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CATALYTIC CONVERSION OF HYDROCARBON OIL

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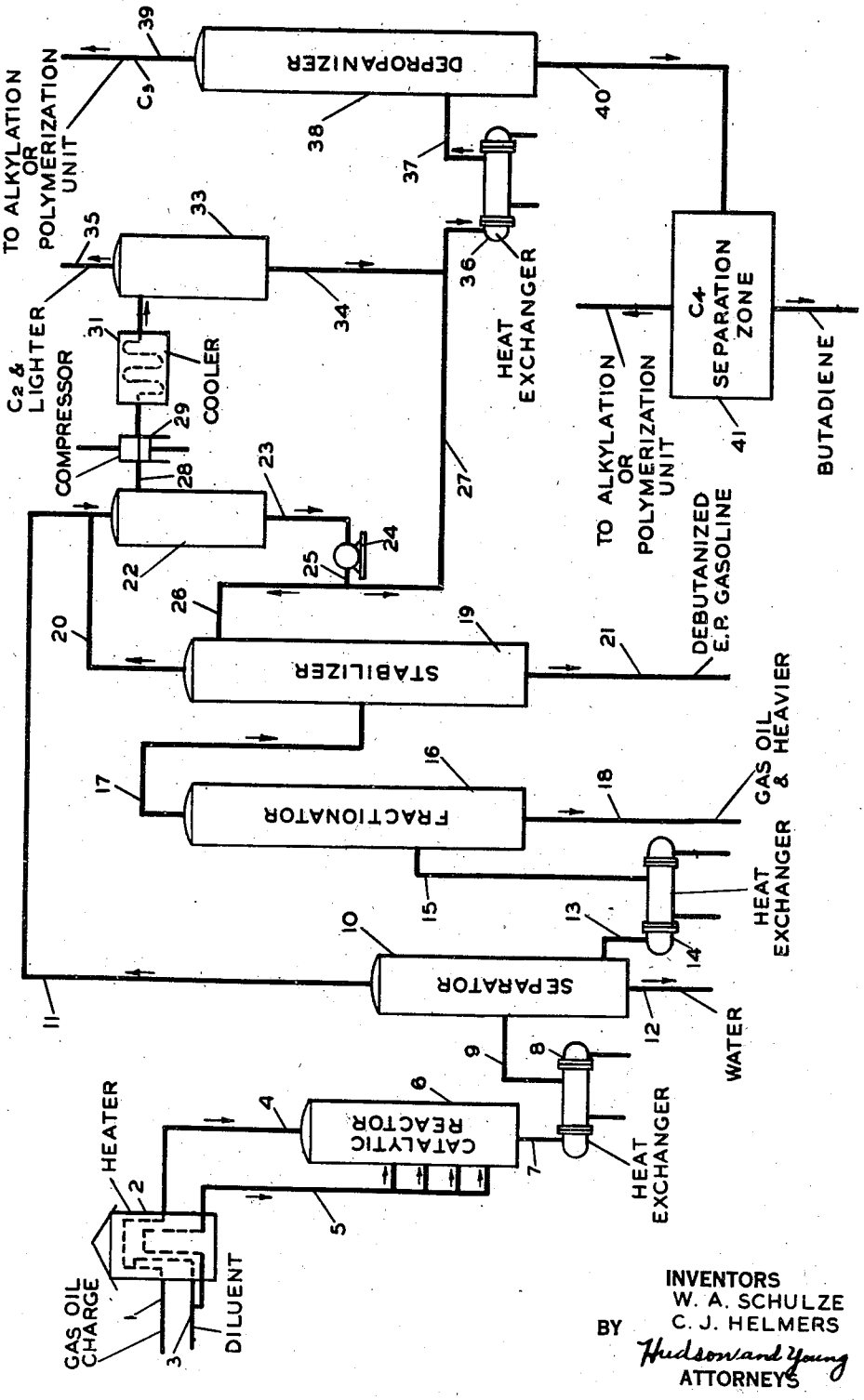


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## CATALYTIC CONVERSION OF HYDROCARBON OIL

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This invention relates to a process for converting hydrocarbon fractions into substantial yields of light unsaturated hydrocarbons with the simultaneous production of valuable stabilized distillate. In one of the more particular applications, the present invention relates to controlled catalytic cracking of normally liquid hydrocarbon materials such as gas oil, kerosene and naphtha to produce normally gaseous olefins and diolefins with concurrent production of by-product distillates rich in aromatic hydrocarbons.

