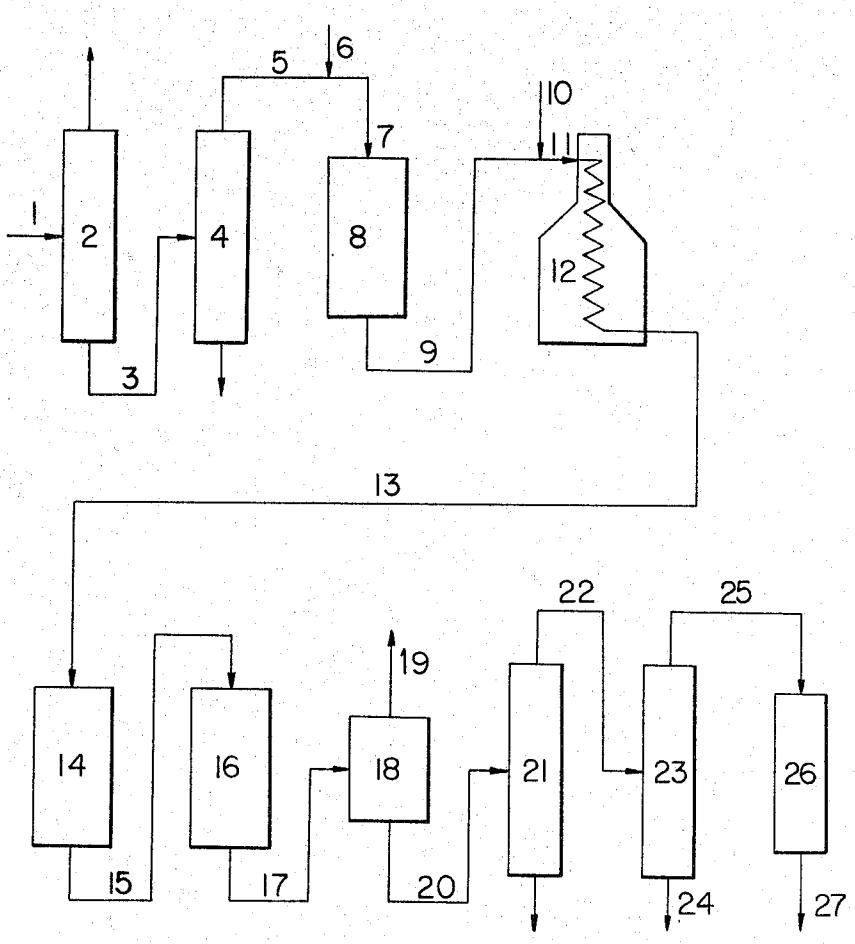
March 21, 1967 JUNICHI FUKUDA ETAL 3,310,592

PROCESS FOR PRODUCING HIGH PURITY BENZENE

Filed April 19, 1965



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United States Patent Office 3,310,592
Patented Mar. 21, 1967

3,310,592

PROCESS FOR PRODUCING HIGH PURITY BENZENE

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Filed Apr. 19, 1965, Ser. No. 449,252
Claims priority, application Japan, Apr. 23, 1964, 39/22,643
9 Claims. (Cl. 260—672)

The present invention relates to a process for producing a large amount of high purity benzene from cracked oils by-produced at the time of gaseous olefin production by means of steam cracking of petroleum hydrocarbons.

Such cracked oils by-produced at the time of steam cracking petroleum hydrocarbons for producing gaseous olefins such as ethylene and propylene normally contain no less than 30% by weight, sometimes even no less than 60% by weight, of aromatic hydrocarbons, and therefore the by-produced cracked oils provide excellent aromatic materials.

However, because such cracked oils contain large amounts of highly reactive unsaturated component, particularly diolefin, they tend to form resinous or coke-like polymer when heated in a heat-exchanger and a tubular pre-heater, which polymer is deposited on the heat-exchanging surfaces and conduit walls at the time of heating to impair their thermal conductivity and furthermore to clog the conduit within a short period. Furthermore the said cracked oils contain sulfur compounds in the order of 0.01–0.1% by weight, most of which is thiophene, which is thermally extremely stable and the hardest to separate from benzene. For these reasons, in the attempts to obtain high purity aromatic hydrocarbons from the cracked oils, economical elimination of diolefin and thiophene presents a most serious problem.

