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RECOVERY AND PURIFICATION OF BENZENE

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This invention relates to the recovery and purification of benzene from crude coke oven or coal tar light oils.

A principal objective of the present invention has been to provide an improved low cost process for producing high purity sulfur-free nitration grade benzene at high yield from a crude coke oven or coal tar light oil in which benzene is contained along with toluene, xylene, paraffinic and sulfur-bearing impurities such as thiophenes.

While coke oven light oil is abundantly available at low cost, the sulfur and paraffinic impurities therein have interfered with extensive use of this raw material as a source of high grade benzene. These impurities have caused the chemical industry increased operating costs and lower yields in subsequent reaction. This impurity problem is so critical that the chemical industry is switching its high grade benzene requirements to the petroleum industry. Also, for this reason the coal tar industry is switching to the petroleum industry's technique of hydrodesulfurization to recover benzene from coal tar light oil, using cobalt molybdenum catalyst, followed by solvent extraction.

At present coal tar producers subject the light oil to an acid treatment which removes some of the impurities, but this treatment does not effectively remove thiophenes and other impurities and does cause a significant loss in benzene content. Benzene of suitable purity for nitration purposes or the like cannot be obtained from the acid-washed material by ordinary methods of fractionation, such as might otherwise be expected, because the boiling point of the thiophenes is too close to the boiling point of the desired fraction.

In the past various proposals have been made to subject a benzenoid hydrocarbon mixture containing methyl benzenes to catalytic cracking conditions in the presence of hydrogen in the expectation of selectively removing methyl groups from toluene and xylene which may be present, thereby to increase the benzene content of the product being treated. However, the actual experience in this type of procedure falls short of the theoretical expectations. As distinguished from dealkylation of benzenes having two or more groups of carbon atoms in the alkyl group, the methyl groups from toluene and xylene are reluctant to crack off selectively. This is particularly true when coal tar light oils form the charge stock. In the presence of conventional catalysts and at a temperature sufficiently high to effect cracking of impurities, the reaction becomes nonselective and only a small amount of liquid end product is obtained along with large quantities of coke and gaseous hydrocarbons. On the other hand, if slightly lower temperatures are employed, so as to prevent destructive cracking of valuable

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components, the conversion of methyl benzenes into benzene is very poor, even at prolonged contact time; hence the yield is very low and the necessity of multi-pass recycling of the end product prevents commercial utilization of the procedure for economic reasons.

In recognition of these difficulties, a small volume of benzene presently is produced from coal tar light oils by a process of hydrodesulfurization to remove sulfur impurities, followed by solvent extraction of the benzene content of the desulfurized light oil from the end product. However, on account of the very high initial cost of installing equipment necessary for such treatment, as well as the relatively high cost of operating the same, the hydrodesulfurization and selective solvent extraction process affords no economic advantage over the production of benzene of equal purity from petroleum refining sources despite the abundance and low cost of the crude light oil, and the process is used only because of the high demand for benzene.

Briefly, the present invention is based upon the discovery that the sulfur impurities such as thiophenes as well as the paraffinic impurities which are present in a coal tar light oil can be removed, and the methyl groups can be selectively cracked from the toluene and xylene which are also present, without destructive effect on the useful components of the light oil by subjecting the light oil to hydro-cracking conditions in the presence of a specific catalyst.

More specifically, and notwithstanding past indications to the contrary, the present invention is based upon the discovery that a high yield of high purity benzene can be obtained by subjecting coke oven or coal tar light oil to catalytic cracking in the presence of hydrogen at temperatures above 1200° F., for example, 1250° F., in a single pass, through a specialized chromia catalyst which is distinguished from conventional chromia catalysts as subsequently explained.

Otherwise expressed, it has been discovered that the particular catalyst, hereafter identified in more detail, enables selective disproportionation to be accomplished at temperatures considerably higher than were heretofore thought possible to employ, and the yield of the selective demethylation is so high in a single pass that recycling of unconverted methyl or alkyl benzene compounds is unnecessary.

