

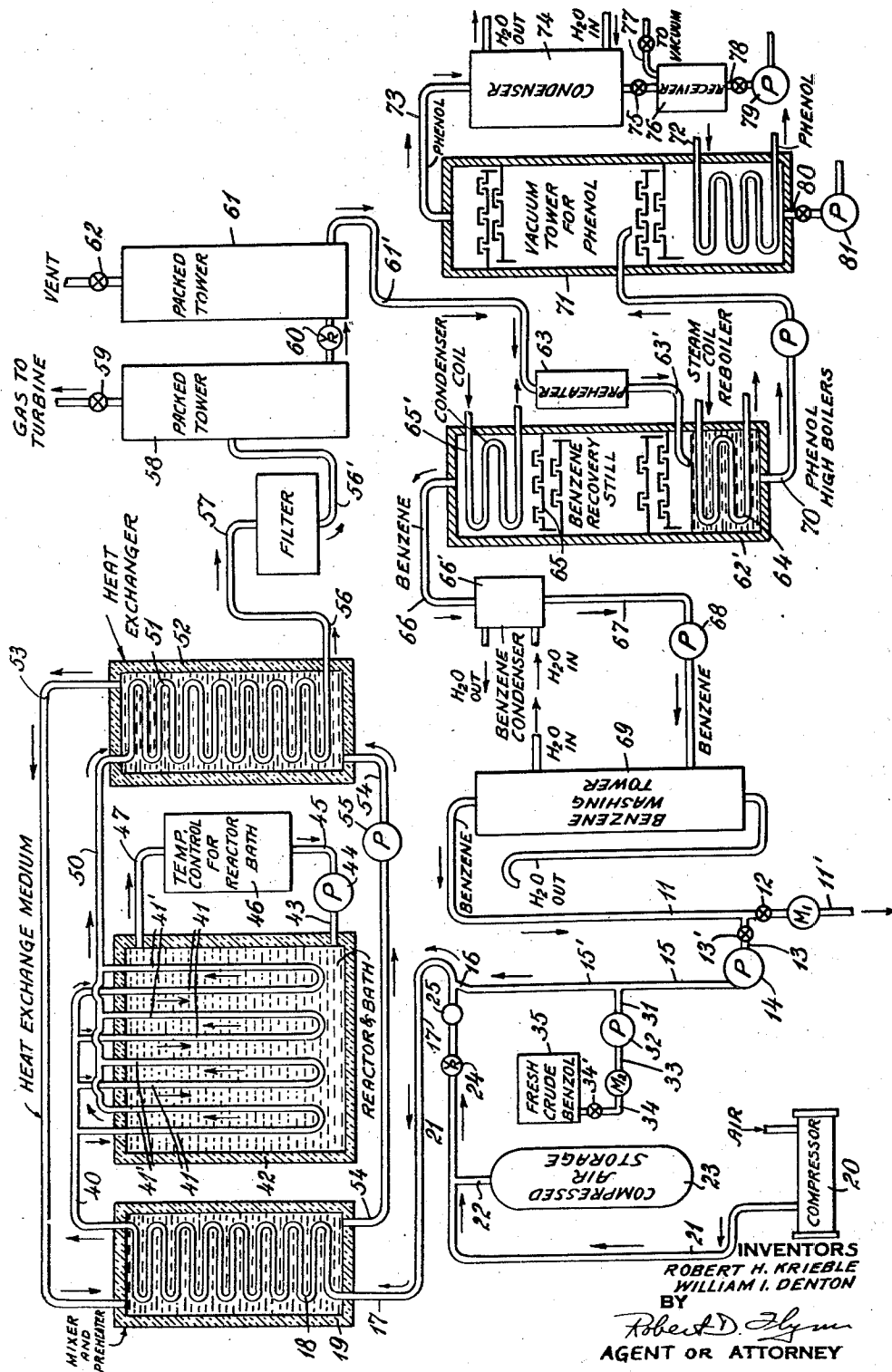
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METHOD OF MAKING PHENOL

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METHOD OF MAKING PHENOL

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This invention has to do with the production of phenol by the oxidation of benzene and is more particularly concerned with that type of process wherein a reaction mixture comprising benzene and oxygen or molecular oxygen-containing gas such as air is passed through a reaction zone void of solid catalyst, under pressure and at elevated temperature.

This application is a continuation-in-part of our copending application Serial No. 465,410, filed November 13, 1942, which, in turn, is a continuation-in-part of our application Serial No. 395,016, filed May 24, 1941.

We are aware of the fact that processes of this general character have heretofore been proposed, and in this regard reference is made to the Bone et al. Patent No. 2,199,585 and the Moyer et al. Patent No. 2,223,383. Each of these patents discloses a process of the general character above referred to, and each mentions that the process therein disclosed can be carried out by recycling. We have discovered, however, that although the process of Bone, for example, if used with a relatively impure grade of commercial benzene, can be operated to obtain a fair yield of phenol on a small number of passes in a recycling operation, the conversion to phenol rapidly decreases with successive cycles, thus materially restricting the scope of the process and rendering it impractical as a recycle operation. We have also observed that if a chemically pure (reagent grade) of benzene is subjected to the process of the Bone patent, no substantial conversion to phenol is obtained.

