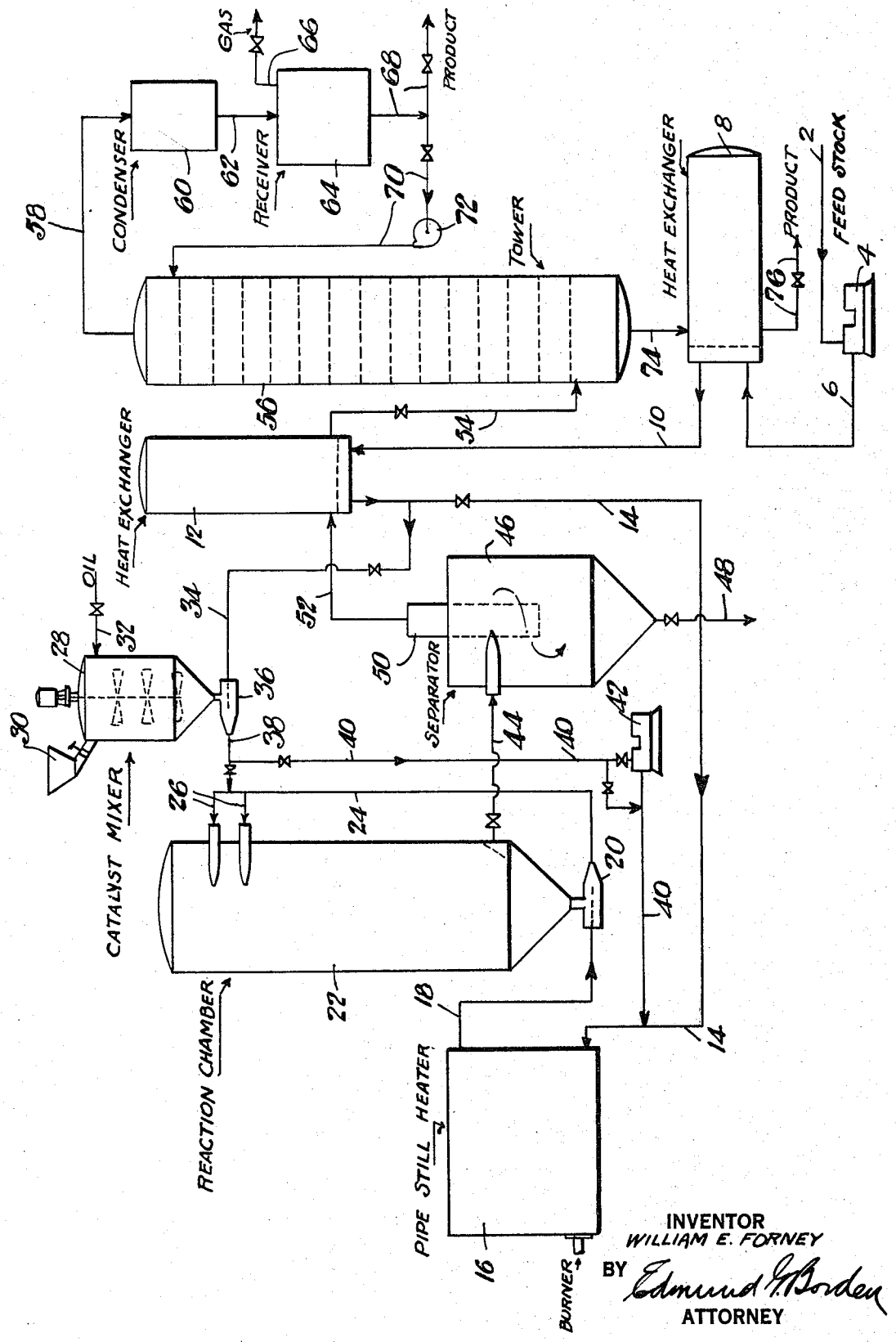
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF HYDROCARBONS

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This invention relates to a process for catalytically converting hydrocarbons of relatively low boiling point and relatively poor antiknock properties into hydrocarbons having high antiknock ratings and suitable for use as motor fuel in high compression engines. More particularly the process of the present invention relates to the catalytic conversion of saturated hydrocarbons such as natural gas gasoline, straight run gasoline, propane, butane and similar hydrocarbons contained in natural gas into motor fuel gasoline of higher octane number than the original stock.

