

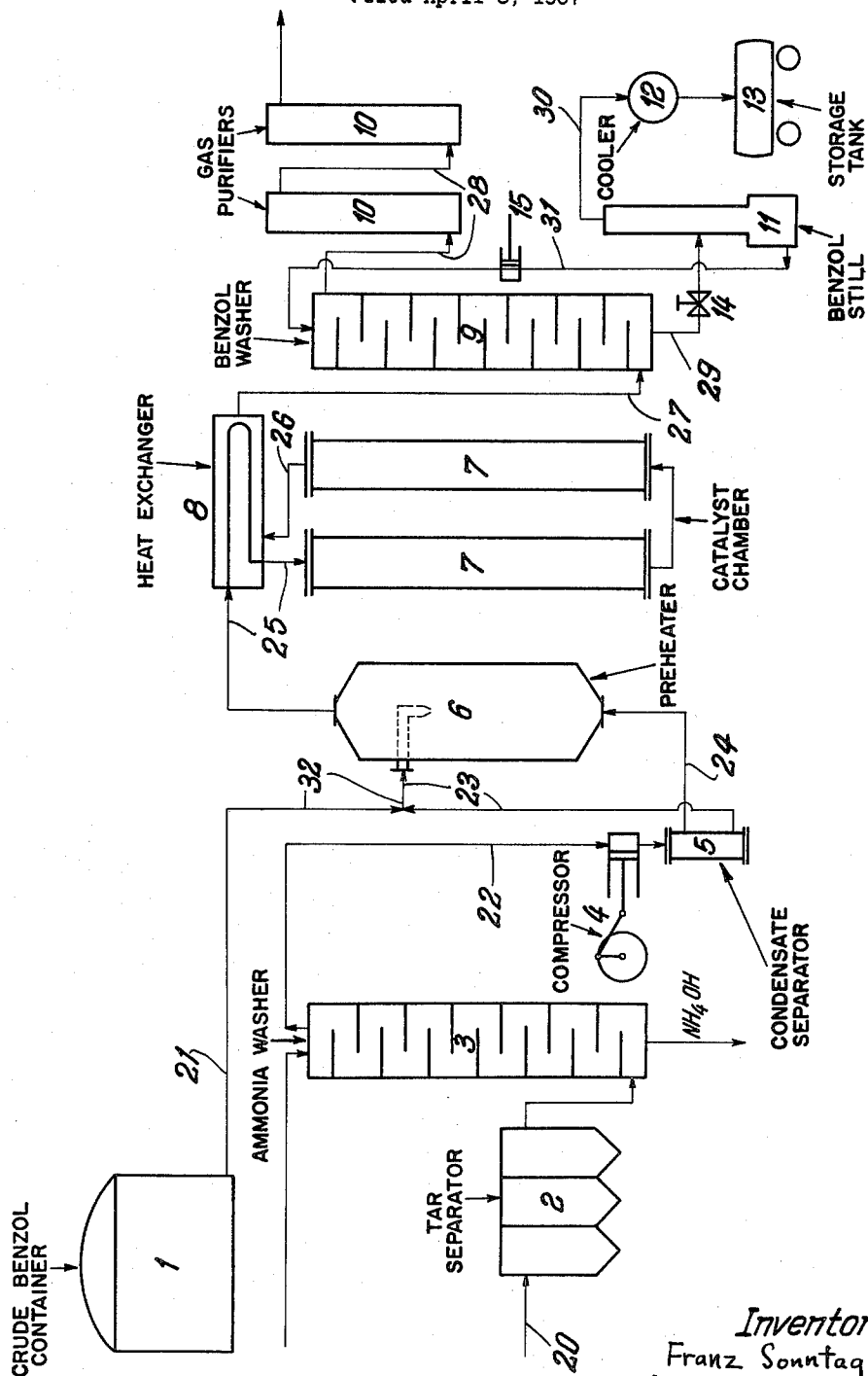
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F. SONNTAG

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METHOD OF PRODUCING REFINED BENZOL

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Inventor:
Franz Sonntag
By Michael S. Stricker
att.

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METHOD OF PRODUCING REFINED BENZOL

Franz Sonntag, Dortmund-Mengede, Germany, assignor to Gelsenkirchener Bergwerks Akt.-Ges., Essen, Germany

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The present invention relates to a method of producing refined benzol, and more particularly it relates to a method of producing refined benzol from coke oven gas containing crude benzol.

