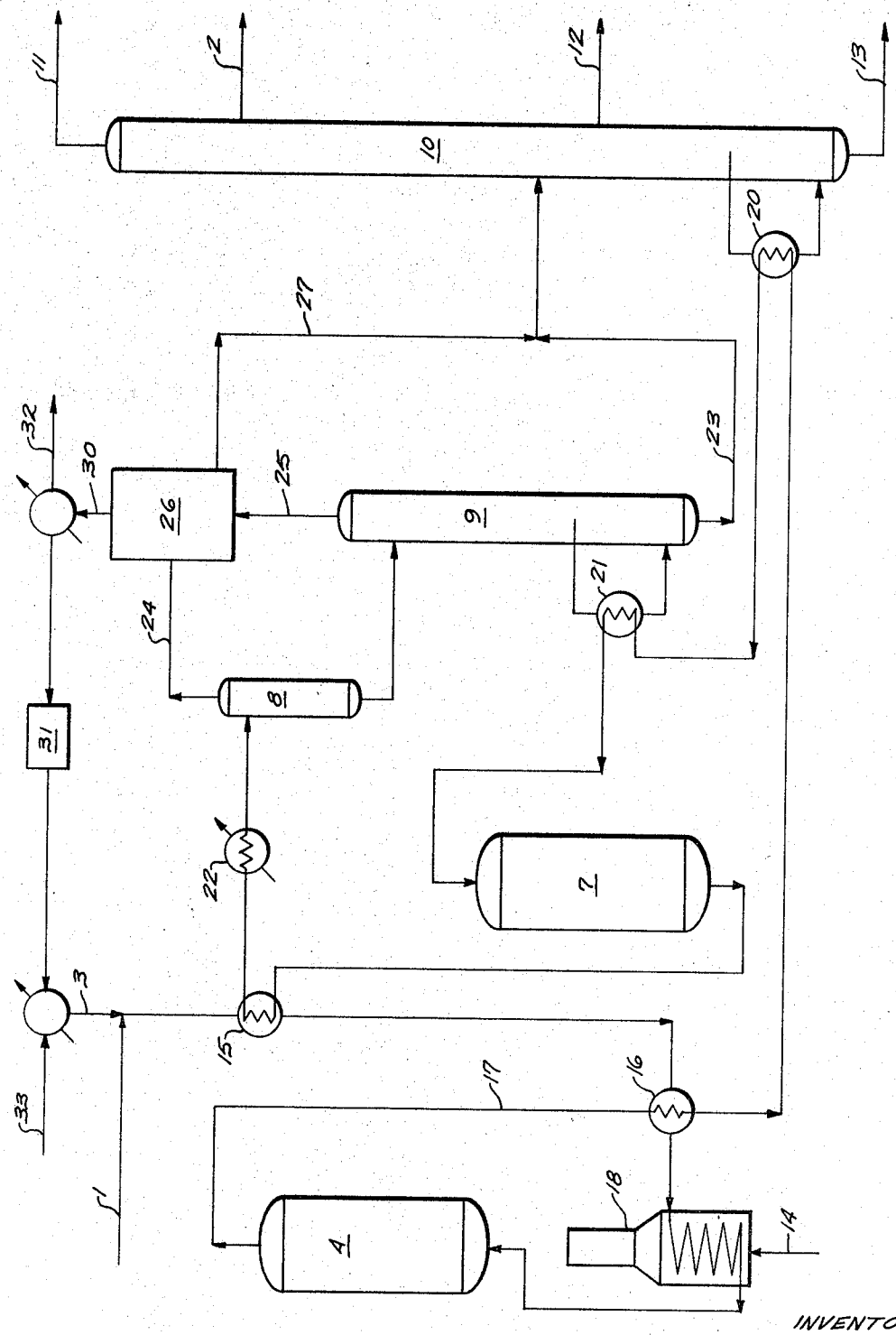
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METHOD FOR IMPROVING THE QUALITY OF DEALKYLATED AROMATIC COMPOUNDS

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METHOD FOR IMPROVING THE QUALITY OF DEALKYLATED AROMATIC COMPOUNDS

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This invention relates to a method for the production of hyperpure dealkylated aromatic compounds from petroleum-derived dealkylated aromatic compounds and more particularly, it relates to a method for producing benzene which substantially exceeds standard commercial specifications.

