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VAPOR PHASE HYDROGENATION OF PHENOLS

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This invention relates to the hydrogenation of tar acids and mixtures and homologues thereof, to produce cyclohexanols. The expression "cyclohexanols" as used herein is intended to include cyclohexanol and homologues thereof, such as methyl cyclohexanols produced in the hydrogenation of cresols and the dimethyl cyclohexanols produced in the hydrogenation of xylenols. The term "tar acids" is used herein to mean (*a*) compounds of the type of phenol and its homologues obtained as by-products in the distillation, carbonization, or gasification of coal, or in the production of combustible gas including water gas; (*b*) such compounds not so derived but made synthetically; and (*c*) mixtures of such compounds.

According to the investigators in this art, the hydrogenation of phenol at atmospheric pressure and at temperatures of 250° to 300° C., using a nickel catalyst, a recognized active catalyst for hydrogenation reactions results in the production of only benzene. Further, the reaction is slow and "much of the phenol passes by unchanged. If the attempt is made to hasten the reaction by raising the temperature, the benzene is attacked with the formation of methane. The three cresols behave the same way and yield toluene" (page 135 of Paul Sabatier's "Catalysis in Organic Chemistry," translated by E. E. Reid, published in 1922 by D. Van Nostrand Company). According to pages 166 and 167 of Sabatier's work, with reference to investigations at atmospheric pressure,

"Phenol, hydrogenated at 180°, gives immediately cyclohexanol, $C_6H_{11}.OH$, containing 5 to 10% unchanged phenol, small quantities of cyclohexanone and cyclohexene, C_6H_{10}. The mixture boiling between 155° and 165° can be purified by a second passage over the nickel at 150°–170° which changes the phenol and cyclohexanone completely into cyclohexanol.

"o.Cresol is regularly transformed by nickel at 200°–220° into o.methyl-cyclohexanol with a yield of better than 90%***.

"m.Cresol, under the same conditions, gives a mixture of the alcohol and ketone which can be rehydrogenated at 180° to give practically pure m.methyl-cyclohexanol.

"p.Cresol is readily hydrogenated at 200°–230° to form p.methyl-cyclohexanol containing only traces of the ketone which are readily eliminated by bisulphite.

"The xylenols, or dimethyl-phenols, are hydrogenated over nickel with varying degrees of success, 1,3-dimethyl-phenol (4), at 190°–200° changes almost completely to the corresponding dimethyl-cyclohexanol with a little ketone and m.xylene."

Heretofore, it has been considered necessary to conduct vapor phase hydrogenations of tar acids over nickel catalysts at the above temperatures and low pressures, i. e., at pressures of about atmospheric, in order to avoid relatively large losses of material due to unfavorable side reactions, such as the formation of hydrocarbons, and also to avoid overheating of the catalyst with consequent deterioration thereof. The low production rate incident to the use of low pressure has been a serious economic disadvantage in the hydrogenation of tar acids. Higher pressures, i. e., pressures substantially above 1 atmosphere, were not used because they were considered to result in undesirable side reactions and deterioration of the catalyst due to overheating thereof.

It is an object of this invention to provide a process of high production capacity for the vapor phase hydrogenation of tar acids and their homologues to produce cyclohexanols, including mixtures of cyclohexanols and cyclohexanones, with a minimum production of undesirable reaction products. Other objects and advantages will appear from the following description.

We have found that the hydrogenation of tar acids can be carried out at surprisingly high rates with unexpectedly low production of undesirable reaction products and low rate of catalyst deterioration by passing tar acids in vapor phase admixed with hydrogen over hydrogenation catalyst in a reaction zone under the following conditions: (1) maintaining in the catalyst zone an absolute pressure of at least 4, and preferably at least 7, atmospheres, (2) controlling the temperature so that the temperature in the reaction zone where the tar acid-hydrogen mixture initially contacts the catalyst is maintained within the range of 180° to 270° C., preferably from 200° to 260° C., and the temperature in the reaction zone where the reaction mixture is withdrawn is maintained within the range of from 180° to 230° C. preferably from 190° to 230° C., these temperatures being determined by thermocouples disposed along the center of the catalyst mass, and (3) utilizing an excess of at least 700 cubic feet of hydrogen measured at the pressure existing in the catalyst zone and at room temperature per pound mol of the tar acid. Preferably the catalyst adjacent the inlet end of the catalyst zone is of lower activity than that adjacent the outlet end of the zone, so that the reaction mixture is passed over catalysts of high activity after con-

tacting catalysts of lower activity, and the average temperature of the reaction mixture is maintained somewhat lower at the outlet end than at the inlet end of the catalyst zone.

