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PROCESS FOR PRODUCING XYLENES

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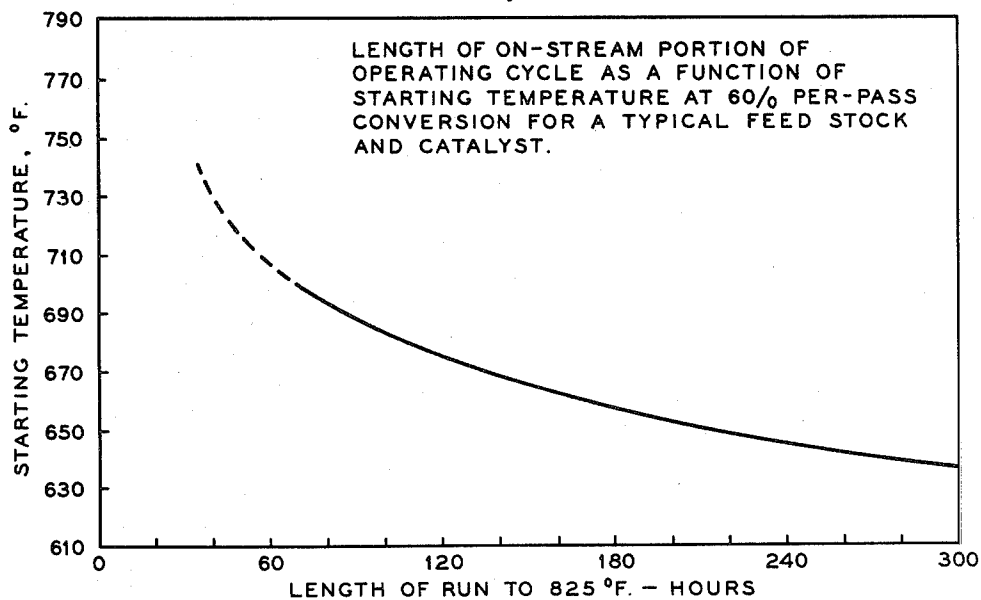


FIG. 2

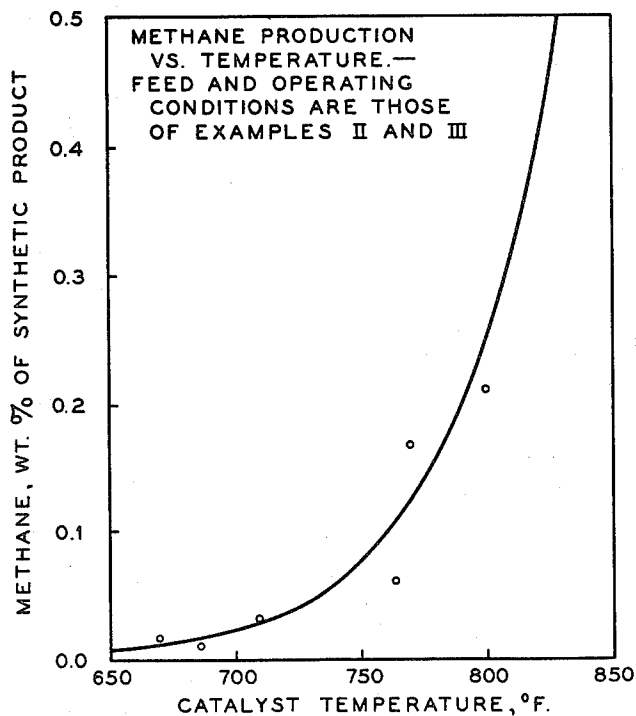


FIG. 1

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PROCESS FOR PRODUCING XYLENES

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8 Claims. (Cl. 260-668)

This invention relates to a process for the production of xylenes and other desired aromatic compounds by the catalytic conversion of aromatic-rich hydrocarbon stocks boiling above about 325° F.

Considered in its broader aspects, this invention is directed to the application of a unique conversion process on an essentially nitrogen-free hydrocarbon fraction of selected boiling range and high aromatic content. This conversion process involves a critical correlation of process variables to attain a multiple combination of reactions in which those of isomerization, disproportionation and selective cracking predominate, and is conducted in the presence of hydrogen over a selective catalyst composition incorporating both hydrogenation as well as highly active cracking components at distinctively controlled temperatures and pressures resulting in substantial consumption of hydrogen.

In order to differentiate and define the distinctive features of this process and to set the same apart from conventional refinery operations, the subject conversion process will hereinafter be referred to as an isocracking process.

The primary application of the subject isocracking process is to produce xylenes, though such other low-boiling aromatic compounds as benzene, toluene, ethyl benzene and the various C₉ benzenes are also of utility. A present source of large volumes of the xylene isomers is the product stream (commonly designated as a reformate) obtained by the catalytic reforming of petroleum naphthas. However, a substantial proportion of the reformate so obtained boils above 325° F. and thus contains no xylenes. For lack of a more economic use, these heavier fractions have heretofore been directed into the gasoline pool, and it would be desirable if a method were available whereby these and other aromatic-rich hydrocarbon fractions boiling above the xylene range could be efficiently converted to xylenes and other aromatics of relatively low boiling point with but extremely small losses to normally gaseous product fractions which are of little commercial value. According to this invention, it has been found possible to utilize the distinctive features of the isocracking process to attain this and such other objects of the invention as will hereafter appear.

The process of the invention involves the selection of a hydrocarbon fraction containing at least 75% by volume of aromatic hydrocarbons, which fraction boils in the range of 325°-450° F. and whose nitrogen content, measured as basic nitrogen, is at a level below about 25 p.p.m. This selected charging stock is introduced into an isocracking zone in admixture with at least 2000 s.c.f. hydrogen per barrel of feed for contact in said zone with a multifunctional catalyst composition comprising a hydrogenating component disposed on an active acidic cracking support, the critical balance of the catalytic components being so regulated as to result in a catalyst severity factor (as the term is hereinafter defined) of from about 0.1 to 2.0.

The isocracking zone is operated under a pressure of

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at least about 400 p.s.i.g. and at instantaneous temperatures in the range of about 450°-800° F., the temperature being so regulated as to initiate the conversion reaction at a temperature below 730° F. and to maintain a periodic average temperature having a value below about 730° F. during at least the first half of any given conversion period (i.e., the period during which the catalyst remains on-stream before being subjected to any regeneration treatment), while maintaining a per-pass conversion of at least 20% over the course of said period. To put the matter in an equivalent fashion, a periodic average temperature below 730° F. is maintained during that portion of the conversion period which is productive of at least one-half of the total synthetic product formed over the course of the entire conversion period.

By virtue of the foregoing critical correlation of feed, catalyst and process variables, it has been found that the feed can be converted in a yield of at least 20% per pass through the isocracking zone to synthetic, xylene-containing product, i.e., that boiling in a range falling essentially below that of the feed. Any portions of the effluent from the isocracking zone boiling above the synthetic product can readily be brought down into said synthetic range as they are recycled to the isocracking zone, it having been found that such recycle streams respond to processing in the isocracking zone in a manner which is generally similar to that of the fresh feed.