Since the percentage conversion of benzene to phenol in an oxidation process of the class described is relatively small, it is obviously essential from the standpoint of practicability that the operation be one in which the unconverted benzene can be continuously recycled with a substantially constant conversion and yield of phenol under a given set of operating conditions. It is the primary object of this invention to provide such a process.

It is a further object of this invention to produce substantially pure benzene by such a process.

This invention is predicated upon the discovery that if the concentration of certain impurities, which act as oxidation promoters under the conditions of the reaction in the process contemplated herein, in crude benzol be maintained above a certain minimum hereinafter defined, the conversion and yield of phenol is substantially improved over the conversion and yield without said impurities. Further, the conversion

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and yield will remain substantially constant in a continuous operation for a given set of operating conditions. As used here, the term "crude benzol" denotes a hydrocarbon fraction, the greater portion of which is benzene and a minor portion of which is made up of reaction-promoting impurities.

The promoters or inductors present in crude benzol may be designated, as in the aforesaid copending application, as those compounds which, under the conditions of reaction, are better hydrogen donors than benzenes.

For the continuous operation contemplated herein, a properly proportioned mixture of benzene and oxygen, air or other oxygen-containing gas (one containing oxygen in admixture with one or more other gases), is thoroughly mixed and preheated to the desired temperature and passed through a reactor tube which has been preheated and which, for the purpose of preheating and dissipating the heat of the exothermic reaction, is immersed in a suitable heat transfer bath, such as salt. The reaction mixture, as will hereinafter be explained, is preferably maintained under pressure. With properly-regulated conditions, a portion of the benzene in the crude benzol is thus oxidized to phenol. This phenol and the gaseous and high-boiling products of oxidation are then separated from the unreacted benzene which may still contain some reaction-promoting impurities, or may be free from such impurities, as is probably the case when the original crude benzol has been continually recycled. A portion of the unreacted benzene is subsequently recycled through the mixer-preheater and reactor. Additional air is, of course, added prior to the admission of the unreacted benzene to the mixer-preheater, and in a continuous operation fresh crude benzol in excess, as defined hereinafter, is also added to replace the benzene converted and, more particularly, to maintain the proper concentration of promoter or promoters in the charge. A portion of the unreacted benzene is withdrawn regularly from the continuous operation in order that the promoter concentration be maintained at a desired level. The unreacted benzene or recycle stock, withdrawn from the operation, contains a much greater percentage of benzene than the original crude benzol charged to the reactor tube; therefore, it is valuable for those processes or operations in which substantially pure benzene is required, and in which crude benzol cannot be used.

The expression "fresh crude benzol" used here-
in describes a charge of crude benzol (defined

hereinafter) which has not previously been used in our process.

In such an operation, we have found that where a commercial grade of crude benzol, such as "90% benzol," obtained from coal tar, which is predominantly benzene and contains impurities such as paraffins, cyclohexane and olefins, is used as the charge stock and is recycled through the reactor with no additions of make-up stock under fixed conditions of temperature and pressure, the benzene in the crude benzol loses its reactivity and, further, that the reactivity may be restored only in part through altering the reaction conditions by going to higher temperatures. The charge eventually becomes unreactive, even at relatively high temperatures. The loss of reactivity is directly traceable to the loss of impurities, which function as reaction promoters in the charge. We have also found that when the procedure just described above is altered by adding just enough fresh make-up crude benzol to replace converted benzene—i. e., a "true recycling" operation—the reactivity and conversion to phenol is not markedly increased. This will be demonstrated hereinafter by the results tabulated in Table I. In this "true recycling" operation, the concentration of impurities (or reaction promoters) steadily decreases and this decrease causes a much greater decrease in conversion of benzene to phenol. However, if the recycle operation just described is modified, such that an excess of fresh make-up crude benzol is continuously added to a portion of the unconverted benzene available for recycling and a portion of said unconverted benzene (which is substantially pure benzene) is continuously withdrawn from the reaction product, a steady conversion performance may be obtained and the reactivity, as indicated by the per cent conversion and yield of phenol at a given temperature, is greatly increased. We have found that the reactivity in the process of the latter class, under a given set of conditions, is greatly increased by maintaining in the reaction mixture a certain concentration of certain impurities which act as reaction promoters, and is accomplished by adding an amount of fresh crude benzol in excess of that required to replace converted benzene and at the same time withdrawing a portion of the recycle stock.

In general, all crude benzol fractions may be used in the process contemplated herein. The most important criteria, however, in the selection of said fractions are: the type of impurities or promoters, and concentration of the same therein. Particularly preferred crude benzol fractions are those in which the impurities are predominantly comprised of cyclohexane or olefins, or of cyclohexane and olefins. Less desirable, although they may be used and are contemplated herein, are those fractions in which the impurities or promoters are chiefly paraffins, for such compounds are active only at greater concentrations than those for cyclohexane and olefins.