At one time a rather static benzene market was largely supplied with benzene obtained as a by-product of the well developed but stabilized coal carbonization industry. Recovery of benzene from crude petroleum in which it usually occurs as a very minor constituent was not a significant factor. However, in recent years the rapid growth in the synthesis of upgraded chemicals from benzene, such as synthetic rubbers, plastics, detergents and fine chemicals, has caused a rapidly increasing and fluctuating demand for benzene which could not be supplied by the coal carbonization industry.

Fortuitously, benzene has lately been produced in relatively large amounts as a by-product in the petroleum naphtha reforming process concurrently with this increasing demand. Various alkyl aromatics such as toluene and the xylenes, which are also produced in the naphtha reforming process, can be dealkylated as a further source of benzene. In this expanding market cycles of over capacity and under capacity have been a natural occurrence. These cycles are expected to continue into the future as the result of future growth and adjustments to changing economic conditions.

Concomitant with this increase in benzene usage is a demand by many users, sometimes without regard to process requirements, for benzene which surpasses the standards of established commercial specifications. In view of this fluctuating and highly competitive market for benzene, it would be most advantageous for a benzene supplier to be able to provide material of a quality that would exceed the most rigid specifications at no greater cost than lower specification material. Thus, not only could he fulfill every user's requirements, but in periods of over capacity he could easily sell his entire output, since users, with cost being equal, will buy the highest specification material whether or not it is required in their process. In the long run this would lead to a general upgrading of benzene and with the ready availability of a purer material should lead to new usages. In accordance with our invention a hyperpure benzene is produced from the alkyl aromatic by-products of the naphtha reforming process at no greater cost than less pure commercial grades of benzene.

In reforming petroleum hydrocarbons a naphtha fraction is first subjected to a hydrogenation-purification step to eliminate poisons to the usually used platinum reforming catalyst. In the subsequent reforming step, conducted in the presence of an excess of hydrogen under suitable conditions of temperature and pressure, naphthenic constituents are converted to aromatics, primarily benzene, toluene, xylene and ethyl benzene. These aromatics are separated from the reformate by solvent extraction and may be distilled into exceedingly pure fractions.

Benzene is classified into a number of grades generally indicative of its purity. Nitration-grade benzene carries the most rigid standard commercial specification as set forth in ASTM D835–50. Under this specification its acid wash color, the most sensitive and significant test, must not be greater than No. 2 on the acid wash color scale as determined by ASTM D848–62. In this test a benzene sample is agitated with 96 percent sulfuric acid and the resulting color of the acid layer is compared with a set of color standards numbered from 0 through 14 with 0 being the color of distilled water.

With strict adherence to the proper processing conditions, it has been possible heretofore to make nitration-grade benzene by the demethylation of toluene without any further treatment after the demethylation other than the customary separative procedures. If this demethylated product does not meet the specifications for nitration-grade benzene, treatment with clay can bring the acid wash color down to No. 2, however, the attainment of a significantly lower number is not practically attainable by clay treatment since the clay quickly loses its effectiveness and must be frequently replaced at a prohibitive expense. Analysis of the untreated demethylation effluent by chromatographic and mass spectroscopic analysis for color producing bodies or impurities has failed to identify any such substances. Notwithstanding this, we have made the surprising discovery that by an appropriate modification of the process, the resultant product will far exceed the rigid specifications for nitration-grade benzene. Our invention is in part predicated upon this discovery.

In our process an alkyl aromatic stream such as a stream of toluene from the reformate separation is subjected to an integrated dual treatment, first hydrogenating with an excess of hydrogen under appropriate conditions to demethylate the toluene and second treating in the presence of this hydrogen under different conditions to ensure that the product will exceed the most rigid commercial specifications. According to our process benzene can be produced with an acid wash color as low at 0+, which is almost water white under the test. We accomplish this by immediately subjecting the demethylation effluent to an elevated temperature and pressure in the presence of hydrogen and a solid particulate material. We do not know what direct effect that this has on the effluent other than the discovery that the benzene product obtained after the final distillation far exceeds the specifications for nitration-grade benzene. Knowing that at least three separate purifying-hydrogenation operations as well as the associated purifying-separative procedures are involved from the original refinery distillation through this demethylation, it is wholly unexpected and highly surprising that a further treatment of this essentially pure demethylated product under these conditions would produce a strikingly superior-specification material.