In the preferred practice of the invention, the synthetic product fraction is regarded as that having an end point of from about 300° to 325° F., it having been found that the xylene isomers present in said fraction comprise at least 50% by volume of the total amount of aromatic compounds present therein. Within said range, the precise temperature generally corresponding to the end point of the synthetic fraction will vary depending on the cut point employed in working up the isocracker effluent to separate the product from any higher boiling fractions possibly employed as recycle. However, it also falls within the purview of this invention to obtain a somewhat higher boiling synthetic product stream which, though rich in xylenes, also contains an appreciable proportion of C₉ components, said stream normally having an end point of from about 325 to 350° F. Thus, in the case of a feed boiling in a 350-450° F. range, one may obtain a synthetic product stream having an approximate end point of, for example, 300, 315, 325 or 350° F., it being recognized, however, that as said end point appreciably exceeds 325° F. the product will contain increasing amounts of C₉ aromatic components. In any case, the portion of the synthetic product stream boiling below about 325° F. will be found to contain at least 50% by volume of xylene isomers based on the volume of aromatics present in said 325° F. portion.

As employed herein, the term "instantaneous catalyst temperature" means the (average) temperature which prevails in the catalyst bed as measured at any given point in time. The term "periodic average catalyst temperature" refers to the average of the instantaneous catalyst temperatures as measured at substantially equal time intervals over the duration of the period in question, the latter normally comprising an initial portion of the total on-stream or conversion phase of any given processing cycle.

The references to boiling points or ranges expressed herein are those measured in accordance with either of the ASTM distillation procedures D-86 or D-158, depending upon the reference boiling range. It is furthermore to be understood that, in respect to the designations of boiling ranges and of feed and product distillation cut or end points, a 10% by volume tolerance is to be permitted in order to approximate more closely the practical limitations of refinery distillation equipment and

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practices. Thus, the designation of a feed boiling range between 325° F. and 450° F. resolves itself to those feeds wherein at least the 10 and 90% distillation points fall within the stated range, while a product designated as boiling below 325° F. includes a product fraction wherein at least the 90% point is at 325° F. or below.

The isocracking process of this invention is characterized by certain definite features. Firstly, it is productive of a synthetic product stream wherein the portion having an end point falling in approximately the 300–325° F. range contains at least 50% (and normally more) of xylene isomers, based on the total volume of aromatics present in said fraction. While the process does entail a moderate reduction in aromatic content (comparing the content of aromatics in the feed with that of the synthetic product), nevertheless the amount of aromatics present in the synthetic product remains high due to the fact that the feed stream, by definition, is itself made up in major proportion of aromatic components. The abnormally high proportion of xylenes in the synthetic product has been found to be attributable in large measure to the fact that the feed is essentially free of polynuclear components of the type found in petroleum stocks, said components boiling well above 450° F. as a general rule. As will be brought out below in connection with Example IV, an aromatics-rich, essentially polynuclear feed stream is productive of a synthetic product wherein the xylene content of the 325° F.– fraction is far below 50% in terms of total aromatics present therein.

Secondly, the process is characterized by the fact that the feed is converted in high yield to xylenes and other aromatics boiling below 325° F. (or to such compounds along with C₆ aromatics, if desired) with but little loss to methane and the various C₂–C₃ gases of little commercial value. This result is one which is in part attributable to the balance of the hydrogenating and cracking components of the catalyst, though it is also tied particularly closely to the relatively low temperatures employed in the isocracking zone. Thus, it has been found that the amount of methane produced in a typical run increases by a factor of approximately 20 times as the reaction temperature in the isocracking zone rises from 675 to 800° F., said increase being particularly severe in the range about 750° F.

Thirdly, the process of this invention is characterized by the fact that the unit may remain on-stream at high conversion levels for unusually long periods before reaching those temperatures approaching 800° F. and above where operation no longer becomes feasible due to the rapid increase in the make of light gas and coke which accompanies said temperatures. This result is due to the fact that the unit is brought on-stream at temperatures below 730° F. (preferably at from 450°–675° F.), and can be efficiently operated for long periods of time at said temperatures before resort must finally be had to temperatures approaching 800° F. if conversion is to be maintained at a high level during the terminal phases of the on-stream period without lowering the space rate.

Lastly, mention should be made of the fact that the process is accompanied by a consumption of hydrogen in an amount of at least 1000 s.c.f. per barrel of feed converted to synthetic product, said amount normally averaging between 1000 and 2000 s.c.f. in most operations.

The charging stocks supplied as fresh feed to the isocracking zone in accordance with the subject invention may be any of the conventional hydrocarbon distillate fractions boiling in the range of 325°–450° F. whose (basic) nitrogen content is less than 25 p.p.m. and which contain at least 75% by volume of aromatic hydrocarbons. Such stocks may be of petroleum origin or they may be obtained from shale, gilsonite, coal tar or other natural source. In this connection, the word "aromatic" is employed in the conventional sense to include all those hydrocarbons incorporating an aromatic nucleus which may be either unsubstituted or substituted with one or

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more of various aliphatic or other groups. While referred to as hydrocarbons, they may also contain other atoms such as nitrogen, oxygen, sulfur and the various metals commonly found in petroleum and other distillates of natural origin. The basic nitrogen content of the charging stock can be determined in the conventional manner by dissolving the stock in glacial acetic acid and titrating the solution with perchloric acid, also in glacial acetic acid, crystal violet commonly being employed as the indicator.

Representative isocracker feed stocks normally meeting the criteria of aromatic content and nitrogen level comprise the effluent portions boiling above about 325° F., as obtained from a catalytic reforming unit. Such reformates are conventionally produced by passing straight run, thermally cracked or catalytically cracked naphthas, along with hydrogen, through a reforming unit provided with a platinum-on-alumina or molybdena-alumina catalyst under reforming conditions. The 325° F.+ fractions which are obtained from the reformate streams for use in this invention have a 90° point below about 450° F. and thus are substantially free of polynuclear aromatic components. Other appropriate stocks affording similar results when employed as fresh feed to the isocracking zone include concentrates rich in aromatic hydrocarbons as may be obtained by the extraction of various hydrocarbon fractions with sulfur dioxide, furfural, or the like.

One of the important variables in the conduct of the subject process which has a material effect and, to that extent, permits the production of the desired gasoline products is the control of the nitrogen content of the charge stock. As indicated, an acceptable nitrogen level, expressed as basic nitrogen, is about 25 p.p.m., although appreciable further improvement is obtained as this nitrogen content is reduced to levels below 10 p.p.m. When the stock is not already sufficiently low in nitrogen, these levels may be reached by hydrofining the feed stock by treating the same with hydrogen at elevated temperatures and pressures in the presence of a hydrogenating catalyst which has little cracking activity and little tendency to saturate aromatics under the conditions employed. The effluent from this pretreating or hydrofining step, if satisfying the specification boiling ranges and aromatic content, may be fed directly to the isocracking stage of this invention or it may be first subjected to a preliminary fractionation to recover a specification feed.