For a high degree of reactivity of the benzene in the crude benzol used and a high degree of conversion of the said benzene to phenol, the minimum concentration of impurities or promoters therein should be about 0.25%. Satisfactory results may be obtained, however, with concentrations of said promoters as great as about 15%. Preferred are those crude benzol fractions which contain promoter concentrations of from about 2% to about 10%. Although all of the impurities present in crude benzol fractions may not be promoters, it may be assumed, as a rough work-

ing rule, that all materials other than benzene in the more desirable toluene-free benzol stocks will function as promoters. One impurity normally present in crude benzol stocks that is not a promoter, however, is thiophene, which is not a better hydrogen donor than benzene under the conditions of the reaction zone. The promoter concentration can then be determined by difference from the benzene assay of the crude benzol as estimated by any standard method. For example, the method of specific dispersion described by Grosse and Wackler, Ind. & Eng. Chem. Anal. Ed. 11, 614, 1939, is to be preferred for benzols assaying less than 95% benzene.

As aforesaid, the process contemplated herein is characterized by the joint feature of introducing excess fresh feed of crude benzol and removing a portion of unreacted benzene (substantially pure benzene) in order that the promoter concentration be maintained at a desired level. For a given promoter or impurity content in the crude benzol to be used, the excess of fresh feed required should be accurately calculable. For example, under preferred operating conditions, hereinafter defined, the desired promoter concentration in the total feed (unreacted benzene and fresh crude benzol) is from 0.25% to 5.0% and in particular from about 1% to about 2½%. Assuming that the rate of conversion of benzene in the crude benzol remains constant, the recycle feed rate must remain unchanged. The following equations provide a means for calculating the excess of fresh feed required:

$$I. (a) \quad P = \frac{XY}{X+R}$$

$$(b) \quad C = X + R$$

wherein P is the concentration of reaction-promoting impurities to be maintained in the total benzol feed entering the reaction zone in order to effect the desired conversion; X is the amount of fresh feed (fresh crude benzol) added to maintain the desired promoter concentration (P) and is expressed in units of weight or volume; Y is the concentration of reaction-promoting impurities in the fresh crude benzol; R represents the amount of unconverted benzene used as recycle feed, and is expressed in the same units used for X; and C is the capacity of the reactor expressed in the same units used for X. The expression

$$\frac{XY}{X+R}$$

(which is equal to P), represents the ratio of the amount of reaction-promoting impurities in the added fresh crude benzol to the amount of total feed, fresh crude benzol plus recycled unconverted benzene. The quantity (X+R) represents the amount of total feed, expressed in the same units used for X, and for a single cycle is equal to the capacity (C) of the reactor.

By substituting C for (X+R) in I(a) and solving for X, we find:

$$I. (c) \quad X = \frac{CP}{Y}$$

that is, the number of units of fresh crude benzol feed required to maintain the desired promoter concentration (P) in the total charge may be determined from just three factors, the values of which are readily obtained. The concentration of reaction-promoting impurities (P) necessary to effect the desired conversion can be determined experimentally, and the capacity of the reactor (C) and the concentration of reaction-promoting

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impurities (Y) in the fresh crude benzol can be similarly determined. For example, Y can be determined by analysis as pointed out above.

The amount of unconverted benzene to be removed (D), that is, not to be recycled in a succeeding operation, is determined from the following equation:

$$D = uC - (C - X)$$

wherein u is the percentage of total benzol charge which remains unconverted to phenol and other oxidation products; uC in units of weight or volume is the total unconverted benzene available for recycling and $(C - X)$ is the quantity of unconverted benzene recycled in a succeeding operation; and C and X being as defined above. Thus, D is determined from C and X since u can readily be determined by simply measuring the amount of unconverted benzene and representing such amount as a per cent of the total benzol charge for a single cycle from which it was obtained.

The foregoing mathematical representations are applied practically in such a case as the following. Using a "90% benzol" having a promoter concentration (Y) of approximately 4% and maintaining a preferred promoter concentration (P) of 1% in a reactor having a capacity (C) of 8 units, we determine the number of units of fresh feed (X) required, by solving the expression obtained above:

$$X = \frac{CP}{Y} = \frac{(8)(0.01)}{(0.04)}$$

$$X = 2 \text{ units}$$

If the conversion of the total benzol charge to phenol and other oxidation products is 14% per pass, the total unconverted benzene available for recycling is 86% of the total benzol charge for a single cycle or 6.9 units. We can determine the number of units of unreacted benzene (D) to be withdrawn by solving Equation II for D:

$$D = uC - (C - X) \\ = (0.86)(8) - (8 - 2) = 0.9 \text{ unit}$$

Thus, the amount of unconverted benzene recycled is 6 units (from 6.9 units less 0.9 unit).

In effect, removing a portion, 0.9 unit, of the recycle stock (unreacted benzene) and adding 2 units of the fresh feed (fresh crude benzol) to the remaining recycle stock should provide the same performance as a "true recycling" operation with the use of a fresh feed containing 3% of added promoter. This is determined in the following manner. In order that the promoter concentration remain about 1% with the same conversion rate of 14%, Y must equal 7% as obtained by use of Equation I (c):

$$X = \frac{CP}{Y}$$

$$Y = \frac{P}{\left(\frac{X}{C}\right)} = \frac{0.01}{0.14} = 0.07$$

wherein

$$\frac{X}{C}$$

represents the conversion per pass of benzene to phenol and other oxidation products. Now, as the original promoter concentration was 4%, the added promoter in the "true recycling" operation is 3% (from $Y - 0.04$) of the fresh feed.

