

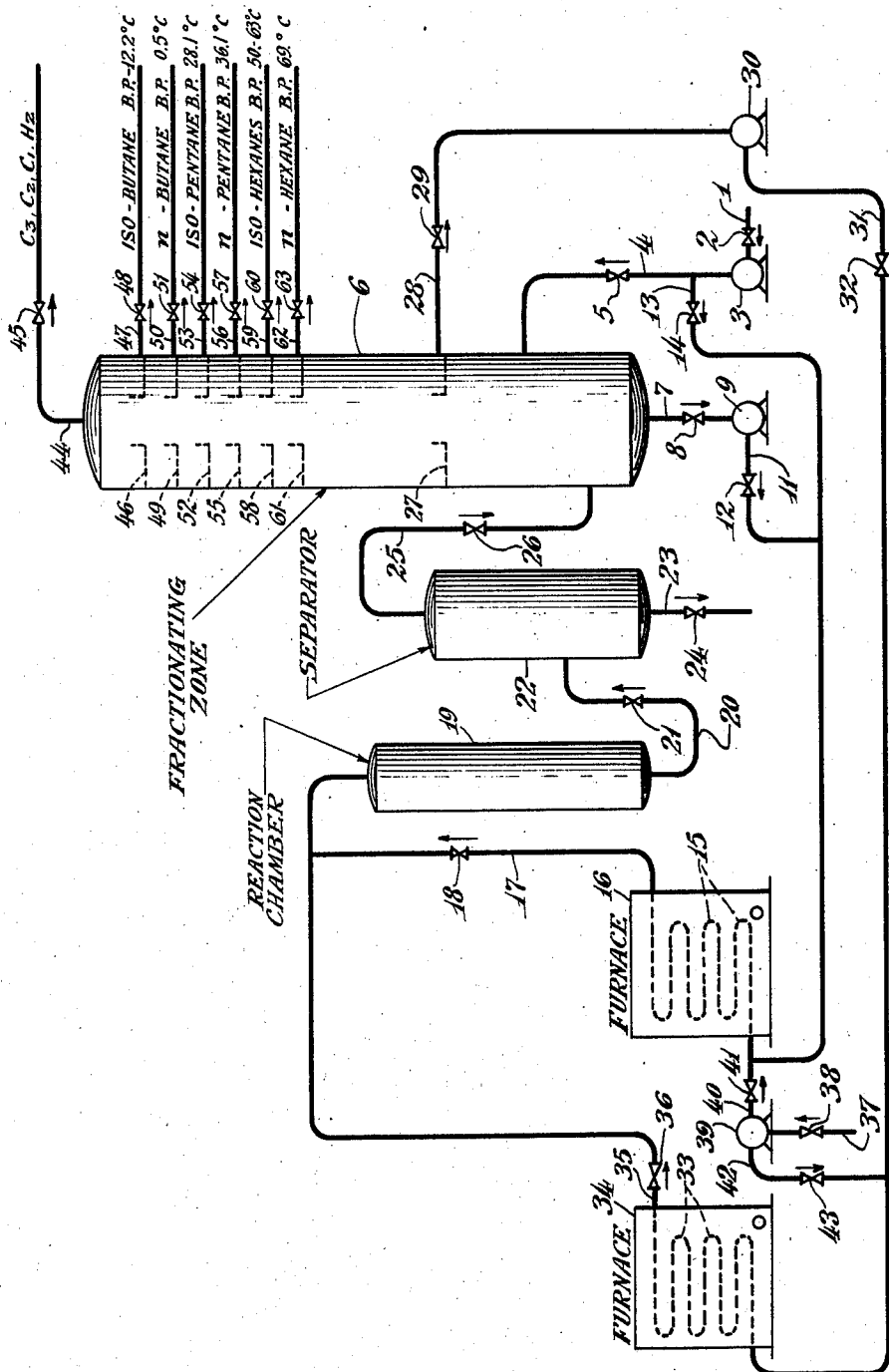
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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5 Claims. (Cl. 196—48)

This invention relates to the treatment of hydrocarbons for the conversion thereof into lower boiling hydrocarbons suitable for use as motor fuel, and particularly to the production of individual low boiling hydrocarbons of an iso character which can be used as the base material in synthetic processes or directly as high antiknock constituents of motor fuel blends.

The invention is more specifically concerned with the use of metal halide catalysts and particular process flows for accomplishing the objects mentioned.

