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PRODUCTION OF AROMATIC HYDROCARBONS

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This invention relates to treatment of hydrocarbon material. In a more specific aspect, this invention relates to the conversion of aliphatic hydrocarbons to aromatic hydrocarbons. In a still more specific aspect, this invention relates to the conversion to aromatic hydrocarbons of aliphatic hydrocarbons having at least six carbon atoms connected together in a linear chain, particularly paraffins, olefins, and diolefins. In yet another specific aspect, this invention relates to upgrading of hydrocarbon streams, such as reformer stocks, poly-gas stocks, and the like, by converting aliphatics contained therein to aromatics. In other specific aspects, this invention relates to the conversion of long chain paraffin hydrocarbons to high boiling benzenes which are desirable for conversion to their sulfonic acid derivaties; to the treatment of sulfur and sulfur compound-containing straight run gasoline and naphtha fractions to convert aliphatics contained therein to aromatics; to the treatment of natural gasoline or streams separated therefrom to convert the n-hexane, n-heptane, etc., therein to benzene, toluene, and higher boiling alkylated benzenes; and to the conversion of n-hexane to benzene and n-heptane to toluene.

This application is a continuation-in-part of our copending application, Serial No. 186,120, filed September 21, 1950, now abandoned, and discloses and claims the subject matter covered thereby.

Aromatic hydrocarbons, such as benzene and toluene, are in innumerable instances the starting material in the synthesis of a great many of industry's widely used organic chemicals and products. They are very valuable organic chemicals. Aromatic hydrocarbons have high anti-knock ratings, and are desirable in engine fuels. Usually, the anti-knock ratings of aromatic hydrocarbons are substantially higher than those of aliphatic hydrocarbons, particularly those aliphatic hydrocarbons having six or more carbon atoms in a linear chain found in natural gasoline, and the intermediate and higher boiling fractions, such as straight run gasoline and naphtha streams, and gas oil fractions, separated from crude petroleum in refining operations. Alkylated benzenes having relatively high boiling points are desirable and are in demand for sulfonation to produce their sulfonic acid derivaties which are commercial detergents. Straight chain saturated aliphatic hydrocarbons are in great supply from natural gasoline separated from natural gas, and from refinery streams separated from crude petroleum. Olefin hydrocarbons and olefin hydrocarbon fractions are available as a result of the common cracking operations, particularly catalytic cracking operations, which are carried on in refining operations today. The chemical and petroleum industries are continually carrying on research and development to find better processes by which to convert aliphatic hydrocarbons to aromatic hydrocarbons. Catalysts and methods are known which can be used to give such conversions. Some dehydrogenation catalysts have dehydrocycling power, such as chromia or molybdenum oxide catalysts, which give substantial conversions of aliphatics to aromatics. Other dehydrogenation catalysts, such as

activated alumina, bauxite, and activated charcoal, have no power alone to catalyze the conversion of aliphatics to aromatics. We have invented a new process to convert aliphatic hydrocarbons to aromatic hydrocarbons. Our new process gives good yields, and offers industry an efficient and economical method to produce aromatic hydrocarbons.

By the process of our invention aliphatic hydrocarbons are converted into aromatic hydrocarbons, by contacting the aliphatic hydrocarbons with a dehydrogenation catalyst in the presence of an oxide of sulfur. Dehydrogenation catalysts having no dehydrocycling power can be used in the process of our invention with good yields of aromatic hydrocarbons, and dehydrogenation catalysts having dehydrocycling power can be used with resultant increase in conversion to aromatic hydrocarbons. The process of our invention is particularly valuable, since it can be used with good results to upgrade petroleum hydrocarbon streams containing aliphatic hydrocarbons by converting them to aromatic hydrocarbons, or relatively pure streams of aliphatic hydrocarbons, such as n-hexane, n-heptane, or the corresponding olefins can be converted to benzene and toluene, respectively. Hydrocarbons and other materials normally associated with the aliphatic hydrocarbons in natural gasoline and in refinery streams do not interfere with the conversion of the process of our invention. In a specific embodiment of the process of our invention, sulfur and the sulfur in the sulfur compounds contained in aliphatic hydrocarbon containing streams which presently result from refining certain sulfur-containing crude oils, are converted to a sulfur oxide by reaction with oxygen with additional conversion of the aliphatic hydrocarbons to aromatic hydrocarbons. This application of the process of our invention has been found to be particularly valuable since not only is the hydrocarbon material stream upgraded, but in addition, and as a result, the undesirable sulfur and sulfur compounds are removed. The process of our invention offers the petroleum industry a method to upgrade gasoline stocks which are used as such or for blending to high octane engine fuel, as well as a process to produce aromatic hydrocarbons for use or sale as such. Engine fuel requirements in regard to anti-knock rating are ever increasing, and those familiar with the present and who visualize the future requirements of the petroleum industry, will realize the importance of the process of our invention.

It is an object of our invention to provide a process for the treatment of hydrocarbon material.

It is another object of our invention to provide a process for the conversion of aliphatic hydrocarbons to aromatic hydrocarbons, specifically aliphatic hydrocarbons having at least six carbon atoms connected together in a linear chain, particularly paraffins, olefins and diolefins.

Still another object of our invention is to provide a process for increasing the anti-knock rating of gasoline and naphtha stocks by converting aliphatic hydrocarbons therein to aromatic hydrocarbons.

Yet another object of our invention is to provide a new process for the conversion of relatively high boiling aliphatic hydrocarbons to alkylated benzenes of relatively high boiling point and which are suitable for sulfonation to their sulfonic acid derivatives, thus providing detergents.