To further explain the application of the fore-

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going equations, if a 2½% promoter concentration is maintained in the total feed, with the same "90% benzol" and the same conversion rate under proper operating conditions but with a reactor of 16 units capacity, we then have: 2.2 units converted and 13.8 units unconverted; the number of units of fresh crude benzol (X) required to maintain the desired promoter concentration is 10, as obtained from:

$$X = \frac{CP}{Y} = \frac{(16)(0.025)}{(0.04)}$$

and the number of units of unconverted benzene (D) to be withdrawn from the total amount of unconverted benzene (13.8 units) is:

$$D = uC - (C - X) \\ = (0.86)(16) - (16 - 10) \\ = 7.8 \text{ units}$$

Thus, of the unconverted benzene available for recycling, 7.8 units are withdrawn and the remainder, 6 units, are combined with 10 units of fresh feed for recycling.

Accordingly, the withdrawal of 7.8 units of the unconverted benzene available for recycling, and the addition of 4.55

$$\left(\text{from } \frac{10}{2.2}\right)$$

as much fresh feed as is required for a "true recycling" operation, should provide the same performance as the use of the required amount of fresh feed containing 13.9% of promoter. As indicated above, this is determined by the following. In order that the promoter concentration remain about 2½% with the same conversion rate of 14%, Y must equal 17.9%, as obtained with Equation I(c):

$$Y = \frac{P}{\left(\frac{X}{C}\right)} = \frac{0.025}{0.14} = 0.179$$

As the original promoter concentration was 4%, the added promoter in the "true recycling" operation is 13.9% of the fresh feed.

It will be apparent from the foregoing that in a continuous operation of the type contemplated herein, the unreacted benzene withdrawn from the recycle stream is continuously withdrawn at a suitable rate, such as, for example, D units per minute, and fresh crude benzol is thereafter continuously added to the recycle stream at X units per minute.

It will also be apparent from the foregoing that in a continuous process of the type contemplated herein, the ratio of the amount of added fresh crude benzol to the amount of unreacted benzene recycled remains substantially constant. Further, it will be apparent that the total quantity of fresh crude benzol plus recycle unreacted benzene charged to the reactor is substantially constant.

The foregoing indicates one manner by which the excess of fresh feed required to maintain a desired promoter concentration in the total feed may be calculated. Any excess over and above that required for a "true recycling" operation, however small, will show improvement in the reactivity of the benzene in the crude benzol and in the conversion of said benzene to phenol. As a lower practical limit, 50 percent excess fresh feed is preferred.

As will be readily apparent to those skilled in the art, the apparatus used in carrying out a process of the type contemplated herein may take

various forms. In the accompanying drawings, however, we have shown diagrammatically one form of apparatus which may be satisfactorily used in carrying out an operation for the continuous production of phenol from benzene in crude benzol. As will hereinafter appear, the conditions of operation embody a number of variables which may be changed with respect to one another over relatively wide limits, and no attempt will be made in describing the apparatus to take account of these possible changes in variables.

Referring now to the drawing, reference number 11 indicates a conduit which carries unreacted benzene and is connected through a suitable valve 13' with the inlet 13 of a pump 14. The conduit 15 or discharge side of the pump is connected with conduit 31 which is a means for adding fresh crude benzol to the system. Conduit 31 is connected with the discharge side of variable-speed pump 32. The suction side of pump 32 is connected with conduit 33 which is fitted with meter M_2 and which, in turn, is connected with conduit 34. Fresh crude benzol reservoir 35 is connected with conduit 34 which is fitted with adjustable valve 34'. Conduit 15' which carries unreacted benzene and fresh crude benzol is connected to a T-connection 16, where it connects with mixing conduit 17 leading to the coils 18 of a mixer and pre-heater mounted in an insulated case 19 which is filled with a suitable heat-exchange medium, such as "Dowtherm."

Reference number 11' indicates an outlet fitted with adjustable valve 12 and meter M_1 , and is a means by which all or a part of the unreacted benzene may be withdrawn from the system.

Reference number 20 indicates an air-compressor which discharges into pipe 21 connected through the connection 22 to a compressed air storage reservoir 23. The pipe 21 discharges through a pressure-reducing valve 24 and an orifice flow-control 25 into the conduit 17, through which the air-and-crude benzol reaction mixture is conducted to the mixing and pre-heating coil 18.

The pre-heating and mixing coil 18, wherein the crude benzol-air mixture is intimately mixed and pre-heated to a temperature below the temperature at which reaction will take place, discharges into header 40, which connects with a series of reactor tubes 41. The reactor tubes are suspended in a suitable heat-transfer bath, such as a fused salt bath, capable of maintaining a close temperature control, such bath being contained in the insulated case 42, which is provided with an inlet conduit 43 having a pump 44, the inlet 45 of which connects with a heat-exchanger 46 which can be used to raise the temperature of the salt bath for initiating the reaction and, after the exothermic reaction has started, can be used to dissipate the heat of reaction and maintain a constant temperature. The heat-exchanger 46 receives the heat-exchange medium from the tank 42 through a discharge conduit 47.

In the form of the apparatus shown in the drawing, the reactor tubes are illustrated as being U-shaped, and the discharge portion 41' of the respective reactor tubes connects with a header conduit 50 which discharges into the coil 51 of a heat-exchanger 52. For the thermal balance of the process, this heat-exchanger 52 is shown as being connected through conduits 53 and 54 with the mixer and pre-heater 19 so that the heat-exchange medium is circulated by means of pump 55 from the bottom of the mixer and pre-

heater 19 to the bottom of the heat-exchanger 52 and back to the mixer and pre-heater through the pipe 53.

