

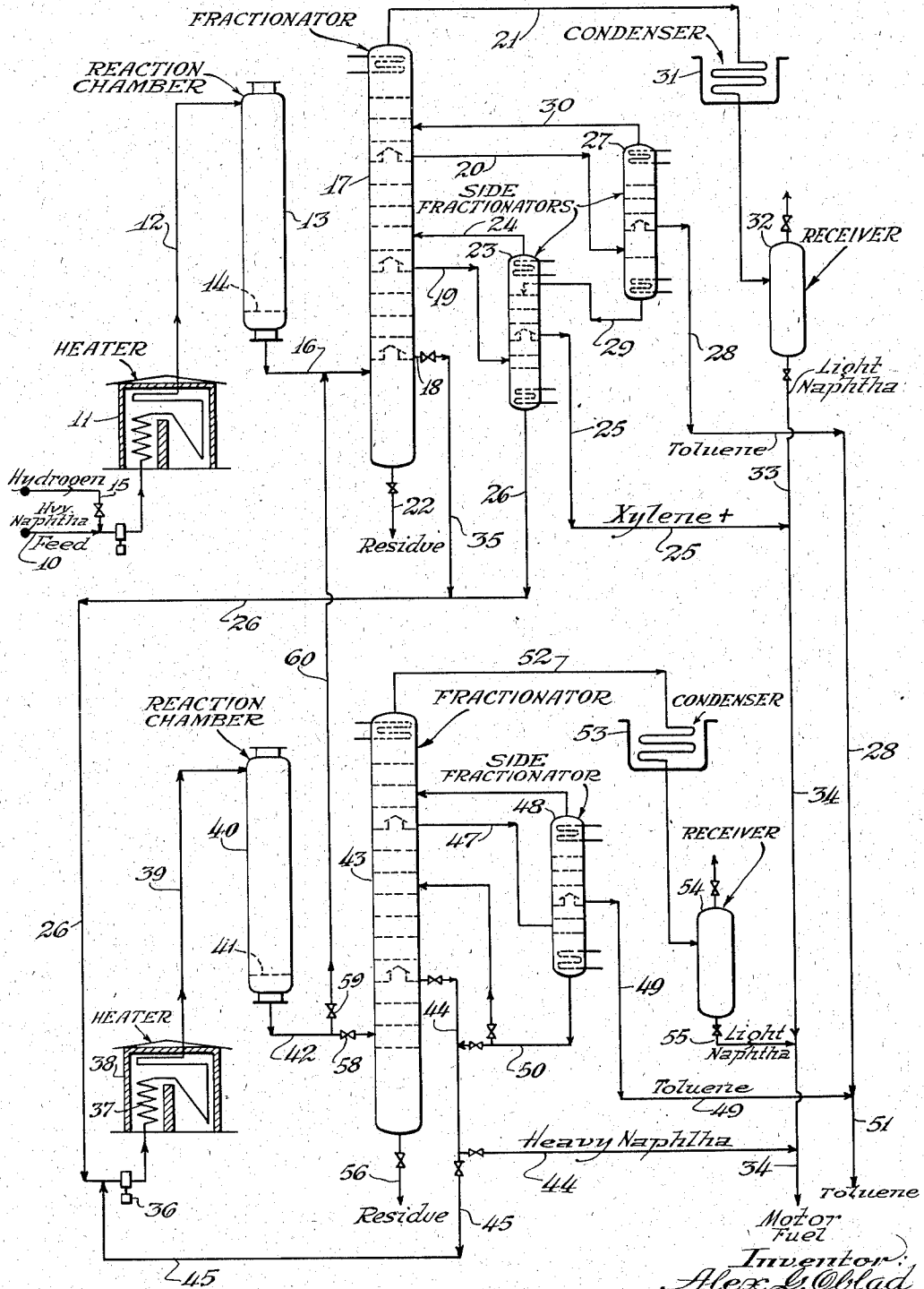
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PRODUCING TOLUENE

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PRODUCING TOLUENE

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This invention relates to a process of producing toluene from petroleum hydrocarbons. An object of the invention is to produce both toluene and high knock rating motor fuel simultaneously with the aid of catalysts without the destruction of large amounts of the petroleum hydrocarbons such as occurs in the case of high temperature pyrolysis for the production of toluene from petroleum. Other and more detailed objects will be shown in the description of the invention.

In the manufacture of benzene and toluene from petroleum by high temperature pyrolysis, for example, at temperatures of the order of 1400° F. to 1600° F., a large proportion of the paraffin hydrocarbons is degraded to coke and permanent gases. Yields of aromatic distillates and particularly toluene are relatively low. I have now discovered that by the use of catalysts at moderate temperatures within the cracking range, I may obtain substantial yields of toluene from petroleum naphtha, accompanied by relatively little degradation of the naphtha into gas and carbon.