Still another object of our invention is to provide a process for increasing the aromatics content of sulfur and sulfur compound-containing straight run gasoline and naphtha fractions and to provide for the removal of the sulfur therefrom.

It is yet another object of our invention to provide a process for the production of aromatic hydrocarbons from

natural gasoline or fractions thereof, separated from naturally occurring hydrocarbon material gas.

It is still another object of our invention to provide a new process for converting n-hexane to benzene and a new process for converting n-heptane to toluene.

Other objects and advantages of the process of our invention will become apparent to one skilled in the art upon reading this disclosure.

Following is a discussion and description of the process of our invention in which is set forth preferred specific embodiments and applications of the process, along with preferred operating conditions, materials, catalysts, etc. However, it is to be understood that such discussion and description is not to unduly limit the scope of our invention.

The process of our invention can be used to convert aliphatic hydrocarbons, having at least six carbon atoms connected together in a linear chain, to aromatic hydrocarbons. Aromatic hydrocarbons can be produced readily by the process of our invention by conversion of paraffin hydrocarbons, such as n-hexane, n-heptane, octanes, higher boiling saturated aliphatic hydrocarbons, including those having from ten to twenty-four carbon atoms, such as hexadecane, heptadecane, octadecane and branched chain high boiling paraffins having at least six carbon atoms in a linear chain, mixtures of such hydrocarbons, and the like. Olefins can easily be converted with good yields, such olefins as the n-hexenes, the n-heptenes, the octenes, high boiling olefins, such as result from catalytic cracking processes, mixtures of such, and the like. Diolefins can be converted to aromatics, such diolefins as the n-hexadienes, the n-heptadienes, the octadienes, higher boiling diolefins, mixtures of these diolefins, and the like. Paraffins, olefins and diolefins can and do exist together in some petroleum refinery and chemical plant streams, and in admixture they can be treated by the process of our invention to produce aromatic hydrocarbons. Benzene can be produced by the process of our invention from n-hexane, the n-hexenes and n-hexadienes; n-heptane, the n-heptenes and the n-heptadienes can be converted to toluene; and the higher boiling paraffins, olefins and diolefins, respectively, can be converted to higher boiling alkylated benzenes. The aliphatic hydrocarbons can be treated either in the pure state, in admixture with each other, or in admixture with other hydrocarbons, as in hydrocarbon material streams containing substantial quantities of the aliphatic hydrocarbons, such as natural gasoline (sometimes called casinghead gasoline) which is separated from natural gas and usually contains substantial quantities of n-hexane, n-heptane and higher boiling paraffins; straight run gasoline streams, naphthas and similar hydrocarbon mixtures, referred to as reformer stocks, and which are many times subjected to reforming operations to improve engine fuel quality; refinery olefin streams resulting from cracking operations, including thermal, fixed catalyst bed, and moving catalyst bed, both bead and fluid, which are known olefin producers; and the like. Long chain, high boiling paraffin hydrocarbons can be converted to high boiling alkyl benzenes which are suitable and desired for sulfonation to their sulfonic acid derivatives, which are desired as synthetic detergents. Sulfur and/or sulfur compound-containing straight run gasoline and naptha reformer stocks, such as are obtained from "Santa Maria Valley," California, crude oils, Wyoming crude oils, and the like, can be treated by the process of our invention by adding O_2 to the feed or reaction zone, the aliphatics therein being converted to aromatics to improve quality, and in addition to improving octane rating, undesirable sulfur is removed. The sulfur and O_2 provide the sulfur oxide in the conversion zone. Additional sulfur oxide over that formed from sulfur in the feed can be added, if desired. So-called poly-gas made by polymerizing butenes under controlled conditions has substantial quantities of olefins therein having six and more carbon atoms connected in a linear chain, and such can be treated by the process of the invention to produce aromatic hydrocarbons.

The oxide of sulfur used to carry on the process of our invention can conveniently be SO_2, SO_3, mixtures of same, and the like. We have found that the oxides of sulfur can be added to the hydrocarbons to be converted and/or to the zone wherein conversion takes place as the oxide itself and/or in acid form, such as H_2SO_4, H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_7$, the polythionic acids, mixtures of same, and the like. To provide the oxide of sulfur at conversion, sulfur and/or sulfur-containing compounds, added separately to the hydrocarbons to be converted or present therein and/or therewith, can be used along with oxygen. The O_2 can be added to the food stream and/or reaction zone as can be the sulfur or sulfur-containing compound. Pure O_2 can be used, or air, or enriched air can be used. Ozone can be used, if desired. Sulfur and O_2, and H_2S and O_2 can be used, and sulfides, mercaptans, other sulfur-containing compounds, and mixtures of such, together with O_2 or ozone can be used. Certain advantages have been found through the use of excess O_2 and/or O_3 with the sulfur oxides or sulfur oxide yielding compounds and with the sulfur-containing compounds, resultant longer catalyst life being of particular importance. It has been found economical and preferable to use relative pure SO_2 which can conveniently and easily be added to the hydrocarbon feed stream.