The cooled reaction mixture containing the phenol and other products of the reaction discharges from the heat-exchanger 52 through pipe 56—56' and filter 57 into a high-pressure mist-breaking tower 58 having a high-pressure gas-discharge valve 59 which may lead to a turbine. Discharge valve 59 is controlled by orifice flow-control 25 to maintain a constant flow of air in pipe 17. The liquid product accumulating in the bottom of the high-pressure tower 58 is discharged through a valve 60 into a low-pressure packed tower 61 provided with a valved vent 62 to release gaseous products. The liquid product collecting in the bottom of tower 61 is discharged through conduit 61'. This liquid product, which is a mixture of phenol, recycle stock (substantially pure benzene), and "high-boilers," is delivered to the benzol-recovery still 62. In the still, as illustrated, the liquid products pass through a pre-heater 63 and are discharged through the discharge pipe 63' into the bottom of the still 62, where the benzol is distilled off by a steam coil reboiler 64. The still 62 is shown as being equipped with bubble plates 65 and a water coil reflux-condenser 65'. The recycle benzol vapors (unreacted benzene) are discharged through conduit 66 into a recycle benzol condenser 66', from which the liquid product discharged through conduit 67 is pumped by means of pump 68 into a recycle benzol-washing tower 69, from which the recycle benzol (unreacted benzene) enters the benzol conduit 11'.

The bottom of the benzol-recovery still 62 is provided with a discharge conduit 70 through which the mixture of phenol and high-boilers is pumped into a vacuum still 71, wherein the phenol is distilled off by means of the steam reboiler coil 72 into the phenol-discharge conduit 73, which connects with the phenol condenser 74 from which the condensed phenol is discharged through the conduit 75 into a receiver 76 provided with a valved vacuum line 77 and a valved phenol-discharge pipe 78 connected with a phenol-discharge pump 79. The high-boiling products of oxidation, which are referred to as "high-boilers," are discharged from the still 71 through the conduit 80 by means of a pump 81.

The mathematical representations discussed hereinabove are useful when applied in the following manner. Using an apparatus of the type described above in which the reactor tubes 41 have a capacity of, say, 8 gallons per minute of total benzol charge, a promoter concentration of 1% and a conversion rate of 14%, the amount of unreacted benzene continuously discharged from the benzene washing tower 69 through conduit 11 is 6.9 gallons per minute. As determined hereinabove, with Equations I(c) and II, the amount of unreacted benzene is to be continuously withdrawn (d) is 0.9 of a gallon per minute and the amount of fresh crude benzol to be continuously added (X) is 2 gallons per minute. Therefore, valve 12 of conduit 11' is regulated such that 0.9 gallon per minute of unreacted benzene is continuously metered through meter M_1 and withdrawn from the system concurrently with the continuous addition of 2 gallons per minute of fresh crude benzol to the remaining 6 gallons per minute of unreacted benzene in the recycle stream conduit 15—15'. The fresh crude benzol is pumped from the fresh crude benzol reservoir 35 by means of variable-speed pump 32 through ad-

justable valve 34' and meter M₂ to conduit 15—15'. The rate at which the fresh crude benzol is added to the recycle stream conduit 15—15' is regulated by suitable adjustment of pump 32. The total charge of fresh crude benzol and recycle unreacted benzene is delivered to the reactor tubes as indicated hereinabove.

As has been previously pointed out, the process contemplated herein embodies a number of variables which are susceptible of adjustment with respect to one another to obtain optimum operation conditions for a given set of variables. These variables include: The ratio of oxygen to total benzol; the ratio of recycle benzol (unreacted benzene) to fresh feed of crude benzol; the reaction time; the pressure under which the operation is carried out; the temperature of reaction; the material, internal diameter and length of the reactor tube; the internal diameter and length of the pre-heater coil and the temperature of the pre-heater bath; and the promoter concentration is the total feed of fresh crude benzol and recycle unreacted benzene maintained at a concentration above the limits hereinabove defined. As aforesaid, the feature of maintaining such a promoter concentration is the essence of this invention.

In order that some indication may be afforded as to the effect of these variables, each of them will now be discussed individually.

Reaction mixture

The proportion of air that can be used to advantage in the reaction mixture has an upper practicable limit that varies with the conditions used and particularly with the internal diameter of the reactor tube (41—41').

In tubes, having an internal diameter of from 0.2 inch to 0.35 inch, operating at a pressure of 1000 pounds per square inch, good yields of phenol are readily obtainable with mixtures which are not richer in oxygen than a mixture containing 4 mols of hydrocarbon charge (unreacted benzene and fresh crude benzol) to 1 mol of oxygen and 4 mols of nitrogen. Mixtures of higher oxygen content result in a greatly increased production of "high-boilers," which greatly lowers the yield of phenol even though the conversion to phenol may be moderately greater. Also, good yields of phenol have been obtained in reactor tubes of this size with mixtures in the ratio of 2 mols of benzene to 1 mol of oxygen and 4 mols of nitrogen by keeping the reactor bath temperature low enough to permit the consumption of only half of the oxygen, but this requires very accurate temperature control and presents no advantage either in conversion or in yield of phenol over the use of the 4:1:4 mixture first referred to. Under the conditions just described, we prefer to use mixtures of from 8 to 4 molecular proportions of benzene to 1 molecular proportion of oxygen.

