

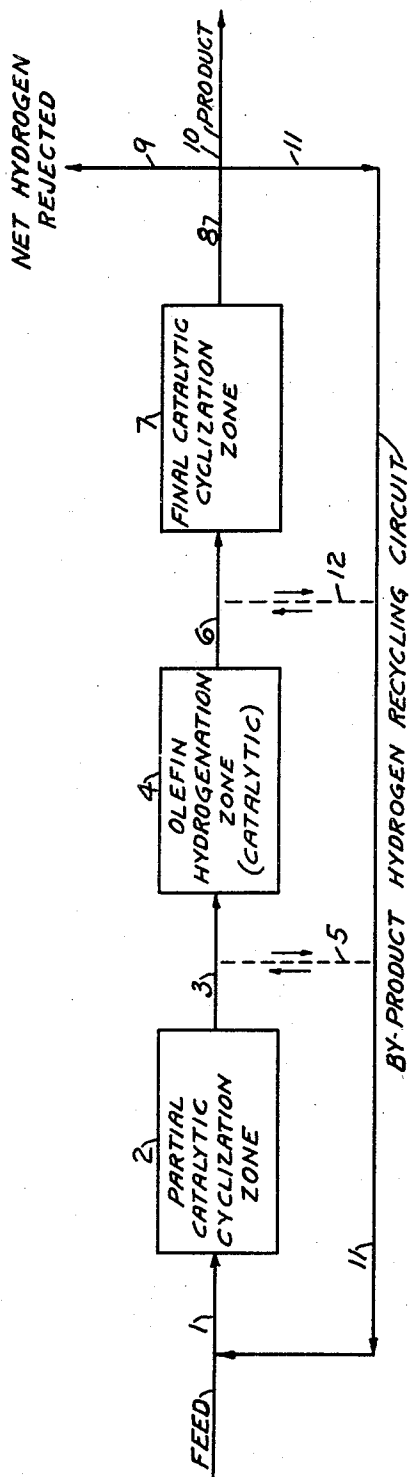
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PROCESS FOR CYCLIZING HYDROCARBONS

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PROCESS FOR CYCLIZING HYDROCARBONS

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This invention relates generally to the catalytic dehydrogenation of hydrocarbons, and particularly to the conversion of paraffinic hydrocarbons into cyclic hydrocarbons by the action of a catalyst.

Theoretically, it should be possible to convert paraffinic hydrocarbons into naphthenic and aromatic hydrocarbons catalytically without forming any by-products other than hydrogen. In practice, however, this ideal is never attained; solid carbonaceous matter is invariably deposited upon the catalyst and in time accumulates to such an extent that the activity of the catalyst is impaired. Removal of the contaminating deposit restores the catalyst to its initial activity or very nearly so, but in continuous large-scale operations such removal is by all methods now known quite expensive, entailing investment and operating costs which are frequently greater than those associated with the conversion step itself.

One of the objects of my invention is to provide a method of decreasing the amount of solid carbonaceous matter formed during the catalytic conversion of paraffin hydrocarbons into cyclic hydrocarbons.

Another object of my invention is to provide an improved catalytic paraffin cyclization wherein contamination of the catalyst takes place more slowly, and wherein regeneration of the catalyst is necessary less frequently than in prior known processes. Other objects of the invention will be apparent during the course of the following description.

When vaporized paraffinic hydrocarbons are contacted with a cyclization catalyst in accordance with known methods of cyclization, the paraffins are apparently converted successively to compounds having lower and lower hydrogen-carbon ratios until, if the treatment is sufficiently severe, aromatics are formed. At least some of the paraffins are first converted into olefins before being sufficiently dehydrogenated to form cyclic compounds. Supposedly because of differences in the rates of the paraffin-to-olefin and olefin-to-cyclic reactions, the olefin content of a mixture undergoing cyclization builds up during the early stages of conversion, and is not entirely depleted even after a major portion of the paraffins have been cyclized.

I have discovered that a substantial if not a

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major proportion of the carbonaceous matter deposited upon catalysts during paraffin cyclization is derived in some way from transitory olefins, and that the greatest amounts of carbonaceous matter are laid down during those stages of the cyclization in which the olefin content of the reactants is greatest. This may be due to polymerization of the olefins to high molecular weight solid compounds, or to thermal cracking accelerated by the instability or reactivity of hydrocarbons containing olefinic double bonds.