The bromine index of benzene is frequently used in commercial dealings in substitution of or to supplement the acid wash color test although it is not a part of the official specifications. In typical examples the effluent from the toluene demethylator exhibited a bromine index of about 20 as determined by ASTM D1491–60. This without further treatment is superior by several orders of magnitude to material produced by prior processes even after special treatment. For example, in U.S. Patent No. 2,701,267, crude benzene obtained by the steam distilla-

tion of wash oil used in the recovery of light oil from coal distillation gases is prepurified and then is subjected to a catalytic treatment with a large quantity of hydrogen at elevated temperature and pressure. This gives a final benzene, stated to be pure, having a bromine number of 0.2 which corresponds approximately to a bromine index of 200. It is therefore highly unexpected that the bromine index of the demethylation effluent, which is lower by a factor of about 10 than the pure benzene resulting after final treatment under this patent, can be substantially reduced by our treatment. Despite this, we have made the surprising discovery that, if the demethylation effluent is subjected to suitable conditions of temperature and pressure in the presence of a solid particulate material, a benzene having a bromine index less than 5 and in many instances under 1.0 is produced.

The drawing illustrates an arrangement for carrying out our invention. Toluene **1** from the naphtha reformate separation admixed with recycle toluene **12** is introduced into the system and hyperpure benzene **2** is obtained as the primary product. The toluene is first mixed with an excess of hydrogen **3** and the mixture heated prior to introduction into the demethylation unit **4**. After demethylation, the benzene-rich effluent is treated in upgrading unit **7** to reduce the acid wash color and bromine index of the final benzene product to an extremely low value. After gas-liquid separation in **8** and final removal of gases and light ends in stripper **9**, the liquid effluent is separated in fractionator **10** into hyperpure benzene **2** as the major product as well as a more volatile fraction **11**, unreacted toluene **12** suitable for recycling, and less volatile by-products **13**. This less volatile bottoms product can be further separated into one or more of its components in a hyperpure state, if desired, including naphthalene, biphenyl, fluorene, phenanthrene, and pyrene, or this fraction may be fed into the refinery fuel oil stream.

In more specific detail the toluene-hydrogen feed is sequentially heated in heat exchangers **15** and **16** by the effluent stream from the upgrading unit **7** and by the demethylator effluent stream **17** and in furnace **18** fired with refinery fuel gases **14** to bring the mixture to reaction temperature for thermal demethylation. This reaction occurs between about 1150° and 1800° F. with 1250° to 1350° F. being the preferred range and about 100 to 1000 p.s.i.g., preferably in the range of 400 to 600 p.s.i.g. An excess of 1.5 to 20 mols of hydrogen per mol of hydrocarbon is generally used with the preferred molar ratio being 3 to 8 mols of hydrogen per mol of hydrocarbon. The mixture is retained in reactor **4** for sufficient time, from one to 600 seconds and preferably from 10 to 100 seconds, to obtain the desired demethylation. This procedure as described merely represents a preferred mode of operation. Demethylation may also be performed hereunder in a catalytic reaction using a suitable dealkylation catalyst at a temperature somewhat lower, such as 1000° to 1400° F., than is used in the non-catalytic reaction.

Heat economy is effected by utilizing the hot effluent **17** from the demethylator to sequentially heat the feed in heat exchanger **16**, to heat the fractionator bottoms in heat exchanger **20**, and to drive the stripping column in heat exchanger **21** prior to its introduction into treating unit **7**. This upgrading operation is broadly carried out at about 150° to 600° F., at 100 to 1000 p.s.i.g., and at a liquid hourly space velocity at 1 to 20 volumes of liquid per hour per volume of solid particulate material. Preferred conditions for operation are about 200° to about 550° F., about 300 to about 500 p.s.i.g., and a liquid hourly space velocity of 1 to 8. Suitable solid particulate materials for use in the upgrading unit include the metals, metal oxides and sulfided metals of Group VI (left column) and Group VIII of the Periodic Table alone or in admixture, distended on non-acidic supports. These include nickel-cobalt-molybdenum, cobalt molybdenum, sulfided nickel, sulfided tungsten-nickel, sulfided tungsten on such non-acidic carriers as alumina, clay, and kieselguhr and the like. Primary process control is effected by varying the liquid hourly space velocity.

The effluent stream from treating unit **7** passes through heat exchanger **15** which provides the initial heating to the toluene-hydrogen feed stream and through cooler **22** into gas-liquids separator **8** for separation of the gases, primarily hydrogen and methane, from the liquid portion of the cooled stream. Residual gases and light hydrocarbons are removed in stripper **9** and the liquid bottoms product **23** is fractionated into super specification benzene **2** and the other previously described fractions.

Gas-vapor streams **24** and **25** from the gas-liquids separator and the stripper are introduced into the vapor recovery unit **26** from which a small amount of separated liquids **27** is passed to the fractionator. The gases **30** from the vapor recovery unit are recycled through compressor **31** after bleeding off a small slip stream **32** to maintain the hydrogen content of the feed stream at an appropriate level. Makeup hydrogen **33** from the reformer off-gases or other available source is added to the recycle gas stream.