More specifically, I have found that a catalyst consisting of approximately 10–15% by weight of chromium oxide on a high purity, low sodium content, gamma type alumina support is capable in the presence of hydrogen of enabling selective demethylation of benzenoid hydrocarbons contained in coal tar light oil or the like and concurrent conversion of sulfur-bearing and paraffin impurities, with little or no coking effect, at temperatures above 1200° F. and preferably at approximately 1250° F. The catalyst which enables such results to be obtained, in contrast to the poor results obtained in the use of conventional chromia and other catalysts on conventional supports, is commercially available from The Girdler Corporation, Louisville, Kentucky under their trade designation G-41. X-ray diffraction patterns show the chromia oxide to be present in the form of hexagonal crystals as distinguished from chromia aluminum co-gel catalysts which have also been available but which are incapable of providing similar results. The total chromia content of the commercial product is calculated as 11.8% Cr₂O₃.

by weight, the remainder of the product being the specified high purity, low sodium content chromia type alumina. In use the catalyst is employed in the form of tablets, for example, $\frac{3}{16}$ " x $\frac{3}{16}$ " in size, forming a fixed bed through which the feed stock and hydrogen are passed continuously.

The process of this invention is effected by contacting the charge of coal tar light oil with the catalyst and hydrogen at a temperature above 1200° F., and preferably at a temperature of approximately 1250° F., at a charge flow rate providing a contact time of approximately ten to twelve seconds. Since demethylation of the methyl benzenes present in the charge stock is accompanied by heat liberation, the feed is preferably held at a temperature somewhat lower than the preferred 1250° F. temperature at which the conversion is effected; for example, where hydrocracking is to be conducted within the reactor at a temperature of 1250° F., the feed temperature may be approximately 1150° F. The feed temperature provides a convenient means of limiting peak temperature at the contact zone.

Within the contact zone demethylation occurs rapidly, but even at the high temperature indicated there is little destructive cracking of hydrocarbons into coke or normally gaseous products and little formation of undesirable polybenzenes or biphenyl. In the cracking zone methyl groups split off the toluene and xylene to yield benzene, while the sulfur impurities are converted into hydrogen sulfide and the paraffin impurities are cracked to gas. The normally liquid products from the hydrocracker are then condensed, and the gaseous products are separated from the liquid products by means of a flash drum and absorber. Dry gas products may be used for plant fuel, while the liquid products are stabilized to remove entrained or absorbed gas, and the liquid products are then subjected to fractionation to separate benzene, toluene, and xylene from one another as desired.

In a typical crude benzol or acid-washed coal tar light oil, the benzene content is approximately 60%, the toluene content approximately 20%, the xylene content approximately 10%, the balance being paraffins and other impurities, the total sulfur content approximating 2000 parts per million. In terms of yield, the following table illustrates the practice of the invention on a typical acid-washed coal tar light oil.

MATERIAL BALANCE FOR CRACKING

Crude benzene-toluene-xylene

Feed:	
BTX—	
Benzene	Barrels/day 307
Toluene	108
Xylene	44
Total BTX	459
Paraffins	41
Total feed	500
Products:	
BTX—	
Benzene	336
Toluene	92
Xylene	23
Total BTX	451
Light hydrocarbons:	
Ethane and lighter	114.6 million B.t.u./day.
Propane	2.2 bbls./day.
Butane	21.9 bbls./day.

From this table it will be seen that the benzene yield of the process is in excess of 100%, taking into account the fact that 336 barrels of benzene are recovered for

every 307 barrels of benzene charged. Thus, substantial disproportionation and little gas or coke loss is obtained in a single pass through the reactor. At the same time the paraffin content of the feed is substantially eliminated; the resultant benzene is essentially sulfur-free and meets commercial specifications for nitration grade benzene.

The temperature at which hydrocracking is effected not only has a bearing on the extent to which toluene and xylene are demethylated but has a bearing on the degree of desulfurization obtained, which, in the production of pure benzene, is of great importance. For example, in respect to a feed stock having a sulfur content of approximately 2000 p.p.m., the following table shows sulfur content of the end product under varying temperature conditions.

Reactor temperatures:	Sulfur content, p.p.m.
1050° F.	346
1150° F.	135
1250° F.	99

A sulfur content of 100 p.p.m. is considered to be essentially sulfur-free in the trade. The benzene produced according to the present invention, whether obtained from coal tar light oil, catalytic reformate, or other benzenoid or alkyl benzene sources, is of 99.5+ % purity, boils within a range of 0.8° C., and is negative to the copper strip corrosion test.