Conventionally, therefore, for obtaining high purity aromatic hydrocarbons from the cracked oils, very complicated procedures such as, in sequence, first stage hydrogenation, second stage hydrogenation, solvent extraction and distillation, have been employed. The first stage hydrogenation is performed for converting the diolefin contained in the cracked oils to mono-olefin and/or paraffin hydrcarbons by means of hydrogenation, and the second stage hydrogenation is for converting the mono-olefin to paraffin hydrocarbon as well as for converting the sulfur compounds contained in the cracked oils to hydrogen sulfide by means of hydrocracking to separate and remove the same. In the conventional methods, after the two-stage hydrogenation, the aromatic component is extracted with solvent and thereby separated from aliphatic hydrocarbons, and the solvent containing the aromatic component is distilled to yield such aromatic hydrocarbons as benzene, toluene and xylene.

Among those aromatic hydrocarbons, particularly benzene commands the greatest demand and, therefore, when production of large amounts of benzene is desired, conventionally the alkyl-substituted aromatic hydrocarbons such as toluene and xylene obtained as in the above are further converted to benzene by means of hydrodealkylation.

Such conventional methods, however, require extremely complicated procedures, and particularly because of the additional separation step of the aromatic hydrocarbons from aliphatic hydrocarbons by means of solvent extraction, they can hardly be economically satisfactory methods.

Incidentally, the above solvent extraction step is necessary because a part of the aliphatic hydrocarbons formed by the preceding hydrogenation forms an azeotropic mixture with benzene or toluene, and since the same has a

boiling point close to that of benzene or toluene, an attempt to separate non-aromatic hydrocarbons by distillation does not give a satisfactory result even when a distillation tower with many plates is used.

Accordingly, the principal object of this invention is to provide a process for producing high purity benzene from the cracked oils by-produced at the time of the production of gaseous olefins such as ethylene and propylene by means of steam cracking of petroleum hydrocarbons with relatively few operations.

A further object of this invention is to provide a process for producing high purity benzene from the cracked oils directly at high yield, without the solvent extraction step.

Still another object of this invention is to provide an economically advantageous process for obtaining high purity benzene from the cracked oils with low cost.

Other objects and advantages of this invention will become apparent from reading the following disclosures.

In the present invention, among the cracked oils by-produced at the time of producing gaseous olefins such as ethylene and propylene by means of steam cracking of petroleum hydrocarbons, those having a boiling point in the range of 60–200° C. at atmospheric pressure, are used as the feed stocks. Therefore, hereinafter such cracked oils are referred to as the material cracked oils. As the material cracked oils of this invention, particularly those composed chiefly of hydrocarbons of 6–9 carbons are preferred. The present invention is concerned with a process for directly obtaining high purity benzene at high yields from such material cracked oils.

According to this invention, such material cracked oils as described in the above are: (1) as the first step contacted with 0.2 to 2.0 mol times the material cracked oils of hydrogen in the presence of hydrogenation catalyst at temperatures ranging from room temperature to 250° C. and pressures of no less than 10 kg./cm.^{2} to convert the diolefin in the material cracked oils to mono-olefin and/or paraffin hydrocarbons.

(2) As the second step, the oil obtained in the above first step is contacted with 2–20 mol times the oil of hydrogen at temperatures ranging from 500 to 800° C. and pressures of no less than 10 kg./cm.^{2} to convert the mono-olefin and/or paraffin hydrocarbons to lower saturated hydrocarbons such as methane and ethane by means of hydrocracking as well as to dealkylate the alkyl-substituted aromatic hydrocarbons contained in the cracked oils.

