United States Patent Office 2,957,925
Patented Oct. 25, 1960

2,957,925

METHOD OF TREATING A CRUDE BENZENE WITH PURIFIED COKE OVEN GAS

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No Drawing. Filed Sept. 26, 1956, Ser. No. 612,094

Claims priority, application Germany Nov. 18, 1955

4 Claims. (Cl. 260—674)

This invention relates to an improved method for the treatment of a crude benzene with a purified coke oven gas.

The crude coke oven gas as well as the coke oven gas purified by known processes, e.g. by the application of iron oxide or iron ores, contain impurities which cause deposits and stoppages in the compressor and in the pipes, when the gas is compressed to pressures above 20 atmospheres.

By the purification of the crude coke oven gas with the aid of known processes only the bulk of the impurities, especially hydrogen sulfide, is eliminated, whereas small amounts of impurities as for example unsaturated hydrocarbons, sulfur compounds and/or oxygen compounds remain in the gas. The gas thus partly purified is fit for the combustion in heaters and so on, but it is not suitable for the compression to pressures above 20 atmospheres, for the said impurities form resinous substances which cause the deposits and stoppages mentioned above.

I have now found and this is the object of my invention that the said disadvantages can be avoided by first compressing the unpurified or only partly purified coke oven gas to a pressure up to about 20 atmospheres, e.g. 3, 5, 10 or 15 atmospheres, leading it at elevated temperature over a hydrogenation catalyst and further compressing the gas thus treated to a higher pressure.

As hydrogenation catalysts there come into question the compounds of metals of the 1st to 8th groups known in this art, as for example the oxides, sulfur compounds and phosphorus compounds of the heavy metals, advantageously the metals of the 4th to 8th groups, as well as metals of the platinum and palladium groups. The said compounds can also be applied to carriers. Suitable catalysts are for example the sulfides or oxides of molybdenum and tungsten, preferably in combination with nickel sulfide or nickel oxide, further the sulfides or oxides of molybdenum on activated alumina or mixtures of the sulfides or oxides of molybdenum with the sulfides or oxides of cobalt preferably on activated alumina. The catalysts may be rigidly arranged in the reaction chamber or may be brought into contact with the gas to be treated while they are in moving condition, for example in a fluidized bed.

As the reaction temperature for the hydrogenation of the injurious constituents, temperatures between 150° C. and 300° C., advantageously between 180° and 250° C., are chosen. The throughput of the gas mounts to at least 100 litres, advantageously more than 500 litres, preferably 1,000 litres or more per litre of catalyst volume per hour. After the catalytic treatment, the coke oven gas can be cooled and any liquid formed separated.

The gas thus treated is free from noxious constituents and can be compressed to pressures higher than 20 atmospheres, e.g. 30, 50, 100, 300, 500 atmospheres or more, without any deposition occurring in the apparatus.

The gas is suitable for use for the cracking, aromatizing and refining hydrogenation, and it can also be used

with good results for the refining of benzene hydrocarbons, for example for the refining of light oil fractions boiling about between 80° and 150° C. or 80° and 220° C.

Also when the coke oven gas pretreated according to this invention is used for the production of heat, no stoppages occur in pipes, burner nozzles and the like.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

Example 1

Crude coke oven gas is compressed to 15 atmospheres. The gas leaving the compressor at about 120° C. is heated up to 200° C. by heat exchange with gas already treated and by additional supply of heat with the aid of a preheater and then led over a catalyst consisting of active alumina which has been provided with cobalt molybdate, in an amount of 1,500 litres per litre of catalyst volume and per hour. At the beginning of the reaction the gas has a temperature of 200° C., while on leaving the reaction chamber it has a temperature of 220° C. The hot gas gives up its heat in the heat exchanger to the fresh gas, is then further cooled and compressed in a compressor to 70 to 100 atmospheres or more.

Whereas by the compression of the crude coke oven gas to 70 to 100 atmospheres stoppages occur in the compressor and attached pipes even after 2 days, the catalytically treated coke oven gas can be compressed without disadvantageous deposits becoming evident.

