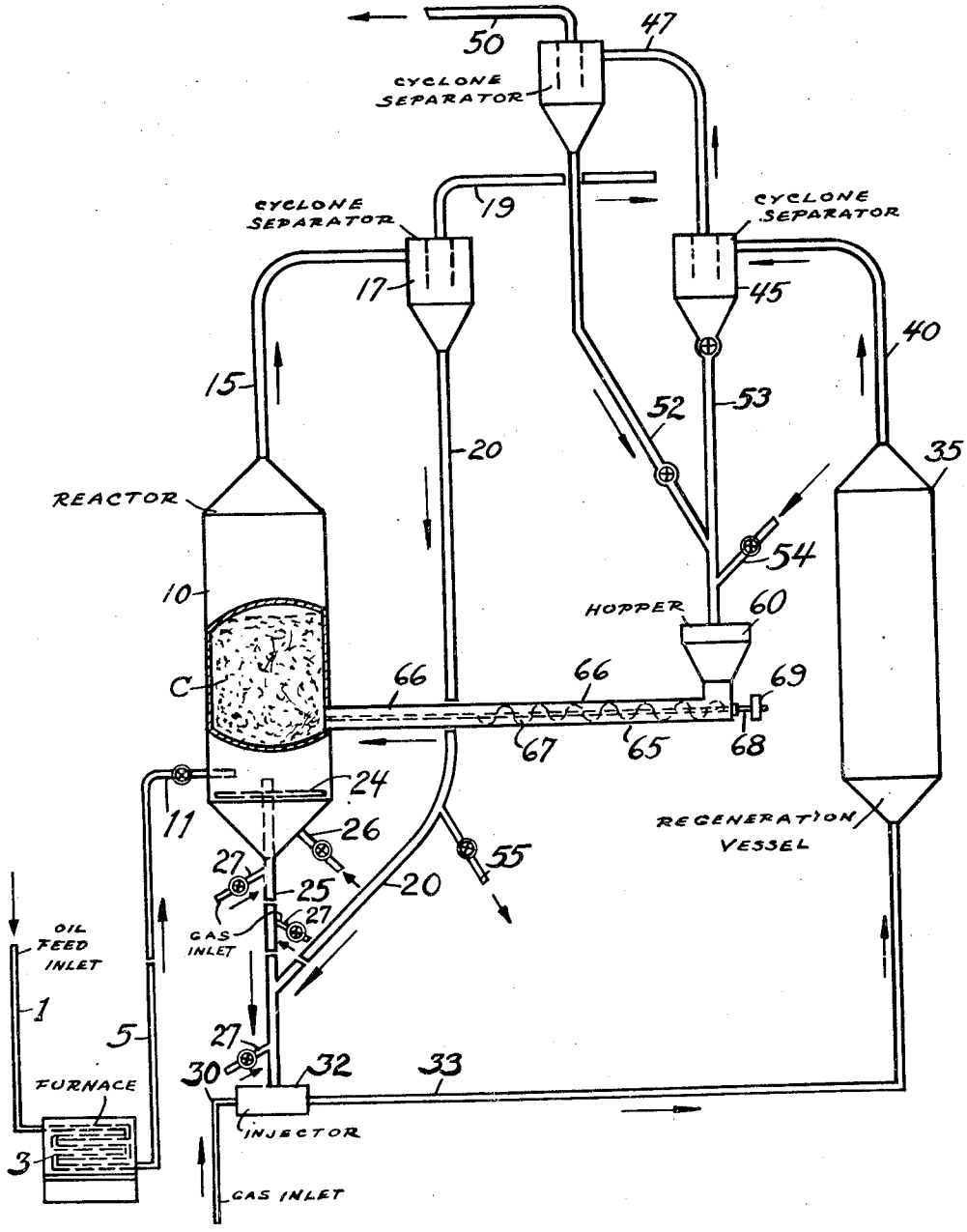
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CHEMICAL PROCESS FOR THE CATALYTIC CONVERSION OF HYDROCARBON OILS

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CHEMICAL PROCESS FOR THE CATALYTIC CONVERSION OF HYDROCARBON OILS

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2 Claims. (Cl. 196—52)

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This application is a continuation-in-part of my copending application, Serial No. 363,866, filed November 1, 1940 now abandoned.