(3) Thereafter, as the third step the product obtained in the second step is heated to a temperature between 100–250° C. in the presence of catalyst for hydrodesulfuration to decompose the sulfur compounds contained in the said product (mainly thiophene) and to separate and remove the same in the form of hydrogen sulfide.

(4) As the fourth step, benzene is separated from the product of the third step by suitable means known per se such as distillation.

Each of the above steps performed in accordance with this invention will be explained in detail hereinbelow.

The first step

The hydrogenation treatment of the first step can be performed either on fixed bed using shaped catalyst or in suspended bed using powder catalyst. As the catalyst, any known hydrogenation catalyst may be used. For example, oxides and sulfides of the metals of Groups VI and VIII of the Periodic Table may be used. Again any other compound which performs catalytic activity in the hydrogenation may be used either alone or as a mixture with other catalyst. Suitable hydrogenation catalysts include, for example, Ni, Pd, Pt, cobalt molybdate, WS_2, NiS, MoS_2, MoS_3, $CoMoO_4$-Al_2O_3, MoS_2-activated car-

bon, Co-Fe-Ni, WS_2-NiS-Al_2O_3 and Cr-Mo-W sulfides, etc. At the time of the hydrogenations, these metal compounds may be used with suitable carriers, such as activated alumina, artificial or natural silicate, oxides of magnesium, zirconium and titanium, and other similar substances. Particularly suitable catalysts are Pd and CO-Mo catalysts.

Suitable reaction conditions vary depending on the type of catalyst employed, but generally the feed stocks are contacted with the catalyst at reaction pressures of above 10 kg./cm.^{2} and temperatures ranging from room temperature to 250° C. in the presence of hydrogen. In this case, care must be always taken to avoid temperature rise beyond 250° C. in order to prevent polymerization of diolefin.

When a Co-Mo catalyst is used, particularly preferred reaction conditions to hydrogenate selectively diolefin and a portion of mono-olefin without causing polymerization of diolefin are reaction temperatures ranging from 150–230° C., and reaction pressures of 10–80 kg./cm.^{2}.

When Pd catalyst is used reaction temperatures of 20–60° C. and pressures of 10–80 kg./cm.^{2} are satisfactory, but in case the feed stock employed contains catalyst poisons such as carbon monoxide and hydrogen sulfide, it is desirable that those gases be eliminated in advance.

The reaction pressure of the first step is required to be at least 10 kg./cm.^{2}, because at pressures below that, the catalytic activity is lowered and consequently the hydrogenation of diolefin is insufficient. However, there is no rigid upper limit present for the pressure condition. Generally pressures of above 80 kg./cm.^{2} do not appreciably increase the catalytic activity and therefore employment of such high pressures is not justified when the constructional and operational problems incidental to high pressures are considered.

By performing the above-described first step, the highly active component such as diolefin present in the cracked oils is stabilized, and so treated feed stocks now can be the material for dealkylation.

The cracked oils thus subjected to the first step hydrogenation, therefore, are led to the site of the second step operation, in which the excessive hydrogen gas of the hydrogenation step is used as the gas necessary for the second step reaction as it is.

The second step

The object of the second step is to dealkylate the alkyl-substituted aromatic hydrocarbons as well as to completely decompose the non-aromatic hydrocarbons present so that they may be readily separated from the aromatic hydrocarbons in the form of gaseous hydrocarbons such as methane and ethane. The reaction conditions satisfactory to fulfill this object are reaction temperatures of 500–800° C., preferably 650–730° C., space-velocity of the liquid of 1–6, preferably 2–4, and molar ratio of hydrogen to the oil of 2–10. The reaction pressure must be no lower than 10 kg./cm.^{2}, since too low a reaction pressure causes small amounts of non-aromatic hydrocarbons such as olefins to remain with the aromatic hydrocarbons. Further, while there is no particular upper limit to the reaction pressure, employment of such high pressures as above 60 kg./cm.^{2} does not give particular advantage and therefore meaningless when the constructional and operational difficulties incidental to such high pressures are considered.