Example 2

A dust-free unpurified coke oven gas compressed to 3 excess atmospheres is heated to 215° C. and then led at this temperature through a reaction chamber which has been filled with a catalyst consisting of tungsten sulfide and nickel sulfide on alumina. The amount of coke oven gas amounts to 1,000 litres, measured without pressure, per litre of catalyst per hour. After leaving the reaction chamber the gas is cooled. A small amount of an aqueous liquid thereby separates and is removed. The gas is further compressed to 60 atmospheres. In the compressor and the associated pipes, no deposits are observable even after operation for long periods.

Example 3

Unpurified coke oven gas which contains 54% of H_2, 5.9% of CO, 3% of unsaturated hydrocarbons, 0.8% of H_2S and for the rest CH_4, CO_2, N_2, O_2 and also small amounts of NO (5 ccs. of NO in 1 cubic metre of gas), is compressed to 15 atmospheres, heated to 210° C. and then led at this pressure and this temperature over cobalt molybdate on alumina as catalyst. For each litre of catalyst and each hour, 2.1 cubic metres of gas are led into the reaction chamber filled with catalyst. The gas thus purified is then further compressed to 60 atmospheres, 235 litres of this gas (measured without pressure) are heated with circulating gas together with 1 kilogram of crude benzene to a temperature of 200° C. and supplied to an evaporator vessel. In this vessel the substances tending readily to form resins which are contained in the benzene are wtihdrawn at the lower end. The vaporizable benzene fraction, which leaves the evaporator vessel at the top, is further heated up to 350° C. and then passes over 2 litres of a catalyst consisting of cobalt molybdate on alumina. The vapors leaving the catalyst chamber are cooled and led into a pressure separator. Herein the gas is withdrawn at the top and 1,270 litres per hour returned in circulation. The liquid pressure raffinate is withdrawn at the lower part. In order to maintain the necessary hydrogen partial pressure of 20 atmospheres in the reaction chamber, 138 litres are decompressed each hour from the gas circulation.

By working in this way undesirable depositions of polymers do not occur either upon compression of the coke oven gas or upon heating the crude benzene and coke oven gas.

Example 4

The coke oven gas is compressed as described in Example 3 and heated up together with the crude benzene to 200° C. and led at this temperature over a catalyst consisting of nickel sulfide and tungsten sulfide on alumina. The catalyst loading amounts to 0.5 kilogram of crude benzene per litre of catalyst per hour. The gas and oil vapor leaving the catalyst chamber at 230° C. is further heated up to 350° C. and led through a second reaction chamber which is filled with the same catalyst. The gas and oil vapor leaving the reaction chamber at 375° C. is further treated as described in Example 3.

Also in this case no deposition of polymers is observed.

I claim:

1. A process for treating a crude benzene with purified coke oven gas which comprises subjecting coke oven gas to pressures above about 3 atmospheres but not about about 20 atmospheres, heating the compressed gas to from 150° to 300° C. while subjecting said heated gas to catalytic treatment with hydrogenation catalysts, and thereafter subjecting said gas to further compression to a pressure above 20 atmospheres, heating said gas together with recycle stock gas and a crude benzene to a temperature of about 200° C., supplying the mixture to an evaporator vessel from which the formed resins are downwardly withdrawn, the vaporizable benzene fraction coke oven gas and recycle stock gas upwardly withdrawn, further heating the vaporized benzene, recycle and coke oven gas to about 350° C. and passing said mixed gases over a hydrogenation catalyst, cooling the gases leaving the catalyst chamber and leading them into a pressure separator, withdrawing the liquid raffinate and returning the uncondensed gases as recycle stock.

2. A process for treating a crude benzene with purified coke oven gas which comprises subjecting coke oven gas to pressures above about 3 atmospheres but not above about 20 atmospheres, heating the compressed gas to from 150° to 300° C. while subjecting said heated gas to catalytic treatment with hydrogenation catalysts, and thereafter subjecting said gas to further compression to a pressure above 20 atmospheres, heating said gas together with a crude benzene to a temperature of about 200°, passing the mixture over a hydrogenation catalyst, further heating the gas and benzene vapor up to about 350° and leading the mixture over a hydrogenation catalyst, cooling the gases leaving the catalyst chamber, leading them into a pressure separator and separating the so-treated benzene from said gas.

3. A process as claimed in claim 2, wherein each of the hydrogenation catalysts is cobalt molybdate on alumina.

4. A process as claimed in claim 2, wherein each of the hydrogenation catalysts is a mixture of nickel sulfide and tungsten sulfide on alumina.

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