

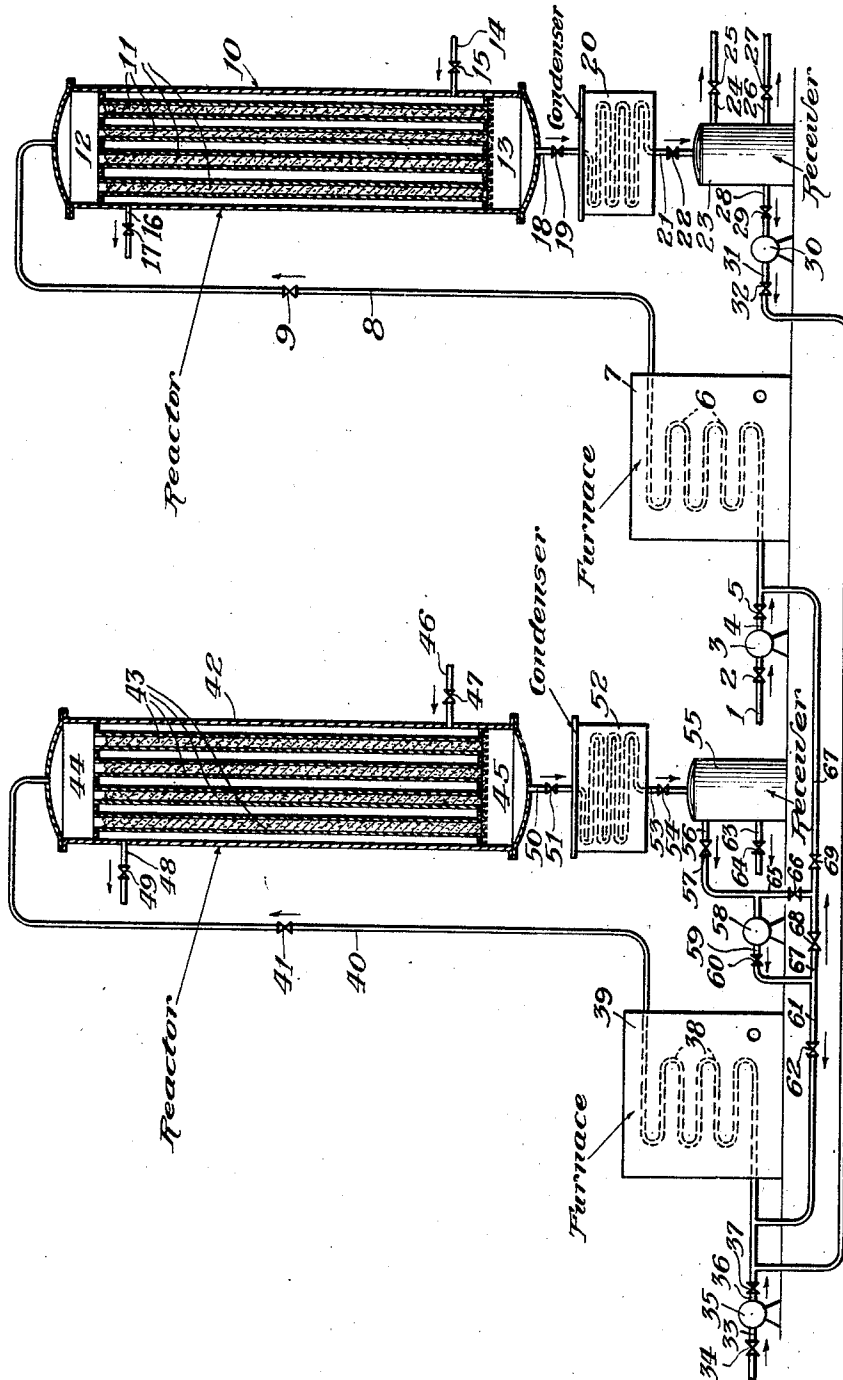
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HYDROGENATION

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# UNITED STATES PATENT OFFICE

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## HYDROGENATION

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2 Claims. (Cl. 260-676)

This invention relates more particularly to processes involving the direct addition of hydrogen to unsaturated hydrocarbons in the presence of catalysts.

5 More specifically it is concerned with a process which finds applicability in the saturation of mono olefinic hydrocarbons boiling within the range of gasoline such as, for example, the mono olefinic liquid polymers produced by the polymer-  
10 ization of normally gaseous olefin hydrocarbons either by thermal or thermal-catalytic methods.