It has been recognized for some time that there is a distinct limitation both as to quality and yield of product in strictly thermal cracking processes aimed at the production of optimum yields of high antiknock value gasoline. Even though cracking plants have been developed which are more or less perfect mechanically and wherein individual fractions of hydrocarbon charges and intermediate insufficiently converted conversion products are subjected individually to sets of conditions best suited to their effective conversion, it has been found that high antiknock value materials useful as motor fuel are difficult to obtain without sacrifice of yields and increased losses due to formation of fixed gases on the one hand and heavy carbonaceous residual materials on the other. To overcome these limitations, a wide variety of catalytic materials have been examined with varying degrees of success. The present process is an improvement over ordinary thermal and catalytic cracking processes in the combination of particularly effective catalysts and a process flow which is adapted to produce increased yields of low boiling products, particularly those of an isoparaffinic character which have high antiknock value.

In one specific embodiment the present invention comprises fractionating a hydrocarbon oil along with products of catalytic cracking to produce a relatively light and a relatively heavy reflux material, separately converting these light and heavy refluxes in the presence of metal halide catalysts, passing the products from these conversions to a reaction zone in which time is given for the completion of the desired conversion reactions, passing the conversion products thereafter to a separation zone preferably operated under reduced pressure wherein heavy reaction products are separated from normally vaporous materials and fractionating said vaporous materials to produce a plurality of individual hydro-

carbon fractions and the light and heavy refluxes mentioned.

The features and advantages of the present invention will be further evident from a consideration of the following description of a characteristic operation in connection with the attached drawing which shows diagrammatically in general side elevation and without regard to exact proportioning of interconnected units an arrangement of apparatus in which the process of the invention may be carried out. The plant is not represented in the drawing in complete detail, since the drawing has been simplified to assist in the description of the flow and to bring out the more salient features of the process.

Referring to the drawing, a hydrocarbon charging stock which may comprise a gas oil cut from the primary distillation of a crude oil is introduced to a plant by way of a line 1 containing a valve 2 and into a charging pump 3 which discharges either through line 4 containing valve 5 into a point in the final fractionating zone 6 or directly to a heating element 15 by way of branch discharge line 13 containing valve 14, heater 15 being arranged to receive heat from a furnace 16. Whether the charging stock is introduced directly to a conversion zone or into a fractionating zone will depend upon the characteristics of the stock and both methods of introduction are comprised within the scope of the invention as may be expedient. When introduced to the fractionating zone a charge is preferably admitted at a point between the collection of a light reflux condensate and the admission of vapors from a preceding separator. As shown in the drawing, the heavier fractionated cracked products are withdrawn from fractionating zone 6 by way of a line 7 containing valve 8 to a pump 9 which discharges through a line 11 containing valve 12 and leading to line 13 containing whatever portion of the charging stock is to be fed directly to primary heating element 15. Light reflux condensate is removed from a cooling plate 27 by way of line 28 containing a valve 29 to a pump 30 which discharges through line 31 containing valve 32 to a secondary heating element 33 arranged to receive heat from a furnace 34. It will thus be seen that a charging stock may be converted in admixture with heavy reflux condensates while the light reflux condensate is separately converted.

In accordance with the present process light and heavy reflux condensates from the fractionation of the cracked products and the charging stock are separately catalytically cracked in the

presence of metal halide catalysts, particularly aluminum chloride and similarly acting materials. These catalysts are preferably introduced in a finely divided and substantially anhydrous condition in suspension in oils at moderate temperatures although they may be injected as vapors wherever feasible as in the case of aluminum chloride. As indicated in the drawing, line 37 containing valve 38 and leading to catalyst pump 39 is provided for the admission of the catalytic material, the pump discharging partially through line 40 containing valve 41 to primary heating element and conversion zone 15 while the remaining portion of the catalyst is directed through line 42 containing valve 43 to secondary heating element 33. Conditions of temperature and pressure, amount of catalyst and size of the two individual heaters will be determined by the characteristics of the charging stock. However, as a rule more moderate conditions will be employed in the conversion of the mixture of heavy reflux and charging stock while more severe conditions are employed in the conversion of the light reflux. Temperatures of from 450-750° F. may be employed at the exit of the two heating elements and superatmospheric pressures up to 500 lbs. per square inch, the conditions of each coil being preferably regulated to produce maximum yields of low boiling iso-paraffinic hydrocarbons. Hydrogen halides such as hydrogen chloride may be admitted at any point in the conversion zones to assist in promoting the primarily desired production of iso-paraffins.

