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MANUFACTURE OF DIOLEFINS

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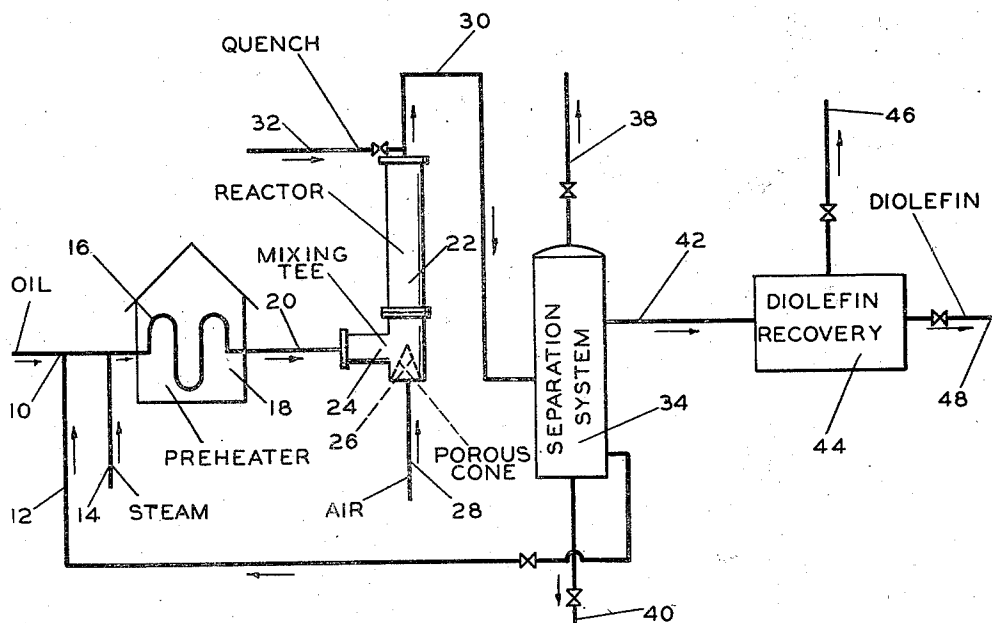


FIG. -1

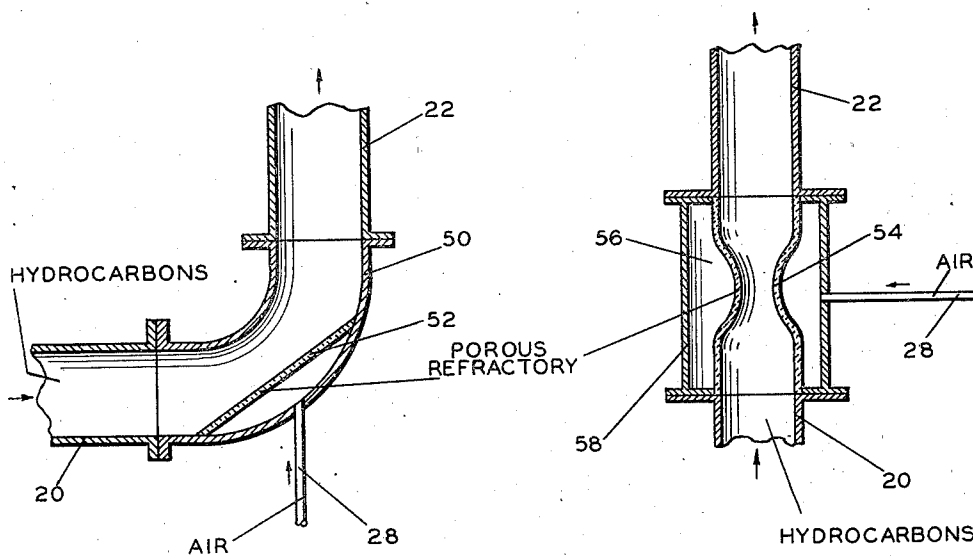


FIG. -2

FIG. -3

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## MANUFACTURE OF DIOLEFINS

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12 Claims. (Cl. 260—680)

This invention relates to the conversion of hydrocarbons and to the production of diolefin hydrocarbons. A preferred modification relates to the decomposition of light normally liquid hydrocarbons under conditions chosen for optimum production of diolefins aided by the action of free oxygen on said hydrocarbons. Specific aspects include an apparatus and method of operating which favor a partial oxidation of hydrocarbon reactants in such manner that a very rapid temperature rise to the desired range is attained.