With a smaller reactor tube having an internal diameter of, say, 0.086 inch, the situation is somewhat different. In a tube as small as this, the reaction is very much less temperature-sensitive, making it a relatively simple matter to control the bath temperature in such a way that only a part of the oxygen in the mixture is consumed. With this tube, the best results have been obtained with the mixture $2C_6H_6 + O_2 + 4N_2$ at temperatures where from $\frac{1}{4}$ to $\frac{1}{2}$ of the available oxygen is consumed. Under these conditions a higher yield of phenol is obtained than

with the mixture $8C_6H_6 + O_2 + 4N_2$, although the conversions to phenol are not greatly changed.

With a small tube of this character, higher pressures in the neighborhood of from 2000 to 3000 pounds per square inch are also desirable.

Reaction time

For the purpose of this discussion, the reaction time may be defined as the time taken for a molecule of the reaction mixture to pass through the reactor tube under operating conditions. The reaction time is not an important variable provided it exceeds a certain minimum value which varies with the apparatus and the conditions of use. Above this so-called critical minimum value an increase in reaction time can be compensated for by a small decrease in reaction temperature. However, for reaction times below the minimum value there is a sharp rise in the production of high-boilers and a corresponding decline in phenol yield, although the actual conversion to phenol is not greatly affected. The value of this so-called critical minimum reaction time, as aforesaid, is dependent upon the apparatus and conditions of use, and it is probable that the controlling factor rests in the ability of the apparatus to dissipate heat. The critical minimum reaction time is about 5 seconds under the following conditions:

Fresh feed: "90% benzol" is added at a rate equal to 3.4 times the rate at which benzene is converted, the excess unreacted benzene being withdrawn.

Reactor: 0.35" internal diameter stainless steel tube 60' long.

Mixture: $4C_6H_6 + O_2 + 4N_2$.

Pressure: 750 pounds per square inch.

If the reaction time is about 8.5 seconds, the optimum reaction temperature is about 840° F., the conversion to phenol about 4.7% and the ultimate yield of phenol about 30%.

Pressure

We have obtained phenol in good conversion at pressures of from 60 pounds per square inch to 3000 pounds per square inch. The higher the pressure, the lower the optimum reactor temperature, other conditions being the same. Thus, while at 60 pounds per square inch, temperatures of the order of 1200° F. are required, at 2000 pounds pressure good results have been obtained at 675° F. Since ferrous metal surfaces strongly catalyze total combustion at temperatures above 1000° F., it is necessary to use inert surfaces such as glass, enamel, silica, etc., in the reactor when operating at low pressures and the concomitant high temperatures. In this connection, good results have been obtained in nickel tubes at a pressure of 350 pounds per square inch where the optimum reaction temperature was about 1030° F., and probably still lower pressures and higher temperatures could have been successfully used. With iron tubes, sufficient pressure to keep the reaction temperature below 1000° F. is required, usually at least 500 to 1000 pounds per square inch. However, at 1000 pounds pressure, the use of nickel tubes instead of iron or stainless steel tubes presents no advantage.

The use of high pressure has certain fundamental advantages, however. At low pressures, even though a glass-lined reactor be used, the loss to oxides of carbon is materially higher than at high pressures in stainless steel equipment.

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Furthermore, the minimum critical reaction time apparently increases with decreasing pressure; and, since for a constant reaction time the rate of feed varies directly with the pressure (by definition), the maximum permissible rate of throughput falls off very rapidly with decreasing pressure.

There is also an upper useful limit of pressure. As the pressure is raised, the temperature required to initiate reaction decreases, as explained above. Furthermore, the boiling point of benzene in crude benzol is raised until the critical temperature of liquid benzene (550° F.) is reached, where it remains unchanged as the pressure is further increased. Since it is advantageous to mix thoroughly the crude benzol vapor and air before initiating reaction, in order that local regions of undesirably high oxygen-concentration be eliminated, it is not desirable to indefinitely lower the reaction temperature by the use of extremely high pressures. There is a relationship between the maximum useful pressure and the internal diameter of the reactor tube, since we have found that the smaller the internal diameter of the reactor tube, the higher the temperature necessary to initiate reaction. Thus, pressures at least as high as 3000 pounds per square inch and probably higher can be used to advantage in a 0.086 inch internal diameter reactor tube, while in a 0.35 inch internal diameter reactor tube 2000 pounds per square inch appears to be about the upper limit, and we prefer a pressure of 1000 pounds per square inch. Because of this same relationship between internal diameter and reaction temperature and the catalytic effect of the iron tube walls discussed above, a 0.086 inch internal diameter tube requires a pressure of at least 1000 pounds per square inch, while a 0.35 inch internal diameter tube has given fairly good results at 500 pounds per square inch.

Temperature

The optimum reaction temperature can be varied from 650° F. to 1225° F. by changing the operating conditions, among the most effective of which are pressure, promoter concentration and internal diameter of reactor tube. This is discussed in the section entitled "Pressure."