My process involves treating petroleum naphtha in two successive steps under specific conditions of catalyst treatment and separation of intermediate products. In the first step of my process the petroleum naphtha is treated under aromatizing conditions in the presence of a hydrogenation-dehydrogenation catalyst at elevated temperature whereby the aromatic hydrocarbon content of the naphtha is greatly increased, partly by cyclization of paraffinic and/or olefinic hydrocarbons and partly as a result of dehydrogenation of naphthenic hydrocarbons. Toluene is separated from the products and higher boiling aromatic hydrocarbons are subjected to a second high temperature catalytic treatment with a cracking or hydrocarbon splitting catalyst whereby certain of the higher boiling aromatic hydrocarbons are decomposed to produce additional toluene. Other aromatic hydrocarbons not decomposed or decomposable in the second stage of the process are separated and employed as high knock rating motor fuel, high solvency naphtha suitable for lacquer and paint solvents, etc.

The process will be readily understood by referring to the drawing which accompanies this specification and is a part thereof. The drawing shows diagrammatically a layout for a plant to produce toluene and high knock rating motor fuel from petroleum naphtha in accordance with my invention.

Referring to the drawing, heavy naphtha is charged by line 10 to heater 11 wherein it is vaporized and heated to a high conversion temperature and conducted by transfer line 12 to reaction chamber 13 where it undergoes conversion in the presence of a catalyst. The naphtha employed in my process may suitably be either straight run or cracked petroleum naphtha, preferably the former. I prefer to employ a heavy naphtha having an initial boiling point of about 200 to 300° F. and a final boiling point of about 450° F. Somewhat heavier naphthas may be employed, however, including a material commonly classed as kerosene and a light gas oil having final boiling points as high as 600 to 650° F. Paraffinic and olefinic naphthas may be employed though somewhat better yields of toluene are obtained from the more aromatic or naphthenic types of naphtha.

Reaction chamber 13 is charged with a suitable catalyst for effecting conversion or reforming of the naphtha. The catalyst which is a porous, granular mass, is supported on perforated plate 14. Catalysts of the hydrogenating-dehydrogenating type are preferred, including the difficultly reducible oxides such as vanadium, chromium and molybdenum oxides and oxides of other metals in the left columns of groups V and VI. It is preferred to employ these oxides supported on a suitable base, particularly granular alumina or magnesia. Activated alumina, magnesite or bauxite activated by acid treating may be employed as a base. The amount of hydrogenating-dehydrogenating metal oxide supported on the alumina, for example, may be of the order of 5 to 25%.

Hydrogen may be employed in the reactor 13, the hydrogen being introduced, for example, by line 15, and passed through the furnace with the naphtha. The amount of hydrogen may suitably equal the volume of hydrocarbon vapors undergoing treatment or it may exceed that volume by as much as 2 to 5 fold. When employing hydrogen, it is desirable to maintain the pressure in reactor 13 within the range of 50 pounds to 600 pounds, preferably about 100 to 250 pounds per square inch. The rate of contacting the oil vapors with the catalyst in 13 may suitably be about 0.2 to 5.0 volumes of liquid hydrocarbon per gross volume of catalyst per hour. The rate will depend partly on temperature, partly on the character of the stock and the activity of the catalyst. A temperature in reaction chamber 13 of the order of 900 to 1050° F. is satisfactory.

Vapors leaving reactor 13 pass by line 16 to

fractionator 17 where they are fractionated into several streams as indicated by the drawoff lines 18, 19 and 20 and vapor line 21. In the operation, the reflux in tower 17 is trapped out at different levels and the highest boiling fraction is withdrawn at the base of the fractionator by drawoff line 22. The fraction withdrawn at line 19 is further fractionated in side fractionator 23 where lighter materials are taken overhead and returned by line 24 to main fractionator 17. A side cut boiling above about 115° C., containing principally xylenes and heavier aromatic hydrocarbons, is withdrawn by line 25 and employed in the blending of motor fuel or as a high solvency naphtha. A still heavier cut is withdrawn from fractionator 23 by line 26 which leads to heavy naphtha conversion furnace hereinafter described.

Another side cut containing most of the toluene is withdrawn by line 20 and is fractionated in fractionator 27 from which a toluene cut is withdrawn by side drawoff line 28. A higher boiling fraction, containing in part xylenes and toluene, is withdrawn from fractionator 27 via bottom drawoff line 29. This bottom fraction serves as part of the reflux in fractionator 23. Lighter materials in 27 are driven off from the toluene and returned to the main fractionator 17 by line 30.