The production of low-boiling diolefinic hydrocarbons such as butadiene, isoprene, piperylene, etc., has recently become of vital importance for the manufacture of synthetic rubber-like materials. In perhaps the most important type of synthetic rubber the diolefinic constituent comprises about 75 per cent of the raw material. While relatively high yields of diolefins may be obtained through carefully controlled selective catalytic processes, for example, the catalytic dehydrogenation of normal butenes to butadiene, such processes suffer somewhat from the disadvantage of requiring a careful isolation of feed stocks which may be needed for other purposes. Furthermore, a high initial capital expenditure is required.

In order to obtain a substantial production of diolefins in a relatively short period of time and to utilize less valuable stocks in so doing, attention has been directed to the non-catalytic cracking of petroleum oils. By virtue of the advantages of the present invention I may obtain optimum reaction conditions for converting relatively light normally liquid hydrocarbons into lower boiling diolefins in a very effective manner. In order to obtain substantial yields it is required that the hydrocarbon charging stock be maintained at a relatively high temperature, preferably from about 1400 to about 1600° F., for a very short period of time such as in the range of 0.1 to 0.2 second, the longer time being used at the lower temperatures. Unless this temperature range is attained very rapidly, and unless the reaction products are in turn rapidly cooled, the hydrocarbons will undergo extensive reactions other than those desired, with consequent reduction in yield. I have found that an effective way to attain the desired temperature level almost instantaneously is to admix an oxygen-containing gas, with or without inert diluents, with a partially preheated charge stock in a particular manner chosen to promote a partial oxidation of the hydrocarbons, as more fully hereinafter disclosed and discussed.

An object of my invention is to effect conversion of hydrocarbons.

Another object of my invention is to produce low-boiling diolefin hydrocarbons.

Further objects and advantages of my invention will become apparent, to one skilled in the art, from the accompanying disclosure and discussion.

In the preferred manner of carrying out the production of low-boiling diolefins in accordance with the principles of this invention, a non-aromatic hydrocarbon distillate such as cracked or straight-run naphtha is diluted with steam or other non-oxidizable diluent, is brought to a temperature of about 1100° F. or slightly higher, and then passed rapidly past the incandescent surface of a porous refractory material through which air in carefully controlled proportions is being introduced. The resulting gaseous admixture is maintained at the desired reaction temperature for the short time required and quenched immediately thereafter to stop the reaction. The porous refractory material referred to preferably is coated with a catalyst, such as a metal oxide, which catalyzes the oxidation of hydrocarbons. The introduction of oxygen through said refractory member in the manner described provides a very rapid and intimate intermixture of hydrocarbon charge with oxygen and the desired oxidation is at least partially effected at the refractory surface. The result is the maintenance of a highly heated surface past which the hydrocarbon stream flows. It will be seen that the temperature of the hydrocarbon stream is raised almost instantaneously several hundred degrees from the preheat temperature to the reaction temperature. Due to the intimate mixture of oxygen with hydrocarbons thus effected the oxidative reaction continues in the portion of the reaction zone immediately following the incandescent refractory and serves to maintain the temperature of the mixture in the desired range in spite of the highly endothermic cracking reaction which is being effected. In other words, the hydrocarbons are first rapidly raised to reaction temperature and second maintained at reaction temperature by the introduction of limited amounts of oxygen in the particular manner described.