Many processes have been devised for the reforming of straight run gasolines, naphthas and similar hydrocarbon mixtures in order to produce gasolines of higher octane value. However, most of the processes employed in such operations involve the use of extremely high temperatures upwards of 1100° F. as well as high pressures. Some processes operate at slightly lower temperatures but excessively high pressures are employed. Temperatures of the order of 1300° F. and higher are used for the conversion of hydrocarbons of the type of butane and propane into constituents suitable as a gasoline motor fuel. Such processes require expensive and elaborate equipment and are in many cases economically impracticable because of the loss occasioned from the conversion of the hydrocarbons into substantially fixed gases such as hydrogen and methane. In the conversion of straight run gasoline and natural gasoline to products of higher octane value, losses of this character make the resulting products too expensive to warrant production except for special purposes.

The primary object of the present invention therefore is to provide a catalytic process for converting hydrocarbons of the type referred to into high octane products in a relatively simple and inexpensive manner.

A further object of the present invention is to provide a process for catalytically converting relatively low boiling hydrocarbons into high octane motor fuel products by the use of relatively low conversion temperatures and moderate pressures.

Accordingly, the improved process of the present invention comprises the steps of heating the hydrocarbon to be converted to a moderate temperature of from 750° to 850° F. and intimately contacting the heated material with a catalytic metallic salt comprising the iron, aluminum, copper, zinc, molybdenum, chromium, manganese or nickel salts of phosphoric acid, sulfuric acid, hydrochloric acid, silicic acid or boric acid. These catalytic materials may be for convenience deposited on inert carriers such as fuller's earth, coke particles, or other similar material, or they may be used by themselves.

Other features and advantages of the process of the present invention will be apparent to those skilled in the art from the following detailed description taken in connection with the accompanying drawing in which:

The single figure is a diagrammatic flow sheet illustrating an apparatus particularly adapted for carrying out the improved process.

Referring to the drawing the hydrocarbon to be converted which for purposes of illustration is natural gasoline, is introduced into the system of the apparatus through a feed line 2 and forced by means of a pump 4 and a line 6 through a high pressure heat exchanger 8 in which the charging stock is passed in heat exchange with a portion of the product produced in the conversion operation. The material discharged from the pump 4 should be at a pressure of from 550 to 800 pounds per square inch. The preheated charging stock is conducted from the heat exchanger 8 at a temperature of about 400° F. and passed by means of a line 10 through a second heat exchanger 12 in which the charging stock is heated to a higher temperature by heat exchange with high temperature vapors in the conversion process. The preheated oil leaves the heat exchanger 12 at a temperature of about 550° F. and is conducted through a line 14 into and through a pipe coil heater mounted in a pipe still furnace 16. In passing through the pipe still furnace the natural gasoline charging stock is raised to a temperature of from 750° to 850° F., and maintained at this temperature in a portion of the coil for a substantial period of time and then discharged through a transfer line 18. At the temperatures and pressures given above the period of time referred to is preferably from 8 to 14 minutes.

The pipe still heater 16 may be of conventionally known construction in which tubes of three or four inch internal diameter are employed, and in which the pressure drop may be from 200 to 300 pounds per square inch, so that the pressure in the transfer line 18 will be from 250 to 600 lbs. per square inch.

The highly heated products discharged through the transfer line 18 are conducted into an ejector mixing nozzle 20 mounted at the bottom of an enlarged reaction chamber 22. The products are then conducted from the ejector 20 through a line 24 and discharged tangentially into the up-

per part of the reaction chamber 22 through one or more vertically spaced lines 26.