Several processes of refining a crude benzol obtained from coke oven gas are known. Recently several methods have been published all of which have in common that they are based on a so-called catalytic refining pressure hydrogenation. These latter methods are based on what has been proposed in the German Patent No. 550,123 to M. Pier. According to these pressure refining processes, the crude benzol is vaporized at pressures exceeding 36 atmospheres in a stream of pure hydrogen gas or in a stream of free hydrogen-containing gas, and is then passed over a catalyst maintained at a temperature of between 350 and 400° C. The catalyst consists of sulfides of elements belonging to the sixth and eighth group of the periodic system and causes a cracking hydrogenation of the oxygen, nitrogen and sulfur bonds in the crude benzol, as well as saturation of easily hydrogenizable unsaturated compounds. Aromatic constituents of the crude benzol are not attacked under the above conditions of refining hydrogenation.

These known processes of refining the crude benzol contained in coke oven gas have in common that the crude benzol has first to be removed from the coke oven gas by a scrubbing process by absorption on activated carbon or by any other suitable process, and that the thus isolated crude benzol has then to be evaporated into a relatively small quantity of a free hydrogen-containing gas, prior to being passed over the catalyst. Thus, the recovery and refining of crude benzol from coke oven gas is a multi-step high-pressure process requiring a relatively large investment and involving considerable operating costs.

It is therefore an object of the present invention to overcome the above mentioned disadvantages in the production of refined crude benzol from coke oven gas.

It is another object of the present invention to devise a process for the production of refined benzol from coke oven gas, which process may be carried out in a simple and economical manner.

It is a further object of the present invention to provide a process for producing refined benzol from coke oven gas, without the addition of hydrogen containing reducing gases other than those contained in coke oven gas.

It is still another object of the present invention to produce refined benzol from coke oven gas without requiring separation of crude benzol from the coke oven gas.

Other objects and advantages of the present invention will become apparent from a further reading of the description and the appended claims.

With the above objects in view, the present invention mainly comprises in a method of producing refined

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benzol from ammonia-free coke oven gas containing crude benzol, the steps of compressing the ammonia-free coke oven gas, contacting the compressed gas with a sulfide catalyst so as to partially crack and hydrogenate the crude benzol contained in the compressed gas, thereby refining the crude benzol, and scrubbing the thus treated gas with a wash oil so as to form a solution consisting essentially of the refined benzol dissolved in the wash oil.

According to a preferred embodiment, the present invention consists in a method of producing refined crude benzol from coke oven gas containing crude benzol, comprising the steps of freeing the coke oven gas of ammonia, compressing and heating the substantially ammonia-free coke oven gas to a pressure of between about 13 and 16 atmospheres and a temperature of between about 350 and 380° C., contacting the heated and compressed crude benzol-containing ammonia-free coke oven gas with a sulfide catalyst so as to at least partially crack and hydrogenate the crude benzol contained in the compressed coke oven gas, thereby refining the crude benzol, scrubbing the thus treated gas with a fully hydrogenated wash oil so as to form a solution consisting essentially of the refined benzol dissolved in the wash oil, and separating the refined benzol from the wash oil.

Surprisingly it has been found that it is not necessary to remove from the coke oven gas the crude benzol, which generally is present therein in a quantity of about 25 grams per normal cubic meter of coke oven gas, and to subsequently evaporate the crude benzol and mix the same with a small quantity of a suitable gas before subjecting the crude benzol to catalytic pressure refining.

According to the present invention, two steps which were essential according to the prior art processes, namely separation of the crude benzol from the coke oven gas and subsequent evaporating and mixing of the separated crude benzol with a hydrogen containing gas can be omitted, and the crude benzol can be refined at relatively low overpressures while still being contained in the coke oven gas. This is accomplished by passing coke oven gas from which ammonia has been removed but which still includes its original contents of crude benzol, over any one of the sulfide catalysts conventionally used for refining hydrogenation of crude benzol, whereby the temperature and pressure of the crude benzol-containing, ammonia-free coke oven gas, as well as the period of time for which the gas is to be in contact with the catalyst are to be so adjusted as to achieve the desired refining effect.

Thus, according to a preferred embodiment of the present invention, the coke oven gas after removal of tar and ammonia therefrom is compressed and heated to the temperature of the catalyst and passes in this condition through the catalyst-containing vessel, in contact with the catalyst, prior to removal of hydrogen sulfide and separation of the refined benzol from the gas. It depends primarily on the type of wash oil which is to be used whether removal of hydrogen sulfide is to be carried out prior or after separation of the refined benzol from the remainder of the gas.

The novel features which are considered as characteristic for the invention are set forth in particular in the appended claims. The invention itself, however, both as to its construction and its method of operation, together with additional objects and advantages thereof, will be best understood from the following description of specific embodiments when read in connection with the accompanying drawing, in which the figure is a schematic representation of the process of the present invention.