It has been found that the best results are obtained when a diluent, such as steam, nitrogen, an oxide of carbon, etc., is mixed with the selected hydrocarbon charge stock prior to its passage through the preheat zone. This serves to minimize any reaction in said zone and permits

a relatively higher temperature to be maintained therein without the occurrence of an appreciable amount of coking. The diluent serves during the reaction to help control temperatures and partial pressure of reactants and enables the attainment of a high conversion to diolefins. Preferably the mol ratio of diluent to oil vapor is in the range of from about 3:1 to about 6:1. While the total pressure of the reaction mixture should generally be above atmospheric, the use of a great superatmospheric pressure will appreciably reduce the yield of low-boiling diolefins. In most cases a preferred operation will involve the use of only a sufficient superatmospheric pressure to overcome the pressure drop through the apparatus and provide a few pounds of superatmospheric pressure at the exit of the reaction zone.

Any suitable source of oxygen may be utilized, but air is ordinarily found to be most convenient. The inert constituents of the air have an advantageous diluting effect in the reaction zone. The amount of free oxygen utilized must be carefully controlled to obtain a sufficiently rapid and great temperature rise on the one hand, while avoiding undue destruction of hydrocarbons on the other hand. With the type of charging stocks described herein and under the given temperature and time conditions, it is necessary that free oxygen be used in an amount substantially between about 0.15 and 0.25 pound per pound of hydrocarbon material to attain the most satisfactory results. In the case of air, this requires an air-hydrocarbon weight ratio in the range of about 0.7 to 1.2.

An important feature of the present invention is the catalyst-covered porous refractory body, particularly with respect to its composition and to its position relative to the steam-hydrocarbon stream. The body proper should have a relatively large surface area, and may comprise any suitable refractory material which is stable at the high temperatures encountered. The porosity is such that the required flow of air or other oxygen-containing gas may be maintained without requiring too high a pressure drop across the body, while at the same time providing for a very intimate admixture of oxygen with hydrocarbon. The catalyst coating may comprise one or more high-melting oxides of metals of Groups IIIB, IVA, VA, VIA, or VIIA of the periodic system as grouped by Mellor, *Modern Inorganic Chemistry*, Longmans, Green & Co. (1939), page 118. Such coating may be applied in any suitable manner, exemplary of which is the impregnation of the body with, or spraying upon the surface of the body, a solution of a metal salt, followed by calcining to convert the salt to the oxide. Preferred combustion catalysts are  $\text{ThO}_2$ ,  $\text{ZrO}_2$ , and  $\text{WO}_3$ . The body thus coated with the combustion catalyst is placed in the apparatus in such way with respect to the flow of hydrocarbon reactants that the latter contact the same for only a very short period of time, and then pass away to the remainder of the reaction zone. As stated above, this provides sufficient combustion to raise the temperature to the desired range, while maintenance of temperature during the ensuing endothermic cracking is provided by continued action of the admixed oxygen with the hydrocarbons in the balance of the reaction zone. The shape of the porous body will be somewhat dependent on the design of the reactor and its location therein. One preferred shape is that of a cone, with oxygen introduced into the base thereof and the apex of the cone extending partially into the hydrocarbon

stream. This and other arrangements are shown in more detail in the drawing.

The preheated hydrocarbon-steam mixture is passed rapidly into contact with or adjacent to the catalyst-coated porous refractory body through which oxygen is being introduced, and then immediately away from said body. This insures a rapid temperature increase only to the desired level whereas if the hydrocarbon were allowed to remain in close contact with the incandescent body for a more substantial portion of the total reaction time a decomposition entirely too extensive for satisfactory diolefin production would be encountered. The reaction time allowed between introduction of preheated charge to admixture with air and the subsequent shock cooling is preferably between about 0.1 and about 0.2 second. Usually an empty reaction chamber is provided, the size of which is correlated with flow rates to give the proper reaction time. However, the reaction zone may be partially filled with metal or refractory packing to provide a more extended surface which seems to favor the continuance of the already initiated combustion. Immediately upon completion of the conversion the total reaction mixture is quenched, preferably to about 400° F. or lower.