Reactor tube

As we have previously indicated, it is highly desirable that the reactor tube be void of solid catalyst and that it be of a material which will have no substantial catalyzing effect in accelerating the oxidation of benzene in the crude benzol. We have observed in this connection that the chief effect of a solid catalyst is to increase the loss to total-combustion products and therefore to be avoided in the reactor tube (41-41'). At the relatively high temperatures encountered in low-pressure oxidation the use of extremely inert (non-catalytic) inner surfaces of the reactor tubes, such as glass, enamel, glazed porcelain, or silica, is imperative.

At moderate pressures (several hundred pounds per square inch) nickel is satisfactory. At pressures in the neighborhood of 1000 pounds per square inch, low-carbon steel and stainless steel are satisfactory, and nickel presents no advantage.

As to the internal diameter of the reactor tube (41-41'), successful operation has been obtained in tubes varying from 0.086 inch to 0.875 inch

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in internal diameter. For iron tubes, the smaller the internal diameter, the higher the required pressure. We prefer to use a tube having an internal diameter in the neighborhood of 0.35 inch to operate with pressures in the range of from 500 to 2000 pounds per square inch. Smaller tubes are equally satisfactory, but they require higher operating pressures. For a tube having an internal diameter of 0.086 inch, pressures of from 2000 pounds to 3000 pounds per square inch are recommended.

The length of the reactor tube (41-41') apparently determines the rate of throughput, and the existence of a critical minimum reaction time for a tube of fixed length and internal diameter has already been discussed. Satisfactory results in the operation of a process of the class described have been obtained with tube lengths of 15 feet, and tubes of at least this length are recommended.

Mixer-pre-heater tube

As to the mixer-pre-heater tube (18), any material having suitable mechanical properties such as stainless steel is satisfactory. The internal diameter of this tube should be sufficiently small to prevent reaction taking place therein, and the tube should be sufficiently long to provide the heating surface necessary for a heat-exchange that will maintain the feed temperature within 25° F. to 50° F. of the temperature of the pre-heater bath. The temperature of the pre-heater bath should be such that the reaction mixture discharged from the pre-heater coil (18) is at a temperature of about 50° F. to 150° F. below the temperature maintained in the reactor bath in the case 42. The required pre-heat may be obtained by indirect heat exchange of the product against the feed.

Promoter and concentration of promoter

The crude benzol stocks, the promoters and concentration of promoters therein have been discussed hereinabove.

The following experimental data clearly support Equation I given in the foregoing. A fresh feed of "90% benzol" which contained 4% of reaction promoting impurities was charged at a rate equal to 3.4 times the rate at which benzene was converted, that is, 3.4 times more fresh crude benzol than that required for a "true recycling" operation. The reaction conditions were: 750 pounds per square inch, 840° F., 8.5 seconds reaction time and sufficient air to give the mixture $4C_6H_6 + O_2 + 4N_2$. The excess recycle stock, phenol and high-boiling products were continuously removed. The yields and conversions contained are given in Table I below, together with similar data obtained under identical conditions but with "true recycling" operation.

Table I

Product	Yield with true recycling, weight per cent	Yield with 3.4 fold excess fresh feed, weight per cent
Phenol.....	9	30.4
Diphenyl.....	1.7	20.6
Other liquid products.....	20	23.9
Per pass conversion of benzene.....	3.0	15.5
Per pass conversion to phenol.....	0.27	4.7

When these data are used in Equation I(c), it will be seen that the promoter concentration (P) of the total feed maintained during the process

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contemplated herein is within the preferred limits of 1% to 2½%:

$$X = 3.4(0.155C)$$

$$\therefore \frac{X}{C} = 0.53$$

$$\text{But by I(c): } P = \left(\frac{X}{C}\right)Y$$

$$\therefore P = (0.53)(0.04) = 0.021$$

$$\therefore P = 2.1\%$$

The results tabulated above clearly demonstrate the superiority of our process, in which an excess of fresh feed is used, over a process in which a "true recycling" operation is used without the addition of some promoter to the fresh feed.

It will be noted from Table I that a considerable amount of another valuable chemical—diphenyl—is obtained in the process contemplated herein, and that such amount is far in excess of that obtained with the "true recycling" operation. Diphenyl may be separated from phenol, other oxidation products and unreacted benzene in the reaction mixture by suitable separation and distillation means. For example, diphenyl may be isolated from the fraction of "high-boilers," discharged from the vacuum still 71, as indicated hereinabove, by distillation.

As aforesaid, one object of this invention is to produce substantially pure benzene from crude benzol by the process contemplated herein. The unreacted benzene or recycle stock obtained in the experiment, wherein a 3.4 fold excess of fresh feed was used (Table I), was water-washed and re-distilled before the following properties were determined. The properties of the removed recycle stock are tabulated below in Table II, along with the same properties for the original "90% benzol" and for pure benzene.

Table II

Property	Pure benzene	Recycle stock	"90% benzol"
Specific gravity, D _{60° F.} ^{60° F.}	0.8843	0.8800	0.8783
Index to refraction, n _D ^{20° C.}	1.5011	1.5007	1.4961
Thiophene content.....	0	0.13	0.46
Initial freezing point, °C.....	5.49	5.1	2.3

The rise in specific gravity and rise in the index of refraction are indicative of the increase in aromatic content of the recycle stock over the "90% benzol," i. e., substantially all of the non-aromatic hydrocarbons have been removed from the "90% benzol." The thiophene content has been greatly reduced as well. The increase in melting point demonstrates conclusively that the recycle stock is a great deal purer than the "90% benzol."