Vapors from tower 17 are conducted by line 21 to condenser 31 and receiver 32 where fixed gases are separated and the light naphtha, which is a low boiling light condensate, is withdrawn by line 33. This stock may be combined with the heavier naphtha in line 25 to produce a motor fuel which is withdrawn by line 34.

Stock which contains aromatics boiling within the range of from about 146° C. to about 210° C. is trapped out at 18 from tower 17 and is conducted by line 35 to line 26 where it is combined with the bottoms from tower 23 and charged by pump 36 to coil 37 in heater 38 from which the hot oil vapors are conducted by line 39 to catalyst chamber 40. Different conversion conditions and different catalysts are employed in chamber 40 from those employed in reactor 13. In chamber 40 the principal reaction is one of carbon to carbon bond rupture rather than dehydrogenation and ring formation, typical of the catalyst and conditions in 13. In 40 the temperature is preferably within the range of 950 to 1200° F. and the predominant reaction appears to be a splitting or dealkylation reaction apparently involving removal of heavy side chains from aromatic rings.

After separating toluene and lighter hydrocarbons from the reaction products derived in the aromatization or first stage of my process, I may subject all the higher boiling hydrocarbons, particularly those boiling up to the end boiling point of gasoline, i. e., 210° C., to the second stage or dealkylation step of the process. In one form the process may be carried out by passing the hot products from the first stage directly to the second stage without any separation whatever. However, it is desirable to avoid disproportionation by alkylation of the lighter alkyl aromatics in reactor 40 and hence the xylenes, toluene and benzene are preferably removed from the feed passing to reactor 40. A stock having an initial boiling point of about 146 to 150° C. is suitable and this stock may be obtained by proper regulation of fractionating conditions in tower 17 and side fractionator 23. Thus, referring to tower 23 the xylene may constitute a large proportion of the naphtha in line 25, which is employed for

motor fuel or high solvency naphtha. A heavier fraction withdrawn from tower 17 by line 35 and/or from fractionator 23 by line 26 may contain a large amount of alkyl substituted toluene in which alkyl groups of 2 or more carbon atoms are present. Ethyl toluene having a boiling point of about 158° C. is characteristic of this material. Tower 40 is filled with porous, granular catalyst of the conversion or splitting type such as active silica, the alumina-silica complexes, acid treated clays, acid treated bentonite, etc. Super Filtrol is an example of the latter type of catalyst. Silica gel impregnated with small amounts of magnesia, alumina, or with small amounts of alumina and zirconia may also be used supported on porous plate 41. The vapors pass downward through the catalyst bed in reactor 40 and escape by line 42 leading to fractionator 43.

Two side streams may be withdrawn from fractionator 43; the lower stream by line 44 has an initial boiling point of about 150° C. or higher and is suitable for blending with light naphtha from 32 making a motor fuel of high knock rating which leaves the system by line 34 previously described. A part of this stream may be recycled to furnace 38 by line 45 is desired. A toluene fraction is taken from tower 43 by line 47 leading to side fractionator 48 where lighter fractions are eliminated as overhead and relatively pure toluene is withdrawn by side drawoff line 49. A higher boiling fraction may be withdrawn from fractionator 48 by line 50 leading to line 44. Alternatively, this heavy fraction may be returned to the tower 43 for refluxing therein. The toluene removed by line 49 may be combined with the toluene in line 28 and discharged from the system by line 51.

Vapors from fractionator 43 are led by line 52 to condenser 53 and receiver 54 where the gases are separated and a light naphtha having a boiling range of about 30 to 110° C. may be led by line 55 into admixture with the stocks from lines 25 and 33 to motor fuel line 34.

Residual fractions containing relatively high boiling material may be discarded from the system by drawoff lines 22 and 56.

As an alternative method of operation, I may close valve 58 in line 42 and open valve 59 in line 60 and discharge the reaction products from tower 40 directly into fractionator 17 where these products commingle with the reaction products from tower 13. The separation of distillate and side fractions in tower 17 may be conducted in regular manner previously described without substantial change. By this system of operation substituted toluene compounds boiling above 150° C. are conducted by line 35 and pump 36 back to heater 38 where they are reprocessed until completely converted into toluene.

As pointed out hereinabove, the conditions employed in reaction tower 40 are generally more stringent than those employed in reaction chamber 13. Contact rates represented by space velocities of about 0.2 to 2 volumes of oil charged per hour per apparent volume of catalyst are characteristic. The preferred temperature is about 950 to 1050° F. and the pressure about atmospheric to 50 pounds per square inch. The principal reaction occurring in reactor 40 is dealkylation of alkyl side chains on the aromatic nucleus. The amount of toluene produced in the operation of reactor 40 is, therefore, primarily dependent on the amount of polyalkylated benzene available in the process. In general, with average feed stocks, such as Mid-Continent and East Texas naphtha

charged to heater 11, the amount of polyalkylated aromatic hydrocarbons is about equal to the amount of toluene in the products leaving reactor 13.