In case of practicing the second step, addition of catalyst is unnecessary, but rather the absence of catalyst is preferred, because often the catalyst is poisoned by the small amount of sulfur compounds and other impurities present in the feed stock and its activity is impaired. However, the second step of this invention can be performed either thermally (in the absence of catalyst) or catalytically.

The second step of this invention is highly advantageous over the conventional thermal dealkylation process in which pure toluene, xylene or catalytic reformate, etc. is used as the feed stock, in the point of construction material. To wit, when in conventional thermal dealkylation process a steel reactor is used, because of the contact catalysis of the steel surface, nuclear decomposition of benzene ring is caused to precipitate large amounts of carbonaceous matters. Consequently, aromatic hydrocarbon yield is very much lowered and continuous operation over long periods is made impossible. In contrast, the present invention is advantageous in that even when conventional steel reactors are used, no precipitation of carbonaceous matters is observed because of the trace amount of sulfur compounds always present in the cracked oils and the minor amount of hydrogen sulfide formed by the first step hydrogenation present in the hydrogen gas remaining in the product of the first step.

The third step

The desulfuration treatment of the third step is similar to the first step, but the material fed to this step is the product of the second step composed of hydrogen, methane, ethane and aromatic hydrocarbons (mostly benzene), and the remaining sulfur compounds herein consist mostly of hydrogen sulfide and thiophene. The catalyst and reaction conditions of the third step therefore must be so selected that the thiophene is decomposed and removed to leave no more than 0.0001 g./100 cc. of the same in the aromatic hydrocarbons while avoiding nuclear hydrogenation of benzene ring.

As the catalyst, conventionally well known hydrodesulfuration catalysts of the metals of Groups VI and VIII of the Periodic Table may be used similarly to the first step, while Co-Mo catalyst is particularly preferred. Ni-containing catalysts are undesirable because they show strong activity for nuclear hydrogenation of benzene ring.

The suitable temperature condition in case a Co-Mo catalyst is employed is 100–250° C., preferably 150–200° C. Temperatures above 250° C. should be avoided because they cause hydrogenation of benzene ring. The reaction can proceed at atmospheric pressure, but pressures of 10–40 kg./cm.^{2} are preferred. Pressures above 40 kg./cm.^{2} are not particularly deleterious to the reaction but neither provide any advantage.

The fourth step

The liquid product obtained by removing gaseous substances such as methane and ethane from the product of the third step consists mostly of benzene and contains minor amounts of toluene and a tar-like substance.

Accordingly, in this invention benzene is separated from the liquid product of the third step by suitable means such as distillation. Further the so obtained benzene can be made a product of very high purity by such simple treatment as with activated clay.

In accordance with this invention, thus high purity benzene is obtained by simple operations at very high yield, while simultaneously a minor amount of by-product such as toluene is also obtained. If desired, this toluene may be further converted to benzene by subjecting the same to the second step together with the feed stock of the said step.

As the hydrogen employed in this invention, not only purified hydrogen but also any hydrogen-containing gas such as those by-produced from catalytic reforming, from dehydrogenation plant of ethyl benzene, ethylene production plant, or methane reformed gas and the circulation gas of this invention.

Hereinafter an embodiment of the process of this invention will be explained with reference to the attached drawing, while it should be understood that of course the same is not intended to limit the present invention in any sense. The drawing shows the minimum necessary for

the explanation of the subject process and therefore, accessory equipments such as pump, heat exchanger and compressor are not shown thereon.

The cracked oils by-produced at the time of producing gaseous olefins such as ethylene and propylene by means of thermal cracking of petroleum hydrocarbons are fed into a preliminary distillation tower **2** through a pipe **1**. From the top of the tower **2**, light oil of no more than five carbons are removed, and the distillate collected at the bottom of the tower **2** is fed into another preliminary distillation tower **4** through pipe **3**. From the bottom of the tower **4**, heavy oils of no less than nine carbons are removed, and the fractions of the distillate of C_6–C_8 boiling in the range of 65–145° C. are withdrawn from the top of the tower **4** through a pipe **5**, mixed with the hydrogen from a pipe **6** and through a pipe **7** fed into a hydrogenation reactor **8** in which the first step is performed.