In general, the effect of a basic nitrogen content in excess of 25 p.p.m. is a reduction in catalyst activity which is reflected in both operational efficiency and product distribution. As the nitrogen content increases above the specification maximum, higher reaction temperatures are necessary to maintain an economic per-pass conversion level or, in other words, a per-pass production of synthetic product boiling below the initial boiling point of the feed. These requisite higher reaction temperatures entail a disproportionate increase in the amount of product converted to light gases and carbonaceous residues which form on the catalyst surface and thus decrease catalyst activity. Any such decrease in activity must be compensated for by resort to still higher operating temperatures if conversion is to be maintained at the desired level, and thus the on-stream portion of the cycle is shortened as limiting temperatures of 800° F. and above are reached much sooner than would otherwise be the case. The criterion employed to determine the necessity of catalyst regeneration in a constant conversion operation is the prescribed specification limit of isocracking at 800° F.

This effect of nitrogen is in contrast to that observed in other hydrocracking operations which, though employing an intrinsically acidic catalyst system, are conducted at temperatures above 800° F. In such operations the effect of nitrogen in the feed even when present in substantial amounts becomes progressively smaller as reaction temperatures increase above 800° F., and be-

comes substantially lost at temperatures above 850° F. Under the conditions encountered in the present isocracking operations, on the other hand, and particularly at temperatures below about 750° F., the (basic) nitrogen compounds present in the feed or formed in the isocracking zone becomes chemisorbed upon the catalyst surfaces and thus drastically reduce the activity of the catalyst.

While reference is uniformly made to feeds having a maximum basic nitrogen content of 25 p.p.m., this assumes a total nitrogen content of less than about 100 p.p.m. since conventional refinery stream normally contain from about 3 to 4 times as much total nitrogen as basic nitrogen. However, in view of this known distribution of the nitrogen compounds, it is now common in the art to make only the basic nitrogen determination since this test is much easier and less expensive to make than is that for total nitrogen. It also is known that the non-basic nitrogen components present in the feed are quickly converted to basic nitrogen compounds once contact is made with the isocracking catalyst. Hence, when dealing with isocracker feed streams which contain only basic nitrogen compounds or with those wherein the distribution between basic and nonbasic nitrogen compounds is other than that conventionally encountered, it is appropriate to define the isocracker feed as one which contains a total of less than about 100 p.p.m. of nitrogen.

The conversion or isocracking process to which the foregoing charge stocks are subjected further involves a critical correlation of process variables to achieve the unique combination of conversion reactions which are manifested in the physical and chemical characteristics of the synthetic product. The principal process variables effecting the desired combination of reactions, and therefore identifiable with the isocracking process, are catalyst composition and reaction temperature or temperature control. This is not intended to imply that other process variables are not significant to the isocracking process, but rather to emphasize the degree of criticality in the various process variables.

As previously indicated, the catalyst employed is a multifunctional catalyst composition comprising a hydrogenating-dehydrogenating component disposed on an active acidic cracking support wherein the catalytic components are critically balanced to result in a catalyst severity factor of from about 0.1 to 2.0. The cracking component or support may comprise any one or more of such acidic materials as silica-alumina, silica-magnesia, silica-alumina-zirconia composites, as well as certain acid-treated clays and similar materials; provided, however, that such acidic materials possess substantial cracking activity, it being recognized that in some cases the acidic nature of the cracking component may be enhanced, as by the addition of halides or the practice of other known means for developing Lewis or Brønsted type of acidity in the finished catalyst composition. More specifically, the cracking component of the catalyst should be one having an activity, in terms of gasoline production, of at least about 25 as measured by the "Cat. A" method (J. Alexander and H. G. Shimp, National Petroleum News (1944), vol. 36, at page R-537. J. Alexander, Proc. Am. Petroleum Inst. (1947), vol. 27, at page 51). Preferably, the cracking component of the present isocracking catalyst has a Cat. A value of at least 30.

A preferred cracking support for the subject catalyst composition is comprised of synthetically prepared composites of silica and alumina containing from about 75 to 90% of the silica component. A material of this type, in crushed aggregate form, was employed in the various exemplary runs described herein, said material containing about 87% silica, having a Cat. A activity of 46, and a surface area of about 430 M²/g. when first placed in service.

The hydrogenating-dehydrogenating component of the catalyst may be selected from any one or more of the

various group VI and group VIII metals, as well as the oxides and sulfides thereof, representative materials being the oxides and sulfides of molybdenum, tungsten, chromium and the like, together with such metals as nickel or cobalt and the various oxides and sulfides thereof. Also suitable are certain group I(B) or group II(B) metals, such as copper or cadmium and their oxides and sulfides. If desired, more than one hydrogenating-dehydrogenating component may be present, e.g., composites of two or more of the oxides and/or sulfides of molybdenum, cobalt, nickel, copper, chromium and zinc.

Depending on the activity thereof, the amount of the hydrogenating-dehydrogenating component may be varied within relatively wide limits of from about 0.1 to 15%, based on the weight of the entire catalyst composition. Within these limits, the amount of said component present should be sufficient to provide a reasonable catalyst on-stream period at required conversion levels, but insufficient under the reaction conditions employed to effect substantial saturation of any except highly substituted aromatic ring compounds and of any small amounts of polynuclear aromatic compounds which may be present.

The balance of catalytic components necessary to effect the desired selectivity in the multiphase reactions of the process is determined by reference to the "severity factor" (S_a) of the catalyst composition. This characteristic of the catalyst may be determined by subjecting the catalyst to a standardized test wherein the reference feed stock is a trimethylbenzene, such as pseudocumene, or an equilibrium mixture of trimethylbenzenes which may be obtained from a catalytically reformed naphtha. When employing the latter trimethylbenzene concentrate, a narrow boiling fraction having a D 86 distillation range from about 313°-335° F. and a C₉ aromatic content of at least 95 volume percent should be used. The test involves passing the reference feed stock through the test catalyst at a liquid hourly space velocity of 2.0 with 9000 s.c.f. of hydrogen per barrel of feed which maintaining a catalyst temperature of 650° F. and a pressure of 1200 p.s.i.g. This test operation is continued for a period of time (usually about 2 to 5 hours) sufficient to stabilize the system, and thereafter for a time sufficient to provide an adequate product sample. After flashing to atmospheric pressure the liquid product is then fractionated to determine the volume percent of product boiling below 300° F., relative to feed. This is taken as the synthetic product. Aromatic contents of the reference feed and said synthetic product are determined, as by chromatographic analysis (FIAM method), and the severity factor, S_a , is calculated from the expression:

$$S_a = \frac{A_f}{A_p} - 1$$

where A_f = volume percent aromatics in the feed, and A_p = volume percent aromatics in said product.