Referring now to the drawing, it may be seen that crude coke oven gas enters tar separator 2 as indicated

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by arrow 20. The gas then passes through ammonia washer 3 in countercurrent flow to water which is introduced into the ammonia washer 3 as indicated by arrow 21. As indicated by arrow 22, the gas which thus has been freed from tar and ammonia passes through compressor 4 into condensate separator 5. The gas then passes, as indicated by arrow 23, into preheater 6. The condensate which has been separated from the gas in condensate separator 5 may be sprayed into preheater 6 as indicated by arrow 24. From preheater 6, the gas then passes as indicated by arrow 25 through heat exchanger 8 into catalyst chamber 7 in which contact is made between the catalyst and the crude benzol containing coke oven gas. From catalyst chamber 7, the gas containing the now cracked and hydrogenated crude benzol passes through heat exchanger 8, as indicated by arrow 26, and from there after giving off heat, the gas reaches benzol washer 9 as indicated by arrow 27. Between heat exchanger 8 and benzol washer 9, a hydrogen sulfide remover of conventional construction (not shown in the drawing) may be arranged. In benzol washer 9, the refined benzol is dissolved in wash oil and separated from the remainder of the coke oven gas. The gas passes from benzol washer 9 through gas purifier 10 as indicated by arrows 28. The solution of refined benzol in wash oil leaves benzol washer 9 as indicated by arrow 29 and passes through expansion valve 14 into benzol still 11. In benzol still 11, the refined benzol is distilled-off and passes in vapor form, as indicated by arrow 30, to cooler 12, and from there in liquid form to stationary or movable tank 13. The wash oil from which benzol has been distilled-off in benzol still 11 passes from there through pump 15 into benzol washer 9, as indicated by arrow 31.

An installation such as described above is primarily designed for use in connection with and adjacent to a central coking plant. In addition to refining crude benzol contained in the coke oven gases produced in the central coking plant, the installation may also be employed for refining crude benzol obtained in small coking units the capacity of which would not warrant a separate installation as described above. In such small coking plants, the crude benzol may be washed out of the coke oven gas in conventional manner and transported to container 1 of the drawing. From container 1 crude benzol may be added, as indicated by arrows 32, to the ammonia-free crude benzol-containing coke oven gas originating from the central coking plant, preferably prior to introduction of the coke oven gas into preheater 6.

The following example is given as illustrative of the process of the present invention only, the present invention, however, not being limited to the specific details of the example.

Example

Crude coke oven gas from which ammonia has been removed is passed from the ammonia washer through a one-stage compressor in which the gas is compressed to between 13 and 16 atmospheres. The compressed gas is heated in a heat exchanger to a temperature of between about 350 and 380° C. The thus heated and compressed gas then passes through a catalyst chamber in such a manner that 0.5 cubic meters of compressed gas per minute and per cubic meter of contact space flow through the catalyst chamber.

As previously stated, any crude benzol which might have condensed during compression of the coke oven gas, is separated from the compressed gas in condensate separator 5, and is introduced into preheater 6 by means of a small injection pump (not shown in the drawing). In preheater 6 such crude benzol condensate evaporates and becomes again part of the gaseous mixture of crude benzol containing coke oven gas.

The coke oven gas leaving catalyst chamber 7 and containing refined benzol, passes through a heat exchanger

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in which some of the heat of the refined benzol-containing gas is given off for heating crude benzol-containing coke oven gas, prior to its introduction into the catalyst chamber. Thereby a small portion of the refined benzol is condensed. However, the major portion of the refined benzol is removed from the remainder of the coke oven gas by washing with a completely hydrogenated wash oil such as Arsol-II-Fraction, dekalin or tetralin. Generally, a wash oil incapable of forming resinous or gummy substances should be used.

The coke oven gas coming from the ammonia washer contains 25.5 grams of crude benzol per normal cubic meter.

The composition of the crude benzol contained in the coke oven gas entering the catalyst chambers is of approximately the following composition:

Bolling range, °C.	Liquid volume, percent	Bromine Number g./100 g.
30-79.5	4.5	10
79.5-80.5	66.0	4.5
80.5-109.5	1.5	15
109.5-110.5	13.5	5.5
110.5-133	1.0	12
133-145	7.0	8.5
145-180	1.5	45
>180	5.0	20

The crude benzol is cracked and hydrogenated in the catalyst chamber and thereby refined so that the coke oven gas leaving the catalyst chamber contains refined benzol of approximately the following composition:

Bolling range, °C	Liquid volume, percent	Bromine Number g./100 g.
57-70	1.0	2.6
70-70.5	3.0	1.2
70.5-79.5	1.0	0.27
79.5-80.5	67.0	0.05
80.5-109.5	1.0	0.68
109.5-110.5	13.0	0.10
110.5-123.0	0.5	0.10
123.0-123.5	4.5	0.22
123.5-138.0	0.5	0.28
138.0-138.5	4.0	0.65
138.5-200	3.0	>2.0

¹ Benzene.