The present invention contemplates the contacting of paraffinic hydrocarbons with a cyclization catalyst under cyclizing conditions, the interruption of the ensuing conversion at an intermediate stage thereof, and the elimination of olefins which have been formed. The invention further contemplates starting anew with the partially cyclized material of reduced olefin content and continuing the cyclization reaction.

It is within the scope of my invention to eliminate olefins from a partially-cyclized mixture by simple removal, for example by treating the mixture either in the liquid or vapor phase with a substance such as sulfuric acid having a selective affinity for olefins. However, I prefer to eliminate olefins by preferential catalytic hydrogenation, converting them back into paraffins so that they may be cyclized in a subsequent stage of treatment. This method has the advantage of involving the least departure from cyclization conditions intermediate the cyclization stages.

The type of hydrogenation I employ is a mild one, involving only the saturation of olefinic double bonds. In general this is a comparatively low-pressure process and is not to be confused with the so-called destructive hydrogenation process which is conducted ordinarily at very high pressures. The mild type of hydrogenation does not produce significant changes in the average number of carbon atoms per molecule with an accompanying increase in volatility, which apparently is characteristic of destructive hydrogenation.

In further cyclizing material which has been subjected to the intermediate olefin-eliminating step, additional olefins will be formed, but the average olefin content and hence the total degradation to carbonaceous material will, for the process as a whole, be substantially reduced. In some

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instances, it is contemplated by my invention to interrupt a cyclization reaction repeatedly and interpose olefin-eliminating steps, whereby the average olefin content of the reactants and the total deposition of catalyst contaminants may be further reduced.

It will be seen that paraffin cyclization in accordance with my invention, because of the retarded catalyst contamination associated therewith, enables an increased amount of hydrocarbons to be converted before regeneration of the catalyst is necessary. The catalyst then need be out of service for regeneration during a smaller percentage of the time, and cyclization may be accomplished more cheaply and efficiently.

A more detailed description of my invention will now be given with reference to the annexed drawing, which is a diagrammatic flow sheet illustrating one form of the invention. In the drawing, rectangles are used to designate successive zones of hydrocarbon treatment, and lines are used to show the paths of materials entering and leaving the zones.

As illustrated by line 1 of the drawing, a vaporized paraffinic hydrocarbon fraction is introduced into the presence of a cyclization catalyst in a zone 2 maintained under conditions favorable to cyclization. The time of residence of the reactant material in the zone is such that the conversion occurring therein will be preferably not less than about 20% nor more than about 60% of that desired in the final product.

Partially converted reactants pass from zone 2, as indicated by line 3, into zone 4 in which are maintained conditions favorable to olefin hydrogenation but not sufficiently severe to hydrogenate the cyclic compounds produced in zone 2. The cyclization occurring in zone 2 may produce greater or less amounts of hydrogen depending upon the type of feed stock and the extent of conversion. In the event that olefin hydrogenation is desired to be effected in the presence of a greater or less amount of hydrogen than that produced in zone 2 the excess or the deficiency is corrected by the respective withdrawal or addition of hydrogen as indicated by dotted line 5, any added hydrogen being obtained from the final products of the process as hereinafter described. Hydrogen may be separated from the partially cyclized hydrocarbon reactants by condensing them to liquids, after which revaporization of the latter will be necessary before proceeding with olefin elimination.

After contacting a suitable hydrogenation catalyst in zone 4 and being freed of olefins the reactants pass as indicated by line 6 into a second cyclization zone 7 wherein they are subjected to further cyclization in a manner similar to that described with reference to zone 2, except that the treatment is made sufficiently severe and prolonged to complete the desired conversion. Thereafter, as indicated by lines 8, 9 and 10, by-product hydrogen (in admixture with other normally gaseous by-products) is separated in any suitable manner from the cyclized product and rejected from the process via line 9.

It has been found that the contamination of dehydrogenation catalysts during cyclization is retarded appreciably by the presence of hydrogen, or a gas mixture containing hydrogen, added to reactants before conversion commences. I may take advantage of this fact to enhance the efficacy of my invention by recirculating by-product hydrogen-containing gas and admixing it with material about to enter a cyclization zone.