Conversion of the aliphatic hydrocarbons to aromatic hydrocarbons by the process of our invention is accomplished in the presence of a dehydrogenation catalyst, including those which have dehydrocycling power as well as dehydrogenating power. The presence of the sulfur oxide will increase conversion to aromatics with any suitable dehydrogenation catalyst. Some catalysts which can be used to carry on the process of the invention are activated carbon; activated alumina; bauxite; fuller's earth, particularly attapulgite; silica gel; supported platinum catalysts, such as platinizel asbestos, platinized alumina, platinized carbon; bentonite; synthetic silicates; metals, such as platinum, nickel and copper; molybdenum oxide; chromium oxide; nickel sulfide; tungsten sulfide; or any of a number of oxides or sulfides of metals of groups IV, V, VI, VII and VIII of the periodic system. Mixed catalysts can be used, if desired. The catalysts can be used alone or in supported form on either inert or active carriers, and contact can be had with the catalyst in a fixed bed, moving bed or in fluidized state, as desired. Chromia-containing activated alumina and molybdenum oxide-containing activated alumina catalysts have been found to give excellent results. Catalyst regeneration causes no difficulty, burning in air to remove carbon deposits, sulfur, if any, etc., working well. Sulfur deposit has been found to poison the catalysts drastically and should be avoided. Potassium carbonate treatment of the catalysts has been found to prolong their life, but with some decrease in activity.

In the process of our invention, the proportion of oxide of sulfur to hydrocarbon material to be converted can vary over a wide range from as low as 0.1 mole to as high as several moles per mole of hydrocarbon, preferably in the range of from 0.25 to 4 moles per mole of hydrocarbon, more preferably in the range of 0.3 to 3 moles per mole of hydrocarbon. It is desired that from 0.4 to 3 moles of SO_2 per mole of hydrocarbon to be converted be employed in carrying out the process of our invention, more preferably 0.7 to 1.8 moles per mole of hydrocarbon. When the SO_2 is provided at conversion conditions by using an SO_2 yielding material, or by providing for conversion of sulfur to SO_2 so that such is present at conversion conditions, it is desirable that the above set forth preferred quantities be maintained, that is, moles of SO_2 per mole of hydrocarbon to be converted in the ranges set forth at conversion conditions.

When treating reformer stocks by the process of the invention, additional SO_2 over that provided and used to give conversion of aliphatics to aromatics is generally desirable, since naphthenes in mixture with convertible paraffin hydrocarbons are preferentially converted to aromatics. It has been found preferable to use from 1.2 to 1.3 moles of SO_2 per mole of n-hexane and/or n-heptane when converting same to aromatics. H_2S is produced as a product of the process of our invention, and such can be separated from the conversion products and converted to SO_2 for use in further conversion. Also, hydrogen is produced. In carrying on the process of our invention, it has been found desirable to avoid excess SO_2, because if an excess of SO_2 exists, H_2S formed in the conversion reacts therewith to give sulfur which deposits on the catalyst to poison same. SO_2 in the conversion effluent should be avoided and appearance of SO_2 in the effluent usually indicates a decrease in catalyst activity, making it advisable to regenerate the catalyst.

In carrying out the process our our invention, a suitable temperature is maintained for conversion, preferably a conversion temperature in the range of from 400° to 700° C., more preferably in the range of from 475° to 600° C., and still more preferably in the range of from 500° to 575° C.

A suitable conversion pressure is maintained on the reaction zone in carrying on the process of our invention. Conversion can be carried on at pressures considerably less than atmospheric down to 1 p.s.i.a. and at relatively high pressures up to 2000 p.s.i.a. and more can be used, if desired. It is preferred to use pressures in the range of atmospheric to 100 p.s.i.a. Excellent results have been obtained at atmospheric pressure and up to 200 p.s.i.a.

In operating the process of our invention, the hydrocarbons to be converted are maintained in contact with the catalyst in the presence of the oxide of sulfur for a suitable length of time to give the desired conversion, preferably from 0.3 to 20 seconds, more preferably a time in the range of from 0.6 to 6 seconds.

Operational procedures in carrying on the process of our invention can be any of the common mixing, contacting, separation and recycling methods which are suitable to convert the aliphatic hydrocarbons to aromatic hydrocarbons. We have found it desirable to preheat the aliphatic hydrocarbons to be converted, or the hydrocarbon material stream containing the aliphatics to be converted, and the sulfur oxide prior to contact with the catalyst. The sulfur oxide can be added to the aliphatic hydrocarbon stream to be contacted with the catalyst somewhat prior to contact, just prior to contact, or it can be introduced directly into the catalyst bed during conversion, as desired. The process of our invention is exothermic, and such should be taken into account in determining the degree of preheat. For example, preheat to within 25° to 75° C. of the desired conversion temperature for the conversion of n-hexane to benzene has been found to work well, allowing for adequate control of conversion temperature.

The dehydrogenation catalyst used in the process of our invention can be employed in a fixed bed, a moving bed with continuous catalyst regeneration associated therewith, if desired, or the catalyst can be employed in fluidized form, again with continuous regeneration associated therewith, if desired. Burning to remove deposits of carbonaceous material and sulfur has been found desirable. Steam to control regeneration temperature during burning is preferably used.

The common and usual separation means can be used to separate and remove desired products of the process of our invention, such as fractional distillation operations, selective adsorption processes, employing activated charcoal, silica gel, etc., or selective absorption processes, using for example, cuprous salts. If desired, one can employ liquid-liquid absorption separation processes, or liquid-gas absorption separation processes to separate the reaction effluent and recover desired constituents thereof. Water produced by the process of our invention can be separated from the hydrocarbons by condensing and decanting.