Generally speaking, in the refining practice of the past, catalytic cracking processes have been concerned with the manufacture of high yields of superior motor fuels. A recognized advantage of such processes has been the production and conversion of high percentages of gaseous olefins to higher boiling hydrocarbons. However, with the advent of recent developments in the design of aircraft engines, the demand for special high-quality fuels shifted refining technology from motor fuel production to the manufacture of aviation gasoline. The need for the latter fuels has created a demand for light olefins suitable for use in the production of alkylate gasoline and for aromatic hydrocarbons valuable for their favorable effect on the rich-mixture performance of aviation gasoline. Existent catalytic processes have partially solved this problem in that distillates rich in aromatic hydrocarbons have been produced, but this has been accomplished at the expense of potential olefin and diolefin production. Since operating variables favorable to one reaction are unfavorable to the other, a definite lack of flexibility is evident in catalytic cracking processes described heretofore.

It is an object of the present invention to provide a process for the catalytic conversion of hydrocarbon oils to substantial yields of light olefins and diolefins with the simultaneous production of a high quality aviation blending stock.

Another object of this invention is to provide a catalytic cracking process for hydrocarbon oils wherein novel means of control of temperature and contact time within the catalyst zone is provided.

Other objects and advantages will be apparent from the following disclosure.

We have now discovered that with the application of the present invention, normally liquid petroleum hydrocarbons such as gas oil, kerosene and/or naphtha may be catalytically treated under reaction conditions leading to the production of valuable light olefins and diolefins in substantial yield along with concurrently valuable

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aromatics-containing distillates. This unusual result is realized through effective control of temperature and contact time in different sections of the catalyst bed. Thus when the catalyst case is arranged for downward flow, a relatively long contact time at conversion temperature in the upper portion of the catalyst case favors the formation of a large proportion of $C_4$ and lighter hydrocarbons along with the considerable conversion of the feed to aromatic types, while at one or more suitable points along the length of the bed a large proportion of heat-carrying steam or other inert diluent is introduced. This diluent, heated to a desired temperature, furnishes additional heat necessary for dehydrogenation of butenes to butadiene and at the same time reduces the contact time, thus preventing further appreciable conversion of the olefins and diolefins to polymers and/or cyclic compounds. By addition of the preheated diluent at one or more selected points in the catalyst chamber, the temperature and contact time in both the upper and lower portions of the catalyst bed may be controlled to give the unit the high degree of flexibility required to process feed stocks through the range of naphtha and gas oil fractions.

In order to permit the coexistence of aromatizing and dehydrogenating conditions in the same catalyst bed, so as to obtain both aromatic fractions and olefin- and diolefin-containing fractions, it is necessary to provide relatively long contact time in the aromatizing zone and relatively short contact time in the dehydrogenation zone. This is accomplished by introducing steam or other inert gaseous diluent, such as nitrogen, into that point in the catalyst bed at which the treated vapors have been subjected to the desired contact time for the aromatizing reaction to have taken place. At this point sufficient diluent is introduced to provide the desired effective dehydrogenation contact time in the remaining portion of the bed. The contact time for the cracking-aromatizing portion of the reaction is preferably between about 0.5 and 3 seconds, while the contact time for the dehydrogenation portion of the reaction is between about 0.05 and 0.5 second.

Lower-boiling paraffins such as methane and ethane are also relatively inert since the reaction conditions are not sufficiently severe to induce extensive cracking and may also be used as diluents.

In order to obtain substantial dehydrogenation in the second zone it is necessary to compensate for any endothermic loss of heat occurring in the initial cracking-aromatizing reaction.