The above expression is derived, as shown below, from the following general relationships:

$$S_a = \frac{\text{Aromatics hydrogenation index } (A_h)}{\text{Aromatics cracking index } (A_c)}$$

where

$$A_h = \frac{\text{Percent Aromatics in feed } (A_f) \text{ minus percent aromatics in the product portion boiling below initial boiling point of feed } (A_p)}{\text{Percent Aromatics in feed } (A_f)}$$

$$A_c = \frac{\text{Percent Aromatics in the product portion boiling below initial boiling point of feed } (A_p)}{\text{Percent Aromatics in feed } (A_f)}$$

Combining the above equations:

$$S_a = \frac{A_f}{A_p} - 1$$

For operations in the subject isocracking process, the severity factor (S_a) must have a value falling within the range of from about 0.1 to 2.0. An S_a value greater than 2.0 reflects an undesirable loss in aromatic content in the product, as well as a high hydrogen consumption. On the other hand, S_a values below 0.1 normally reflect actual formation of aromatics and such reactions are undesirable for the purposes of this invention since they involve rapid catalyst deactivation due to deposition of coke, etc. Catalysts having S_a values higher than the desired range can usually be brought into compliance by suitably adjusting the amount of the hydrogenating-dehydrogenating component present. While the activity of the particular catalysts will vary, depending upon methods of preparation and other customary variables, as a general rule exemplary catalysts having satisfactory S_a values are those containing from about 1 to 10% of one or more of the oxides and/or sulfides of molybdenum, nickel or cobalt, together with the hydrogen-reduced counterparts of said oxides, it being recognized that many of these oxides are reduced to the metal state and remain as such once the oxide has been exposed to hydrogen at elevated temperatures and pressures, either before the conversion reaction takes place or under the conditions prevailing in the isocracking unit as the same is placed on-stream.

Particularly good results from the standpoint of high per-pass conversion, even at relatively low operating temperatures, coupled with good selectivity and the ability to withstand repeated regeneration with relatively minor decrease in activity, are obtained with catalysts composed of from 1 to 10% nickel sulfide deposited on the aforementioned synthetically prepared silica-alumina composites.

The following catalysts are representative of those which are particularly well adapted for use in the present invention.

Nickel sulfide (2.5% Ni) on silica-alumina

This catalyst (No. 425-2) was prepared by impregnating 11 liters of a crushed (8-14 mesh) SiO_2 (87%)- Al_2O_3 aggregate with 2896.9 grams of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, dissolved in enough water to make 8800 milliliters total solution, following which the beads were held for 24 hours at 70° F. The catalyst was then dried for 10 hours at 250° F. and thereafter calcined at 1000° F. for 10 hours. The calcined material was reduced in an atmosphere of hydrogen at 580° F. and 1200 p.s.i.g., following which the resulting nickel-bearing catalyst was sulfided in an atmosphere containing 8% H_2S in hydrogen at 1200 p.s.i.g. and 580° F., thereby converting the nickel essentially to nickel sulfide. This catalyst, when sulfided using an excess of a mixture of dimethyl disulfide in mixed hexanes, had a severity factor of about 0.6.

Nickel sulfide (2.5% Ni) on silica-alumina

This catalyst (No. 316) was prepared by impregnating 11 liters of the crushed SiO_2 - Al_2O_3 support with a solution prepared by mixing 1500 milliliters water and 500 milliliters of ammonium hydroxide solution with 1082 grams of ethylenediamine tetraacetic acid (EDTA) and 469 grams of nickel carbonate, the solution being made up to a total of 4000 milliliters with water. The impregnated material was held for a period of 24 hours at 70° F., following which it was centrifuged and calcined for 10 hours at 1000° F. in air to convert the nickel chelate to nickel oxide. The catalyst was then reduced in an atmosphere of hydrogen at 650° F. and 1200 p.s.i.g. and sulfided in situ in the reactor by the use of a feed stream made up of a catalytic cycle oil (49 volume percent aromatics) to which 0.1% by volume of dimethyl disulfide has been added at a pressure of 1200 p.s.i.g., and in the presence of approximately 6500 s.c.f. H_2 per barrel of feed. This catalyst, when sulfided using an excess of a mixture of dimethyl disulfide in mixed hexanes, had a severity factor of approximately 0.36.

Nickel sulfide (2.5% Ni) on silica-alumina

This catalyst (No. 353) was prepared by impregnating approximately 7.5 liters of the crushed SiO_2 - Al_2O_3 support, which had been dried in air for 24 hours at 400° F., with 2183.7 grams of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in water and made up to a total of 7760 milliliters. The impregnated base material was then held for 24 hours at 70° F., following which it was drained, dried for 10 hours at 250° F. and calcined for 10 hours at 1000° F. The catalyst was then sulfided by treatment in an atmosphere of hydrogen containing 8% hydrogen sulfide at 1200 p.s.i.g. and 580° F. It was found that this catalyst, when sulfided using an excess of a mixture of dimethyl disulfide in mixed hexanes, had a severity factor of about 0.42.

Cobalt sulfide (4% Co) on silica-alumina

This catalyst (No. 248-2) was prepared by impregnating 2000 milliliters of the crushed SiO_2 - Al_2O_3 support with 1600 milliliters of an aqueous solution containing 172.5 milliliters ammonium hydroxide solution and 373 grams EDTA along with 168 grams cobalt carbonate, the solution being heated until bubbling ceased before being added to the silica-alumina material which, in turn, had previously been dried for 24 hours at 400° F. Following impregnation, the catalyst was centrifuged and calcined for 4 hours at 1000° F., thus yielding a material having an amount of cobalt oxide equivalent to 2.2 weight percent Co. A second impregnating solution was then made up as above, using 150.2 grams cobalt carbonate, 334 grams EDTA and 154 milliliters of ammonium hydroxide and added to the catalyst. Following a holding period of 24 hours at 70° F., the catalyst was centrifuged and calcined for 10 hours at 1000° F. The calcined product so obtained was then alternately reduced in hydrogen and oxidized in air (repeating the cycle 5 times) at 1000° F. and 1200 p.s.i.g. The catalyst was then sulfided by treatment with an excess of a solution comprising 10% by volume of dimethyl disulfide in mixed hexanes at 1200 p.s.i.g. and 675° F., hydrogen also being present in the amount of about 6500 s.c.f. per barrel of feed. The catalyst had a severity factor of about 0.24.