Usually olefins are produced as a product of the process of our invention as well as aromatic hydrocarbons. These olefins can be recycled along with unreacted paraffin hydrocarbons for additional conversion of those olefins having six or more carbon atoms in a linear chain. A particular advantage of the process of our invention is that with some dehydrogenation catalysts, particularly those with cyclizing power, a relatively small amount of paraffins are formed when olefins are converted in the presence of the sulfur oxide, resulting in a higher yield of aromatics. Dehydrocyclizing catalysts are known to, and have been found by us to, give relatively large amounts of paraffins when olefins are converted in their presence and in the absence of a sulfur oxide. In our process we have found that internal olefins give considerably higher yields of aromatics than can be obtained without the use of an oxide of sulfur. This is advantageous because usually terminal olefins are rapidly shifted to internal olefins in the presence of dehydrogenation catalysts at elevated temperatures. Further, it is known that internal olefins give a much poorer yield of aromatics than do 1-olefins in the presence of dehydrocyclizing catalysts and in the absence of an oxide of sulfur. However, in the process of our invention, all olefins give excellent conversions to aromatics independent of the position of the double bond. As a result of this, particular advantages stem from our process when treating thereby streams containing both internal and 1-olefins.

H_2S is produced as a product of the process of our invention. It can be separated and removed from the effluent resulting from our process by any suitable means. Since it is in all cases present as a product of our process, the use of excess sulfur dioxide should be avoided. The presence of sulfur dioxide in the reaction effluent results in sulfur being formed by reaction of sulfur dioxide with the H_2S. Formation of sulfur should be avoided, because it deposits on the catalyst poisoning same, and if produced in any substantial quantity, it will plug up and foul up equipment. We have found it desirable and advantageous to control our process by detecting sulfur dioxide in the reaction effluent. When such occurs, the catalyst usually needs regenerating, or if a moving bed or fluidized catalyst system is being employed, more regeneration of the catalyst or less time in contact during conversion is usually needed.

In the following is set forth examples of the process of our invention. It is to be understood that the aliphatic hydrocarbon feed material, oxides of sulfur, catalysts, times, temperatures, pressures, proportions, etc., set forth in these examples are not to unduly limit the scope of our invention, since such examples only set forth specific and preferred embodiments of the process of our invention.

EXAMPLE I

Pure n-hexane (99.5+% pure) was passed through a bed of activated alumina at a temperature of 500° C. and at atmospheric pressure. The activated alumina was granular and of a 4–10 mesh size. The activated alumina catalyst was placed in a 22 mm. I.D. Pyrex reaction tube; the depth of catalyst bed was 10 cm.; and the volume of catalyst was approximately 38.6 ml. The liquid n-hexane was charged to a preheater at an average rate of 0.7 ml./min., vaporized and preheated over porcelain Raschig rings to 440° C., and passed through the activated alumina bed at 500° C. The average space velocity during the run was about 1.3 (vol. liq/vol. cat./hr.). The refractive index of the liquid product, resulting from condensing the reactor effluent, was 1.3752 at 20° C., that of pure n-hexane being 1.3750. The specific gravity of the liquid

product was 0.658 @ 20° C., that of n-hexane being 0.659.

These data indicate that n-hexane undergoes no substantial change over activated alumina up to temperatures of 500° C.

Using this same alumina without removing it from the reaction tube or disturbing it in any way and with the same entire apparatus, n-hexane and SO_2 were passed through the alumina at 500° C. The SO_2 feed rate was about 69.5 ml./min., and n-hexane 0.7 ml./min.,, this being a mol ratio of SO_2 to hexane of 0.58. Again the reactor effluent was condensed and collected, and the refractive index of the total liquid product was 1.3987 at 20° C., that of n-hexane 1.3750. The specific gravity of the liquid product was 0.701 at 20° C., that of n-hexane 0.659 at 20° C. During the course of the experiment many samples had refractive indices as high as 1.4020 or higher.

To one skilled in the art, the production of aromatics would immediately be assumed. However, a sample of the liquid product was subjected to adsorption analysis, using silica gel adsorbent, employing the ASTM procedure. The aromatic plateau by silica gel analysis was approximately 20%. It is known, however, that thiophenes and other sulfur compounds could be present in that portion of the product which gives the aromatic plateau. Consequently, the samples constituting the aromatic plateau were combined and treated with excess sulfuric acid. Such a treatment removes thiophenes, sulfur compounds and unsaturates. Some of the benzene would also be dissolved under such treatment. The combined aromatic portion, when so treated, underwent a loss of 25%, indicating it was 75% benzene, or about 13½% benzene was present in the original product. A rough estimate of the total benzene produced was made from the values of the specific gravity and the refractive index. This calulation gave a figure of approximately 19 vol. percent benzene produced based on the n-hexane feed.

EXAMPLE II

Test No. 1

Vaporized n-hexane was continuously passed once through a fixed bed of chromia-on-Porocel catalyst at a substantially constant rate and at atmospheric pressure. The n-hexane was 99+ mol percent pure. The temperature of reaction was 500° C. measured at the outside wall of the reactor containing the catalyst. The reactor was an elongated one inch internal diameter tube and was insulated. The average liquid space velocity during the run was 0.75 cu. cm. hexane/cu. cm. catalyst/hr. The time of the run was 2 hours and 48 minutes. The resulting effluent from the reactor was condensed, collected and analysed for aromatics using fluorescent indicator analysis and for trans-internal olefins using infra-red analysis. The liquid recovery of effluent was 80% (vol. product/vol. feed). The liquid product contained 21% aromatics, 17% trans-internal olefins and 62% unreacted n-hexane. The aromatics recovery was 17% (vol. aromatics/vol. feed).