In order to minimize the production of undesirable reaction products and to avoid excessive catalyst deterioration, the reactants should be passed over the catalyst at a linear velocity sufficiently high to obtain turbulent flow of the gases and thus promote distribution of heat in the reaction chambers and the time of contact of the reactants with the catalyst should be relatively short. In practice, the linear velocity of the gases passing over the catalyst should not be less than 1' per second. Thus, in the case of reaction tubes about 4'' in diameter containing common catalysts such as pumice base nickel catalysts or nickel turnings a linear gas velocity of at least 4' per second has been found advantageous. The apparent time of contact of the reactants with the catalyst is not more than 30 seconds, preferably not more than 10 seconds. The use of pressure of at least 4 atmospheres, a temperature of from 180° to 270° C. in the neighborhood of the inlet of the reaction zone, a temperature of 180° to 230° C. in the neighborhood of the outlet, and an excess of at least 700 cubic feet of hydrogen per pound mol of tar acids permits passing the reactants over the catalyst at high linear velocity and utilization of a short period of contact of the reactants with the catalyst while promoting high throughput and reaction rates and minimizing undesirable side reactions such as the formation of hydrocarbons and water.

We have found that in accordance with the invention, the throughput of tar acid-hydrogen reaction mixtures through hydrogenation converters of given size may be greatly increased with corresponding increase in the production rate of cyclohexanols including cyclohexanol-cyclohexanone mixtures with only slight production of undesirable products such as hydrocarbons, e. g. cyclohexane and water. The production rates of the desired hydrogenated products may be increased at least about four-fold as compared with that of prior art vapor phase tar acid hydrogenation processes carried out at about atmospheric pressure. Furthermore, the invention permits the use of higher temperatures than were heretofore considered feasible with consequent increase in the reaction rate while the tendency of the reaction to reverse and reform tar acids from the hydrogenated products is reduced. To obtain optimum results all of the conditions above mentioned should be observed. However, substantial improvement over prior art procedures may be obtained by observing the above specified pressures and temperatures, preferably utilizing the aforementioned excess of hydrogen in the reaction mixture.

As hydrogenation catalysts, promoted or unpromoted nickel, and nickel mixtures, e. g., those containing copper or cobalt, are employed in carrying out the invention. For example, catalysts produced by treating pumice, Alundum, Carborundum, or other support with nickel nitrate solution and decomposing the nitrate to form catalytically active nickel or nickel oxide may be used. Nickel catalyst in the form of turnings, rings, helices, gauze, etc., activated by producing an adherent layer of nickel oxalate on the nickel masses and decomposing the oxalate by oxidation, e. g., heating in air at temperatures of from 300° to 380° C., to convert the oxalate into an adherent layer of catalytic nickel or nickel oxide are suitable. Nickel catalysts produced by treating nickel masses such as turnings, helices, rings or gauze with nitric acid vapors to form an adherent layer of nickel nitrate and decomposing the nitrate layer by roasting to produce an adherent catalytically active layer on the masses may also be employed. Spent nickel hydrogenation catalysts reactivated by heating in air, or otherwise, are suitable.

The reaction may advantageously be carried out in apparatus involving several, e. g., five, catalysts containing reaction tubes or converters arranged in series, which tubes may be maintained at the proper temperature by any suitable means, for example, water under pressure or a water-steam mixture in jackets surrounding the tubes. The phenol or other tar acid is vaporized in a stream of hydrogen which will provide an excess of at least 700 cubic feet, measured at working pressure (the pressure in the reaction tubes) and room temperature, per pound mol of the tar acid, and the vapor mixture passed over the catalyst in the reaction tubes, the hydrogen being preheated prior to mixing with the tar acid so that the vapor mixture is supplied to the catalyst at a temperature not below 180° C. and preferably from 200° to 260° C. The excess hydrogen is separated from the reaction product from the reaction chambers, and mixed with additional tar acid prior to entry of the vapors into the reaction chambers, sufficient make-up hydrogen being supplied to provide the desired excess. As above indicated, the amount of hydrogen circulated through the catalyst should be at least 700 cubic feet, measured at the working pressure (pressure in the reaction zone) and room temperature, per pound mol of tar acid in excess of that required to react with the acid to form the desired cyclohexanol. The maximum amount of hydrogen which may be used depends upon the equipment employed, i. e. the capacity of the hydrogen supply pump, etc.; while any desired amount of excess hydrogen above the minimum may be used, for economic reasons the amount used may be limited to about 3000 cubic feet of excess hydrogen per pound mol of tar acid. The excess hydrogen used in accordance with our invention, we have found, facilitates the control of the temperature in the reaction zone in that it absorbs reaction heat and transfers some of the heat to the converter and also aids in distributing the heat uniformly through the catalyst resulting in the elimination of hot spots and thus minimizing undesirable side reactions. Further the excess hydrogen maintains the tar acids in the vapor phase under the pressure and temperature conditions of the invention, thus preventing condensation of the acids on the catalyst and promoting long catalyst life.

