

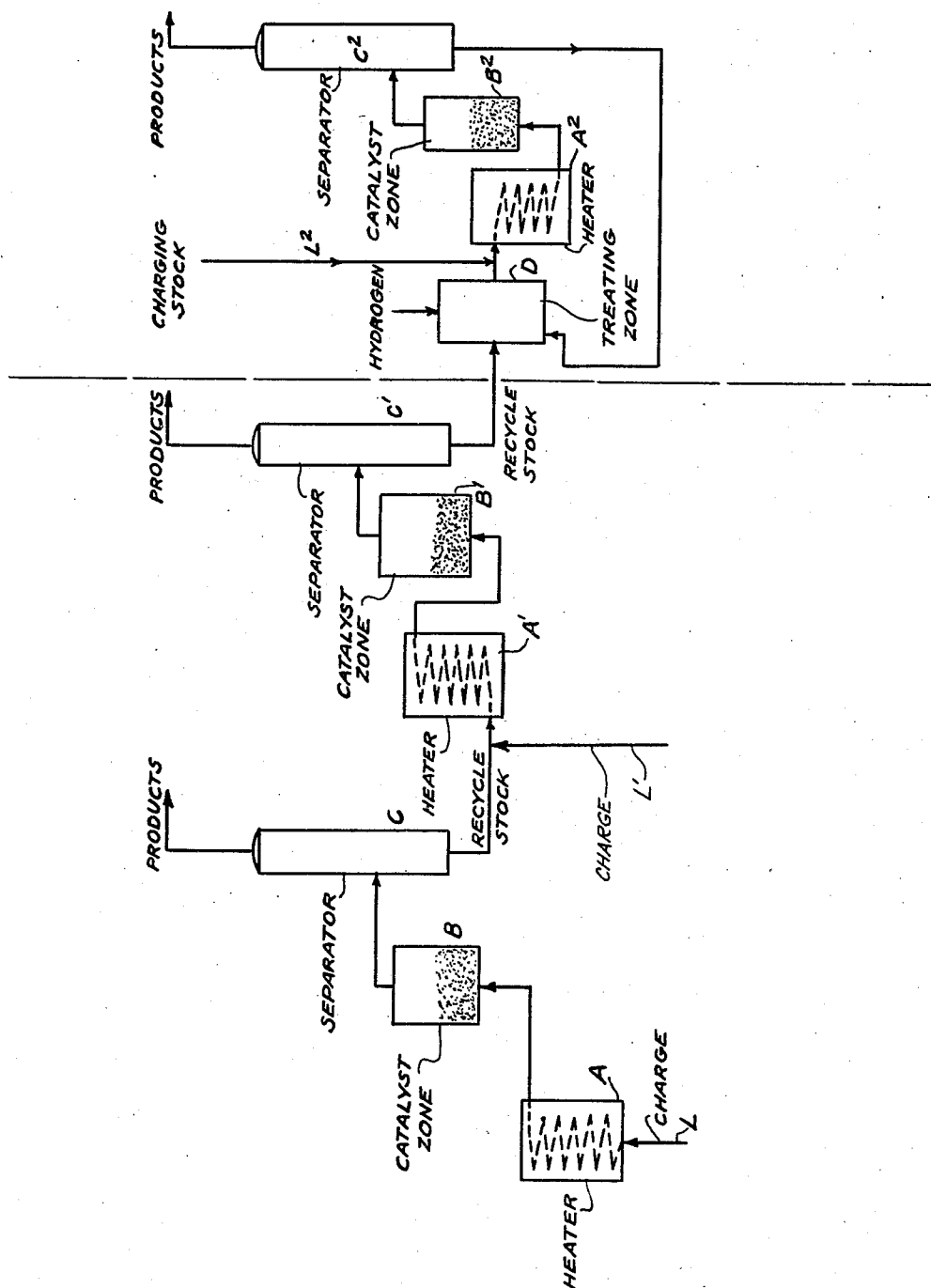
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PRODUCTION OF LOW BOILING HYDROCARBONS

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PRODUCTION OF LOW BOILING HYDRO-CARBONS

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1 Claim. (Cl. 196—50)

This invention relates to catalytic or contacting operations for producing low boiling hydrocarbons, including those in the gasoline boiling range, from higher boiling hydrocarbons. More particularly the invention is concerned with treating the residue of one or more catalytic transforming operations in a manner to adapt it to further catalytic transforming operations.