The present invention relates to improvements in the art of treating heavy hydrocarbon oils catalytically and for the purpose of converting them into relatively lower boiling range hydrocarbons, including hydrocarbons boiling within the gasoline range. For example, the present invention includes the injection of a preheated reduced or topped petroleum crude oil onto an active catalyst such as magnesia-silica catalyst under conditions such that the heavy hydrocarbon oil is cracked to produce a gasoline and a coke which is deposited on the catalyst.

Heretofore, it has been the practice in producing gasoline, either thermally or catalytically, to use as a charging stock, a gas oil, that is to say, a hydrocarbon oil boiling substantially within the range of from 400–900° F. Such a gas oil was previously obtained by distilling the crude to obtain a virgin gas oil and then viscosity reducing or coking the topped or reduced crude thermally to produce a further quantity of gas oil.

My present invention obviates the necessity of coking or viscosity reducing a topped or reduced crude, for it provides means whereby such an original or topped crude may be preheated to incipient cracking temperatures or temperatures below cracking temperatures, and thereafter sprayed onto an active catalyst, preferably a magnesia-silica gel.

The main object of my present invention therefore, is to produce a high quality gasoline by cracking an oil catalytically in a continuous operation in which the preheated oil is injected in at least partial liquid form onto a catalyst under conditions such that the oil is reduced to coke which is deposited on the catalyst and volatile products, including a substantial quantity of gasoline of high octane number.

My invention will be best understood by reference to the accompanying drawing which shows diagrammatically a flow plan illustrating a method of carrying my invention into practical effect.

Referring in detail to the drawing and an illustrative example, a topped East Texas crude, a crude having an A. P. I. gravity of about 25°, in this specific case, is fed into the system through line 1 and thence heated in a furnace 3 to a temperature of about say, 900° F. or any temperature within the cracking range. The oil is preferably fed through the coil at such a flow rate that substantially no cracking takes place within

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the coil or in any event to prevent more than 10% conversion of the charged oil to gasoline and thereafter the heated oil is withdrawn through line 5 and discharged into the bottom of a reactor 10. The reactor 10 contains a mass of catalyst C, say a mixed or plural magnesia-silica gel containing 20% to 60% magnesia (the balance silica) by weight. The entering liquid oil is sprayed through distributing pipe 11 into the body of the mass of catalyst C. The catalyst which is in powder form and has a particle size of from about 50 to 400 mesh, is introduced into the reactor by means of a screw-conveyor 65, in a manner hereinafter more fully described, at a temperature above that of the incoming oil, say at about 1100° F. The amount of catalyst fed to and maintained in the reactor is such as to increase the temperature of the oil to an average temperature of about 980° F. within the reactor; that is to say, where the catalyst which is at an inlet temperature of about 1100° F. and the oil at a temperature of about 900° F., as it enters the reactor should be fed to the reactor at a ratio of about 5.5 parts by weight of catalyst, per one part of oil, whereupon after admixture, the oil acquires a temperature of about 980° F.

In the reactor the catalyst is maintained in a state of turbulence or ebullient motion by a gasiform material such as steam. The gasiform material is introduced through pipe 26 and flows upwardly through the reactor 10 at a velocity of from about 0.5 to 10 feet per second, thus imparting the above-mentioned turbulence. The concentration of catalyst is such in the lower part of the reactor that a cubic foot of the vapors, steam and catalyst weighs from 15–25 lbs. In the upper part of the reactor the concentration of catalyst is much less, so that vapors may be withdrawn from the top containing only about say 0.025 lb. of catalyst per cubic foot of vapors, or thereabouts.