The use of pressure of at least 4 atmospheres and temperatures of from 180° to 270° C., preferably 200° to 260° C., at the inlet end of the system and from 180° to 230° C., preferably 190° to 230° C. at the outlet end of the system, permits high conversion and high throughput of reactants with high production rates of reaction products. Furthermore, the use of such pressures and excesses of at least 700 cubic feet of hydrogen, measured at the working pressure and room temperature, per pound mol of the tar acid minimizes at the specified temperatures the tendency of reversal of the desired reaction to occur. We have discovered that the disadvantages which prior investigators have indicated to be associ-

ated with the use of such high pressures and temperatures in hydrogenation of tar acids, namely, undesirable side reactions, such as the production of cyclohexane, do not occur to an objectionable extent when operating in accordance with the conditions of this invention. While any pressure above 4 atmospheres may be employed, we prefer to utilize pressure above 7 atmospheres; higher pressures may be employed and the upper pressure limit is determined only by the safe working capacity of the equipment. Preferably the temperature at the exit end of the system is maintained somewhat lower than the temperature at the inlet end, e. g., an average temperature of about 210° C. may be maintained at the exit end and an average temperature of about 220° C. maintained at the inlet end.

It is advantageous to employ catalyst of high activity near the outlet of the catalyst zone and catalyst of lower activity near the inlet. The hydrogenation of tar acids to cyclohexanols is an exothermic reaction liberating substantial amounts of heat so that passage of the initial reaction mixture of tar acid vapors and hydrogen into contact with catalysts of high activity liberates large quantities of heat near the inlet end of the reaction zone rendering it difficult to control the reaction. On the other hand, passage of the gas mixture over catalyst of high activity prior to leaving the reaction zone is desirable in order to promote maximum conversion of the reactants to the desired products. As is well known, nickel-type hydrogenation catalysts lose activity during use. In accordance with the invention, freshly prepared highly active catalyst is used near the outlet of the reaction zone and partially spent catalyst of lesser activity is employed near the inlet end of the zone. As the catalyst loses activity during use, it may be shifted from the outlet end toward the inlet end of the reaction zone and fresh catalyst of high activity introduced in the neighborhood of the outlet end, for example, one or more cages of spent catalyst may be removed from the inlet end of the reaction zone, the remainder of the catalyst in the zone shifted toward the inlet end and freshly activated catalyst introduced into the system at the outlet end. If desired, a number of individual converters may be connected by valves and piping so that a converter containing spent catalyst can be withdrawn from service at the inlet end and another converter containing highly active catalyst added to the system at the outlet end of the reaction zone without interruption of operations. Thus a gradient of catalytic activity may be established and maintained in the system, the reactants progressively contacting catalysts of higher activity, permitting control of the reaction and promoting maximum conversion of the tar acid vapors to the desired hydrogenated products. Hydrogenation of about 85–90 per cent of the tar acid may be accomplished while the reaction mixture is passing over catalyst of relatively low activity at a temperature of 180°–270° C. and the remainder of the tar acid hydrogenated while passing over more active catalyst at a temperature of 180–230° C.

Among the materials that may be hydrogenated in accordance with the invention to produce cyclohexanol and mixtures of cyclohexanols and cyclohexanones, may be mentioned phenol, the cresols, the xylenols and other substituted phenols containing from one to five alkyl substituents, each having not more than four carbon atoms. The expression "phenol and its homologues" is intended to include these materials. The material should preferably contain less than .01 per cent each of sulfur and chlorine to avoid excessive deterioration of the catalyst due to poisoning.

The following examples are illustrative of preferred embodiments of the invention.