In the case of a naphtha having a distillation range of 230° F. to 404° F. derived from the distillation of MC crude oil, there was obtained about 15% of toluene after catalytic reforming in reactor 13 of 950° F., 1 volume per hour per volume of catalyst, and 150 pounds per square inch pressure. About 15% additional toluene was obtained from side fractionator 48 as a result of the dealkylation of heavier substituted aromatic hydrocarbons in reactor 40, thus making the total yield of toluene about 30%, based on the heavy naphtha charged to heater 11.

It is believed that the reaction occurring in reactor 13 is largely one of dehydrogenation and aromatization. High aromatic compounds may be converted into aromatics by the former reaction and straight chain paraffin compounds are also converted to aromatics by cyclization. Hydrogen exerts a beneficial effect upon the catalyst, increasing the catalyst life and maintaining activity. Hydrogen for the process may be obtained partially or entirely from the spent gases discharged from separator 32 where it occurs in admixture with fixed hydrocarbon gases.

When the catalysts in reactors 13 and 40 become spent they may be restored to substantially their original activity by oxidizing off the carbonaceous material with air or mixtures of air with flue gas or other inert gas after purging the reactors of hydrocarbon vapors. Purge lines and catalyst regeneration lines are not shown on the drawing.

Although I have described my invention with respect to a specific apparatus for carrying out the process, I do not intend that it be limited except as described in the following claims.

I claim:

1. The process of making toluene from petroleum naphtha which comprises initially subjecting said naphtha to catalytic conversion in the presence of hydrogen and a hydrogenating-dehydrogenating catalyst under aromatizing conditions of temperature and pressure whereby said naphtha is substantially converted into a mixture of aromatic hydrocarbons containing toluene, xylene and heavier aromatics, fractionating said hydrocarbons and removing therefrom a toluene fraction and a fraction heavier than xylene boiling chiefly in the range of about 146° to about 210° C., subjecting said heavier than xylene fraction to conversion in the presence of a porous, solid cracking catalyst at a high conversion temperature and a pressure of about 0 to 50 pounds per square inch gage, whereby additional toluene is produced and separating said additional toluene from the conversion products.

2. The process of claim 1 wherein a xylene fraction is combined with a fraction lighter than toluene to produce a motor fuel of high knock rating.

3. The process of producing toluene from petroleum naphtha which comprises subjecting said naphtha to the action of a solid hydrogenating-dehydrogenating catalyst of the metal oxide type in the presence of hydrogen at a temperature within the range of 900 to 1100° F. and a space velocity of about 0.2 to 5 volumes per hour per volume of catalyst whereby aromatic hydrocarbons are produced, fractionating said aromatic hydrocarbons and separating therefrom a toluene fraction, a xylene fraction and a fraction boiling between about 145° C. and 210° C., subjecting said last-mentioned fraction to the action of a porous, solid cracking catalyst at a pressure of about 0 to 50 pounds per square inch gage, a temperature within the range of 950 to 1150° F. and space velocity of about .2 to 2 volumes per hour per volume of catalyst, thereby converting a substantial amount of heavier aromatic hydrocarbons into toluene, and recovering said toluene from the conversion products by fractionation.

4. The process of claim 3 wherein the hot conversion products obtained from said cracking catalyst are conducted without condensation directly to the fractionation step following said hydrogenation-dehydrogenation catalyst treatment and fractionated therein to recover toluene.

5. The process of claim 3 wherein the said hydrogenation-dehydrogenation catalyst is an oxide of a metal of the left columns of groups V and VI of the periodic system.

6. The process of claim 3 wherein the hydrocarbon cracking catalyst is a compound comprising essentially activated silica.

7. The process of producing toluene from paraffin hydrocarbons which comprises subjecting a paraffinic petroleum naphtha to cyclization in the presence of hydrogen and a dehydrogenating catalyst at a cyclization temperature of about 900 to 1050° F., thereby converting a substantial portion of the paraffin hydrocarbon into toluene and other aromatic hydrocarbons, separating from the aromatic hydrocarbon products a toluene fraction, a xylene fraction and a heavy fraction substantially all boiling above the boiling point of xylene, subjecting said heavy fraction to the action of a porous, solid, cracking catalyst at a pressure of about 0 to 50 pounds per square inch gage and a temperature of about 950 to 1150° F., thereby converting heavy aromatic hydrocarbons into lower boiling aromatic hydrocarbons including toluene, and recovering the desired toluene from the products of said conversion.

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