The partially converted products and catalyst from primary heating element 15 pass through line 17 containing valve 18 while similar products pass from secondary heating element 33 through line 35 containing valve 36, both sets of products passing to a reaction chamber 19 which is provided to permit continued conversion of the products to a desired point. The total products from reaction chamber 19 pass through line 20 containing valve 21 to a separator 22 which preferably operates under a pressure lower than that employed in the preceding reaction chamber. In this separator, aluminum chloride or other metal halide sludges and heavy residual reaction products drop out and are removed through line 23 containing valve 24 while the vapors from the separator pass through line 25 containing valve 26 to fractionating zone 6 already mentioned. While a single fractionator has been shown in the drawing to represent the fractionating zone in the interest of simplicity, it is to be understood that a more elaborate system will be necessary to effect the desired fractionation of the products into individual hydrocarbons. Thus instead of the upper set of collecting plates 46, 49, 52, 55, 58, and 61, there may be used a corresponding number of separate fractionating columns which act successively to fractionate the vapors evolved above collecting plate 27. By the choice of fractionators of suitable design and capacity, it is preferred to separate by way of line 44 containing valve 45 a light fixed gaseous fraction comprising essentially hydrocarbons of three, two and one carbon atoms and hydrogen, which are removed and used in any desired manner such as, for example, fuel in the furnaces of the process.

As shown in the drawing, a line 47 containing a valve 48 removes iso-butane which may thereupon be alkylated with normally gaseous olefins to produce liquid iso-paraffin hydrocarbons including hexanes, heptanes, and octanes.

Line 50 containing valve 51 is shown in the drawing as removing a normal butane fraction which may be further treated by isomerization or dehydrogenation processes to produce more reactive compounds useful in the synthesis of high antiknock value hydrocarbons.

Line 53 containing valve 54 is indicated as a means of removing an iso-pentane fraction which is utilizable directly as a high antiknock constituent of motor fuel or which may be alkylated readily as in the case of iso-butane to form high boiling iso-paraffin hydrocarbons which may be used as ingredients of the so-called safety fuels.

Line 56 containing valve 57 permits the recovery of a normal pentane fraction which may be utilized by methods similar to those suggested for the utilization of normal butane.

Line 59 containing valve 60 permits the removal of a mixture of iso-hexanes which are utilizable directly in ordinary motor fuel or in aviation fuels.

Line 62 containing valve 63 permits the withdrawal of a normal hexane fraction which may be separately utilized in the production of other hydrocarbons of good antiknock value.

The following example is introduced to indicate in a general way the types and yields of products normally obtainable in the operation of the present process although the scope of the invention is not to be considered as limited by the character of the specific data introduced.

The charging stock to the process may be a Mid-Continent gas oil having an A. P. I. gravity of 30, which is introduced to a fractionating zone in the manner described in the process flow. By operating a primary conversion element at a temperature of approximately 500° F. and a secondary heating element at a temperature of 600° F. utilizing pressures of 100 lbs. per square inch at the exit of the heating elements and in the succeeding reaction chamber, approximately 5% by weight of aluminum chloride being suspended in the fractions undergoing conversion in each zone. The final weight per cent yield of products may be as follows:

	Per cent
Gases lighter than butanes.....	15
Iso-butane	25
Normal butane.....	5
Iso-pentane	20
Normal pentane.....	5
Iso-hexanes	15
Normal hexane fraction and heavier.....	15

I claim as my invention:

1. A process which comprises heating a mixture of hydrocarbon oil and metal halide catalyst to catalytic conversion temperature in a heating zone, simultaneously heating a lighter oil, together with additional metal halide catalyst, to independently controlled higher conversion temperature in a second heating zone, introducing the reaction products including the suspended catalysts from both said zones into a reaction zone maintained under catalytic conversion conditions and therein continuing conversion, separating the commingled products into vapors and residue, fractionating the vapor to separate a plurality of fractions therefrom, including a relatively heavy reflux condensate and a lighter reflux condensate, and returning the heavy reflux condensate to the first-mentioned heating zone and the lighter reflux condensate to said second heating zone.

2. The process of claim 1 further characterized

in that said metal halide comprises aluminum chloride.

3. The process of claim 1 further characterized in that hydrogen halide is added to the oil undergoing conversion in both of said heating zones.

4. A process which comprises heating a mixture of hydrocarbon oil, metal halide catalyst and hydrogen halide to catalytic conversion temperature in a heating zone, simultaneously heating a lighter oil, together with additional metal halide catalyst and hydrogen halide, to independently controlled conversion temperature in a second heating zone, introducing the reaction products including the suspended catalysts from both said zones into a reaction zone maintained

under catalytic conversion conditions and therein continuing conversion, separating the commingled products into vapors and residue, fractionating the vapors to separate a plurality of fractions therefrom, including a relatively heavy reflux condensate and a lighter reflux condensate, and returning the heavy reflux condensate to the first-mentioned heating zone and the lighter reflux condensate to said second heating zone.

5. The process of claim 4 further characterized in that the metal halide catalyst comprises aluminum chloride and the hydrogen halide comprises hydrogen chloride.

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