One method of practicing the invention continuously on a commercial scale as an adjunct to a petroleum refinery operation to which coal tar light oil readily can be shipped by rail for conversion is illustrated in the accompanying diagram according to which the hydrogen employed for the hydrocracking operation is furnished as hydrogen off-gas from a catalytic reformer. This is supplied through line 1 to a gas compressor 2. The coal tar light oil is supplied through line 3 to a feed pump 4, and the hydrogen gas and charge stock, commingled in line 5, pass through a heater 6 wherein the temperature of the mixture is elevated to a temperature sufficient to inaugurate and support selective cracking, or provide desired autocatalytic effect, for example, to a temperature of 1150° F. or more. This temperature may vary depending upon the weight hourly space velocity in the reactor and may be considerably higher if the reactor is provided with a coolant to remove excess heat therefrom. A weight hourly space velocity of 1.0 pound of coal tar light oil per pound of catalyst is suitable but may be increased up to approximately 5. The molal hydrogen to coal tar light oil ratio may be from 1.0-10; a ratio of approximately 5.0 has been found practical. These ratios may be varied to accommodate variations in the impurity level of the stock.

The hot feed stream passes through line 7 to the reactor 8 wherein a pressure of approximately 500 p.s.i.g. is maintained as provided by the compressor 2 and feed pump 4. The reactor contains a fixed bed of catalyst as described through which the reactor feed is passed. As previously indicated, flow rate is preferably adjusted to provide a contact time or time of residence within the reactor of approximately twelve seconds. As will be understood by those skilled in the art, the reactor pressure may be varied from approximately 100 to approximately 1000 p.s.i.g., the 500 p.s.i.g. pressure disclosed herein being an operating pressure which is practical to employ.

The reactor output passes through line 9 and a cooler 10 into a condenser 11 wherein the liquid product is condensed. The output stream then passes through line 12 into a flash drum 13 which may be maintained for example at a pressure of approximately 490 p.s.i.g. and a temperature of 100° F. Gases non-condensable under the flash drum conditions of temperature and pressure are liberated from the stream at this point.

Gases from the flash drum 13 pass through line 14 into an absorber 15 which may be held at a pressure of

approximately 400 p.s.i.g. and a temperature of 100° F. The absorber operates in conjunction with a stabilizer 16 and a recirculating liquid product stream which is passed into the absorber as lean oil through line 19. Liquid product collected in the flash drum is led through line 18 to be commingled with fat oil from the absorber in line 17. In this manner valuable liquid product contained in the flash drum vapor is recovered in the absorber while the dry gas from the absorber is withdrawn through line 21 for use as plant fuel. The stabilizer may be operated for example at a temperature of approximately 155° F. and a pressure of 75 p.s.i.g. The necessary heat of vaporization for the stabilizer is supplied by reboiler 22 with the vapors returning to the stabilizer through line 23.

A portion of the stabilizer bottom liquid is used as lean oil and is passed through a cooler 24 which discharges at a temperature of approximately 100° F. to a recirculation pump 25. Also, the stabilizer overhead, withdrawn through line 26, operates in conjunction with a reflux system comprising condenser 27 and receiver 28, the liquid reflux collecting in the receiver at a temperature of approximately 100° F. and being recirculated to the stabilizer by pump 29.

The other portion of the stabilizer bottoms is withdrawn through line 30 and passes into a fractionation system comprising one or more fractionating columns which may be of conventional design and which therefore are not shown in detail. In the fractionation system shown, benzene is withdrawn from the first fractionating tower 31, the overhead being finished benzene, while the bottoms product of fractionator 31 is charged into fractionator 32 from which toluene is the overhead product. Similarly, the bottoms product from fractionator 32 is passed to fractionating column 33 which provides mixed xylenes as the overhead while the bottoms product of fractionator 33 is a heavy end oil which may be used as fuel oil. In this procedure the total equipment cost is less than half the amount required for production of benzene of equal purity by the process of hydrodesulfurization and solvent extraction which is now being installed by some coke oven operators and is the only known commercial alternative to such recovery.

It will be noted that the time of contact during which the feed is in contact with the catalyst, for example only ten to twelve seconds as indicated, is very short. It is also apparent, however, that the catalyst activity is very high inasmuch as the catalyst effects rapid demethylation in a single rapid pass of the stock through the fixed bed in this short time period. The unusual and unexpected result is that a catalyst possessing such a high degree of catalyst activity at the prevailing unusually high temperature, is nevertheless selective in its action, effectively splitting methyl groups from toluene and xylene and effectively cracking sulfur-bearing impurities and paraffins without degrading the benzene content of the feed.

