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PROCESS FOR PRODUCING HIGH-PURE
AROMATIC HYDROCARBONS

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The present invention relates to a process for producing high-purity aromatic hydrocarbons such as benzene and toluene by thermally cracking crude hydrocarbon oils containing aromatic hydrocarbons, particularly C_6 – C_8 aromatic hydrocarbon.

Crude hydrocarbons containing C_6 – C_8 aromatic hydrocarbons, such as benzene, toluene, etc., contain as impurities paraffinic hydrocarbons such as n-hexane and n-heptane, naphthenic hydrocarbons such as cyclohexane and methylcyclohexane, olefinic hydrocarbons such as hexene, sulfur compounds, nitrogen compounds, oxygen compounds, etc. In order to produce high-purity benzene, toluene and the like by removing such impurities from these hydrocarbons, various processes and apparatus have been used with considerable effects. Particularly excellent processes include hydrogenation and extraction steps. According to these processes, high-purity benzene, toluene, etc., of a purity above 99% can be produced through, generally, the steps of pre-distillation, hydrogenation, extraction, and distillation.

According to the present invention, the thermal cracking reaction of crude hydrocarbon oils containing aromatic hydrocarbons, such as benzene, toluene, etc., takes place in the presence of a hydrocarbon or hydrocarbons having particularly large numbers of carbon atoms, which results in accelerating selectively the thermal cracking reaction. Therefore, the process of this invention is quite different from conventional processes and, by the process of this invention, aromatic hydrocarbons, such as benzene, toluene, and the like of purities not lower than those of the aromatic hydrocarbons obtained by the conventional processes can be obtained without using an extraction process which is an important process in the conventional processes.

That is, the present invention relates to a process for producing the high-purity aromatic hydrocarbons, such as benzene and toluene, which comprises thermally cracking crude hydrocarbon oils containing aromatic hydrocarbons such as benzene and toluene, said hydrocarbon oils containing almost no paraffinic hydrocarbons and naphthenic hydrocarbons having above 9 carbon atoms as impurities, at temperatures of 500–800° C., at a contact period above 0.01 second, and at normal pressure or a raised pressure, in the presence of hydrogen or a hydrogen-containing gas in a mole ratio of 0.5–20.0 of hydrogen to the feed oils, with the addition of paraffinic hydrocarbons, naphthenic hydrocarbons, or a mixture thereof, said hydrocarbons having above 9 carbon atoms, preferably 15 carbon atoms, thereby promoting the thermal cracking reaction of hydrocarbons having paraffin bonds, naphthene bonds and olefine bonds of comparatively low number of carbon atoms mixed in the feed oils as impurities, without affecting the benzene ring, mainly by the action of free radicals formed from the paraffinic hydrocarbons and/or the naphthenic hydrocarbons having above 9 carbon atoms, and thereby producing hydrocarbons having boiling points lower than those of the aforesaid aromatic hydrocarbons such as benzene.

The main reason for adding the paraffinic hydrocarbons and/or naphthenic hydrocarbons having above 9 carbon atoms, preferably above 15 carbon atoms, which

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is a main feature of this invention, is that these hydrocarbons are directly decomposed thermally by the thermal cracking reaction in the reaction system to form easily free radicals, which are further decomposed or cause reactions and gradually form free radicals having lower carbon atoms, such as methyl and ethyl. These free radicals promote selectively, by chain reaction, thermal cracking of the hydrocarbons having paraffin bonds and naphthene bonds of comparatively low number of carbon atoms, mixed in the feed oils as impurities (without, in this case, affecting the benzene ring in the reaction system) and these impurities are converted into hydrocarbons having boiling points lower than those of benzene and toluene or finally into gaseous hydrocarbons, whereby high-purity aromatic hydrocarbons such as benzene and toluene are produced.

Therefore, if there are no such free radicals or too small amounts of such free radicals necessary for the above mentioned selective thermal cracking reaction, the desired objects of this invention cannot be attained.