Cobalt sulfide (2% Co) and chromium sulfide (3.53% Cr) on silica-alumina

This catalyst (No. 174-5) was prepared by forming an aqueous slurry with 1130 grams of the chelate of chromium and EDTA, to which slurry was added 196 grams of cobalt carbonate, the solution being then stirred until bubbling action ceased and made up to 1779 milliliters. This solution was warmed to 140° F. and added to 2280 milliliters of the crushed SiO_2 - Al_2O_3 support. The resulting material was then held for 24 hours at 140° F., following which it was centrifuged and calcined 10 hours at 1000° F. The calcined product was reduced in an atmosphere of hydrogen at 1200 p.s.i.g. and 675° F., following which the cobalt and chromium metals present were converted to sulfides by treatment with an excess of a solution comprising 10% by volume of dimethyl disulfide in mixed hexanes at 1200 p.s.i.g. and 675° F., hydrogen also being present in the amount of 6500 s.c.f. per barrel of feed. This catalyst had a severity factor of about 0.4.

Molybdenum sulfide (2% Mo) on silica-alumina

This catalyst (No. 226) was prepared by forming 530 milliliters of an ammoniacal solution containing 41.4 grams of ammonium molybdate. This solution was then added to the crushed SiO_2 - Al_2O_3 support, previously dried for 24 hours at 400° F., present in an amount sufficient to yield a dried product containing the equivalent of 2 weight percent Mo. After being held for 24 hours at 70° F., the impregnated material was centrifuged and calcined for 5 hours at 1000° F. It was then reduced

in an atmosphere of hydrogen at 1200 p.s.i.g. and 650° F., following which it was sulfided in situ by treatment under these same conditions of temperature and hydrogen pressure with a hydrofined cycle oil (49% aromatics) containing 1% by volume dimethyl disulfide. This catalyst, when sulfided using an excess of a mixture of dimethyl disulfide in mixed hexanes, had a severity factor of about 0.19.

Nickel sulfide (1% Ni) and molybdenumsulfide (1% Mo) on silica-alumina

This catalyst (No. 296) was prepared in the following manner. 28.6 milliliters of ammonia were mixed with 80 milliliters water and added to 49.3 grams EDTA, and to this solution was added 22.3 grams of nickel carbonate. After being heated to evolve carbon dioxide, this solution was mixed with another solution prepared by dissolving 78.7 grams of ammonium molybdate in a mixture of 80 milliliters of ammonia hydroxide and 80 milliliters of water. The resulting solution, on being made up to 480 milliliters by the addition of water, was then used to impregnate 600 milliliters of the $\text{SiO}_2\text{-Al}_2\text{O}_3$ mixture. The impregnated material, after being held for 24 hours at 70° F., was centrifuged and calcined for a period of 10 hours at 1000° F. It was then reduced in an atmosphere of hydrogen at 1200 p.s.i.g. and 650° F., following which it was sulfided under these same conditions of temperature and hydrogen pressure with a solution containing 10 volume percent dimethyl disulfide in mixed hexanes. This catalyst was found to have a severity factor of about 0.41.

In the operation of the isocracking process, the charge stock may be introduced to the reaction zone, in admixture with hydrogen, as either a liquid, vapor or mixed liquid-vapor phase, depending upon the temperature, pressure, proportions of hydrogen and boiling range of the charge stocks utilized. This charge stock is introduced in admixture with at least 2000 s.c.f. of hydrogen per barrel of total feed (including both fresh, as well as recycle feed), and this amount of hydrogen may range upwardly to 15,000–20,000 s.c.f. per barrel of feed. From about 1000 to 2000 s.c.f. of hydrogen is consumed in most instances in the isocracking reaction zone per barrel of total feed converted to synthetic product, i.e., that boiling below the initial boiling point of the fresh feed. The hydrogen stream admixed with incoming feed is conventionally made up of recycle gas recovered from the effluent from the hydrofining and/or isocracking zones, together with fresh make up hydrogen. The hydrogen content of the recycle stream in practice generally ranges upwardly of 75 volume percent.

Basically, the pressures employed in the isocracking zone are in excess of about 400 p.s.i.g. and may range upwardly to as high as 3000 or even 5000 p.s.i.g., with a preferred pressure range being from about 600 to 1500 p.s.i.g. Pressures below about 400 p.s.i.g. result in decreased conversions per pass, as well as in shorter on-stream or reaction periods by reason of an accelerated tendency to induce dehydrogenation of naphthenes to aromatics, a reaction accompanied by carbonaceous fouling of the catalyst composition. On the other hand, pressures above about 2000 p.s.i.g. normally tend to induce undue saturation of aromatics. However, if pressures above 2000 p.s.i.g. are desired (e.g., for non-regenerative operations), this pressure-induced tendency toward aromatic saturation may be offset or balanced by employing a catalyst composition of decreasing severity factor or, in other words, a catalyst wherein the hydrogenation component is composed of catalytic metals and their compounds which are relatively less active as, for example, the compounds of cobalt, chromium and/or molybdenum, as well as nickel when present in the sulfided form.

Generally, the isocracker feed may be introduced to

the reaction zone at a liquid hourly space velocity (LHSV) of from about 0.2 to 5 volumes of hydrocarbon (calculated as liquid) per superficial volume of catalyst with a preferred rate being from about 0.5 to 3 LHSV.

Probably the most characteristic and, to that extent, critical process variable in the subject isocracking process is the specification on reaction temperatures. As hereinabove prescribed, the process may be conducted at instantaneous catalyst temperatures in the range of about 450° to 800° F., provided the conversion reaction is initiated at temperatures below 730° F. and is maintained at a periodic average temperature having a value below about 730° F. during at least the first half of the conversion period. As previously mentioned, the reference to "instantaneous" temperatures means the average temperature which prevails in the catalyst body or bed as measured at any given point in time, and the "periodic average temperature" refers to the average of the instantaneous temperatures as a function of time during the conversion reaction.

In the preferred practice of this invention, the temperature at which the reaction is initiated in a given on-stream period should be as low as possible (commensurate with the maintenance of adequate per-pass conversion levels, as discussed below) since the lower the starting temperature the longer will be the duration of the said on-stream period, particularly that portion thereof employing instantaneous catalyst temperatures below 730° F. For any given conversion, the permissible starting temperature is a function of catalyst activity since the more active catalysts (i.e., those capable of effecting a relatively high per-pass conversion under given operating conditions) naturally permit the unit to be placed on-stream at lower starting temperatures than would otherwise be the case. In any event, the conversion reaction should be initiated at temperatures below about 730° F., with a preferred range being from 450° to 675° F. In some cases it may be desirable to initiate the reaction at temperatures below 450° F., with higher temperatures then being reached in a relatively short period of time as the catalyst becomes conditioned. Moreover, with all except the most refractory feed stocks, and assuming the use of a catalyst of relatively good activity, instantaneous catalyst temperatures below about 730° F. can be maintained during at least the first half of the on-stream portion of any given processing cycle (or the portion productive of at least one-half of the total product, as aforesaid), and this method of operation is observed in a preferred practice of the invention.