Under the conditions stated, the charging oil undergoes conversion to form a solid carbonaceous product or a coke which is deposited upon the catalyst and also vapors containing gasoline, gas oil and normally gaseous hydrocarbons. The cracked vapors are withdrawn from the reactor through line 15, discharged into a cyclone separator 17 to remove entrained catalyst and thence withdrawn from separator 17 through line 19 and delivered to a recovery system (not shown) to recover the gasoline and other desired products. The catalyst is withdrawn from cyclone separator 17 through line 20 and thence discharged

into catalyst draw-off line 25. Catalyst which has become contaminated as a result of contact with the oil in reactor 10 is substantially constantly withdrawn from the reactor 10 through said line 25 extending above grid 24. To purge the catalyst in line 25 of hydrocarbon vapors, steam may be injected into pipe 25 through branch pipes 27. It will be understood that instead of withdrawing catalyst from the bottom of the reactor, as shown, it may be withdrawn from the side of the reactor. The withdrawn catalyst is mixed with a regeneration gas introduced into the system through line 30, in injection means 32 to form a suspension, which suspension is then discharged through line 33 into a regeneration vessel 35. The regeneration gas introduced into line 30 may be ordinary air but preferably, in order to avoid overheating the catalyst, is a mixture of air and flue gas in such proportions as to form a mixture containing from 5–10% free oxygen. As I have shown the regeneration vessel, the flow of catalyst and gas is concurrent upward and eventually, all of the catalyst being withdrawn overhead through pipe 40. However, it is preferable to regulate the gas velocity in vessel 35 say within the range of from 0.5 to 10 feet per second so that while the catalyst moves generally upward, the catalyst moves at a slower rate than does the gas and hence remains in the regenerator for a longer period of time. This effect can be attained by fixing the gas velocity as previously indicated. Of course, it is also possible to feed fouled catalyst by means of a screw directly into the regenerator, in a manner analogous to that in which catalyst is fed to the reactor 10, as shown and described herein. The regenerated catalyst is withdrawn in the modification shown, from regenerator 35 through line 40 and discharged into a cyclone separator 45. The catalyst is separated from the regeneration products in cyclone separator 45 to the extent of about 90% of its catalyst content and the flue gas is withdrawn through line 47 and discharged into a second cyclone separator where a further quantity of the catalyst is separated from the flue gas, which flue gas may be then rejected from the system through line 50. The regenerated catalyst recovered from cyclones 45 and 47 is delivered by gravity through lines 52 and 53 to a feed hopper 60 which is in communication with a catalyst feeding means 65, such as an ordinary screw conveyor consisting of a casing 66, a screw member 67 attached to a shaft 68 carrying a pulley 69 adapted to be driven by a motor or other motivating means. The catalyst is fed into the reactor and is at a temperature of about 1100° F., as previously indicated. As also previously indicated, the catalyst is preferably fed to the reactor at a rate such that about 5.5 parts of catalyst per part of oil by weight forms the mixture in reactor 10. Obviously a greater or lesser amount of catalyst may be fed to the reactor, depending upon the final temperature conditions desired therein, but normally it is desirable in the process herein described to operate at temperatures above 850° F. in reactor 10 and preferably above 900° F. In some process it may be desirable to operate at 1200° F. or higher to produce increased quantities of normally gaseous and liquid olefins.

It is also pointed out that it is desirable to feed a minimum of 5 lbs. of oil per hour per lb. of catalyst in the reactor because this condition gives a desirable "product distribution," that is, maximum quantities of desired products such as gasoline and gas oil.

To recapitulate, my present invention relates to a process of catalytically cracking a heavy petroleum oil, and it is to be distinguished from operations in which the feed stock to a catalytic cracking operation is wholly vaporized. My process involves the injection of a charging hydrocarbon oil, at least partly in liquid phase, into a mass of catalyst under conditions such that the liquid oil is reduced to coke and volatilizable hydrocarbons, including 30–50%, based on the feed stock, of hydrocarbons boiling within the gasoline range having an octane rating of 91–95 according to the method of the Committee on Fuel Research, A. S. E. "Research 1939." I prefer to use a catalyst which is more active than acid treated clay, namely a catalyst such as a magnesia-silica gel, principally for the reason that this catalyst may be regenerated safely and without injury to the catalyst at temperatures as high as 1100° F. or higher, say at 1200° F. This hot catalyst recovered from the regeneration zone is fed directly and substantially uncooled to the reaction zone where use is made of its sensible heat to superheat the heavy oil undergoing conversion and to compensate for the heat losses due to the endothermic nature of the reaction taking place in reactor 10.