One object of the invention is to provide a process for obtaining high yields of low boiling products from an original charging stock. Another object is to reduce the components in a residue which forms undesirable products during a catalytic cracking operation without decreasing the liquid volume of the residue. Another object is to reduce the refractory aromatic compounds contained in a residue by conversion to compounds which are readily cracked to gasoline by catalytic processes. Other objects will be apparent from the detailed description which follows.

In the contact treatment of high boiling hydrocarbons involving the use of suitable catalytic adsorptive masses which include those made up solely or in part of materials from the group comprising silicates of alumina of natural or synthetic origin, the recoverable products from the process consist of overhead vapors which are mainly the desired low boiling products with a small proportion of fixed gases and a liquid residue consisting of higher boiling hydrocarbons. The contacting operations are usually carried out at temperatures between 700° and 950° F., and during the production of the low boiling product, carbon is deposited on the catalyst or contact material which is later removed by oxidation over a period of time, depending on the amount of carbon which has been deposited. The period during which the carbon is removed or the regeneration period is unproductive since during this time the catalyst cannot be used for obtaining the desired low boiling products. For the most efficient operation it has been found that the coke deposit during the productive or on-stream period should be limited to a small amount in relation to the contact material in order that the latter may have sufficient activity throughout such period to give a high yield of desired products and also in order to limit the duration of the periods of regeneration.

The rapidity and amount of coke deposition during the initial pass or first cracking in the presence of a contact mass, under given conditions of operation, will vary, of course, with different charging stocks but the rapidity of the

coke deposit from residues or recycle stocks, it has been observed, tends to increase after the first pass and to continue to increase with each successive pass and not only that but the percentage of the residual charge which is transformed to the desired low boiling hydrocarbons tends to decrease after the first pass and to continue to decrease with each successive pass. It will be apparent from these facts that the catalytic or contacting treatment of hydrocarbons tends to produce coke forming compounds which remain in a residue or recycle stock and at the same time tends to reduce the compounds which can be cracked to the desired low boiling hydrocarbons.

Due to the tendency of catalytic cracking operations to produce components which form coke, difficulty has been experienced in the past in obtaining an economical cycle of alternate on-stream and regeneration reactions when the residual material is recycled with fresh charge. This is due to the increased rapidity of coke formation when the residual material is cracked and necessitates changes in the operating conditions, such as a shortening of the on-stream period or a modification of the rate of feed of the charge, in order to prevent the formation of too great a coke deposit which would require a longer period of regeneration than is usually provided for in the cycle of operation.

Basing our experiments on the above observations relative to the catalytic treatment of hydrocarbons, examinations of various original charging stocks indicate that the catalytic or contacting operations have a tendency to form high boiling or highly refractory aromatics which remain in the residue and when the residue is used in a succeeding catalytic operation the refractory aromatics increase the rapidity of the coke deposit while producing little or none of the desired low boiling hydrocarbons. It is further indicated that the refractory aromatics are formed from the naphthenic content of an original charge or from the naphthenic content of a residual oil since when no naphthenes or naphthenic compounds including tetrahydronaphthalenes are present in a charge the production of refractory aromatics during the catalytic cracking operation is negligible. Even though the naphthenes and naphthenic compounds provide good material for producing the desired low boiling products, a portion of these compounds apparently undergoes different reactions which form the refractory aromatics.

An examination of a 37.8 A. P. I. Mid-Continent

virgin gas oil which was cracked in the presence of a synthetic silica-alumina catalyst maintained at a temperature of approximately 800° F. showed that about 80% of the naphthenic portion of the virgin charge was cracked during the first pass and that the residue then contained about 5 times as much high boiling or refractory aromatics as naphthenes. When this residue in untreated condition was subjected to the same or a somewhat more severe catalytic cracking operation on the same or similar contact material, the naphthenic portion thereof was again reduced or cracked about 80 per cent but the residue from this pass contained about 10 times as much refractory aromatics as naphthenes, indicating that the untreated residues tend to increase progressively in refractory aromatic content with each pass.