This may be accomplished by superheating the steam or other diluent to a point sufficiently above the temperature of the reactants at the point in the bed at which the diluent is introduced, to elevate the temperature in the dehydrogenation zone to the desired point. Preferably the cracking-aromatizing reaction is carried out at a temperature between about 1100–1300° F. while the dehydrogenation reaction is also carried out at temperatures within this range.

In the practical operation of the present conversion steps, time-temperature relationships may be relied on to determine the amount and location of the injection of diluent to the catalyst case. Thus in the cracking section of the catalyst case, the diluted hydrocarbon vapors are permitted a temperature drop of about 100° F. as representing the optimum depth of cracking in this process. Sufficient diluent preheated to 1200–1400° F. then enters the chamber in amount sufficient to raise the vapor temperature to about 1150° F. and at the same time to reduce the hydrocarbon partial pressure and residence time. In the dehydrogenation section of the catalyst bed, additional diluent may be injected at points corresponding to temperature drops of about 50° F., so that the overall temperature in the after section of the catalyst bed is maintained between about 1100–1150° F., and the hydrocarbon partial pressure at about 0.05 to about 0.01 atmosphere.

Thus the point in the bed at which cracking has proceeded to an optimum extent is represented by the temperature drop of about 100° F. and at and beyond that point sufficient diluent is introduced to provide the hydrocarbon partial pressure and contact time necessary to give the desired dehydrogenation conditions in the remainder of the bed.

The accompanying diagram shows in conventional side elevation one particular embodiment of the invention. It should be emphasized, however, that modifications and variations in the equipment apparent to those skilled in the art may be made as desired without departing from the broad scope of the invention.

With reference now to the drawing, the feed stock to the operation, which may comprise a gas oil such as that fraction boiling between 450° and 650° F. and which may be obtained either by the straight distillation of a crude oil or by the mild cracking of a reduced crude, is led through transfer line 1 into the furnace 2. A diluent, comprising steam or other inert gas, may be introduced by line 3, heated in the furnace 2 and added to the vaporized hydrocarbon. The heated mixture of gas oil and diluent then passes by line 4 into the reaction chamber 6 to which an additional amount of superheated steam or other inert diluent is added through line 5 to serve as heat carrier and to reduce the contact time. Means are illustrated for introducing the diluent at one or more points in the latter portion of the bed, as desired.

The reaction chamber 6 may be any of various reactors known to those versed in the art. Inasmuch as the invention pertains to a novel and advantageous cracking procedure rather than to a particular type of equipment, no attempt will be made to describe the catalyst chamber in detail. An appropriate reaction vessel for use in this process, however, may suitably be a multiple-bed type of chamber provided with suitable arrangements for the injection of heat carrier media at different points. It is not intended, however, that the invention should be limited to this particular type of reactor.

Leaving the catalyst chamber, the reaction mixture passes through line 7 with appropriate cooling by the heat exchanger 8 and, where steam is used as diluent, through line 9 into the separator 10 from which water is withdrawn at the bottom through line 12. The overhead vapors from the separator are taken through line 11 into the accumulator 22 while the normally liquid hydrocarbon material is withdrawn at the side of the separator and taken through line 13 through a suitable heat exchange element 14 and through line 15 into the fractionator 16. The fractionator bottoms, comprising gas oil and higher boiling material, are removed through line 18 while the overhead from the fractionator is taken through line 17 to the stabilizer 19. The stabilizer bottoms withdrawn by line 21 comprise debutanized end-point gasoline which, upon refractionation and further treatment, is suitable for utilization as a high-octane, aromatic aviation fuel. The overhead from the stabilizer, comprising $C_4$ and lighter gases, is taken through line 20 to the accumulator 22. A portion of the liquid condensed in accumulator 22 and comprising essentially $C_3$ and $C_4$ hydrocarbons is withdrawn through line 23 and pump 24 and returned to the stabilizer through lines 25 and 26 as reflux. The remainder of the $C_3$—$C_4$ hydrocarbon is taken through line 27, the heat exchanger 36 and line 37, to the depropanizer 38. The gaseous material from the accumulator 22 is taken through line 28, the compressor 29 and the cooling coil 31 to the accumulator 33 from whence the $C_2$ and lower-boiling products are vented to an ethylene recovery system or to the refinery gas plant through line 35. The liquid condensate from the accumulator 33 comprising predominantly propane and propylene is combined through line 34 with the excess reflux liquid in line 27. The bottoms from the depropanizer, comprising the $C_4$ cut is taken through line 40 to an appropriate system 41 for effecting the separation of the fraction into such components as butadiene which is of use in the manufacture of synthetic rubber and into butylenes and isobutane which may be used as feed to alkylation and polymerization processes. The amount of isobutane available for these processes may be increased by the use of isomerization reactions. The $C_3$ overhead from the depropanizing column may be taken through line 39 for further treatment or for use in alkylation or polymerization processes.