The amount of hydrogen introduced from the pipe **6** and the reaction conditions in the hydrogenation reactor **8** differ depending on the type of catalyst employed. In case Pd catalyst is used, it is preferred to introduce 0.2–0.5 mol times the material oil of hydrogen. In that case, the circulation gas from a pipe **19** should not be used because it contains hydrogen sulfide. The suitable reaction conditions are temperatures of 20–60° C. and pressures of above 10 kg./cm.^{2}, preferably below 80 kg./cm.^{2}. Whereas if a Co-Mo catalyst is used, use of 0.5–2.0 mol times the material oil of hydrogen and temperatures of 150–200° C. is preferred while care should be taken in selecting the temperature at the entrance of the reactor to prevent the temperature at the exit from becoming above 230° C. because of the temperature rise in the reactor due to the heat of reaction.

The hydrogen-oil mixture which left the hydrogenation reactor **8** through a pipe **9** is mixed with the hydrogen from a pipe **10** and fed into a preheater **12** through a pipe **11**.

It is necessary to introduce hydrogen from the pipe **10** at such a rate that the molar ratio of hydrogen to the oil in the pipe **11** should become 2–10. The preheater **12** normally employed is a furnace. The hydrogen-oil mixture is heated in the preheater **12** to 600–700° C. and thereafter led to a hydrocracking reactor **14** through a pipe **13**.

Because the reaction in the reactor **14** is considerably exothermic, when an adiabatic reactor is used, it is sometimes necessary to introduce at a suitable part of the reactor **14** hydrogenated oil, hydrocracked oil or cooled hydrogen to prevent abnormal rise in temperature. The reaction product is withdrawn from the reactor **14** through a pipe **15**, cooled to 100–200° C. and fed to a desulfuration reactor **16** in which the third step is performed. In the reactor **16** thiophene is decomposed, and the reactant is led into a gas-liquid separator **18** through a pipe **17**, wherein the gaseous components such as hydrogen, methane and ethane are discharged outside the system through a pipe **19** while a part of such components are circulated through the system via the pipe **6** or **10**.

The liquid product is introduced into a distillation tower **21** from a pipe **20**. High boiling point fraction of the distillate boiling at above 160° C. is withdrawn outside the system from the bottom of the tower, and the rest is led into another distillation tower **23** from the top of the tower **21** through a pipe **22**. From the bottom of the tower **23** toluene and xylene (as a matter of fact, xylene is substantially absent) are withdrawn through a pipe **24**, and if necessary are circulated through the pipe **1**. The remaining benzene is led to a tower **26** from the top of the distillation tower **23** through a pipe **25** to receive clay treatment to be freed of the trace amount of olefin present therein, and thereafter withdrawn from the system through a pipe **27**.

In order to more clearly understand the present invention, the following specific examples are given.

Example 1

The C_6–C_8 fraction of the distillate obtained by removing from the cracked oils by-produced at the time of olefin production by steam cracking of naphtha, light oil fraction of C_5 and less and heavy oil fraction of C_9 and above, was fed to the first step operation site as the starting material cracked oil of the process of this invention. In the Tables 1–3 below, the properties of the material cracked oil, the composition of its aromatics and the results of its test for fractional distillation are shown.

TABLE 1

Properties of material cracked oil:	
Bromine value	34.0
Diene value	19.7
Sulfur content, wt. percent	0.047

TABLE 2

Composition of aromatics in material cracked oil (by gas chromatography):

	Weight percent
Benzene	25.8
Toluene	23.0
Ethyl benzene	7.1
m-p-Xylene	9.3
o-Xylene	3.5
C_9-aromatics	5.6
Total of aromatics	74.3

TABLE 3

Test for fractional distillation of material cracked oil:

	° C.
Initial boiling point	67.0
5%	77.0
10%	81.5
30%	89.2
50%	98.0
70%	108.0
90%	130.5
95%	137.0
Dry point	144.0

In the first step a Co-Mo catalyst was used, and the feed stock was treated under such conditions as a space velocity of the liquid of 2.3, a molar ratio of hydrogen to oil of 1.0, a reaction pressure of 50 kg./cm.^{2}, an entrance temperature of 200° C. and an exit temperature of 223° C. The product oil had a bromine value of 16.7, a diene value of 1.7 and a 0.034 wt. percent of sulfur content.