Test No. 2

A mixture of vaporized n-hexane and sulfur dioxide was continuously passed once through a fixed bed of chromia-on-Porocel catalyst at a substantially constant rate and at atmospheric pressure. The n-hexane was of the same quality and from the same source as that used in Test No. 1. The chromia catalyst was fresh and from the same sample as that used in Test No. 1. The equipment, procedure, reaction temperature, and average liquid space velocity of n-hexane were the same as those of Test No. 1. The sulfur dioxide was continuously added at a substantially constant rate to the stream of n-hexane prior to contact with the catalyst in an amount of 0.68 mole of sulfur dioxide per mole of n-hexane. The time of the run was 2 hours and 19 minutes. The resulting effluent from the reactor was condensed, collected and analysed under the same conditions and by the same procedure as that used in Test No. 1. The liquid recovery of effluent was 66% (vol. product/vol. feed). The liquid product contained 36% aromatics, 7% trans-internal olefins and 57% unreacted n-hexane. The aromatics recovery was 24% (vol. aromatics/vol. feed).

The production of aromatic hydrocarbons from n-hexane was increased 7% by carrying on the conversion in the presence of sulfur dioxide under the same conversion conditions.

EXAMPLE III

Relatively pure n-hexane (99+% pure) was passed over activated carbon catalyst contained as a fixed bed in a 2.3 cm. internal diameter reaction tube. The depth of the bed was 4.5", and the weight of activated carbon contained therein was 17.2 grams. Prior to contact with the activated carbon catalyst, the n-hexane was preheated to 450° C., and the temperature at contact and in the bed during conversion was approximately 500° C. The time of the run was approximately 140 minutes. Gaseous sulfur dioxide was added to the n-hexane stream prior to preheat. The flow rate of the n-hexane stream and sulfur dioxide were measured, and it was calculated that 0.22 mole of sulfur dioxide were added and present during conversion for each mole of n-hexane. The space velocity was 0.9 vol. liq. feed/vol. cat./hr. The effluent from the reaction was collected after condensation, and the specific gravity of the resulting condensate was measured. From the specific gravity, it was estimated that the product contained 10% aromatics, and the percent aromatics production based on the feed was estimated to be 8% by volume.

EXAMPLE IV

Relative pure n-hexane (99+% pure) was contacted in the presence of sulfur dioxide with a platinized alumina catalyst in a fixed bed. The catalyst was contained in a tube reactor having an internal diameter of 2.3 cm. The bed depth of the catalyst in the reactor was 4.5", and the weight of catalyst used was 36.1 grams. The n-hexane and sulfur dioxide were mixed as gases and preheated to 450° C. prior to introduction into the catalyst bed. The sulfur dioxide was added in an amount so that 1.1 moles were present per mole of n-hexane. Conversion temperature was 500° C.; the space velocity was 0.7 vol. liq. feed/vol. cat./hr.; and the time of the run was 120 minutes. The reaction effluent was condensed and collected, and the resulting condensate was measured for specific gravity. From this specific gravity it was estimated that the production of the reaction contained 24% aromatics, giving an estimated aromatics production of 18% by volume based on the liquid feed volume.

EXAMPLE V

Relative pure n-hexane (99+% pure) was contacted in the presence of sulfur dioxide with a Ni impregnated activated alumina catalyst in a fixed bed. The catalyst was contained in a 2.3 cm. internal diameter reactor tube. The bed depth was 4.5", and the weight of catalyst in the bed was 35.2 grams. The sulfur dioxide was added as a gas to the gaseous stream of n-hexane, and the resulting mixture was preheated to 450° C. prior to introduction into the catalyst bed. Sulfur dioxide was added in an amount so there were 1.2 moles present per mole of n-hexane. The conversion was carried on at a temperature of 500° C., and the space velocity was 0.7 vol. liq. feed/vol. cat./hr. The time of the run was 120 minutes. The effluent from the reaction was condensed and collected, and the specific gravity of the resulting condensate was measured. From this specific gravity, it was estimated that the reaction product contained 22% aromatics, giving an estimated aromatics production of 16% by volume based on the liquid feed volume of n-hexane.

EXAMPLE VI

Conversion of n-hexane to aromatics in the presence of sulfur dioxide and a chromia catalyst was carried out varying the amount of sulfur dioxide present during conversion. The runs set forth in the following Table I were all carried out at a conversion temperature of 550° C. and at a conversion pressure of atmospheric. The time of each of the runs was 45 minutes. Contacting was carried on in a reactor containing the catalyst in a fixed fluidized bed, the catalyst in each of the runs being Cr_2O_3 on Porocel with 10% of the total weight of the catalyst being Cr_2O_3. The mesh size of the catalyst was minus 70 plus 200, and 700 grams of fresh catalyst from the same batch was used for each of the runs. The n-hexane and SO_2 in gaseous state were preheated separately to the conversion temperature and mixed together just prior to introduction into the reaction chamber. The reaction chamber had an internal diameter of 2⅜". The reaction effluent in each case was condensed and collected as the product of the run after equilibrium conditions were obtained.

TABLE I

Mole Ratio SO_2:Hexane	Liquid Recovery, Wt. Percent	F.I.A.[1]			Yield, Vol. Percent on hex. chgd.	Calculated Ultimate Yld., Volume Percent
		Percent P	Percent O	Percent A		
0.802	78.0	71.1	6.8	22.1	15.6	34.6
1.05	72.8	67.9	5.7	26.4	17.1	32.7
1.05	74.6	66.6	5.9	27.5	18.4	35.8
1.17	70.8	63.6	6.7	29.7	18.6	33.4
1.19	71.6	64.6	7.4	28.0	17.7	32.3
1.43	67.5	59.2	7.4	33.4	19.6	32.5
1.45	68.4	57.5	6.9	35.6	20.8	33.8
1.46	70.7	58.0	6.7	35.4	21.3	35.4
1.62	57.9	55.1	6.2	38.7	18.9	27.5

[1] Fluorescent Indicator Analysis of reaction product, percent paraffins, percent olefins, percent aromatics.