The lower boiling polymers produced from the normally gaseous olefins are generally of a character permitting their direct blending with hydrocarbon motor fuels of inferior knock rating, since the mono olefins have relatively little tendency to undergo extensive changes under average gasoline storage conditions and this slight tendency may be readily counteracted by the use  
15 of small quantities of antioxidants or inhibitors. Similarly, cracked gasolines which have been freed from their more reactive olefinic hydrocarbon constituents by light treatment with sulfuric acid or adsorbents such as fuller's earth are also  
20 readily inhibited. However, the more stringent specifications for airplane motor fuels generally demand a hydrocarbon mixture which is substantially completely saturated to eliminate all tendency to gum formation and deposits in feed lines  
25 and which at the same time has a very high antiknock value. These requirements are met only by hydrocarbon mixtures consisting of naphthenes of limited boiling range and the isoparaffins, and of the two groups, isoparaffins are preferable on account of their higher antiknock rating. The process of the invention to be presently described is particularly applicable to the complete saturation with hydrogen of the dimers produced by the polymerization of the butenes to  
30 produce mixtures consisting principally of iso-octanes.

In one specific embodiment the present invention comprises the substantially complete hydrogenation of normally liquid olefins and particularly  
35 octenes in two stages wherein the olefins undergoing hydrogenation are treated in the first stage with quantities of hydrogen or hydrogen-containing gas insufficient to completely saturate the olefins, the supply of gas being that separated  
40 from the product of the second stage and wherein the partially hydrogenated olefins are contacted in a second and final stage with an excess of hydrogen over that necessary to effect total saturation, this excess being maintained by the  
45 introduction of hydrogen or gas mixtures rich in

hydrogen and the forced recirculation of the residual hydrogen containing gas remaining after condensation of the completely hydrogenated product.

The process thus comprises generally a counter-current hydrogenating treatment in which the relative concentration of hydrogen in the final stage is increased by rapid recirculation of hydrogen-containing gases and for this reason the process is specially adapted to the utilization  
5 of hydrogen-containing gas mixtures of fairly high hydrogen content rather than the more expensive pure hydrogen produced by such processes as the electrolytic process and processes involving the action of mineral acids on metals. To  
10 further show the features of the process, the attached drawing has been provided which shows the essential parts of a plant in which the process may be conducted. The figures are conventional  
15 and not drawn to any exact or relative scale. The description will be made in connection with the hydrogenation of octenes such as those resulting from the primary polymerization of butylenes to form dimers, though it is to be understood that the principles of the process are as applicable to  
20 other olefins or olefin-containing hydrocarbon mixtures, or unsaturated hydrocarbons generally.

Referring to the drawing, octenes may be admitted to the plant through a line 1 containing a valve 2 from a storage not indicated, to a charging pump 3 which discharges through line 4 containing a valve 5 into and through a pre-heating element 6 arranged in a furnace setting 7. The hydrogen necessary for partially saturating the hydrocarbons is admitted to line 4 from line 6  
25 and valve 69, the source of this gas mixture being described in connection with the second stage of the hydrogenation. Since the process is not limited to any particular catalyst or conditions of temperature, pressure, and rate of flow in the two  
30 stages, only general ranges need be given. The hydrogenation of mono olefins as a rule requires only moderate temperatures of the order of approximately 300-600° F. and moderate pressures of the order of substantially atmospheric to 500  
35 lbs. per square inch. It is preferred in the present instance to maintain substantially vapor phase conditions in the hydrogen-olefin mixture passing over the catalysts.

The preheated mixture of hydrogen and olefin passes through line 8 containing valve 9 into the upper section 12 of a reactor 10 which preferably consists of multiple parallel tubes of relatively small diameter which contain granular catalyst 11. The mixture of hydrogen and olefin  
40 45 50 55

passes downwardly through the granular catalyst and enters lower section 13. Since the reactions of hydrogenation are exothermic, cooling is necessary to maintain a constant temperature and provision is made for circulating cooling fluid around the nest of tubes by introducing said fluid through line 14 containing valve 15 and discharging it through line 16 containing valve 17. The partially hydrogenated hydrocarbon plus fixed gases which may consist of unused hydrogen and of methane or any other gases present in the original hydrogen-containing gas mixture pass through a line 18 containing a valve 19 and through a condenser 20, the condensed liquids and fixed gases then passing through line 21 containing valve 22 to a receiver 23 which has a vent line 24 containing a valve 25 for the release of the fixed gases which are too low in hydrogen to make their re-use worth while. If desired a portion of the partially hydrogenated product may be withdrawn through line 26 containing valve 27.

The liquid in receiver 23 is now further subjected to hydrogenation in the second stage of the process and is taken through line 28 containing valve 29 by a pump 30 and discharged through line 31 containing a valve 32 to mix with the fresh and recirculated hydrogen-containing gas. The primary hydrogen supply is introduced through line 33 containing a valve 34 and brought up to the required pressure by means of the compressor 35 which discharges through line 36 containing a valve 37. Recirculated hydrogen from the receiver of the second hydrogenating stage enters line 36 by way of line 61 and the mixture of partially saturated olefin plus an excess of hydrogen is preheated to a proper temperature during passage through a heating coil 38 arranged to receive heat from a furnace 39. The general conditions of operation in the second stage will be broadly the same as those employed in the first stage though in the case of any given charge they will obviously be modified in consideration of the degree of saturation of the partially saturated material from the primary stage and the excess of hydrogen which is present.