Then the product of the first step was admixed with hydrogen gas containing 20 mol percent of methane in an amount to make the molar ratio of pure hydrogen to oil about 4.5, and subjected to hydrocracking which is the second step. By the reaction under the following conditions:

Pressure, kg./cm.^{2}	20
Entrance temperature, ° C.	665
Exit temperature, ° C.	693

Residence time about 28 seconds.

(calculated under an assumption that the mol numbers do not change by the reaction) a reaction product as shown in Table 4 was obtained.

TABLE 4

Composition and properties of the product of second step:	
Methane —wt. percent/material cracked oil—	18.0
Ethane —do—	18.5
Propane —do—	0.6
Benzene —do—	51.5
Toluene —do—	8.1
C_8 aromatics —do—	0.8
Heavy oil —do—	3.1
Bromine value of the liquid product	0.073
Sulfur content of the liquid product, p.p.m.	450

The second step product was led to the desulfuration which is the third step in the form as obtained. In the desulfuration step, a Co-Mo catalyst was used, and the treatment was performed at a reaction temperature of about 180° C., and a pressure of 20 kg./cm.². The liquid product obtained from the third step was then subjected to the fourth step treatment, i.e., distilled in a distillation tower with about 40 plates, and the benzene fraction of the distillate was separated and treated with clay. The resultant benzene yield was 50.3% by weight to the material oil. The properties of the product benzene were excellent as shown in Table 5 below.

TABLE 5

Properties of product benzene:	
Specific gravity (15/4° C.)	0.8835
Solidifying point (° C.)	5.45
Thiophene (gr./100 cc.)	Below 0.0001.
Carbon disulfide (gr./100 cc.)	Below 0.0001.
Copper corrosion	No discoloration recognized.
Sulfuric acid coloration	No. 1 or lighter with reference to the standard color comparison liquid.
Reaction	Neutral.
Color	Satisfactory.
Test for fractional distillation:	
I.B.P.	79.7° C.
50%	80.1° C.
E.P.	80.1° C.
Total distillate (vol. percent)	98.0.

Example 2

The same starting material as used in Example 1 was treated in the first step using Pd catalyst at reaction temperatures of 25–45° C., a pressure of 40 kg./cm.², and a molar ratio of hydrogen to oil 0.25. The resultant product oil had a diene value of 1.3, a bromine value of 23.2 and a sulfur content of 0.044% by weight.

The above first step product was admixed with a hydrogen gas containing 5 mol percent of methane in an amount to make the molar ratio of pure hydrogen to oil about 3, and led to the second step.

The reaction in the second step was performed at a reaction pressure of 35 kg./cm.², an entrance temperature of 613° C. and an exit temperature of 645° C., and as the result a reaction product of the composition and properties as shown in Table 6 below was obtained.

TABLE 6

Composition and properties of second step product:	
Methane — wt. percent/material cracked oil	15.4
Ethane —do—	19.4
Propane —do—	0.8
Benzene —do—	50.5
Toluene —do—	9.4
C_8 aromatics —do—	1.1
Heavy oil —do—	3.8
Bromine value of the liquid product	0.054
Sulfur content of the liquid product, p.p.m.	520

From the second step product, the gaseous components contained therein were removed, and the resultant liquid product was admixed with hydrogen in an amount to make the molar ratio of pure hydrogen to oil 0.5 and led to the third step, which was performed at a reaction temperature of about 150° C. and a pressure of 40 kg./cm.² employing a Co catalyst.

The liquid product of the third step was distilled in a distillation tower with about 40 plates as the fourth step, and the benzene fraction of distillate was separated and treated with activated clay. Benzene of excellent properties similar to the product of Example 1 was obtained at the yield of about 49.8 wt. percent of the material oil.