The following is a specific example of the operation of the invention in which hyperpure benzene is produced from toluene. Fifteen thousand lbs./hr. toluene from the reformate extraction which includes a relatively small proportion of recycle toluene from the fractionator is combined with a mixed stream of reformer off-gas and recycle hydrogen having a net hydrogen content of about 75 mol percent to form a hydrogen to toluene mol ratio of 3.5 to 1. This mixture is preheated to about 1170° to 1250° F. and charged to the demethylator operating at a pressure of about 460 p.s.i.g. Two reactors in series are used with cooling between stages to maintain the desired temperature of reaction. After a total contact time of about 40 seconds, the demethylated effluent is quenched by heat exchange with the input stream. After cooling the effluent stream by heat exchange in the fractionator and in the stripper reboiler as described, it is fed to the treating unit at a temperature and pressure of 450° F. and 350 p.s.i.g. and a flow rate of four liquid volumes per hour per volume of solid particulate material. The solid particulate material in the treating unit is a presulfided mixture containing 2.3 percent nickel, 1.4 percent cobalt, and 9.2 percent molybdenum supported on alumina. After separation from the gases, the liquid effluent from the treating unit is fractionated to produce 10,700 pounds of hyperpurse benzene per hour. The following is an actual analysis which is representative of this operation:

	Stripper Bottoms [1]	Benzene From Fractionator [1]	Stripper Bottoms [2]	Benzene From Fractionator [2]
Acid Wash Color	>14	6−	>14	0+
Bromine Index	24.1	20.5	4.3	<1
Thiophene, p.p.m.	9.4	1.5	6	<.1
Sulfur, p.p.m.	3	1	<1	<1
Solidification Point, ° F.		5.5		5.4
Over Point, ° C.		79.6		79.7
Dry Point, ° C.		80.7		80.2

[1] Treating unit by-passed.
[2] Treating unit in operation.

It is of particular interest to note that the improvement in acid wash color does not show up until after fractionation while the improvement in bromine index does not appear to be significantly improved by fractionation. Of further significance are the excellent results obtained after long usage of the solid particulate material. In many runs over the range of preferred conditions of operation the benzene product consistently displayed an acid wash color of 1− or better and a bromine index under 5, indicating a good tolerance to reasonable variations in operation. Furthermore, both the selectivity of toluene to benzene and the per-pass conversion efficiency ex-

ceeded 90 percent in these runs. This high degree of selectivity and conversion efficiency can be consistently obtained with proper operation within the preferred conditions.

At the more rigorous conditions of operation some cyclohexane is produced in the upgrading operation. For example, three runs were carried out at a pressure of 400 p.s.i.g., a temperature of 550° F., and a total gas rate of 10,500 s.c.f./bbl. aromatics, the gas consisting of 50 percent hydrogen and 50 percent methane. For liquid hourly space velocities of 2, 3 and 4 the cyclohexane product amounted to .035, .025 and .015 volume percent respectively. In order to decrease the amount of cyclohexane, the temperature or pressure may be reduced or the liquid hourly space volicty may be increased, or more than one of these variables may be mutually adjusted in the appropriate direction.

It is of critical importance to the successful economical utilization of our process that it be integrated into an energy conserving system as described. Although toluene was specifically described as the feed material, other petroleum-derived materials are also suitable including xylene, ethyl benzene and other monoalkyl and polyalkyl benzene compounds alone or in admixture with toluene. These aromatic compounds are also converted to hyperspecification benzene at high conversion efficiency and good selectivity. In addition, this process can be used to produce hyperpure dealkylated polynuclear aromatic compounds, such as naphthalene, from the corresponding alkylated polynuclear compounds.

It is to be understood that the above disclosure is by way of specific example and that numerous modifications and variations are available to those of ordinary skill in the art without departing from the true spirit and scope of our invention.

We claim:

1. A process for the production of hyperpure dealkylated aromatic compounds which comprises heating a composition selected from the group consisting of an alkyl aromatic compound and a mixture of alkyl aromatic compounds and about a 1.5 to 20 molar excess of hydrogen to a temperature and pressure between about 1000° to 1800° F. and 100 to 1000 p.s.i.g. for about one to 600 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds to a temperature and pressure between about 150° to 600° F. and 100 to 1000 p.s.i.g. in the presence of a solid particulate material selected from the group consisting of metals, metal oxides and sulfided metals of Group VI (left column) and VIII of the Periodic Table, and mixtures thereof, distended on a non-acidic suport; and separating the treating effluent mixture into fractions of hyperpure dealkylated aromatic compounds.