Typical operating conditions which may be employed to carry out the process are approximately as follows:

The hydrocarbon oil change stock is vaporized in the furnace coil, being heated to temperatures markedly higher than those normally utilized for the production of motor fuels by thermal treatment of heavier oils, these temperatures employed being in the approximate range of 1100° to 1300° F. The hydrocarbon vapors are passed over the catalytic mass which preferably comprises a naturally-occurring material such as bauxite. Certain activated adsorbent clays may also be used as well as synthetic materials such as alumina or alumina admixed with minor proportions of certain activating agents such as various metal oxides or salts. In some instances, synthetic materials comprising various combinations of silica gel and metal oxides such as silica-alumina or silica-alumina-zirconia catalysts may be suitable.

In order to control carbon deposition and to favor the production of light unsaturates, the feed to the catalyst case is vaporized and admixed with steam or other inert gases to the extent of about 0.5 to 5 mols of diluent per mol of feed. Additional diluent equivalent to from 10 to 25 mols per mol of feed, preheated to 1200–1400° F., is injected into the catalyst case at suitable points spaced along the catalyst case in the direction of flow. Since the cracking reaction is highly endothermic, the introduction of the auxiliary heat carrier ordinarily occurs after the charge vapors have traversed about one-third of the length of the catalyst bed. Additional injection points may be provided along the latter two-thirds of the length of the bed. This method of operation, by virtue of the high temperature level maintained and low partial pressure of reactants, favors additional dehydrogenation reactions to further increase olefin and diolefin production. On the other hand, the addition of auxiliary diluent greatly shortens the contact time, thereby preventing excessive polymerization and cyclization of the gaseous olefins and diolefins.

The operation may be carried out under moderately superatmospheric pressure which may range from atmospheric to about 250 pounds per square inch gage in order that the desired contact time may be achieved for a given diluent ratio. Ordinarily, in order to produce increased yields of diolefins, relatively low near-atmospheric pressures are preferred, as for example between about zero and 50 pounds gage.

In order to indicate the novelty and utility of the process, the following example is given of a specific embodiment of the invention which employs the preferred conditions of temperature and pressure and flow rate along with a preferred feed stock and catalyst. This example is merely illustrative of results normally obtained and should not be construed as a limiting feature of the invention, as various changes in the catalyst and catalyst chamber design as well as modifications in the reaction conditions apparent to those versed in the art may be made.

*Example*

A 42 degree A. P. I. gravity kerosene having an initial boiling point of 400° F. was admitted to a catalyst chamber filled with a regenerated 10–20 mesh bauxite catalyst, at a charge rate of about 1 liquid volume of kerosene per volume of catalyst per hour, with steam at the inlet in the proportion of 1 mol of kerosene to 2 mols of steam per hour. The feed was introduced into the catalyst bed at a temperature of 1200° F. and after traversing about one-third of the bed the temperature at that point was found to have dropped to about 1100° F. Additional steam was introduced at this point at a temperature of 1400° F. at the rate of 5 mols per mol of hydrocarbon feed per hour, raising the temperature to 1150° F. When the hydrocarbon-steam mixture had traversed approximately another third of the bed the temperature drop was about 50° F. and at this point additional steam at a temperature of about 1400° F. and a rate of about 8 mols per hour per mol of hydrocarbon feed was introduced. The effluent product left the bed at a temperature of about 1100° F. Fractionation of the effluent yielded a $C_4$ fraction amounting to 11.5 per cent by volume of the charge and of this fraction 32 per cent by volume was butadiene, while 64.3 per cent of the fraction consisted of butenes, of which