Running the same virgin charge on a 30 minute cycle of operation, that is, 10 minutes on stream and 20 minutes for purging and regenerating the catalyst, it was necessary to reduce the rate of feed of the charge materially after the first pass in order to attain the desired degree of cracking and also to limit the coke deposit to that which could be removed by oxidation within the regeneration period of the cycle. During the first pass the virgin charge was fed at a rate of 25 liters per hour of charge to 20 liters of catalyst but the residue after this pass and the next pass had to be charged at the rates of 20 and 12 liters per hour, respectively, in order to keep the coke deposit down. On the other hand, however, similar residues from the first and second passes after being treated to make them more suitable for catalytic operation can be supplied at the same rate in subsequent passes as the virgin charge without affecting the cycle of operation. The low boiling products recovered from the treated second pass residue constituted about 35 percent by volume of the charge, which is only about 5 percent less than the products recovered from the virgin charge, and the coke deposited during the 10 minute run was only 1.4 grams per liter of catalyst. On the other hand the products recovered from a similar residue which was untreated were only 15 percent of the charge and about 25 percent less than the virgin charge and the coke deposited was about 3.5 grams per liter of catalyst or more than twice as great as the deposit of the treated charge.

According to our invention a residue or recycle stock may be used alone or with a particular charging stock in a process involving a timed cycle of alternate on-stream and regeneration reactions, wherein the time of the cycle has been predetermined, under given conditions of operation, for the particular charging stock and the residue may be used in the process without in any way affecting the conditions of operation or the cycle of operation. This is accomplished by treating the residue to reduce its refractory aromatic content below that which forms too great a coke deposit and preferably to reduce the aromatic content entirely before the residue is recycled.

One practical method which has been used is hydrogenation of a residual stock to convert all or a sufficient portion of the refractory aromatics after each pass to naphthenes or naphthenic compounds in order to reduce the coke formation and at the same time increase the yield of the low boiling product of gasoline. If the residue contains as little as 10 percent of the refractory aromatics the coke deposit is not sufficiently increased to affect adversely the operating condi-

tions or the cycle of operation, consequently a residue containing such a small amount of the aromatics can be recycled economically without its being hydrogenated. When the percentage goes above this, however, improved results are obtained by the hydrogenation step. The increase in gasoline production and the decrease in coke formation from the hydrogenated residue have both been found to be proportional to the extent or degree of the hydrogenation. This is due to the fact that when the residue is 100 percent hydrogenated all the aromatics are converted back to naphthenes which give high yields of gasoline and low coke formation, while with less than 100 percent hydrogenation a portion of the aromatics only will be converted to naphthenes and the remainder to such partially hydrogenated naphthenic compounds as the tetrahydronaphthalenes which crack to gasoline along with the naphthenes but not quite so readily. By hydrogenation of the recycle stock after each pass 100 percent liquid recovery may be had from a virgin charge.

The hydrogenation step may be carried out in a variety of forms of apparatus and also under known conditions for effecting a simple hydrogenation of the residue, that is, under such conditions of operation that little or no cracking of the residue is effected during the hydrogenation step. The temperatures employed may range between 250° and 800° F. and pressures as high as 3000 pounds per square inch, during the hydrogenation, may be used, depending on the percentage of refractory aromatics in the residue which is to be treated and the degree of hydrogenation or the extent of conversion of the aromatics it is desired to effect. Any known hydrogenation catalyst may be employed to assist in the hydrogenation, for example, the metals, oxides or salts of nickel, cobalt, copper, iron, aluminum, zinc, etc., which become poisoned by sulphur compounds during the hydrogenation and necessitate frequent reactivation, or the sulphide catalysts, the activity of which is less affected during hydrogenation.