Example 3

The fraction of the distillate boiling in the range of 67–190° C. of the cracked oil by-produced in olefin production by steam cracking of naphtha was used as the material cracked oil of this example.

In the first step, the above material oil was treated in the presence of an Ni-Mo catalyst under such conditions as a reaction pressure of 60 kg./cm.², a molar ratio of hydrogen to oil of 1.8, an entrance temperature of 185° C. and an exit temperature of 222° C. The resultant product was admixed with a hydrogen gas containing 15 mol percent of methane in an amount to make the molar ratio of pure hydrogen to oil 6.4, and led to the second step.

The second step was performed under the conditions of a reaction pressure of 15 kg./cm.², an entrance temperature of 680° C. and an exit temperature of 746° C., and the so obtained product was cooled to 200° C.

In the third step the above second step product was contacted with a Co-Mo catalyst at a reaction pressure of 11.4 kg./cm.², and the resultant product was led to the fourth step to be distilled in a distillation tower with about 40 plates. The benzene fraction of the distillate was thus separated and treated with activated clay to give a purified benzene yield of about 45.8 wt. percent to the material oil. The quality of the product benzene was excellent similar to the product of Example 1.

Hereinbelow the results of practices under the conditions outside the scope of this invention are given as Controls by way of comparison with the present invention.

Control 1.—The fraction of distillate boiling in the range of 63.2–153° C. among the cracked oils by-produced at the time of olefin production, having a bromine value of 36.2, a diene value of 20.4 and a total sulfur content of 0.036 wt. percent was used as the material cracked oil. The said oil was hydrogenated under such conditions as a reaction temperature of 350° C. which is beyond the upper limit of temperature condition of the first step of this invention, a pressure of 60 kg./cm.² and a molar ratio of hydrogen oil of 1.2. The resultant hydrogenated oil had a diene value of 0, a bromine value of 0.2 and a sulfur content of 13 p.p.m. However after a few hours of operation the pressure fall at the reaction zone became excessive and continuation of the operation was made impossible.

Following the discontinuation of the operation the reactor was opened, and it was found that carbonaceous polymer piled up at the upper part of the reaction zone, in an amount of 0.55 wt. percent to the material oil.

Control 2.—The same starting material as used in Control 1 was reacted in the presence of the same catalyst used in Control 1 in accordance with the conditions required for the first step of this invention, i.e. at a reaction temperature of 185° C., a pressure of 60 kg./cm.² and a molar ratio of hydrogen to oil of 1.2. No pressure fall in the reaction zone was observed over several days and the reaction was smoothly continued.

Then the resultant hydrogenated oil was subjected to hydrocracking in accordance with the conditions of the second step of this invention, i.e. at an average reaction temperature of 690° C., an average reaction pressure of 20 kg./cm.² and a molar ratio of hydrogen to the hydrogenated oil of 4.5 for a residence time of about 28 seconds. (It was assumed that the mol numbers did not change by the reaction.) In this Control, the third step which should follow in accordance with the present invention was omitted, and the liquid product of the above hydrocracking was directly charged in a distillation tower with about 40 plates to separate benzene. Thus obtained benzene had a solidifying point of 5.40° C. and was of considerably good quality but contained about 150 p.p.m. of thiophene.

Control 3.—The hydrogenated oil obtained in the first step of above Control 2 was subjected to, as the second step, hydrocracking under the following conditions.

Average reaction temperature, 690° C.
Reaction pressure, 4 kg./cm.² (a pressure outside the range specified for the second step of this invention).
Molar ratio of hydrogen to the hydrogenated oil, about 4.5.
Residence time, about 28 seconds (it was assumed that the mol numbers did not change by the reaction).

The liquid product thus obtained by the above hydrocracking was directly charged in a distillation tower with about 40 plates without the preceding third step of this invention, and benzene was separated therefrom. The resultant benzene had a solidifying point of 4.85° C. and a thiophene content of about 170 p.p.m., and thus was of still inferior quality to the product of Control 2.