In the preferred practice of the invention process, the isocracking reaction is conducted under conditions of relatively constant conversion of at least 20% per pass and more particularly at constant conversions falling in the range of about 20 to 70% per pass. Under this type of operation, the catalyst temperature is periodically increased to maintain the per-pass conversion at relatively constant levels. Alternatively, the process may be conducted at a constant temperature of about 730° F. or lower, under which conditions the per-pass conversion will gradually decline and the on-stream portion of the processing cycle will be terminated at an arbitrary conversion level. In either case, the decline in conversion level can also be offset to some extent by lowering the space velocity of the feed, though this procedure is not normally recommended for various economic reasons. Additionally, the process in which the catalyst temperature is maintained constant for a periodic interval or for a time interval as determined by a prescribed drop in conversion level, after which the temperature is incrementally increased to again approximate the initial conversion level, and this temperature staging is repeated over the conversion portion of the

processing cycle provided the periodic average temperature is maintained below about 730° F. during at least the first half of the conversion portion of the cycle. Still other methods of operating the process within the spirit of the present invention will suggest themselves to those skilled in the art.

The low-temperature aspect of the subject isocracking process is a distinguishing feature which is evidenced both in product quality and yield, as well as in process advantages. For example, in the operation described in Example I involving the isocracking of a reformat bottom stream, the volume percent yield of the synthetic C₅-300° F. product fraction remained at a general level of approximately 95% in the operating range of 700° to 750° F., though it fell off rapidly to about 90% at 825° F.

As a corollary to the drop in synthetic liquid yields at the higher operating temperatures, a corresponding increase in the production of C₁-C₃ gases is obtained. As an illustration of this weight loss to gaseous products of little economic value, reference is made to the graphical representation of the methane production in the operation of Example II, which is represented in Figure 1. As will be noted, the methane production at operations below about 730° F. is substantially negligible, but as the catalyst temperature is increased above 730° F. the methane production rapidly becomes a limiting factor in the process and, as will be noted from the curve, increases approximately 15-fold between the temperature of 700° F. and one of 800° F. Such methane production not only represents loss of feed stock, but also (where hydrogen is being recirculated, as it must be in commercial operation) necessitates hydrogen purification, withdrawal of a portion of the contaminated hydrogen or use of higher pressures in order to maintain the hydrogen partial pressure of the recycled gas within acceptable limits. This not only increases the cost of the plant, but also reduces yield due to the increased proportion of undesirable fixed gases.

Just as striking and important from a commercial standpoint as the favorable product yields accompanying low-temperature (below 730° F.) operation is the increase in the length of the conversion portion of a given processing cycle which is obtained as the conversion portion of the process is initiated at temperatures below about 730° F. and preferably below 675° F. A graphical illustration of this fact is set forth in the curve shown in Fig. 2, which is based on data obtained from process runs initiated at various starting temperatures but with other conditions remaining generally the same, said conditions being essentially those of Examples II and III given below, wherein the feed is a catalytic reformat of high aromatic and low nitrogen contents. Thus, it may be seen that by starting the on-stream portion of the operating cycle at a temperature of 650° F., the run may be continued at constant conversion for a total time of about 220 hours before the catalyst temperature becomes so high (800° F.-825° F.) as to require termination of the conversion reaction for regeneration of the catalyst. The permissible on-stream times are still relatively long, namely, 120 and 70 hours even when initiating the conversion portion of the cycle at temperatures of 675° F. and 700° F., respectively. These data illustrate the fact that it is important to initiate the on-stream or conversion portion of each processing cycle at temperatures below 700° F. wherever possible.

The absolute on-stream times represented in Figure 2 depend largely upon the particular isocracking catalyst and feed stocks employed. Thus, much longer runs can be obtained with feeds which are altogether free of components boiling above 450° F. However, in all cases, the relation of starting temperatures to run length will remain substantially consistent with the relationship expressed in Figure 2.

In carrying out the foregoing conversion operation,

there is obtained from the isocracking zone an effluent stream containing hydrogen and other normally gaseous products, a normally liquid synthetic product component boiling essentially below the boiling range of the feed, and what may be termed an unconverted, or bottoms fraction. In working up this total product stream, the usual practice is to first recover a hydrogen-rich gaseous fraction which is returned as recycle to the isocracker along with added, make-up hydrogen in an amount sufficient to compensate for that consumed by conversion of the feed. Other normally gaseous components are then removed from the stream, leaving a normally liquid residue which may then be fractionated into the desired cuts.

Taking into consideration first the synthetic portion of the liquid product, there may be separated therefrom a stream rich in xylene isomers, and similar recoveries may be made, if desired, of other aromatics, including benzene, toluene, ethylbenzene and the various C₉ compounds. Any portions of the synthetic product not so segregated make excellent gasoline blending stocks, since they have extremely high octane ratings, good volatility and clean burning characteristics when combusted in automotive engines. However, when the unit is being run to produce a synthetic product stream from which is recovered a xylene-rich fraction, with the balance of the synthetic liquid product being diverted for use as a premium gasoline blending component, the practice is to so work up the normally liquid portions of the isocracker effluent as to recover a gasoline fraction boiling essentially below the xylene range (i.e., below about 270 or 275° F.), then a xylene-rich fraction which may boil as high as about 325° F., and finally a residual fraction boiling above the xylene fraction.

The work-up of the xylene-rich fraction is, of course, somewhat conditioned on which xylene isomer is to be recovered as product. When meta- and para-xylenes are to be recovered, a gross separation thereof from the orthoxylene can be effected by distillation methods, though other separation methods are also available. Thus, Arnold Patent No. 2,541,682 describes a method for separating para-xylene from a mixture of xylene isomers by fractional crystallization, and Brooke et al. Patent No. 2,521,444 describes a method for separating meta-xylene from mixed xylene isomers by extraction with HF-BF₃. Whatever the xylene isomer product, it forms a feature of this invention that the remaining isomer or isomers can be recycled to the isocracker where isomerization of said recycled portion takes place, thus forming more of the desired isomer product. In the preferred practice of the invention, an orthoxylene-rich fraction is recycled, while meta- and paraxylene isomers are recovered as product. Alternatively, any portion of the xylene-rich fraction not recovered as a xylene isomer, per se, can be utilized as a premium gasoline blending component.

The residual fraction from the isocracker boiling above the synthetic product (e.g., above 300° F., 325° F. or 350° F.) may be recycled to substantial extinction or it may be diverted to other appropriate refinery uses, i.e., to various gasolines, cutter stock or the like. Again, in addition to recovering xylene and other desired products of relatively low boiling point from the isocracker effluent, it is possible to recover from the isocracker effluent an intermediate cut having an end point of from about 350° to 400° F., which cut will contain substantial portions of C₁₀ and C₁₁ aromatic hydrocarbons. Such intermediate fraction is characterized by a relatively high octane rating and is useful as a blending fluid for various grades of gasolines or as a source of aromatic hydrocarbons per se. Alternatively, this intermediate fraction may be recycled to the isocracking unit for conversion to lower boiling products of high xylene content.

Examples I, II and III presented below illustrate the practical application of the process of this invention in a number of its embodiments.