In the single figure of the drawing is shown diagrammatically apparatus for carrying out the process steps for treating the residue from a catalytically cracked virgin stock when the residue becomes sufficiently refractory to have an adverse effect on the operating cycle. The portion of the figure on the left side of the dashed line represents a plurality of sets of apparatus which may be used singly or together in cracking a charging stock to form the desired low boiling products and the portion of the figure at the right of the dashed line represents apparatus for treating or hydrogenating the residual oil when it becomes refractory to cracking.

The virgin charge may be admitted to either heater A or A' from lines L or L', depending on the number of times the charge can be passed through a catalytic cracking zone before it becomes sufficiently refractory or contains sufficient refractory aromatics to necessitate treating the residue in order to place it in suitable condition for the on-stream operation without affecting the cycle of operation. From either chamber A or A' the charge, heated to about 800° F. will be sent through one of the catalyst zones B or B' for the length of the predetermined on-stream period of the cycle and from the catalyst zones B or B' the vapors will pass to one of the separators C or C' and the desired low boiling vapor products carried overhead and sent to storage.

If the virgin charge is of a type which does not produce a residue which is too refractory on the first pass the recycle stock from separator C will be then sent to heater A₁ and through catalyst zone B₁ for further cracking and then to separator C' and when the residue from any virgin charge is found to contain sufficient of the refractory aromatics to require hydrogenation, the liquid residue from separator C' will be sent to the treating or hydrogenating zone D and treated under conditions to effect the desired degree of simple hydrogenation and afterwards it will be sent to heater A², mixed with fresh charging stock from line L² and then through catalyst zone B² and the vapors sent to the separator C² where the desired low boiling products are removed while the residue from separator C² is returned to the hydrogenating zone D and again after hydrogenation to the desired degree, the residue after this pass is sent to the cracking zone B₂. The process of separating the residue from the low boiling hydrocarbons, hydrogenating the residue, and mixing it with fresh charge and cracking the mixture is repeated throughout the on-stream period in the zone B₂ which is then regenerated during the remaining portion of the cycle to remove the coke deposit.

In the specification and claims the terms "refractory," or "refractory aromatics" are intended to describe the resistance of the residue or recycle stocks to being catalytically cracked while the term "less refractory" is intended to describe the ability of the stocks to be catalytically cracked due to the presence of naphthenic compounds in the stock. While the drawing indicates two catalytic cracking zones in series in advance of a treating zone, it is to be understood that the sequence may be varied as desired without departing from the spirit of the invention, provided that recycle stocks containing too great a proportion of refractory aromatics for recycling directly with fresh charge or the like are suitably treated to convert aromatics to naphthenes before being subjected to further catalytic cracking.

With many charging stocks only one catalytic cracking zone, such as B, B', B², is needed to which fresh charge, recycle stock, or treated recycle stock, may be fed, singly or in any combination, continuously or intermittently. Any of the catalytic zones indicated in the drawing may contain two or more converters fed from a single heater and feeding to a single separator to permit continuous operation, one or more converters being on stream while the other or others are in regeneration.

We claim as our invention:

In the treatment of high boiling hydrocarbons in the presence of contact material involving a cycle of alternate on-stream and regeneration reactions effected in predetermined time relationship and wherein the on-stream reaction produces desired low boiling products and a residual stock containing refractory aromatics, the process of utilizing the residual stock in the on-stream reaction period of the cycle to obtain high yields of low boiling hydrocarbons from an original charge which comprises feeding the charge of high boiling hydrocarbons under cracking conditions to contact material during the on-stream period at a rate which limits the amount of coke deposit to that which is removable during the regeneration period, removing the products of the on-stream reaction and separating the refractory residual stock from the low boiling hydrocarbons, mixing the residual stock with the high boiling charge and prior thereto hydrogenating, under conditions to prevent cracking, the stock when it contains above 10 per cent of aromatic components to convert the aromatics to compounds more readily crackable so that the mixture may be fed during the on-stream period to the contact material at the same rate as the fresh charge in order to limit the amount of coke deposit to that which is removable during the regeneration period.

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