Many modifications of my invention may be made without departing from the spirit thereof. In the first place I may of course, use a catalyst less active than the magnesia-silica gel. For example, I may use an ordinary acid treated clay or various other known cracking catalysts. Furthermore, the product distribution for the silica-magnesia catalyst is superior at temperatures above 900° F. This is an important aspect of my invention. The pressure conditions prevailing within reactor 10 are substantially atmospheric pressure, or such pressure as is necessary to force the vapors through the system. However, in some cases it is desirable to reduce the cost of the fractionating system and the gas compression equipment by operating at pressure higher than atmospheric. The decreased cost in this equipment will be more than the increased cost of additional regenerating equipment for the higher coke yields resulting from higher pressures. With reduced crudes from crudes containing less than 15% boiling above 950° F. pressures above 10 lbs./sq. in., say 35 lbs./sq. in. are preferred in the reaction zone. The "lead susceptibility" of the gasoline produced will be increased by the increased pressure, increasing from 80 A. S. T. M. octane number to 87 octane number under these pressures, rather than from 80 octane number to 85 octane number, A. S. T. M. with 3 cc. of tetraethyl lead solution per gallon of gasoline at the lower pressures.

The catalyst may become contaminated with NaCl or other salts upon contact with a crude which has not been desalted. To prevent overcontamination, a pound of catalyst per barrel of oil processed may be withdrawn from the system through line 55, a corresponding amount being added through pipe 54.

Another important variation of my invention resides in the concept of injecting cold oil into the hot catalyst in the reactor, the catalyst being at a sufficiently high temperature to crack the oil upon contact therewith. In this connection it will be understood that where the oil is preheated some of it may be vaporized, so that where a reduced crude is heated to 400° F. or thereabouts,

and then injected into the reactor 10, a portion of the oil is cracked in liquid phase and another portion in the vapor phase.

While it is often preferred to avoid cracking in furnace 31, it is true that in the case of a very heavy reduced crude, say 10% bottoms, some viscosity reducing or cracking is desirable in said furnace.

Many modifications of my invention will suggest themselves to those skilled in the art.

What I claim is:

1. A process for the conversion of heavy residual oils into lower boiling hydrocarbons which comprises passing the oil to be converted into the bottom portion of a conversion chamber while at least partially in liquid state, dispersing said oil into a dense turbulent mass of finely divided solid material within said conversion chamber, maintaining said conversion chamber at a temperature sufficient to convert said oil totally into vapors and solid residue, withdrawing the vapors from the upper end of said conversion chamber, providing a velocity of the oil vapors and gases passing upwardly through said conversion chamber to maintain said finely divided solid material in a dense turbulent state, continuously removing finely divided solid material containing solid carbonaceous residue from a lower portion of said conversion chamber, burning the carbonaceous residue from the finely divided solid material so withdrawn, heating said finely divided solid material during the burning of said solid carbonaceous residue to a temperature materially above the temperature maintained in said conversion chamber, and thereafter returning said heated finely divided solid material to said conversion chamber.

2. A process for the conversion of heavy residual oils into lower boiling hydrocarbons which comprises passing said oil into the bottom portion of a cracking chamber, dispersing the oil to

be converted into a dense turbulent mass of finely divided catalytic material within said cracking chamber at a temperature sufficient to convert said oil into vapors and solid residue, removing conversion vapors from the upper end of said cracking chamber, introducing a gasiform material into the bottom portion of said cracking chamber, controlling the velocity of the oil vapors and gasiform material passing upwardly through said cracking chamber to maintain a dense turbulent mass of finely divided cracking catalyst within said cracking chamber, separately withdrawing finely divided cracking catalyst containing solid residue from a lower portion of said cracking chamber, burning carbonaceous residue intermixed with said finely divided cracking catalyst, heating the finely divided cracking catalyst during the burning of said solid residue to a temperature materially above the temperature maintained in said cracking chamber and returning the finely divided cracking catalyst so heated to said cracking chamber.

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