As the feed oils in the process of this invention, crude hydrocarbons containing aromatic hydrocarbons such as benzene, toluene and the like are used. These raw materials contain considerable amounts of aromatic hydrocarbons, such as benzene, toluene, etc., that is, such raw materials are, for example, light oil recovered from coke oven gas, light oil recovered from tar, benzene-toluene and xylenes fractions from naphtha cracking, or benzene-toluene fractions from naphtha reformat. These raw materials contain hydrocarbons having paraffin bonds, naphthene bonds and olefine bonds of comparatively low number of carbon atoms but contain almost no hydrocarbons having high number of carbon atoms in particular hydrocarbons with above 9 carbon atoms. These feed oils may contain above 0.1% by weight based on the weight of the feed oils of hydrocarbons having a high number of carbon atoms, but they may be used as the raw materials in this invention without removing such hydrocarbons. These raw materials may usually contain, as impurities, sulfur compounds, nitrogen compounds and oxygen compounds; however, these impurities may preferably be removed prior to use. For example, it is preferable to pre-remove the sulfur compounds and olefinic hydrocarbons from the feed oils by a pressure-hydrogenating purification process and/or to pre-treat to some extent the removable hydrocarbons having paraffin bonds, naphthene bonds and olefine bonds by a known distilling method.

The paraffinic hydrocarbons and naphthenic hydrocarbons having above 9 carbon atoms, preferably above 15 carbon atoms, which are added in the above feed oils in the process of this invention are paraffinic hydrocarbons with or without branched chains, such as n-decane, n-cetane, 3-methyl nonane, etc., or naphthenic hydrocarbons such as isopropylcyclohexane, or a mixture thereof. The purity of these hydrocarbons may not be high, or the hydrocarbons can be used in the process of this invention if they contain materials easily forming free hydrocarbon radicals as mentioned above. Therefore, materials containing considerable amounts of the aforementioned paraffinic hydrocarbons and naphthenic hydrocarbons having above 9 carbon atoms, preferably above 15 carbon atoms, e.g., petroleum kerosene, gas oil, or high boiling point fractions, e.g. paraffin wax, may be used. The amount of these hydrocarbons relative to the feed oils may be small and is influenced by the compositions of the feed oils and other factors. For example, in the case where the feed oils contain about 0.1–0.5% by weight of high boiling point fractions containing paraffinic and naphthenic hydrocarbons having above 9 carbon atoms, at least 0.2% by weight of the additional hydrocarbons are added in the feed oils. The effective upper limit of the

amount of the hydrocarbons is 10.0% by weight, whereby selective thermal cracking occurs effectively. The preferable amount of the hydrocarbons is about 2-6% by weight based on the amount of the feed oils, the amount being of course influenced by the compositions of the feed oils and other factors. The paraffinic hydrocarbons and/or naphthenic hydrocarbons having above 9 carbon atoms, preferably above 15 carbon atoms may be added into the feed oils at the beginning of the process or during the process.

According to the process of this invention, the feed oils containing a small amount of the effective hydrocarbons as mentioned above are subjected to the thermal cracking reaction in the presence of hydrogen or a hydrogen-containing gas in a mole ratio of 0.5-20.0, preferably of 1-3, of hydrogen to the feed oils, at temperatures of 500-800° C., preferably of 650-780° C., at a contact time above 0.01 second, preferably of 1-8 seconds, and at normal pressure or a raised pressure, e.g., at a pressure of 1-50 atm., preferably 1-10 atm. In the process of this invention, steam may be used instead of the above mentioned hydrogen or hydrogen-containing gas. In this case, the mole ratio of steam to the feed oils may be 0.5-10.0, preferably 2-4, and other reaction conditions are almost the same as those mentioned above.

In the process of this invention, the thermal cracking reaction may be carried out in the presence of catalysts. The catalysts are ones that have been usually used in this kind of reaction, other dehydrogenation, dealkylation, etc., and known metal oxide catalysts, such as Al_2O_3 , Cr_2O_3 , MoO_3 , etc., may be used. In particular, a silica-alumina catalyst or a chrome-alumina catalyst is usually used. Natural clays or sands may also be used as a catalyst. In the case of using catalysts, the reaction temperature can be reduced more than 50° C. lower than that where no catalyst is used.

In the afore-mentioned reaction system, the paraffinic hydrocarbons and/or naphthenic hydrocarbons having above 9 carbon atoms, preferably above 15 carbon atoms, cause thermal cracking and are directly decomposed to form easily free radicals. These free radicals are further decomposed or cause reactions and are gradually converted into free radicals having a lower number of carbon atoms, e.g., ethyl and methyl. These free radicals, on the other hand, promote by chain actions selectively the thermal cracking of the hydrocarbons having paraffin bonds and naphthene bonds of comparatively low number of carbon atoms mainly mixed in the feed oils as impurities (without affecting the aromatic hydrocarbons in the reaction system), and these impurities are converted into hydrocarbons having lower boiling points than benzene and toluene, or finally into gaseous hydrocarbons. Also, the decomposition of the sulfur compounds, nitrogen compounds, and oxygen compounds in the feed oils is promoted by the presence of the above mentioned free radicals, and the impurities are converted into gaseous products.