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As indicated by line 11, I may introduce by-product hydrogen into the material entering zone 2, or via line 12 into the olefin-free material entering zone 7. In the event that more hydrogen remains after the hydrogenation step than is desired in zone 7, transfer in the reverse direction along line 12 may be adopted, in which case condensation of hydrocarbons is again necessary to effect separation of the excess hydrogen. The introduction of by-product hydrogen into line 3 has already been referred to, and any excess hydrogen withdrawn through lines 5 or 12 into line 11 may augment that obtained from line 8 in building up higher hydrogen content wherever necessary.

None of the various stages of treatment contemplated by my invention require to be carried out in any special type of apparatus, and any which is suitable to the contacting of reactant vapors with a catalyst at an elevated temperature and superatmospheric pressure may be employed. Catalyst may remain static in a containing vessel and be subjected alternately to conversion and regeneration, or it may move continuously and alternately through a conversion zone and a regeneration zone.

Conditions suitable to olefin hydrogenation are usually characterized by lower temperature than cyclization conditions, and I may employ any suitable heat-transferring devices such as heat exchangers in altering the temperature of reactants between a hydrogenation stage and a cyclization stage. In the event that hydrogen is to be added to reactants between any two stages, I may introduce the hydrogen relatively hot or cold to alter the temperature of the reactants as desired. Heating or cooling reactants in the conversion zones themselves may be accomplished by locating heat-transferring surfaces therein.

My invention may be applied, with particular advantage, to the manufacture of superior motor fuel from paraffinic naphtha, by conversion of straight chain hydrocarbons of poor anti-knock characteristics into naphthenic and aromatic compounds having high octane numbers. When my invention is so applied I prefer to operate pursuant to the teachings of my co-pending application (with L. C. Rubin) Serial No. 294,784, now Patent Number 2,320,147. In such operation I employ two cyclizing stages maintained under a pressure between about 30 and about 450 pounds per square inch, and at a temperature between about 875° and 1025° F.; I may use any suitable cyclization catalyst, of which chromium oxide and molybdenum oxide supported on activated alumina are exemplary. I prefer that the second cyclization stage shall be characterized by the greater severity factor, as defined in my co-pending application above referred to. That is to say, I prefer that a greater proportion of the desired conversion shall take place in the second stage than in the first, as may be insured by contacting the reactants with a greater quantity of catalyst in the second stage than in the first. Optionally, I may use the same amount of catalyst in both stages while maintaining a higher reaction temperature in the second stage than in the first.

It appears that the olefin content of a mixture undergoing cyclization increases to a maximum during the initial portion of the conversion, and then declines slowly. A lower average olefin content is therefore obtained by interposing olefin elimination approximately at that point where the olefin content has ceased to increase. With

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operating conditions and catalysts different from those preferred by me, however, it may be desirable to put the olefin-eliminating step later or earlier in the cyclization.

I prefer to conduct the cyclization reaction in the presence of hydrogen added to the reactant mixture in amounts as disclosed in my co-pending application, namely 0.5 to 8.0 mols of hydrogen per mole of fresh feed hydrocarbons. I may, however, use different amounts of hydrogen in the different cyclization stages.

In motor fuel manufacture as above described, sufficient hydrogen for the olefin hydrogenation will usually be produced by the initial cyclization stage. I prefer that there shall be two to four times as much hydrogen present as is required to saturate the olefinic compounds present. In the treatment of straight-run paraffinic naphtha, from 0.25 to 1.5 mols of hydrogen per mol of naphtha will usually satisfy the latter preference. This hydrogen need not be in the pure state, but may be admixed with relatively inert gases such as methane and ethane.

For the olefin hydrogenation I preferably employ the same catalysts as in the cyclizing stages, catalytic dehydrogenation of paraffins to olefins being a reversible reaction. Alternatively, I may use a nickel catalyst for the hydrogenating step. The catalyst in the preceding cyclization is then advantageously molybdenum oxide, which will protect nickel from contact with any poisonous sulfur compounds in the feed by reacting with them to form molybdenum sulfide.