In the choice of charging stock for diolefin production in the instant process, a certain amount of latitude is permissible, which adds to the value of the process, particularly for use in a petroleum refinery where changing operations affect the availability of any particular type of stock. As stated before, the ordinarily less valuable stocks are generally utilizable, thus enhancing the economic status of the process. The material used should, however, generally fall within the following classification: it should be non-aromatic, that is, have a content of aromatic hydrocarbons less than about ten per cent, and preferably less than five per cent; it should be normally liquid, and preferably higher boiling than the diolefin to be produced; it should be relatively light, that is, substantially boiling below about 600° F.—preferably the material comprises hydrocarbons having at least four and not more than twelve carbon atoms per molecule. As examples of such materials may be mentioned straight-run naphthas of narrow or wide boiling range, catalytically or non-catalytically cracked naphthas of narrow or wide boiling range, or mixtures of such naphthas.

In order to provide a better understanding of the invention and to illustrate the preferred features thereof, the accompanying drawing is provided which shows in somewhat diagrammatic form one arrangement of apparatus in which the process may be practiced, and which also shows in some detail preferred arrangements of the reaction system which is a particular feature of the present invention. Figure 1 is a simple flow diagram in which one form of reactor is shown in detail, while Figures 2 and 3 illustrate other preferred forms of the reactor.

In Figure 1, the naphtha or other oil to be cracked is introduced via line 10, joined by recycled material from line 12 if desired, and mixed with steam from line 14 in the proper ratio disclosed hereinabove. The resulting mixture is passed through coil 16 in preheater furnace 18 where the temperature is rapidly raised to about 1100–1200° F. The thus preheated material then flows via line 20 into reactor 22, first entering the mixing T 24. Disposed within this T with its axis at a right angle to the entering stream is

a porous refractory cone 26 coated with a combustion catalyst. The cone is inserted about halfway across the bull-head opening of the T so oil vapors flow across the cone in contact with the surface where air enters, yet leaving enough clearance so that there is no great restriction to oil flow. Air is admitted to the base of cone 26 via line 28 in a quantity based on the quantity of charge oil as described herein. The stream of preheated oil and steam flows past the cone 26 and immediately is turned to flow parallel with the axis thereof away from the cone on into the next portion of reactor 22. The air flowing through cone 26 into reactor 22 mixes with the oil and a considerable proportion of the total combustion occurs in T 24 on or adjacent the catalyst-coated surface of cone 26, which is heated to incandescence. The oxygen and the hot products of combustion rapidly mix with the hydrocarbon and immediately raise the temperature of the total stream to the desired cracking range. It will be seen that the construction of T 24 ensures ease of installation and replacement, which is of particular advantage when such high temperatures are encountered.

After cracking is completed in reactor 22, the total effluents leaving via line 30 are immediately quenched by cool liquid, such as water or oil, entering via line 32. The quenched material passes into a separation system indicated diagrammatically by unit 34. Some incompletely converted material may be recycled via line 12, but it should first be separated from aromatic hydrocarbons by suitable means. Low-boiling material is removed via line 38 and high-boiling material via line 40, while a fraction containing desired diolefins is passed via line 42 to diolefin recovery equipment 44. This may include solvent extraction, extractive distillation, azeotropic distillation, formation and decomposition of diolefin-metal salt complexes such as diolefin-cuprous chloride complex, or any other suitable means known to the art. Non-diolefinic material is removed through line 46, while the desired diolefins, such as butadiene, are recovered through line 48. It will be understood that the C<sub>5</sub> and/or C<sub>6</sub> and even heavier diolefins may be similarly recovered.