While the invention has been disclosed principally in relation to the recovery of purified benzene from coal tar light oil, the invention is also useful for the treatment of other types of charge stocks containing benzene such as relatively high boiling catalytic reformat fractions. For example, a catalytic reformat boiling in the 300°-400° F. range, containing 80-85% alkyl substituted benzenes and 15-20% paraffins may be used as the charge stock in the practice of the present invention to produce a high yield of benzene, thereby up-grading the commercial value of the reformat. Thus, the treatment of such feed material at a rate of 49,000 gallons per day yields 23,400 gallons per day benzene, 11,000 pounds per day refined grade naphthalene, and 516 gallons per day of a heavy residue usable for heavy fuel, as well as 2,837,000,000 B.t.u. per day of gas.

Having described my invention, I claim:

1. The process of recovering benzene of at least nitration grade purity from an impure hydrocarbon stock containing benzene and alkyl benzene components which

process comprises subjecting the said stock, in a single pass, to catalytic cracking conditions in the presence of hydrogen and a catalyst consisting of approximately 10 to 15% by weight of chromium oxide on a high purity low sodium content gamma-type alumina support, at a temperature above approximately 1200° F. whereby a high yield of benzene is obtained.

2. The process of recovering and purifying benzene from coal tar light oil, which process comprises subjecting the coal tar light oil, in a single pass, to catalytic cracking conditions in the presence of hydrogen and a catalyst consisting of approximately 10 to 15% by weight of chromium oxide on a high purity low sodium content gamma type alumina support, at a temperature above approximately 1200° F. whereby a high yield of the aromatic product is obtained.

3. The process which comprises subjecting a stock containing benzene and alkyl benzene compounds to a catalyst consisting of approximately 10 to 15% by weight of chromium oxide on a high purity low sodium content gamma type alumina support, at a temperature above approximately 1200° F., in a single pass, and in the presence of hydrogen for a period of time not substantially exceeding approximately twelve seconds but sufficient to convert alkyl benzene components into benzene and gas, then separating the gas from the benzene so produced whereby a high yield of benzene is obtained from the said stock.

4. A process of recovering high purity benzene from crude benzol containing sulfur and paraffinic compounds which method comprises subjecting the crude benzol to catalytic hydrocracking conditions, in a single pass, at a temperature of at least approximately 1150° F. in the presence of a catalyst comprising 10 to 15% chromia by weight supported on high purity low sodium content gamma type alumina, for a period of time sufficient to demethylate alkyl benzene components of the crude benzol and destructively crack sulfur and paraffinic impurities to gas whereby a high yield of the aromatic product is obtained.

5. The process of claim 4 wherein the hydrocracking temperature is approximately 1250° F.

6. The process of claim 4 wherein the catalytic hydrocracking operation is conducted in the presence of hydrogen off-gas obtained from a catalytic reformer.

7. The process of claim 1 wherein the hydrocarbon stock is coal tar light oil.

8. The process of claim 1 wherein the hydrocarbon stock is a catalytic petroleum reformat boiling above the gasoline boiling range.

9. The process of claim 1 wherein the hydrocarbon stock is catalytic petroleum reformat boiling in the range of approximately 300-400° F.

10. The process of claim 3 wherein the catalyst contains approximately 11.8% chromia on the said support.

11. The process of claim 3 wherein the chromia is in the form of hexagonal crystals.

12. The process of claim 4 wherein the hydrocracking operation is conducted by passing a stream of the stock through a fixed bed of the said catalyst.

13. The process which comprises selectively splitting methyl groups from toluene and xylene and concurrently destructively cracking paraffins contained in a hydrocarbon stock containing benzene in admixture therewith which process comprises passing a stream of the stock and a stream containing hydrogen gas into contact with one another, in a single pass, at a temperature above 1200° F. in the presence of a catalyst consisting essentially of approximately 10 to 15% by weight of chromia, the balance of the catalyst composition being high purity low sodium content gamma type alumina whereby a high yield of benzene is obtained from said hydrocarbon.

14. The process of recovering benzene of at least nitration grade purity from hydrocarbon stock containing a substantial proportion of an alkyl benzene component which process comprises subjecting the stock, in a single

pass, to catalytic cracking conditions in the presence of hydrogen and a catalyst consisting of approximately 10-15% by weight of chromium oxide on a high purity low sodium content gamma type aluminum support at a temperature above approximately 1200° F. whereby a high yield of benzene is obtained from said hydrocarbon stock.

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