The preheated hydrogen and olefin vapors follow line 40 containing valve 42 and enter the upper section 44 of reactor 42 which may be of the same general construction as the primary stage reactor 10 and contain granular catalyst 43 in nested tubes, the products of hydrogenation plus excess hydrogen accumulating in lower section 45. Cooling fluids may be introduced around the reaction tubes through inlet line 46 containing valve 47 and discharged through exit line 48 containing valve 49.

Unused hydrogen and other fixed gases along with vapors of hydrogenated hydrocarbons pass through line 50 containing a valve 51 and through a condenser 52 in which the normally liquid constituents are condensed to flow in admixture with the fixed gases through line 53 containing valve 54 to receiver 55, the final completely hydrogenated product being withdrawn to storage through line 63 containing valve 64.

The fixed gas mixture from receiver 55 is vented through a line 56 containing a valve 57 and taken by a compressor 58 to be discharged through a line 59 containing a valve 60. At this point the amount of gas recirculated through line 61 and valve 62 to the final hydrogenating stage is preferably regulated so that there is a considerable excess of hydrogen over that neces-

sary for complete saturation of the partially saturated products from the primary hydrogenating stage. In the operation of the present process the second stage of hydrogenation in which the partially hydrogenated hydrocarbons from the first stage are finally admixed with hydrogen from outside sources and recirculated hydrogen-containing gases, is preferably operated at a somewhat higher pressure than the first stage so that in most instances the pressure in the receiver 55 will be sufficient to cause a flow of hydrogen-containing gas to the first stage of the process from line 56 through line 65 and valve 66 and line 67 and valve 69. However, if the rate of recirculation of hydrogen by pump 58 is high, the pressure in line 56 may be reduced to an extent that it cannot be depended upon to insure a regular flow into line 65, in which event advantage may be taken of the discharge pressure of the pump and the gas passed to the first stage by way of line 67 and valves 68 and 69 with valve 66 closed. In either event valve 69 may be of the automatic regulator type.

The process thus briefly described above is particularly suited to the employment of what may be termed impure hydrogen as long as there are no substances contained therein which poison the catalysts used, such as hydrogen sulfide, chlorine, etc. Thus it is particularly suited to the utilization of hydrogen produced by cracking heavier hydrocarbons or hydrogen-containing mixtures produced by the interaction in the presence of catalysts of methane or other light hydrocarbons with steam to produce mixtures of carbon monoxide and hydrogen. It has been shown by experiments that whereas a molecular excess of 2:1 of hydrogen to octenes may be necessary in a single stage catalytic hydrogenation to produce a mixture consisting of 98% octanes, the present process may require as low as only a 10% excess of hydrogen to effect the same degree of saturation. When operating on octenes with fairly active catalysts, such as, for example, reduced nickel on siliceous supports, circulation of the separated gases from the final stage is maintained at such a rate that with the fresh supply of hydrogen admitted there is present at all times approximately two times as much hydrogen as is necessary to effect the substantially complete saturation of the product from the first stage.

The foregoing specification along with the accompanying numerical data are sufficient to illustrate the commercial value and the nature of the results obtainable by the use of the present process, but neither are intended to unduly limit the scope of the invention.

I claim as my invention:

1. A two-stage hydrogenating process which comprises subjecting unsaturated hydrocarbon material in a first hydrogenating stage to hydrogenating conditions in admixture with a limited quantity of hydrogen such as to effect only partial saturation of the hydrocarbon material, supplying the partially saturated material to a second hydrogenating stage, introducing fresh hydrogen-containing gas to said second stage and therein completely saturating the hydrocarbon material, separating the saturated material from residual hydrogen-containing gas, supplying to the first stage such an amount of said residual gas as will provide said limited quantity of hydrogen in the first stage, and recirculating a sufficient quantity of the residual gas to the second stage to maintain therein an excess of hydrogen

over that required for the complete saturation of the partially saturated hydrocarbon material.

2. A process for converting octenes into octanes which comprises subjecting the octenes in a first hydrogenating stage to hydrogenating conditions in admixture with a limited quantity of hydrogen such as to effect only partial saturation of the octenes, supplying the partially saturated octenes to a second hydrogenating stage, introducing fresh hydrogen-containing gas to the second stage and therein completing the saturation of

the octenes, separating the resultant octanes from residual hydrogen-containing gas, supplying to the first stage such an amount of said residual gas as will provide said limited quantity of hydrogen in the first stage, and recirculating a sufficient quantity of the residual gas to the second stage to maintain therein an excess of hydrogen over that required for the complete saturation of the partially saturated octenes.

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