Figure 2 illustrates another manner of fashioning the portion of reactor 22 containing the porous refractory. An L 50 takes the place of T 24. A porous refractory catalyst-coated plate 52 is placed in the L as shown so that air, entering through line 28, is introduced into the flowing oil stream without too much restriction to the oil flow. The oil-steam mixture passes adjacent plate 52 and then immediately away from it into the reaction zone proper.

Figure 3 illustrates another preferred arrangement for carrying out the process of this invention, which employs a Venturi-shaped porous refractory catalyst-coated tube 54 in the oil-steam flow line, allowing for air injection from all sides of the flowing oil stream. An annular space 56 about Venturi-tube 54 is provided by cylinder 58, into which air from line 28 is introduced. The venturi decreases any possibility of the center portion of the flowing oil stream not receiving contact with the air, and provides an added mixing effect due to the pressure drop across the venturi. The hot gases pass rapidly from glowing tube 54 on into the remaining portion of reactor 22.

The following example is given as a means of illustrating the results which are obtainable in the practice of this invention. It will be understood,

of course, that the exact data given are not to be construed as unduly limiting since the different factors may be varied within the preferred ranges as heretofore set out.

A straight-run naphtha having a boiling range of 200-400° F. is admixed with 5 mols of steam per mol of oil and preheated to 1100° F. This preheated material is then passed into a reactor similar to that shown in Figure 1 in contact with a porous Alumdum body coated with thorium oxide by impregnation with a solution of thorium nitrate followed by burning to convert the thorium salt to the oxide. Air, preheated to 500° F., is introduced through the porous body at the rate of 1.1 pound per pound of oil charged. Based on the volume of material charged, a reaction time of 0.2 second is realized, and the temperature at the outlet of the reactor is 1600° F. The reactor effluent is immediately quenched with water to about 350° F. and passed to separating equipment comprising conventional absorbers and fractionators. The C<sub>4</sub> cut is recovered and the butadiene, which comprises 45 to 50 per cent of the cut, is separated therefrom by extractive distillation with furfural. The weight ratio of butadiene to dry gas (C<sub>3</sub> and lighter) is 0.11, and the over-all yield of butadiene is 4.5 weight per cent based on the charge. Substantial, though lesser, amounts of C<sub>5</sub> diolefins are also recovered from the process effluents.

I claim:

1. A process for producing low-boiling diolefin hydrocarbons, which comprises preheating a gaseous mixture of steam and a nonaromatic hydrocarbon material having four to twelve carbon atoms per molecule to a temperature of at least about 1100° F., passing said preheated mixture to a partial-combustion-reaction zone, passing also to said zone a gas containing free oxygen in an amount between about 0.15 and 0.25 pound of free oxygen per pound of hydrocarbon material, introducing said oxygen-containing gas into said zone through an incandescent porous refractory material of relatively large surface area and coated on the inside surface with a metal oxide combustion catalyst, introducing said preheated steam-hydrocarbon mixture into said zone at a point immediately adjacent said catalyst-coated surface and in a manner such that the resulting gases pass directly away from said surface to and through a reaction zone which is in relatively free communication with but extends away from said surface, retaining said resulting gases in said reaction zone at the resulting temperature for a time such as to effect an optimum production of low-boiling diolefins, shock-cooling said gaseous mixture at the end of said reaction time to effect a cessation of hydrocarbon conversion reactions, and recovering a low-boiling diolefin so produced.

2. A process for producing low-boiling diolefin hydrocarbons of at least four carbon atoms per molecule from a low-boiling nonaromatic hydrocarbon material comprising more-saturated hydrocarbons of at least four carbon atoms per molecule, which comprises preheating such a material to a temperature between about 1000 and 1200° F., passing a gas containing free oxygen upward and outward through a cone-shaped wall consisting of a porous refractory material coated on the outside with a metal oxide combustion catalyst, the outside surface of said cone-shaped wall forming one end of an elongated partial-combustion-reaction zone, passing said preheated hydrocarbon material into said zone adjacent to

said catalyst-coated outside surface of said cone and at a perpendicular to the axis of said cone, portioning the amounts of said hydrocarbon material and said oxygen-containing gas such that between about 0.15 and 0.25 part by weight of free oxygen enters said zone per part of said hydrocarbon material, passing the resulting admixture through said zone in a direction away from said cone and parallel to the axis of said cone, maintaining a reaction time such as to effect an optimum production of low-boiling diolefins, shock-cooling said gaseous mixture at the end of said reaction time to effect a cessation of hydrocarbon conversion reactions, and recovering a low-boiling diolefin so produced.