² Toluene.

³ Xylene.

The catalyst employed in catalyst chambers 7 was produced in customary manner by imbibing activated carbon with a solution of molybdenum oxide and cobalt nitrate in ammonia, and subsequent drying of the thus treated activated carbon. The thus prepared catalyst becomes fully effective only in an atmosphere containing large quantities of hydrogen sulfide.

As stated above, all of the sulfide catalysts customarily used for refining crude benzol may be used in accordance with the present invention preferably sulfides of chromium, molybdenum or tungsten which are deposited on carriers such as aluminium oxyde, pumice, activated carbon or clay. These sulfides may also contain as promoters small amounts of ferric-, nickel- or cobalt sulfide.

Such catalysts under the selected process conditions cause an effective refining of the crude benzol. Such catalysts are traded ready for use and are described for instance in "Petroleum Processing," August 1955, p. 1174, lines 14ff, p. 1188, left side, p. 1190 left side, p. 1194 left side, and in the German Patent 665,228 as well as in various newer patents.

The best result was reached with a catalyst which contained about 10% Mo and 1% Co in sulfide form deposited on carbon of commercial quality obtained by gas adsorption.

However the process does not depend on using a par-

ticular catalyst but a main condition is that the gas contains about 5 to 15 grams H_2S per cubic meter.

Prior to removing the refined benzol from the remainder of the coke oven gas, it is preferred according to the present invention to remove from the gas hydrogen sulfide which usually is present in a quantity of about 15 grams per normal cubic meter of gas leaving the catalyst chambers. Removal of hydrogen sulfide from the gas may be carried out in any conventional manner such as is described, for instance, in Gluud and D. L. Jacobson International Handbook of the By-product Coke Industry, New York 1932, Chapter 9, pp. 533-583.

Preferably, the coke oven gas containing the crude benzol is subjected to catalytic treatment at a pressure of between 5 and 30 atmospheres and a temperature of between 300° and 450° C., and most preferably the catalytic treatment is carried out at a pressure of between 13 and 16 atmospheres and at a temperature of between 350° and 380° C.

The coke oven gas remaining after removal of refined benzol and hydrogen sulfide is, if desired, further purified prior to being pumped into pipes for long-distance gas supply.

The small portion of refined benzol which is condensed in heat exchanger 8 may be combined with the major portion of refined benzol which has been distilled off from the wash oil, and the entire thus refined benzol may be either used as motor fuel or may be further fractionated into its constituents such as benzene, toluene, xylene, etc.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

What is claimed as new and desired to be secured by Letters Patent is:

1. A method of producing refined benzol from coke oven gas containing crude benzol, comprising the steps of removing ammonia from said coke oven gas; compressing and heating the thus formed substantially ammonia-free coke oven gas to a pressure of between about

5 and 30 atmospheres and a temperature of between about 300° and 450° C.; contacting said heated and compressed substantially ammonia-free coke oven gas with a sulfide catalyst so as to at least partially crack and hydrogenate the crude benzol contained in said compressed coke oven gas, thereby refining said crude benzol; and scrubbing the thus treated gas with a wash oil free of gum-forming constituents so as to form a solution consisting essentially of said refined benzol dissolved in said wash oil.

2. A method of producing refined benzol from coke oven gas containing crude benzol, comprising the steps of removing ammonia from said coke oven gas; compressing and heating the thus formed substantially ammonia-free coke oven gas to a pressure of between about 13 and 16 atmospheres and a temperature of between about 350° and 380° C.; contacting said heated and compressed substantially ammonia-free coke oven gas with a sulfide catalyst so as to at least partially crack and hydrogenate the crude benzol contained in said compressed coke oven gas, thereby refining said crude benzol; and scrubbing the thus treated gas with a wash oil free of gum-forming constituents so as to form a solution consisting essentially of said refined benzol dissolved in said wash oil.

3. A method of producing refined benzol from coke oven gas containing crude benzol, comprising the steps of freeing said coke oven gas of ammonia; compressing and heating the substantially ammonia-free coke oven gas to a pressure of between about 13 and 16 atmospheres and a temperature of between about 350° and 380° C.; contacting said heated and compressed crude benzol-containing ammonia-free coke oven gas with a sulfide catalyst so as to at least partially crack and hydrogenate said crude benzol contained in said compressed coke oven gas, thereby refining said crude benzol; scrubbing the thus treated gas with a fully hydrogenated wash oil so as to form a solution consisting essentially of said refined benzol dissolved in said wash oil; and separating said refined benzol from said wash oil.

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