EXAMPLE I

The feed stock for this run was derived from the effluent from a catalytic reformer unit, said stock having the following specifications:

Gravity, ° API	28.8
Aniline Pt., ° F.	60M
Aromatic Content, vol. percent	91
Basic Nitrogen, p.p.m.	1
ASTM D-86 Distillation: ° F.	
Start	330
10%	334
30%	346
50%	354
70%	370
90%	424
End Point	506

The foregoing feed, along with 0.1 vol. percent dimethyl disulfide (to maintain the catalyst in the sulfided condition) and 6600 s.c.f. of hydrogen-rich recycle gas per barrel of feed was preheated to a temperature of about 710° F. and passed at an LHSV of 1.5 and pressure of 1200 p.s.i.g. through No. 316 catalyst, as described above, containing nickel sulfide (2.5% Ni) supported on the SiO₂-Al₂O₃ base. During the first 20 hours of the run, some variation in temperature occurred, and at the expiration of said period, when the temperature was approximately 720° F., it was observed that the conversion level was 60% per pass to product boiling essentially below 300° F. Since it was desired to operate at a 50% conversion level, the temperature was now lowered to 710° F., and it was calculated that had the temperature been adjusted downwardly in this initial portion of the run to give the desired 50% conversion, the starting temperature would have been approximately 660° F.

The operation was conducted under essentially extinction recycle conditions wherein both unconverted feed and high pressure gases containing in excess of 75% hydrogen were continuously recycled to the isocracking zone. Make-up hydrogen and fresh feed were added on a demand basis so that overall space velocity and gas recycle rates were held constant, the hydrogen consumption rate being observed to be about 1510 s.c.f. per barrel of feed converted to synthetic product. The product was continuously fractionated to produce a bottoms recycle stream, a 60-300° F. synthetic product, and a C₄- gas stream which was not recirculated.

Once the unit had leveled out at a 50% conversion level at a temperature of 710° F. after the initial 20-hour operating period, the conversion was maintained at said level by gradually increasing the catalyst temperatures in order to compensate for catalyst fouling due to the accumulation of coke. More specifically, the average instantaneous catalyst temperature reached levels of approximately 715° F. at the end of 40 hours, 740° F. at the end of 70 hours, 760° F. at the end of 90 hours, 775° F. at the end of 120 hours, and 795° F. at the end of about 144 hours. While the run was terminated at this point, it was estimated that a temperature of about 825° F. would have been reached at the end of 160 hours and one of 850° F. at 170 hours. Expressed otherwise, the catalyst had a periodic average temperature having a value of about 725° F. during the first 80 hours of the run, one of about 765° F. during the succeeding 40 hours, and one of about 780° F. during the terminal 14-hour period.

A 60-300° F. synthetic product fraction was recovered from the unit in a yield of about 96% at 700° F., and about 92% at 800° F., and from the slope of the yield curve it appears that the yield would have been down to about 90% at 825° F. This synthetic product fraction was found to have a total aromatics content of 66% by volume, and of said aromatics, approximately 65 volume

percent was made up of xylene isomers. This product fraction had the following boiling point characteristics:

ASTM D-86 Distillation: ° F.	
Start	102
5%	151
10%	189
30%	253
50%	270
70%	279
90%	289
95%	296
End Point	327

EXAMPLE II

The feed stock for this run was derived from the effluent from a catalytic reformer unit, said stock being one of California origin and having an aromatic content of 94%. Its boiling point characteristics were as follows:

ASTM D-86 Distillation: ° F.	
Start	370
10%	371
50%	382
90%	420
End Point	523

The foregoing feed, along with 6500 s.c.f. of hydrogen-rich recycle gas per barrel of feed, was preheated to a temperature of 580° F. and passed at an LHSV of 1.67 and a pressure of 1200 p.s.i.g. through No. 353 catalyst, as described above, containing nickel sulfides (2.5% Ni) supported on the SiO₂-Al₂O₃ base. The catalyst had previously been employed in four isocracking runs and had been regenerated at the conclusion of each of said runs and reduced in an atmosphere of hydrogen before again being resulfided for use in the succeeding run, including that on which the present example is based.

During the first five hours of the run, the temperature was gradually raised until the desired conversion level of 60% per pass was reached at 680° F., said conversion being to product boiling below approximately 350° F.

The operation was conducted under essentially extinction recycle conditions wherein both unconverted feed and high pressure gases containing in excess of 75% hydrogen were continuously recycled to the isocracking zone. Make-up hydrogen and fresh feed were added on a demand basis so that overall space velocity and gas recycle rates were held constant, hydrogen consumption being observed to be approximately 1550 s.c.f. per barrel of feed converted to synthetic product. The product was continuously fractionated to produce a bottoms recycle stream, a 60-350° F. synthetic product, and a C₄- gas stream which was not recirculated.

Once the unit had leveled out at a 60% conversion level at a temperature of 680° F. after the initial five-hour operating period, the conversion was maintained at said level by gradually increasing the catalyst temperatures in order to compensate for catalyst deactivation due to fouling. More specifically, the average instantaneous catalyst temperature reached the levels shown below at the indicated point of the on-stream period.

Catalyst temperature, ° F.:	Cumulative on-stream time, hours
685	15
690	25
697	35
705	45
715	55
720	65
735	75
750	85
775	95
825	101

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It will be seen from the foregoing table that while the temperature was raised at a relatively moderate rate up to about 85 hours, it was thereafter necessary to raise the temperature at a much more rapid rate in order to keep the conversion of the unit at the desired 60% level. Based on an analysis of the product from the unit when operating at a temperature of approximately 725° F., it was found that the C₅-350° F. synthetic product contained 64 volume per cent of aromatics, of which approximately 44 volume percent were C₉ aromatics boiling in essentially a 320° F.-350° F. range. Of the aromatics in the remaining C₉- synthetic product, xylenes were found to constitute about 62 volume percent.

EXAMPLE III

In a companion operation (Run 8-949) conducted in the same fashion as that described above in Example II, but at a space velocity of 1.17, it was found that the 60% per-pass conversion level was reached at a temperature of but 664° F. instead of at 680° F. Due to this lowering of the starting temperature, it was found that the run could be extended to 157 hours before reaching a temperature of 825° F., this in contrast to the 101-hour period of the foregoing operation. Here the following temperature time pattern was observed:

Catalyst temperature, ° F.:	Cumulative on-stream time, hours
622	20
675	30
677	40
680	50
682	60
690	70
700	80
705	90
715	100
720	110
725	120
735	130
760	140
785	150
825	157

The character of the product stream as regards aromatic content and the distribution therein of the various aromatic components was essentially the same in this run as in that of 8-948.