Thus, by the process of this invention, the impurities in the feed oils are easily converted into gaseous and liquid hydrocarbons. That is, as the converted products are lower paraffins, lower olefins, toluene and xylenes, high-purity benzene, toluene and the like can be easily recovered by a general distilling process.

The purities of benzene and toluene obtained by the process of this invention are higher than 99.00% and generally above 99.50%. In addition, valuable ethylene can be produced in the gaseous components in the reaction products.

As mentioned above, by the process of this invention wherein a small amount of the paraffinic and/or naphthenic hydrocarbons having above 9 carbon atoms, preferably above 15 carbon atoms, are added in the feed oils and the thermal cracking is carried out under the specific reaction conditions, the operation can be simplified by reducing the number of operations, e.g., eliminating an

extraction process which is an important process in conventional processes, and aromatic hydrocarbons such as benzene and toluene having purities not lower than those obtained by the conventional processes can be produced.

The invention will be explained more in detail by the following practical examples:

EXAMPLE 1

As the feed oils, crude aromatic hydrocarbons having the following properties and compositions were used.

Properties of feed oils:

Specific gravity	0.88 (15° C.)
Initial boiling point	82.0° C. (Englar distillation method).
50%	88.0° C.
End point	144.0° C.

Composition of feed oils (mole percent):

C_6 - C_8 aromatic hydrocarbons	97.85.
C_4 - C_6 paraffins and C_5 naphthenes	0.18.
C_5 - C_8 paraffins-naphthenes	1.97.

By reacting 100 parts of the feed oils and n-decane (a mixture of 95.23 weight percent of the feed oils and 4.77 weight percent of n-decane) by using a flow system apparatus at the following reaction conditions, 90.62 parts of liquid products and 3.97 parts of gaseous products were obtained.

Reaction conditions:

Reaction temperature	° C.	734
Hydrogen to raw material mole ratio		1.1
Contact time	sec.	4.4
Pressure		Normal pressure

Composition of liquid products (mole percent):

C_6 - C_8 aromatic hydrocarbons	99.37
C_4 - C_6 paraffins, olefins and C_5 naphthenes	0.34
C_6 naphthenes	0.02
C_7 - C_8 paraffins-naphthenes	0.27

Composition of gaseous products (mole percent):

Hydrogen	7.56
Methane	32.24
Ethane	4.79
Ethylene	48.61
Propane	0.50
Propylene	6.30
$\pm \text{C}_4$	0.00

From the above liquid products were recovered by a known distilling method benzene of 99.70 mole percent purity and toluene of 99.95 mole percent purity.

EXAMPLE 2

The feed oils same as in Example 1 and isopropylcyclohexane (95.23% of the feed oils and 4.77% of isopropylcyclohexane) were caused to react by using a flow system apparatus under the following reaction conditions and 90.52 parts of liquid products and 5.20 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	° C.	734
Hydrogen to feed oil mole ratio		1.0
Contact time	sec.	4.9
Pressure		Normal pressure

Composition of liquid products (mole percent):

C_6 - C_8 aromatic hydrocarbons	99.07
C_4 - C_6 paraffins, olefins and C_5 naphthenes	0.69
C_6 naphthenes	0.02
C_7 - C_8 paraffins-naphthenes	0.23

Composition of gaseous products (mole percent):

Hydrogen	8.85
Methane	25.39
Ethane	2.88
Ethylene	53.27

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Composition of gaseous products (mole percent)—
Continued

Propane	0.77	
Propylene	6.92	
±C ₄	1.93	5

From the above liquid products, benzene of 99.70 mole percent purity and toluene of 99.90 mole percent purity were recovered by a known distilling method.