The calculated ultimate yield is based on the hexane charged and infinite recycle, and ultimate yield includes aromatics resulting from olefins produced being recycled.

In each of the runs set forth in Table I, the material balance was within plus or minus 10%.

EXAMPLE VII

Tests were made treating n-hexane over a fuller's earth catalyst, in one case without SO_2 being present and in the other case in the presence of SO_2. The fuller's earth was Attalpulgus type which was treated in the following manner. A pulverized sample of the earth was wetted with water, extruded, crushed to 4 to 8 mesh size, and heat treated for about 2 hours at 500° C. in a nitrogen atmosphere. Fresh fuller's earth out of the same batch was used in each of the two tests.

The contacting was carried on with the fuller's earth in a fixed bed in each of the tests, and 99+ mole percent pure n-hexane from the same batch was used in each of the two tests. The conversion temperature in each of the two tests was about 500° C., and the conversion pressure atmospheric.

The first test was run in the absence of sulfur dioxide. The time of the run was 1 hour and 40 minutes, using a hexane feed rate of 0.77 cu. cm. hexane/hr./cu. cm. cat. The effluent from the reaction was condensed and collected, and the specific gravity of the resulting condensate was measured. This specific gravity was the same as that of n-hexane, showing that practically no conversion of the hexane took place.

In the second test, 0.66 mole of SO_2 per mole of n-hexane were added to the hexane feed stream prior to contact with the fuller's earth. In this test, the hexane feed rate was 0.75 cu. cm. hexane/hr./cu. cm. cat., and the time of the run was 1 hour and 9 minutes. Again the reaction effluent was condensed and collected. The resulting product condensate contained 35% aromatics as estimated from its specific gravity. Infra-red analysis of the product condensate showed 7% trans-internal olefins. The aromatics production per pass was 21%, vol. aromatics per vol. feed, and a calculation of ultimate aromatics production upon recycle gave a potential yield of 32%, vol. aromatics produced from infinite recycle/vol. of hexane feed.

In regard to fuller's earth as a catalyst for the purpose of the process of our invention, it has been found that certain of the attapulgites are preferable. Some materials classed as fuller's earths have been found to have no effect in our process to catalyze conversion of aliphatics to aromatics.

EXAMPLE VIII

Two tests were made converting n-cetane to aromatic hydrocarbons over activated alumina. In each of the two tests, 45 ml. of fresh catalyst from the same batch was used, of mesh size 8 to 12, and in a fixed bed 4.5" in depth. The n-cetane was 99+ mole percent pure, and a sample from the same batch was used in each test. The temperature of conversion in both of the tests was approximately the same, about 500° to 505° C., and the conversion pressure was atmospheric.

In the first run no sulfur dioxide was present during conversion. The time of the run was 119 minutes, and the space velocity was 0.74 ml. liq. hy./hr./ml. cat. The reaction effluent from the catalyst bed was condensed and collected, and a fluorescent indicator analysis was run on a sample of resulting condensate. This analysis showed 90.2% n-cetane, 6.6% olefins, and 3.2% aromatics. The aromatic hydrocarbons yield was 2.8 vol. percent based on the liquid volume of n-cetane feed.

In the second test sulfur dioxide was added to the cetane feed stream in the amount of 1.23 moles per mole of n-cetane. The time of the run was 69 minutes, and the space velocity was 0.87 ml. liq. hy./hr./ml. cat. Again the effluent from the reaction was condensed and collected and a fluorescent indicator analysis run on a sample of the resulting condensate. This analysis showed the product condensate to contain 48.0% n-cetane, 13.0% olefins, and 39.0% aromatics. This gave a yield of aromatic hydrocarbons of 23.5% by volume based on the cetane feed.

EXAMPLE IX

Two tests were run to convert n-hexene-1 to aromatics over a chromia-on-Porocel catalyst. One of the tests was made in the presence of sulfur dioxide and the other run was made without the use of sulfur dioxide. In both tests 45 ml. of 8 to 12 mesh catalyst were used in a fixed bed having a depth of 4.5". Fresh catalyst from the same batch was used in each of the two runs. Likewise, samples of n-hexene-1 from the same batch having a purity of 95+ mole percent were used in each of the two tests. The conversion temperature in both of the tests was approximately the same in the range of 500° to 510° C., and both tests were made at atmospheric pressure. The time of the run in each case was the same, being 128 minutes in duration.

In the first test, no sulfur dioxide was present during conversion, and the space velocity was 0.897 ml. liq. hy./hr./cu. cm. cat. The product from the resulting conversion was condensed and collected and a fluorescent indicator analysis was run on a sample of the resulting condensate. This analysis showed that the product condensate contained 31.8% paraffins, 35.1% olefins and 33.1% aromatics. This was a yield of aromatics of 24.0 vol. percent based on the n-hexene-1 feed.

In the second test, 1.21 moles of sulfur dioxide per mole of n-hexene-1 was added to the feed stream and was present during the conversion. The space velocity in this second test was 0.740 ml. liq. hy./hr./cu. cm. cat. Again, the effluent from the reaction was condensed and

collected, and a fluorescent indicator analysis run on a sample of resulting condensate. This analysis showed 2.3% paraffins, 24.6% olefins and 73.1% aromatics. This was an aromatics yield of 38.2 vol. percent based on the n-hexene-1 feed.