It will be seen from the information presented in the foregoing examples that the on-stream periods obtained for a given starting temperature are in general accordance with the relationship shown in the graph of Figure 2 of the drawing. Moreover, other operating experience shows that had one or the other of the runs of these examples been initiated at a higher temperature (e.g., 730° F. or 750° F.) with a corresponding increase in space velocity being made so as to maintain the conversion at the same 50-60% per-pass level, the on-stream period would have been greatly shortened, the same probably falling in a 20-50 hour range. An operation of this character is less economical than that which employs a longer on-stream period, for in the latter case the unit must remain off-stream for regeneration for a much larger proportion of the total operating time than would otherwise be the case.

EXAMPLE IV

This operation was conducted under process conditions generally coming within the scope of this invention except for the fact that the feed utilized, while otherwise meeting feed requirements, consisted essentially of polynuclear aromatic components boiling above 450° F. Further, in order to obtain a satisfactory conversion level of approximately 30% with this feed, it was necessary to resort to the use of relatively high temperatures. As will be seen from the following description, the 50-300°

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F. portion of the synthetic product obtained in this run contained far less than 50% of xylene isomers, based on the volume of aromatic compounds present.

The feed employed in this run comprised the heavy portion of a catalytic reformat. It was made up entirely of aromatic compounds and had the following boiling point characteristics:

ASTM D-86 Distillation:	° F.
Start	467
10%	480
50%	492
90%	539
End Point	658

The foregoing feed along with 6278 s.c.f. of hydrogen-rich recycle gas per barrel of feed was preheated to a temperature of 810° F. and passed at a LHSV of 1.5 and a pressure of 1200 p.s.i.g. through No. 226 catalyst, as described above, containing molybdenum sulfide (2% Mo) on the SiO₂-Al₂O₃ base. During the run, conversion was maintained at an average level of 28.8% per pass by gradually raising the temperature from 810° F. to 900° F., the total run lasting 26 hours. The operation was conducted under essentially extinction recycle conditions wherein unconverted feed and other portions of the product boiling above 400° F. (along with high pressure, hydrogen-rich gases) were continuously recycled to the isocracking zone along with fresh feed and make-up hydrogen, the hydrogen consumption being about 2781 s.c.f. per barrel of feed converted to product boiling below 400° F. The synthetic product portions boiling below 400° F. were continuously fractionated to produce, among others, a 60-180° F. fraction, a 180-230° F. fraction and a 230-300° F. fraction. These fractions had a combined aromatic content of 39 volume percent, and of said aromatics the xylene isomers constituted a total of about 35 volume percent.

I claim:

1. A method of producing xylene isomers from aromatic-rich hydrocarbon distillates, which comprises selecting as a feed stock a petroleum hydrocarbon fraction boiling within a range of from 325 to 450° F., and having an aromatic content of at least 75% by volume and a basic nitrogen content of less than 10 p.p.m., contacting said feed stock in admixture with at least 200 s.c.f. hydrogen per barrel of feed in an isocracking zone with a catalyst comprising a hydrogenating component selected from the group consisting of nickel sulfide and cobalt sulfide, disposed on an active acid cracking support and having a severity factor in the range of about 0.1 to 2.0, said isocracking zone being operated at pressures of at least about 400 p.s.i.g. and at instantaneous catalyst temperatures in the range of about 450° to 730° F., whereby there is produced, in a conversion of at least 20% per pass through the isocracking zone, a synthetic product boiling essentially below the initial boiling point of the feed; said synthetic product being characterized by the fact that of the aromatic present therein boiling below about 325° F., at least 50% by volume consists of xylene isomers, there being consumed in said isocracking process at least 1000 s.c.f. of hydrogen per barrel of feed converted to said synthetic product.

2. The method of claim 1 wherein the synthetic product is one having an end point of from about 300° to 325° F.

3. The method of claim 1 wherein said synthetic product has an end point of from about 325° to about 350° F.

4. The method of claim 1 wherein the conversion reaction is initiated at a temperature between 450° and 675° F.

5. A method of producing xylene isomers from aromatic-rich hydrocarbon distillates, which comprises selecting as a feed stock a petroleum hydrocarbon fraction boiling within a range of from 325 to 450° F., and having an aromatic content of at least 75% by volume and a

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basic nitrogen content of less than 10 p.p.m., contacting said feed stock in admixture with at least 2000 s.c.f. hydrogen per barrel of feed in an isocracking zone with a catalyst comprising a hydrogenating component selected from the group consisting of nickel sulfide and cobalt sulfide, disposed on an active acid cracking support and having a severity factor in the range of about 0.1 to 2.0, said isocracking zone being operated at pressures of at least about 400 p.s.i.g. and at instantaneous catalyst temperatures in the range of about 450° to 730° F., whereby there is produced, in a conversion of at least 20% per pass through the isocracking zone, a synthetic product having an end point of from about 300° to 325° F. which contains at least 50% by volume of xylene isomers in terms of the total aromatic content of said product, and recycling to the isocracking zone the portion of the effluent from said zone boiling above said synthetic product, there being consumed in said isocracking process at least 1000 s.c.f. of hydrogen per barrel of feed converted to synthetic product.

6. A method of producing xylene isomers from aromatic-rich hydrocarbon distillates, which comprises selecting as a feed stock a petroleum hydrocarbon fraction boiling within a range of from 325 to 450° F., and having an aromatic content of at least 75% by volume and a basic nitrogen content of less than 10 p.p.m., contacting said feed stock in admixture with at least 2000 s.c.f. hydrogen per barrel of feed in an isocracking zone with a catalyst comprising a hydrogenating component selected from the group consisting of nickel sulfide and cobalt sulfide, disposed on an active acid cracking support and having a severity factor in the range of about 0.1 to 2.0, said isocracking zone being operated at pressures of at

least about 400 p.s.i.g. and at instantaneous catalyst temperatures in the range of about 450° to 730° F., whereby there is produced, in a conversion of at least 30% per pass through the isocracking zone a synthetic product boiling essentially below the initial boiling point of the feed, said synthetic product being characterized by the fact that of the aromatics present therein boiling below about 325° F., at least 50% by volume consists of xylene isomers; fractionating the effluent from the isocracking zone to recover at least (1) a hydrogen-rich gaseous fraction which is recycled, along with make-up hydrogen, to the isocracking zone, (2) a relatively light product stream boiling below the xylene range, (3) a xylene-rich fraction and (4) a bottoms fraction boiling above the xylene-rich fraction; and subjecting said xylene-rich fraction to a separation step to recover as product at least one desired xylene isomer; there being consumed in said isocracking process at least 1000 s.c.f. of hydrogen per barrel of feed converted to said synthetic product.

7. The process of claim 6 wherein the bottoms fraction recovered from the isocracking zone is recycled to said zone.

8. The process of claim 7 wherein there is also recycled to the isocracking zone that portion of the xylene-rich fraction remaining after separating therefrom the desired xylene isomer product fraction.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,944,089

July 5, 1960

John W. Scott, Jr.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 15, line 75, for "50-300⁰" read -- 60-300⁰ --.

Signed and sealed this 31st day of January 1961.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

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Commissioner of Patents