The catalyst employed in the examples hereinbelow described was a nickel catalyst made by dipping particles of pumice in nickel nitrate solution to form a nickel nitrate coating on the pumice and decomposing this coating by roasting in air to produce a catalytically active nickel oxide layer adhering to the pumice base. The equipment employed involved a vaporizer and 5 reaction tubes, the bottom of each connected to the top of the succeeding tube and each having an internal diameter of 4" and each being 78" long and containing 2 nickel screen catalyst cages. Each cage had an outside diameter of 3⅞", was 36" long was equipped with a central longitudinally disposed tube 1" in diameter, and was packed with about 7 pounds of the nickel catalyst hereinabove described. The catalyst in the last two tubes was of high activity and that in the first three tubes was partially spent catalyst of lower activity. Each reaction tube was fitted with thermocouples located in the central tubes of the catalyst cages. The first three of the reaction tubes in the series were provided with jackets through which were circulated a steam-water mixture for removing the heat generated during the reaction and the other two were electrically heated.

Example I

Synthetic phenol having a melting point of 40° to 41° C. was vaporized and passed through the reaction tubes over the catalyst at the rate of 96 to 100 pounds per hour. The working pressure in the catalyst zone was about 150 pounds per square inch gauge. Hydrogen was mixed with the tar acid vapor prior to contacting the catalyst in the amount of 1100 cubic feet per hour, measured at the working pressure (150 pounds per square inch) and at room temperature, i. e., about 1000 cubic feet of hydrogen, measured at working pressure and room temperature, per pound mol of phenol in excess of that theoretically required to react with the phenol to produce cyclohexanol was employed. The excess hydrogen was separated from the reaction products withdrawn from the reaction tubes, and was recirculated through the reaction tubes with additional phenol vapor, sufficient make-up hydrogen being added to bring the amount of hydrogen introduced into the reaction tubes to 1100 cubic feet per hour, measured at the working pressure and room temperature. A temperature of from 200° to 260° C. was maintained in the first three tubes and a temperature of 200° to 230° C. was maintained in the last two tubes, the average temperature of the last two tubes being about 10° C. lower than in the first three. The reaction mixture passed over the catalyst at a linear velocity of about 6 feet per second and the apparent time of contact of the reactants with the catalyst was about 5 seconds. The run was continued for about 76 hours and produced about 7500 pounds of reaction product which was analyzed and was found to contain about 93.4 per cent of cyclohexanol, 1 per cent of water, 2.5 per cent of cyclohexane, 1.5 per cent of cyclohexanone, and 1.6 per cent of phenol.

Example II

Synthetic phenol having a melting point of 40° to 41° C. was vaporized in a stream of hydrogen and passed through the catalyst at the rate of 108 pounds per hour. The working pressure in the reaction tubes was 200 pounds per square inch gauge. Hydrogen admixed with the phenol vapor prior to contacting the catalyst was in the amount of 1200 cubic feet per hour measured at working pressure (200 pounds per square inch) and room temperature, i. e. about 940 cubic feet of hydrogen, measured at working pressure and room temperature, per pound mol of phenol in excess of that theoretically required to react the phenol to produce cyclohexanol, was employed. The temperatures at the middle of the reaction tubes, as determined for a short interval about half way through the run by thermocouples disposed in the tubes, were as follows: 1st tube, 214° C.; 2nd tube, 245° C.; 3rd tube, 215° C.; 4th tube 216° C.; and 5th tube, 211° C.

The average temperature of the first three tubes was about 225° C. and the average temperature of the last two tubes was about 215° C. Hydrogen was separated from the reaction product withdrawn from the tubes and was recirculated together with make-up hydrogen with additional phenol vapor through the reaction zone. The reactants were passed through the reaction tubes at a linear velocity of about 7.5 feet per second and the apparent time of contact of the reactants with the catalyst mass was about 4 seconds. The reaction product was analyzed and was found to contain about 96 per cent cyclohexanol, 1.2 per cent cyclohexanone, .1 per cent phenol, 2 per cent cyclohexane, and .5 per cent water.