EXAMPLE X

Two tests were made converting n-hexene-2 to aromatics using chromia-on-Porocel as the catalyst, one test in the absence of sulfur dioxide and the other test in the presence of sulfur dioxide. In both tests 45 ml. of fresh catalyst from the same batch of 8 to 12 mesh size was used in a fixed bed having a depth of 4.5". The conversion temperature in each of the two tests was approximately 510° C., and the conversion pressure was atmospheric. The n-hexene-2 for each of the two tests was from the same batch having a purity of 95+ mole percent.

In the first test, no sulfur dioxide was present during conversion. The space velocity was 0.937 ml. liq. hy./hr./cu. cm. cat., and the time of the run was 94 minutes. The effluent resulting from contacting the n-hexene-2 stream and the catalyst was condensed, collected and a fluorescent indicator analysis run on a sample of the resulting condensate. This analysis showed 14.3% paraffins, 64.2% olefins, and 21.5% aromatics. This was an aromatics yield of 13.6% by volume based on the n-hexene-2 feed stream.

In the second test 0.927 mole of sulfur dioxide per mole of n-hexene-2 was added to the feed stream prior to contact with the catalyst. The space velocity was 0.945 ml. liq. hy./hr./ml. cat. and the time of the run was 122 minutes. Condensing and collecting the reaction effluent and running a fluorescent indicator analysis on a sample of resulting condensate showed 1.9% paraffins, 22.1% olefins, and 76.0% aromatics in the product condensate. This was a 34.3 vol. percent aromatics yield based on the n-hexene-2 feed.

EXAMPLE XI

A mixture of 99+% pure n-hexane, air and H_2S was passed over activated alumina contained in a fixed bed. An air and H_2S mixture was added to the hexane feed. The effluent from the reaction was collected and condensed, and the resulting condensate contained aromatic hydrocarbons. The reaction was very exothermic and conversion temperature was in the neighborhood of 650° C.

Another test was run over a fixed bed of activated alumina employing a feed stream of n-hexane, H_2S and relatively pure O_2. Again the reaction was very exothermic and the temperature of conversion was in the neighborhood of 650° C. The reaction effluent was condensed and collected, and contained aromatic hydrocarbons.

EXAMPLE XII

A stream of relatively pure n-hexyl mercaptan was passed through a fixed bed of activated alumina of 8 to 12 mesh and having a bed depth of 4.5". A volume of 45 ml. of catalyst was used. Oxygen of 99.5+% purity was added to the mercaptan feed stream prior to contact with the catalyst. The conversion temperature was 508° C., and conversion pressure was atmospheric. The space velocity was 0.863 ml. liq. hy./hr./cu. cm. of cat., and the time of the run was 95 minutes. The reaction effluent from the catalyst bed was condensed and collected, and an analysis conducted thereon by micro-distillation. This analysis showed the condensate product to contain 15% by weight aromatic hydrocarbons. This was an aromatics yield of 7.5 vol. percent based on the mercaptan feed.

EXAMPLE XIII

A test was made passing 99+% pure n-hexane through a fixed bed of activated alumina and converting said hexane to aromatics in the presence of SO_3. The activated alumina bed was 4.5" in depth, and contained 45 ml. of 8 to 12 mesh catalyst. The SO_3 was added to the hexane feed stream by passing a nitrogen stream through stabilized liquid SO_3 at room temperature, and introducing the resulting stream of nitrogen containing vaporized SO_3 into the hexane feed stream prior to introduction into the bed of catalyst. Conversion temperature was approximately 510° C., and conversion pressure was atmospheric. The space velocity during the run was 1.05 ml. liq. hy./hr./ml. cat., and the time of the run was 99 minutes. The effluent resulting from the conversion was condensed, collected, and a fluorescent indicator analysis was run on a sample of resulting condensate. This analysis showed the condensed effluent to contain 84.3% paraffins, 6.1% olefins and 9.6% aromatics. This was an aromatics yield of 6.8 vol. percent based on the n-hexane feed.

The relatively low yield is believed due to the fact that a very small portion of SO_3 was present during conversion, due to the difficulty encountered in adding the SO_3 to the hexane feed stream.

EXAMPLE XIV

A stream of 99+% pure n-hexane was passed through a fixed bed of chromia-on-Porocel catalyst of 4 to 16 mesh size. The depth of the catalyst bed was 6", and 164 ml. of catalyst were used. The temperature of conversion was approximately 520° C., and the pressure under which conversion took place was 200 lb. per square inch gauge. A total weight of hydrocarbons of 123 grams was passed through the catalyst bed during the run. The effluent resulting from conversion was condensed and collected, and fluorescent indicator analysis was run on samples of the resulting condensate.

In the first portion of the run, nothing was added to the n-hexane feed stream, and analysis of the reaction product condensate showed that no conversion of n-hexane took place.

In the latter portion of the run, quantities of SO_2 were added to the n-hexane feed stream prior to introduction into the catalyst bed, and analysis of the resulting reaction product showed 75.5% paraffins, 8.3% olefins, and 16.2% aromatics. This was an aromatics yield of 11.8 vol. percent based on the n-hexane feed.

It was noticeable in this experiment that the catalyst after the test was cleaner and contained less deposit than would be normal for a corresponding run at atmospheric pressure.

EXAMPLE XV

This experiment was conducted in two separate parts hereinafter referred to as A and B. In part A the only feed was 99+ mol percent pure n-heptane and in part B the feed consisted of n-heptane from the same batch and also sulfur dioxide. In both A and B the catalyst was 52 cc. (57.0 gm.) of −6 +12 mesh molybdenum oxide on Porocel maintained in a fixed bed. The catalyst in each case was contained in a glass reaction tube of 25 mm. O.D., and had a bed depth of 5.5".