When one of the hydrogenation-dehydrocyclization catalysts such as chromium or molybdenum oxide is used in the hydrogenation stage, that stage may be maintained at a relatively high temperature below the cyclization range, for example between 600° and 750° F. Such high temperatures are not essential to the hydrogenation reaction, but they minimize the amount of cooling necessary subsequent to the preceding cyclizing stage and the amount of reheating prior to the succeeding cyclizing stage. If a nickel catalyst is used a somewhat lower temperature, in the vicinity of 200° F., is required.

The hydrogenating stage is suitably maintained at a pressure, in the range specified for the cyclizing stages and preferably at the same pressure as actually used in said stages. Generally speaking, the higher hydrogenation pressures will be used with the higher temperatures, and vice versa, in order to insure that only the olefins, which are the most readily hydrogenated compound encountered in the partially converted products, will be hydrogenated.

In the event that a stock to be cyclized already contains an appreciable amount of olefins, I may interpose a hydrogenation stage preceding the first cyclization stage, so that the latter may enjoy the benefits of an olefin-free feed.

Also cracked naphtha from a thermal conversion operation, or other highly olefinic material, may be introduced directly into zone 4 of the drawing, and the severity of conversion in zone 7 made sufficient to produce a desired product in the absence of the preliminary conversion normally afforded by zone 2 when non-olefinic feed is to be treated.

It has been proposed, by L. C. Rubin in his co-pending application Ser. No. 330,315 to combine or overlap a cyclization stage with an olefin hydrogenation stage by establishing a downward temperature gradient through a zone containing a hydrogenation-dehydrogenation catalyst.

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It is within the scope of my invention to substitute such a zone in place of any two consecutive cyclization and hydrogenation zones, and such substitution may be advantageous when relatively small amounts of olefins are to be eliminated.

While reference has been made in the foregoing description to the cyclization of paraffins, it will be understood that in treating in accordance with my invention a feed stock containing naphthenes as well as paraffin, the naphthenes will be further cyclized by dehydrogenation to aromatics. My invention is therefore not limited to the treatment of purely paraffinic materials.

While various modifications have been referred to, it is to be understood that my invention is not limited thereby, but only in and by the following claims, wherein I wish to claim all novel features of my invention.

1. In a process for the production of hydrogen and aromatic hydrocarbons from paraffinic hydrocarbons within the gasoline boiling range, by contacting such paraffinic hydrocarbons with a dehydrogenating and cyclicizing catalyst at a temperature and space velocity adapted to effect dehydrogenation and cyclization thereof, the improvement which consists in effecting said contact in a plurality of successive stages and treating the reaction products from the first of said stages in an intervening stage to eliminate olefins therefrom by catalytically hydrogenating them to paraffins prior to their passage to the second stage.

2. A process as defined in claim 1 wherein said dehydrogenation and cyclization reaction is effected at a pressure between about 30 and 450 pounds per square inch, at a temperature of about 875 to 1025° F., and in the presence of between 0.5 to 8 mols of added hydrogen per mol of hydrocarbon.

3. In a process for the conversion of paraffinic hydrocarbons within the gasoline boiling range to hydrogen and aromatic hydrocarbons by a catalytic dehydrogenation and cyclization reaction, the improvement which consists in effecting said conversion by passing the reactants in the vapor phase through at least three catalytic stages without intervening condensation and separation of products, the first and third stages being effected under reaction conditions including a relatively high temperature adapted to promote dehydrogenation and cyclization of the paraffinic hydrocarbons and the intervening stage being effected under reaction conditions including a relatively low temperature adapted to selectively hydrogenate olefinic constituents produced in the first stage.

4. A process as defined in claim 3 wherein hydrogen produced in the process is separated from the last stage reaction products and recycled to the reactants entering one of said stages.

5. In a process for the conversion of a low octane paraffinic naphtha to a high octane highly aromatic motor fuel by a catalytic dehydrogenation and cyclization reaction, the improvement which consists in effecting said conversion by vaporizing the naphtha and passing the vapors through at least three catalytic stages without intervening condensation and separation of products, the first and third stage being effected under reaction conditions including a relatively high temperature adapted to promote dehydrogenation and cyclization of the paraffinic hydrocarbons and the intervening stage being effected under reaction conditions including a relatively low temper-

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ature adapted to selectively hydrogenate olefinic constituents produced in the first stage.

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