35 per cent was isobutylene. The $C_3$ fraction accounted for 17.5 volume per cent of the charge and was about 92 per cent propylene. The $C_2$ fraction comprised 75 per cent ethylene and amounted to 30 volume per cent of the charge.

Butane-free gasoline was obtained in a yield of about 24.5 volume per cent of the charge. The clear A. S. T. M. octane number of the gasoline was 82.5 while the Research octane of the unleaded gasoline was 96.0. A high aromatic content of the gasoline is indicated by the refractive index of 1.4795.

In the above example the operation was carried out at a pressure of 5 pounds per square inch gage and for a process period of six hours duration.

Another portion of the same feed stock was catalytically cracked under identical conditions except that 9.3 mols of steam diluent per mol of hydrocarbon was initially introduced with the feed and no further diluent was added. On fractionation a $C_4$ fraction amounting to 10.3 volume per cent of the charge was obtained and of this fraction 22.6 volume per cent was butadiene and 67.9 per cent was butenes. Of the butenes fraction 37 per cent was isobutylene. The $C_3$ fraction accounted for 16.5 volume per cent of the feed of which about 90 per cent was propylene. The $C_2$ fraction amounted to about 29 per cent of the charge and contained about 72 per cent ethylene.

A butane-free gasoline amounting to 25.2 per cent of the charge by volume was obtained and the clear A. S. T. M. octane number of the gasoline was 81.6 while the Research octane of the unleaded gasoline was 95.0. The refractive index was 1.4780.

Comparison of the above results shows that in accordance with the present invention butadiene production is increased about 50%, and somewhat greater overall production of olefins is also obtained. Slightly less of a butane-free gasoline is obtained, but this has a somewhat higher octane number due to the slightly greater olefin and aromatic content.

We claim:

1. A process for the conversion of a normally liquid hydrocarbon distillate to an aromatic fraction and normally gaseous unsaturated hydrocarbons which comprises vaporizing and heating the said distillate to a temperature of 1100–1300° F., passing said vaporized distillate in contact with a solid adsorbent cracking and dehydrogenating catalyst for a contact time of 0.5 to 3 seconds, injecting sufficient steam preheated to 1100–1400° F. at a plurality of points spaced along the length of the catalyst bed in the direction of vapor flow after the initial contact period to allow the distillate a further contact time of 0.05 to 0.5 seconds with said catalyst, and separating butadiene, normally gaseous olefins and an aromatic fraction from the effluent.

2. The process of claim 1 in which the preheated steam is introduced at said points in the catalyst bed in a volume and at a temperature sufficient to raise the temperature to 1100–1150° F. in the dehydrogenation zone and to maintain the temperature in a range of 50° F.

3. The process of claim 1 in which the cracking and dehydrogenation catalyst is bauxite.

4. A process for the conversion of a normally liquid hydrocarbon distillate to an aromatic fraction and normally gaseous unsaturated hydrocarbons which comprises vaporizing and heating the said distillate to a temperature of 1100–1300°

F., passing said vaporized distillate in contact with a solid adsorbent cracking and dehydrogenating catalyst for a contact time of 0.5 to 3 seconds, injecting sufficient steam preheated to 1100–1400° F. at a plurality of points spaced along the length of the catalyst bed in the direction of vapor flow after the initial contact period to allow the distillate a further contact time of 0.05 to 0.5 second with said catalyst and separating said normally gaseous hydrocarbons and said aromatic fraction from the effluent.

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