Control 4.—The starting material prepared by adding to pure benzene 250 p.p.m. of thiophene was subjected to desulfuration tests under three sets of severally different conditions as shown in Table 7 below, in the presence of a Co-Mo catalyst.

In these tests, as the hydrogen source a gaseous mixture containing 15 vol. percent of methane and 10 vol. percent of ethane was used.

TABLE 7

	Conditions outside those for the third step of this invention	Conditions within those for the third step of this invention	Conditions outside those for the third step of this invention
Reaction temperature (° C.)	300	175	70
Reaction pressure (kg./cm.²)	30	30	30
Space velocity of liquid	3	3	3
Molar ratio of hydrogen to oil	3.3	3.2	3.2
Thiophene content of the product (p.p.m.)	0	3	215
Cyclohexane in the product (wt. percent)	3.3	0	0
Benzene recovery (wt. percent)	96.5	99.8	99.8

In the above test, at 300° C. which is a temperature higher than the upper limit of the temperature condition for the third step of this invention, thiophene decomposed completely but nuclear hydrogenation of benzene simultaneously took place and cyclohexane was formed. Again at 175° C., a temperature within the condition for the third step of this invention, thiophene decomposed almost completely and furthermore no nuclear hydrogenation of benzene took place. However, in the test performed at 70° C., a temperature lower than the specified range of this invention, substantially no thiophene decomposition was observed, but the thiophene remained in benzene and no nuclear hydrogenation of benzene took place.

We claim:

1. A process for producing high purity benzene which comprises:

(a) as first process step, contacting the 60–200° C. fraction of cracked oils, which are the by-product in the production of gaseous olefins by steam cracking petroleum hydrocarbons, with hydrogen in a molar proportion of cracked oil fraction:hydrogen of 1:0.2 to 2.00 at a temperature from ambient temperature to 250° C. and a pressure of at least 10 kg./cm.² in the presence of hydrogenation catalyst, to convert the diolefins contained in said fraction to mono-olefins and/or paraffin hydrocarbons;

(b) as second process step, contacting the oil obtained in step (a) with hydrogen in a molar proportion of oil:hydrogen of 1:2 to 10 at a temperature of 500° to 800° C. and a pressure of at least 10 kg./cm.² in the absence of solid dealkylation catalyst, to hydrocrack mono-olefins and/or paraffin hydrocarbons as well as to dealkylate alkyl-substituted aromatic hydrocarbons contained in said last-named oil, and

(c) as third process step, heating the resultant product of the second step of 150° to 200° C. in the presence of hydrodesulfuration catalyst to decompose and remove sulfur compounds contained in said product, and

(d) thereafter separating benzene from the resultant liquid product of the third step.

2. A process in accordance with claim **1** in which the starting fraction of cracked oils is composed chiefly of hydrocarbons of six to nine carbons.

3. A process in accordance with claim **1** in which the second step is performed in substantial absence of the catalyst employed in the first step.

4. A process in accordance with claim **1** in which the third step is performed in the presence of hydrogen, the molar proportion of which relative to the resultant product of the second step is 0.2 to 2:1.

5. A process in accordance with claim **1** in which the product of the second step is freed of gaseous components contained therein and the remaining liquid substance is contacted with hydrogen at 150 to 200° C. and at a pressure from atmospheric to 60 kg./cm.², in the presence of hydrodesulfuration catalyst, the molar proportion of hydrogen relative to said liquid substance is 0.2 to 2:1.

6. A process in accordance with claim **1** in which the product of the second step is heated as such to a temperature between 150° and 200° C. at a pressure between atmospheric and 60 kg./cm.² in the presence of hydrodesulfuration catalyst.

7. A process in accordance with claim **1** in which the first step is performed at a pressure ranging from 10 to 80 kg./cm.².

8. A process in accordance with claim **1** in which the second step is performed at a pressure ranging from 10 to 60 kg./cm.².

9. The process in accordance with claim **1** in which the third step is performed at a pressure ranging from atmospheric to 60 kg./cm.².

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