3. A process for producing low-boiling diolefin hydrocarbons of at least four carbon atoms per molecule from a low-boiling nonaromatic hydrocarbon material comprising more-saturated hydrocarbons of at least four carbon atoms per molecule, which comprises preheating such a material to a temperature between about 1000 and 1200° F., passing thus preheated material through a tube containing a section of restricted cross-section, said section comprising a porous refractory material coated on the inside with a metal oxide combustion catalyst, passing a gas containing free oxygen through the pores of said refractory material to the interior of said tube for admixture with and combustion of hydrocarbon material passing therethrough, portioning the amount of said hydrocarbon material and said oxygen-containing gas such that between about 0.15 and 0.25 part by weight of free oxygen is introduced per part of said hydrocarbon material, maintaining in said tube the resulting admixture at the resulting temperature for a time such as to effect an optimum production of low-boiling diolefins, shock-cooling said gaseous mixture at the end of said reaction time to effect a cessation of hydrocarbon conversion reactions, and recovering a low-boiling diolefin so produced.

4. A process for producing low-boiling diolefin hydrocarbons of at least four carbon atoms per molecule from a low-boiling nonaromatic hydrocarbon material comprising more-saturated hydrocarbons of at least four carbon atoms per molecule, which comprises preheating such a material to a temperature between about 1000 and 1200° F., passing thus preheated material through an L-shaped conduit in the corner of which is disposed a porous refractory plate coated with

a metal oxide combustion catalyst, passing a gas containing free oxygen through said plate to the interior of said conduit for admixture with and combustion of hydrocarbon material passing therethrough, portioning the amount of said hydrocarbon material and said oxygen-containing gas such that between about 0.15 and 0.25 part by weight of free oxygen is introduced per part of said hydrocarbon material, passing resulting gases away from said plate in a direction substantially at right angles to the direction of flow of the entering stream of preheated hydrocarbon material, maintaining said resulting gases as the resulting temperature for a time such as to effect an optimum production of low-boiling diolefins, shock-cooling said gaseous mixture at the end of said reaction time to effect a cessation of hydrocarbon conversion reactions, and recovering a low-boiling diolefin so produced.

5. A process according to claim 1 in which said metal oxide is thorium oxide.

6. A process according to claim 1 in which said metal oxide is zirconium oxide.

7. A process according to claim 1 in which said metal oxide is tungsten oxide.

8. A process according to claim 1 in which said resulting gases are maintained at a temperature in the range of about 1400-1600° F. for a time in the range of about 0.1-0.2 second.

9. A process according to claim 1 in which the mol ratio of steam to hydrocarbon in said first-named gaseous mixture is in the range of about 3:1 to about 6:1.

10. A process according to claim 2 in which steam diluent is admixed with said hydrocarbon material prior to contacting the same with said free oxygen, the mol ratio of steam to hydrocarbon material in the admixture being in the range of about 3:1 to about 6:1.

11. A process according to claim 3 in which steam diluent is admixed with said hydrocarbon material prior to contacting the same with said free oxygen, the mol ratio of steam to hydrocarbon material in the admixture being in the range of about 3:1 to about 6:1.

12. A process according to claim 4 in which steam diluent is admixed with said hydrocarbon material prior to contacting the same with said free oxygen, the mol ratio of steam to hydrocarbon material in the admixture being in the range of about 3:1 to about 6:1.

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