The catalytic agent employed in the conversion operation which may, for example be anhydrous iron phosphate or anhydrous aluminum phosphate, is introduced into a catalyst mixing chamber 28 through a valved feet chute 30, and therein intimately mixed with natural gasoline introduced through a valved line 32. The mixture of oil and catalytic material in the chamber 28 may be made up continuously or in batch for use in the conversion operation, and it may be introduced into the conversion process by taking a part of the charging stock discharged from the heat exchanger 12 through the line 14 and passing it through a valved line 34 into an ejector nozzle 36 at the bottom of the mixing chamber 28. The oil is passed at a high velocity from the line 34 and picks up the catalytic mixture in nozzle 36. The oil mixture may be introduced directly into the line 24 through a valved line 38 or passed through a valved line 40 to the inlet of the pipe still heater 16 with the preheating charging stock in line 14. In accomplishing the latter operation the flow of oil through the lines 34, 38 and 40 (including the bypass) may be controlled by the valves in lines 34 and 14, or a pump 42 mounted in line 40 may be used to force the oil-catalyst mixture from the mixing nozzle 36 into the line 14, regardless of a lower pressure in line 38.

In carrying out the process, it is not necessary to continuously introduce the catalytic material into the reaction chamber 22 or into the pipe still heater, but a continuous operation may be effected by mixing a relatively small proportion of catalyst with the oil in the line 14 passing to the heater 16. The proportion of catalyst may be adjusted by controlling the valve in line 34.

The mixture of high temperature products and catalyst discharged through the line 26 into the upper part of the reaction chamber 22 tend to spiral around the inside of this chamber so that the catalyst together with any small amount of liquid which may be present flows down the walls of the chamber and collects in the conical bottom from which the catalyst and any liquid passes immediately into the nozzle 20. The high velocity in the nozzle 20 remixes the catalytic material with the products discharged from the transfer line and they are again passed into the upper part of the reaction chamber.

At the temperatures employed, that is preferably 800° to 850° F. maintained in the reaction chamber 22, there will be substantially no liquid in this chamber so that the catalyst will fall to the bottom of the chamber or be suspended in the vapors in the chamber. The vapor products are discharged from the reaction chamber 22 through a vapor transfer line 44 and introduced tangentially into the upper part of a cyclone type separator 46 in which the spent or partially spent catalytic material is separated from the converted hydrocarbon vapor mixture. The catalytic material is collected in the conical base of this separator and discharged through a valved line 48, while the separated vapors pass downwardly through the separator 46 and out through a central enlarged conduit 50. These vapors are conducted on through a line 52 into the heat exchanger 12 where they are substantially reduced in temperature to about 575° F., and then conducted through a line 54 into the base of a fractionating tower 56.

In the tower 56 the vapors are rectified under a substantially high pressure to separate a light gasoline product which is sent overhead as vapors from the tower with the uncondensible gases. This mixture of materials is conducted through a vapor line 58 and passed through a condenser 60 in which the condensible constituents are liquefied, the resulting mixture being discharged through a line 62 into a receiver and gas separator 64. The separator 64 is maintained under a relatively high pressure so that substantially only the fixed gases such as hydrogen, methane, ethane and ethylene are discharged through a valved gas line 66. The condensed product passes from the receiver through a valved line 68 and any portion of this product may be returned to the top of the tower 56 through a valved line 70 in which is mounted a pump 72 for controlling the cut temperature on the tower. The product discharged through the line 68 will be a relatively light gasoline having an end point of about 325° F. and this product is preferably blended with heavier stock and stabilized to remove any excessive quantities of lighter materials such as a portion of its "propane" and "butane" content.

The heavier condensate which refluxes downwardly through the tower 56 and collects in the bottom of the tower, is removed through a line 74, passed through the high pressure heat exchanger 8 and finally discharged in a cooled condition through a valved line 76. This product contains some constituents which are heavier than those desired in the usual gasolines. They may be eliminated by a suitable distillation, the overhead products being available for blending with relatively light gasolines such as the gasoline removed through the line 68. The products removed through the lines 68 and 76 however have octane ratings of from 76 to 85, increased lead susceptibility and oxygen bomb stability, and therefore are particularly suitable for blending with lower octane numbered gasolines. The products are the result of molecular rearrangements and additions and not of decomposition. Therefore there is practically no tarry fraction formed.