Example III

A mixture of meta and para cresols was passed through the equipment above described at the rate of 96 to 100 pounds per hour. The working pressure within the catalyst zone was 150 pounds per square inch gauge. About 1100 cubic feet of hydrogen per hour, measured at the working pressure (150 pounds per square inch), and at room temperature, was mixed with the cresol vapors prior to contacting the catalyst. A temperature of from 200° to 260° C. was maintained in the first three tubes and a temperature of 200° to 230° C. was maintained in the last two tubes. The reactants were passed through the reaction tubes at a linear velocity of about 6 feet per second and the apparent time of contact of the reaction mixture with the catalyst was about 5 seconds. The hydrogen was separated from the reaction product after withdrawal from the reaction tubes and was recirculated through the tubes in admixture with additional cresol vapors, make-up hydrogen being added to bring the total amount of hydrogen introduced to about 1100 cubic feet per hour, measured at the working pressure and at room temperature. The reaction product was found to contain 93 to 96 per cent methylcyclohexanols, 1.5 per cent of cresols and 1.2 per cent of methylcyclohexanones.

In carrying out the process of this invention, it was found that throughputs of the order of 4 to 8 times that heretofore obtainable by prior known procedures were possible following the conditions of our invention to obtain cyclohexanols and cyclohexanol-cyclohexanone mixtures without substantial loss of reactants by undesirable side reactions such as the formation of hydrocarbons and water. In view of this substantial increase in hydrogenating capacity, it will be seen that the invention represents a marked advance in the hydrogenation of tar acids on the commercial scale.

Since certain changes may be made without departing from the scope of the invention, it is intended that the above shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A process for the vapor phase hydrogenation of material of the group consisting of phenol and substituted phenols containing alkyl substituents, each having not more than 4 carbon atoms, to produce cyclohexanols, which comprises vaporizing the material, contacting the vapor admixed with hydrogen under a pressure of at least 4 atmospheres with nickel-containing hydrogenation catalyst in a reaction zone, the hydrogen being present in amount at least 700 cubic feet, measured at the pressure within the reaction zone and at room temperature, per pound mol of said material in excess of that theoretically required to hydrogenate the material to the corresponding cyclohexanol, maintaining temperature conditions in the reaction zone within the range of from about 180° to about 270° C., a temperature gradient descending in the direction of the flow of the gases being maintained in at least a substantial portion of the reaction zone, and a gradient of catalyst activity ascending in the direction of the flow of the gases being maintained through at least a substantial portion of the reaction zone.

2. A process for the vapor phase hydrogenation of material of the group consisting of phenol and substituted phenols containing alkyl substituents, each having not more than 4 carbon atoms, to produce cyclohexanols, which comprises vaporizing the material, contacting the vapor admixed with hydrogen under a pressure of at least 4 atmospheres with nickel-containing hydrogenation catalyst in a reaction zone, the hydrogen being present in amount at least 700 cubic feet, measured at the pressure within the reaction zone and at room temperature, per pound mol of said material in excess of that theoretically required to hydrogenate the material to the corresponding cyclohexanol, the catalyst being of greater activity in the neighborhood of the outlet of the reaction zone than in the neighborhood of the inlet of the zone, regulating the flow of the mixture of vapor and hydrogen through the reaction zone so that the apparent time of contact with the catalyst is not more than 30 seconds, maintaining temperature conditions within the range of 180° to 270° C. within the reaction zone, a lower temperature within said range being maintained in the neighborhood of the outlet than in the neighborhood of the inlet of said zone.

3. A process for the vapor phase hydrogenation of material of the group consisting of phenol and substituted phenols containing alkyl substituents, each having not more than 4 carbon atoms, to produce cyclohexanols, which comprises vaporizing the material, passing the vapor admixed with hydrogen under a pressure of at least 7 atmospheres through a reaction zone containing nickel hydrogenation catalyst, the hydrogen being present in amount at least 700 cubic feet measured at the pressure within the reaction zone and at room temperature per pound mol of said material in excess of that theoretically required to hydrogenate the material to

the corresponding cyclohexanol, the catalyst being of greater activity in the neighborhood of the outlet of the reaction zone than in the neighborhood of the inlet of the zone, regulating the flow of the mixture of vapor and hydrogen through the reaction zone so that the apparent time of contact with the catalyst is less than about 10 seconds, and maintaining a temperature in the neighborhood of the inlet of the zone within the range of 200° to 260° C. and a lower temperature in the neighborhood of the outlet of the reaction zone within the range of 190° to 230° C.

4. A process as specified in claim 3 in which the material hydrogenated is phenol.

5. A process as specified in claim 3 in which the material hydrogenated is cresol.

6. A process as specified in claim 3 in which the material hydrogenated is xylenol.

7. A process as specified in claim 1 in which the material hydrogenated is phenol.

8. A process as specified in claim 1 in which the material hydrogenated is cresol.

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