EXAMPLE 3

By reacting 100 parts of the feed oils as in Example 1 and a mixture of n-decane and isopropylcyclohexane (96.15% of the feed oils, 1.93% of n-decane and 1.92% of isopropylcyclohexane) by using a flow system apparatus at the following reaction conditions, 88.88 parts of liquid products and 7.20 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	° C	734	
Hydrogen to raw material mole ratio		1.2	
Contact time	sec	4.3	
Pressure		Normal pressure	

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	98.42	25
C ₄ -C ₆ paraffins, olefins and C ₅ naphthenes	1.53	
C ₆ naphthenes	0.02	
C ₇ -C ₈ paraffins-naphthenes	0.04	

Composition of gaseous products (mole percent):

Hydrogen	5.10	30
Methane	28.55	
Ethane	3.86	
Ethylene	53.66	
Propane	0.69	
Propylene	6.90	35
±C ₄	1.24	

From the above liquid products were recovered benzene of 99.90 mole percent purity and toluene of 99.95 mole percent purity by a known distilling method.

EXAMPLE 4

By reacting 100 parts of the feed oils as in Example 1 and petroleum kerosene (96.15% of feed oils and 3.85% of petroleum kerosene) by using a flow system apparatus under the following reaction conditions, 90.41 parts of liquid products and 3.73 parts of gaseous products having the following compositions were obtained. In addition, the properties and the composition of the used petroleum kerosene are shown below.

Properties and compositions of the petroleum kerosene—

Properties:

Specific gravity	0.79 (15/4° C.)	
Initial boiling point	° C	165
End point	° C	243

Compositions (percent by volume):

Aromatic hydrocarbons	13.3	
Saturated hydrocarbons (C ₁₀ -C ₁₅ paraffins-naphthenes)	82.76	
Olefins	3.94	60

Reaction conditions:

Reaction temperature	° C	734	
Hydrogen to raw material mole ratio		1.1	
Contact time	sec	4.5	
Pressure		Normal pressure	65

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	99.17	
C ₄ -C ₆ paraffins, olefins and C ₅ naphthenes	0.68	
C ₆ naphthenes	0.01	
C ₇ -C ₈ paraffins-naphthenes	0.09	70

Composition of gaseous products (mole percent):

Hydrogen	3.75	
Methane	41.29	
Ethane	2.95	
Ethylene	41.02	75

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Composition of gaseous products (mole percent)—
Continued

Propane	0.54	
Propylene	9.38	
±C ₄	0.04	

From the above liquid products were recovered benzene of 99.80 mole percent purity and toluene of 99.90 mole percent purity by a known distilling method.

EXAMPLE 5

By reacting 100 parts of the feed oils as in Example 1 and petroleum kerosene (99.50% of feed oils and 0.50% of petroleum kerosene) by using a flow system apparatus under the following reaction conditions, 93.00 parts of liquid products and 3.20 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	° C	753	
Hydrogen to raw material mole ratio		1.1	
Contact time	sec	4.4	
Pressure		Normal pressure	

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	99.54	
C ₄ -C ₆ paraffins, olefins and C ₅ naphthenes	0.40	
C ₆ naphthenes	0.00	
C ₇ -C ₈ paraffins-naphthenes	0.06	

Composition of gaseous products (mole percent):

Hydrogen	1.72	
Methane	39.32	
Ethane	5.65	
Ethylene	41.77	
Propane	0.74	
Propylene	9.83	
±C ₄	0.04	

From the above liquid products were recovered benzene of 99.90 mole percent purity and toluene of 99.95 mole percent purity by a conventional distilling method.

(Comparative Example 1)

In order to make clear the effects achieved by the process of this invention, 100 parts of the feed oils as in Examples 1-5 was reacted without adding the hydrocarbons having more than 9 carbon atoms at almost the same reaction conditions as in the examples, i.e., by the following reaction conditions, and 94.20 parts of liquid products and 241 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	° C	734	
Hydrogen to raw material mole ratio		1.1	
Contact time	sec	4.5	
Pressure		Normal pressure	

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	98.91	
C ₄ -C ₆ paraffins, olefins and C ₅ naphthenes	0.41	
C ₆ naphthenes	0.04	
C ₇ -C ₈ paraffins-naphthenes	0.74	

Composition of gaseous products (mole percent):

Hydrogen	7.85	
Methane	75.62	
Ethane	2.07	
Ethylene	9.09	
Propane	0.83	
Propylene	4.55	
±C ₄	0.00	

From the above liquid products was recovered benzene of 99.20 mole percent purity by a known distilling method.

Thus, a large amount of impurities are admixed as is clear from the above example, the purity of obtained benzene is low, and the amount of the effective gaseous products is less.