The pressures maintained in the receiver 64 and tower 56 will be substantially equal to that maintained in the reaction chamber 22 except for the usual pressure drop through the various intervening elements of the apparatus. It will also be apparent that the temperature and pressure in the separator 46 will not be substantially different from that in the reaction chamber 22 and therefore the conversion reaction in contact with the catalytic material will still proceed in the separator 46. The tower 56 and the separator 46 may however be operated at lower pressures if desired. All of the apparatus is heavily insulated.

The theory of the action of the catalytic material on the conversion of the paraffin hydrocarbons into constituents of higher octane value is not definitely understood but it may be explained by the influence of the catalytic substances on the stability of the hydrogen atoms in certain molecules of the paraffins. In any case it appears that the paraffins are converted into increasing proportions of isocompounds, some of which are unsaturated, naphthenes and aromatic hydrocarbons. Some of the aromatic hydrocarbons produced in the operation contain side chains so that some alkylation of simple aromatics must have occurred during the operation. There is apparently a combination of reactions being effected including the alkylation of straight chain

hydrocarbons forming branched chain as well as cyclic hydrocarbons.

The spent catalyst may be revivified by well-known methods, such as the heating of it in a stream of air or oxygen containing gas.

From the foregoing description of the process of the present invention, it will be apparent that certain modifications of the process may be made and that it may be carried out in apparatus substantially different from that described. Low boiling olefin hydrocarbons may be converted to motor fuel either alone or when mixed with paraffins. Such features are contemplated within the spirit and scope of the present invention.

Having thus described the invention in its preferred form, what is claimed as new is:

1. The process of catalytically converting a paraffinic hydrocarbon containing from three to four carbon atoms to the molecule into a mixture of hydrocarbons having a substantially higher molecular weight, which comprises carrying out the process in the absence of added hydrocarbons of other type and hydrogen at a superatmospheric pressure of from 400 to 600 pounds per square inch, preheating the aliphatic hydrocarbon to be converted and mixing it with a relatively small proportion of a solid catalytic metallic salt which is adapted to catalyze isomerization and alkylation reactions, passing the resulting mixture in a stream of restricted cross-section through a long heating zone in the first part of which the mixture is heated to a temperature of at least 750° F. and in the latter part of which the temperature is substantially maintained and raised to a point of approximately 850° F., discharging the resulting heated mixture into an enlarged reaction zone in which intimate contact is maintained between the hydrocarbons and the catalytic material, passing the mixture into a separator in which the catalytic material is separated from the resulting converted hydrocarbon, and recovering the condensable products resulting from the conversion reactions.

2. The process defined by claim 1 in which the preheated mixture is passed in a stream to a heating zone and in which said stream is divided and one portion thereof mixed with said catalytic material and again united with the other portion prior to its introduction into said heating zone.

3. The process defined by claim 1, in which catalytic material is withdrawn from one end of said enlarged reaction chamber and mixed with a stream of oil from the heating zone and reintroduced into the opposite end of said reaction chamber.

4. The process defined by claim 1 in which the catalyst salt is anhydrous iron phosphate.

5. In the process of catalytically converting paraffinic hydrocarbons containing from three to four carbon atoms to the molecule into a mixture of hydrocarbons having a substantially higher molecular weight, the improvement which comprises effecting said conversion at a temperature of 750° to 850° F. and at approximately a pressure of from 250 to 600 lbs. per square inch while intimately contacting the hydrocarbons to be converted with a catalyst adapted to catalyze isomerization and alkylation reactions comprising anhydrous iron phosphate, and separating the desired liquid conversion products from the hot products resulting from the reaction by cooling and condensation.

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