In part A, the liquid feed space velocity was 0.73 cc. heptane/cc. cat./hr., and the time of the run was 45 min. The n-heptane was preheated to 375° C. and then passed into the catalyst bed. The reaction zone was maintained at 510° C. and atmospheric pressure. The products from the reaction were condensed, collected and analysed by fluorescent indicator analysis. It was found that the liquid product contained 18.9% aromatics, 3.6% olefins and 77.7% paraffins. This was a yield per pass of 12.4% aromatics by volume.

In part B, the liquid feed space velocity was 0.67 cc. heptane/hr./cc. cat. Sufficient sulfur dioxide was fed into the system to insure that 1.39 moles of sulfur dioxide were present in the reaction zone for very mole of n-heptane present. The n-heptane and sulfur dioxide were mixed in the gaseous phase, preheated to 350° C. and

passed into the catalyst bed which was maintained at approximately 510° C. and atmospheric pressure. The total time of the run was 36 minutes. The products from the reaction zone were condensed, collected, and analysed by fluorescent indicator analysis. It was found that the liquid product contained 35.1% aromatics, 4.2% olefins, and 60.7% paraffins. This was a yield per pass of 20.1% aromatics by volume.

EXAMPLE XVI

A typical reformer stock and sulfur dioxide were mixed in the gaseous phase, preheated to 360° C. and passed through a reaction zone having a fixed bed of 48 cc. (49.6 gm.) of −8 +12 mesh chromia-on-Porocel catalyst contained in a glass reaction tube 25 mm. O.D. and having a bed depth of 5¼", at approximately 510° C. and atmospheric pressure. A fluorescent indicator analysis of the reformer stock showed it to contain 94.8% paraffins and naphthenes, a trace of olefins and 5.2% aromatics. The liquid hourly space velocity was 0.83 cc. liq./hr./cc. cat., and sufficient sulfur dioxide was fed into the system to insure that 1.41 moles of sulfur dioxide were present in the reaction zone for every mole of reformer stock (av. molec. wt.=108) present. The total time of the run was 61 minutes. The products from the reaction were condensed, collected and analysed by fluorescent indicator analysis. It was found that the liquid product contained 33.0% aromatics, 3.8% olefins, and 63.2% paraffins and naphthenes. This was a yield of 17.4% aromatics by volume per pass, inclusive of the 5.2% aromatics originally in the feed.

As will be evident to those skilled in the art, various modifications of this invention can be made, or followed, in the light of this disclosure and discussion, without departing from the spirit or scope of the disclosure or from the scope of the claims.

We claim:

1. A process for producing aromatic hydrocarbons comprising passing a feed stream containing aliphatic hydrocarbons having at least 6 carbon atoms connected together in a linear chain into a reaction zone having a dehydrogenation catalyst therein capable of catalyzing the reaction to produce aromatic hydrocarbons, passing oxide of sulfur providing materials into said reaction zone in an amount such that there is present in said reaction zone an amount of oxide of sulfur corresponding to at least about 0.4 mole of SO_2 per mole of hydrocarbon to be converted to aromatic hydrocarbon, controlling the amount of sulfur providing materials introduced into said reaction zone such that substantially no oxide of sulfur is present in the reaction effluent, and recovering a reaction effluent from said reaction zone containing a substantially increased amount of aromatic hydrocarbons resulting from the conversion of said aliphatic hydrocarbons.

2. The process of claim 1 in which said dehydrogenation catalyst is activated charcoal.

3. The process of claim 1 in which said dehydrogenation catalyst consists essentially of activated alumina.

4. The process of claim 1 in which said dehydrogenation catalyst is a chromia-containing activated alumina catalyst.

5. The process of claim 1 in which said dehydrogenation catalyst is a molybdenum oxide-containing activated alumina catalyst.

6. The process of claim 1 in which said dehydrogenation catalyst is a supported platinum catalyst.

7. The process of claim 1 in which said reaction is carried out at a temperature in the range of 475 to 600° C., at a pressure in the range of atmospheric to 1000 pounds per square inch absolute, and for a contact time in the range of from 0.3 to 20 seconds.

8. A process for producing aromatic hydrocarbons which comprises passing a feed stream containing aliphatic hydrocarbons having at least 6 carbon atoms connected together in a linear chain into a reaction zone having a dehydrogenation catalyst therein capable of catalyzing the reaction to produce aromatic hyrocarbons, passing sulfur dioxide into said reaction zone in an amount of at least about 0.7 mole of sulfur dioxide per mole of hydrocarbon to be converted to aromatic hydrocarbon, at a temperature of from 500 to 575° C., at a pressure of from atmospheric to 200 pounds per square inch absloute, and for a contact time of from 0.6 to 6 seconds, controlling the amount of sulfur dioxide introduced into said reaction zone such that substantially no sulfur dioxide is present in the reaction effluent and recovering a reaction effluent from said reaction zone containing a substantially increased amount of aromatic hydrocarbons resulting from the conversion of said aliphatic hydrocarbons.

9. A process for producing aromatic hydrocarbons which comprises passing a feed stream containing normal hexane into a reaction zone having a dehydrogenation catalyst therein capable of catalyzing the reaction to produce aromatic hydrocarbons, passing sulfur dioxide into said reaction zone in an amount of at least about 1.2 moles of SO_2 per mole of hexane to be converted to aromatic hydrocarbon at a temperature in the range of from 475 to 600° C., controlling the amount of sulfur dioxide introduced into said reaction zone such that substantially no oxide of sulfur is present in the reaction effluent and recovering a reaction effluent from said reaction zone containing a substantially increased amount of aromatic hydrocarbons resulting from the conversion of said normal hexane.

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