EXAMPLE 6

Fractions of 6-8 carbon atoms obtained by pre-distilling cracked residues obtained by naphtha-cracking naphtha by a Stone and Webster method was used as the raw materials. The properties and the compositions of the raw materials were as follows.

Properties of the feed oils:

API	40.80 (60/60° F.)
Specific gravity	0.825 (15/4° C.)
Initial boiling point	70.0 ° C.
50%	97.0 ° C.
End point	144.0 ° C.

Composition of the feed oils (percent by weight):

Aromatic hydrocarbons	83.0
Saturated hydrocarbons (C ₆ -C ₈ paraffins-naphthenes)	13.73
Olefins	2.67

100 parts of the above feed oils and n-cetane (98.04 wt. percent of feed oils and 1.96 wt. percent of n-cetane) were reacted by using a flow system apparatus under the following reaction conditions, and 71.71 parts of liquid products and 23.35 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	760 ° C.
Hydrogen to raw material mole ratio	3.83
Contact time	4.72 sec.
Pressure	Normal pressure

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	99.08
C ₄ -C ₆ paraffins and olefins	0.09
C ₅ -C ₆ naphthenes	0.72
C ₇ paraffins	0.14

Composition of gaseous products (mole percent):

Hydrogen	---
Methane	43.81
Ethane	5.15
Ethylene	48.50
Propane	0.25
Propylene	2.24
±C ₄	0.34

From the above liquid products was recovered benzene of 99.76 mole percent purity by a known distilling method.

(Comparative Example 2)

For comparison, 100 parts of the same feed oils as in Example 6 were reacted without the addition of the hydrocarbons having more than 9 carbon atoms under almost the same reaction conditions as in Example 6, that is, under the following reaction conditions, and 71.71 parts of liquid products and 21.53 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	760 ° C.
Hydrogen to raw material mole ratio	3.93
Contact time	4.44
Pressure	Normal pressure

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	97.30
C ₄ -C ₆ paraffins and olefins	0.54
C ₅ -C ₆ naphthenes	1.16
C ₇ paraffins	1.07

Composition of gaseous products (mole percent):

Hydrogen	---
Methane	45.92
Ethane	6.64
Ethylene	42.97
Propane	0.37
Propylene	3.86
±C ₄	0.27

From the above liquid products was recovered benzene of 98.01 mole percent purity by a known distilling method.

As clear from the above example and Example 6, in the case of adding no hydrocarbons having more than 9 carbon atoms, a large amount of impurities were mixed, the purity of benzene obtained by the distillation was low, and the amount of the effective gaseous products was less.

EXAMPLE 7

The feed oils as in Example 1 and isopropylcyclohexane (99.0% of feed oils and 1.0% of isopropylcyclohexane) were reacted by using a flow system apparatus packed with a silica-alumina catalyst (15 mole percent silica and 85 mole percent alumina) under the following reaction conditions and 90.2 parts of liquid products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	650 ° C.
Hydrogen to raw material mole ratio	1.7
Liquid hourly space velocity (ml./ml./hr.)	0.315
Pressure	Normal pressure

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	99.10
C ₅ -C ₆ paraffins-naphthenes	0.51
C ₇ paraffins	0.39

From the above liquid products, benzene of 99.50 mole percent purity was recovered by a known distilling method.

EXAMPLE 8

The same feed oils as in Example 1 and n-cetane (97.90% of the feed oils and 2.10% of n-cetane) were caused to react by using a flow system apparatus under the following reaction conditions and 91.50 parts of liquid products and 5.35 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	740 ° C.
Hydrogen to raw material mole ratio	2.0
Contact time	3.5 sec.
Pressure	45.0 atm.

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	99.20
C ₄ -C ₆ paraffins, olefins and C ₅ naphthenes	0.52
C ₆ naphthenes	0.03
C ₇ -C ₈ paraffins-naphthenes	0.15

Composition of gaseous products (mole percent):

Hydrogen	---
Methane	49.21
Ethane	17.60
Ethylene	20.90
Propane	4.20
Propylene	4.04
±C ₄	2.05

From the above liquid products were recovered by a known distilling method benzene of 99.70% purity and toluene of 99.90% purity.

EXAMPLE 9

The same feed oils as in Example 1 and n-cetane (97.0% of the feed oils and 3.0% of n-cetane) were caused to react by using a flow system apparatus under the following reaction conditions and 91.30 parts of liquid products and 4.80 parts of gaseous products having the following compositions were obtained.