2. A process for the production of hyperpure dealkylated aromatic compounds which comprises heating a composition selected from the group consisting of an alkyl aromatic compound and a mixture of alkyl aromatic compounds and about a 1.5 to 20 molar excess of hydrogen to a temperature and pressure between about 1000° to 1800° F. and 300 to 1000 p.s.i.g. for about one to 600 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds to a temperature and pressure between about 200° to 550° F. and 300 to 500 p.s.i.g. in the presence of a solid particulate material selected from the group consisting of metals, metal oxides and sulfided metals of Group VI (left column) and VIII of the Periodic Table and mixtures thereof, distended on a non-acidic support, at the rate of about 1:1 to 8:1 liquid volumes of effluent mixture per hour per volume of solid particulate material, and separating the treated effluent mixture into fractions of hyperpure dealkylated aromatic compounds.

3. A process for the production of hyperpure benzene which comprises heating a composition selected from the group consisting of an alkyl aromatic compound and a mixture of alkyl aromatic compounds and about a 1.5 to 20 molar excess of hydrogen to a temperature and pressure between about 1000° to 1800° F. and 100 to 100 p.s.i.g. for about one to 600 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds to a temperature and pressure between about 150° to 600° F. and 100 to 1000 p.s.i.g. in the presence of a solid particulate material selected from the group consisting of metals, metal oxides and sulfided metals of Group VI (left column) and VIII of the Periodic Table, and mixtures thereof, distended on a non-acidic support; and separating hyperpure benzene from the treated effluent mixture.

4. A process for the production of hyperpure benzene which comprises heating a composition selected from the group consisting of an alkyl aromatic compound and a mixture of alkyl aromatic compounds and about a 1.5 to 20 molar excess of hydrogen to a temperature and pressure between about 1000° to 1800° F. and 300 to 1000 p.s.i.g. for about one to 600 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds to a temperature and pressure between about 200° to 550° F. and 300 to 500 p.s.i.g. in the presence of a solid particulate material selected from the group consisting of metals, metal oxides and sulfided metals of Group VI (left column) and VIII of the Periodic Table and mixtures thereof, distended on a non-acidic support; and separating hyperpure benzene from the treated effluent mixture.

5. A process for the production of hyperpure benzene which comprises heating a mixture of toluene and about a 1.5 to 20 molar excess of hydrogen to a temperature and pressure between about 1000° to 1800° F. and 100 to 1000 p.s.i.g. for about one to 600 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds at a temperature and pressure between about 150° to 600° F. and 100 to 1000 p.s.i.g. to a catalytic material selected from the group consisting of metals, metal oxides and sulfided metals of Group VI (left column) and VIII of the Periodic Table, and mixtures thereof, distended on a non-acidic support; and separating hyperpure benzene from the treated effluent mixture.

6. A process for the production of benzene having an acid wash color less than No. 2 which comprises heating a mixture of toluene and about a 1.5 to 20 molar excess of hydrogen to a temperature and pressure between about 1000° to 1800° F. and 100 to 1000 p.s.i.g. for about one to 600 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds to a temperature and pressure between about 150° to 600° F. and 100 to 1000 p.s.i.g. in the presence of a solid particulate material selected from the group consisting of metals, metal oxides, and sulfided metals of Group VI (left column) and Group VIII of the Periodic Table, and mixtures thereof, distended on a non-acidic support at the rate of 1:1 to 20:1 liquid volumes of effluent mixture per hour per volume of solid particulate material; and separating hyper-specification benzene from the treated effluent mixture.

7. A process for the production of benzene having an acid wash color less than No. 2 which comprises heating a mixture of toluene and about a 3 to 8 molar excess of hydrogen to a temperature and pressure between about 1100° to 1350° F. and 400 to 600 p.s.i.g. for about 10 to 100 seconds; subjecting the effluent mixture which is substantially free of organic sulfur compounds to a temperature and pressure between about 200° to 550° F. and 300 to 500 p.s.i.g. in the presence of a solid particulate material selected from the group consisting of metals, metal oxides and sulfided metals of Group VI (left column) and VIII of the Periodic Table, and mixtures thereof, distended on a non-acidic support at the rate of 1:1 to 8:1 liquid volumes of effluent mixture per hour per volume of solid particulate materials; and sepa-

rating hyper-specification benzene from the treated effluent mixture.

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