Reaction conditions:

Reaction temperature	740 ° C.
Steam to feed oil mole ratio	2.0
Contact time	4.0 sec.
Pressure	Normal pressure

Composition of liquid products (mole percent):

C ₆ -C ₈ aromatic hydrocarbons	99.08
C ₄ -C ₆ paraffins, olefins and C ₅ naphthenes	0.71
C ₆ naphthenes	0.04
C ₇ -C ₈ paraffins-naphthenes	0.17

Composition of gaseous products (mole percent):

Hydrogen	6.20
Methane	23.01
Ethane	8.40
Ethylene	49.55
Propane	0.56
Propylene	10.24
±C ₄	2.04

From the above liquid products were recovered by a known distilling method benzene of 99.60% purity and toluene of 99.90% purity.

EXAMPLES 10 TO 13

The same feed oils and flow system apparatus as in Example 1 were used in each of these examples. By changing the contact time and hydrogen to material mole ratio in each example various results were obtained as shown in the following table.

Example	10	11	12	13
Feed oils (wt. part)	96.2	96.2	98.2	98.2
n-Decane (wt. part)	1.9	1.9	0.9	0.9
Isopropylcyclohexane (wt. part)	1.9	1.9	0.9	0.9
Reaction temperature, °C.	740.0	740.0	740.0	700.0
Hydrogen to raw material mole ratio	4.5	8.1	9.2	1.3
Contact time (second)	1.8	1.1	7.4	8.4
Yield of liquid products (wt. percent)	90.4	95.5	90.7	96.4
Yield of gaseous products (wt. percent)	3.6	2.0	2.9	2.4
Pressure	Normal pressure	Normal pressure	Normal pressure	Normal pressure
Composition of liquid products (mole percent):				
C ₄ -C ₈ paraffin, olefine	0.41	0.40	0.21	0.41
C ₅ -C ₈ naphthene	0.03	0.01	0.00	0.00
C ₆ -C ₈ aromatic	99.17	99.39	99.79	99.49
C ₇ -C ₈ paraffin, naphthene	0.39	0.20	0.00	0.10
Purity of benzene (percent)	99.80	99.80	99.90	99.90

The purity of benzene and toluene obtained by normal distillation showed such a high degree as of above 99.80%, respectively, in all examples. With respect to the gaseous products, those very high in ethylene concentration were also obtained in all examples.

What is claimed is:

1. A process for producing high purity aromatic hydrocarbons which comprises thermally cracking crude

hydrocarbon oils containing predominantly aromatic hydrocarbons, said hydrocarbon oils containing almost no paraffinic hydrocarbons and naphthenic hydrocarbons having above 9 carbon atoms as impurities, at temperatures of 500-800° C., at a contact period above 0.01 second, and at normal pressure or a raised pressure, in the presence of a gas selected from the group consisting of hydrogen, a hydrogen-containing gas and steam, with the addition of at least a member selected from the group consisting of paraffinic hydrocarbons and naphthenic hydrocarbons having above 9 carbon atoms thereby cracking the non-aromatic hydrocarbons initially present along with those added, without affecting the benzene ring, into products having boiling points below those of said aromatic hydrocarbons, and separating high-purity aromatic hydrocarbons.

2. The process as claimed in claim 1 wherein said aromatic hydrocarbon is benzene.

3. The process as claimed in claim 1 wherein said aromatic hydrocarbon is toluene.

4. The process as claimed in claim 1 wherein said aromatic hydrocarbons are benzene and toluene.

5. The process as claimed in claim 1 wherein said thermal cracking is carried out in the presence of said gas selected from the group consisting of hydrogen and a hydrogen-containing gas in a mole ratio of 0.5-20.0 of hydrogen to said feed oils.

6. The process as claimed in claim 1 wherein said thermal cracking is carried out in the presence of steam in a mole ratio of 0.5-10.0 of steam to said feed oils.

7. The process as claimed in claim 1 wherein said thermal cracking is carried out under the presence of a silica-alumina catalyst.

8. The process according to claim 1 wherein the member selected from the group consisting of paraffinic hydrocarbons and naphthenic hydrocarbons has more than 15 carbon atoms.

9. The process according to claim 5 wherein said mol ratio is 1 to 3.

10. The process according to claim 6 wherein said mol ratio is 2 to 4.

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