As will be apparent from the above discussion, the concentration of promoters in the total liquid feed required to cause a maximum degree of conversion of benzene to phenol and other oxidation products will be maintained even in "true recycling" operation if a benzol is selected which contains more than about 10% but less than 35% of promoters. While benzols containing more than 35% of promoters are exceedingly reactive, the phenol produced is seriously contaminated with partial oxidation products of the reaction-promoting impurities. Furthermore, it will be apparent that benzols containing from 0.25% to 5.0%, and in particular from 1.0% to 2.5% of re-

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action-promoting impurities may be greatly purified by a one-pass operation under conditions similar to those disclosed above, wherein fractional distillation of the product will produce a major amount of relatively pure benzene and a minor amount of phenol and other oxidation products.

It will also be seen from the foregoing discussion that a process of the type contemplated herein is susceptible of numerous operating conditions through manipulation of the variables discussed, and the present invention is not concerned with any particular set of operating conditions; but, as aforesaid, it is predicated upon the discovery that greatly improved results and a continuous recycling operation may be obtained by maintaining in the reaction mixture a promoter concentration as hereinabove defined. It is to be understood, therefore, that although we have described and illustrated a specific form of apparatus and have discussed in considerable detail various reaction conditions which may be employed in the operation of such apparatus, the invention is not limited to this apparatus or to any particular set of operating conditions but includes within its scope such changes and modifications as fairly come within the spirit of the appended claims.

We claim:

1. In the method for the continuous manufacture of phenol from crude benzol wherein a crude benzol vapor and oxygen-containing gas is passed under pressure through a heated reaction zone void of solid catalyst to convert a part of the benzene in said crude benzol to phenol and other oxidation products, and wherein unreacted benzene is separated from said phenol and oxidation products and is returned for recycling in the reaction mixture; the improvement which comprises: continuously adding fresh crude benzol to the unreacted benzene at a greater rate than at which benzene is converted and continuously removing excess unreacted benzene prior to admixture of the unreacted benzene with said fresh crude benzol, said fresh crude benzol containing at least one impurity of the type normally present therein, which impurity contains hydrogen and is characterized, under the conditions of the said reaction zone, by the property of being in the gaseous phase and by the property of being a better hydrogen donor than benzene, the said addition of said fresh crude benzol and the said removal of said excess unreacted benzene being so proportioned that a concentration, greater than about 0.25 per cent, of said impurity is maintained in said mixture.

2. In the method for the continuous manufacture of phenol from crude benzol wherein a crude benzol vapor and oxygen-containing gas is passed under pressure through a heated reaction zone void of solid catalyst to convert a part of the benzene in said crude benzol to phenol and other oxidation products, and wherein unreacted benzene is separated from said phenol and oxidation products and is returned for recycling in the reaction mixture; the improvement which comprises: continuously adding fresh crude benzol to the unreacted benzene at a greater rate than that at which benzene is converted and continuously removing excess unreacted benzene prior to said addition of fresh crude benzol, the said fresh benzol containing at least one impurity of the type normally present therein selected from the group consisting of a paraffin, an olefin and cyclohexane, and the said addition of said

fresh crude benzol and the said removal of said excess unreacted benzene being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

3. In the method for the continuous manufacture of phenol from crude benzol wherein a mixture of "90% benzol" vapor and oxygen-containing gas is passed under pressure through a heated reaction zone void of solid catalyst to convert a part of the benzene in said "90% benzol" to phenol and other oxidation products, and wherein unreacted benzene is separated from said phenol and oxidation products and is returned for recycling in the reaction mixture; the improvement which comprises: continuously adding fresh "90% benzol," containing at least one impurity of the type normally present therein selected from the group consisting of a paraffin, an olefin and cyclohexane, to the unreacted benzene at a greater rate than that at which benzene is converted and continuously removing excess unreacted benzene prior to admixture of the unreacted benzene with said fresh "90% benzol," the said addition of said fresh "90% benzol" and the said removal of said excess unreacted benzene being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

4. In the method for the continuous manufacture of phenol from crude benzol wherein a mixture of crude benzol vapor and oxygen-containing gas is passed under pressure through a heated reaction zone void of solid catalyst to convert part of the benzene in said crude benzol to phenol and other oxidation products, and wherein unreacted benzene is separated from said phenol and oxidation products and is returned through a recycle stream to the reaction mixture; the improvement which comprises continuously withdrawing a quantity of the unreacted benzene from the recycle stream and thereafter continuously adding fresh crude benzol to the recycle stream prior to its admission to the reaction zone, said fresh crude benzol containing at least one impurity of the type normally present therein, which impurity contains hydrogen and is characterized, under the conditions of said reaction zone, by the property of being in the gaseous phase and by the property of being a better hydrogen donor than benzene, the quantity of said fresh crude benzol so added replacing the said quantity of unreacted benzene withdrawn from the recycle stream and replacing the benzene consumed in the previous passage through said reaction zone, the ratio of the rate of addition of said fresh crude benzol to the rate of withdrawal of said unreacted benzene being substantially constant and being such that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

5. The method for the continuous manufacture of phenol from crude benzol containing at least one impurity of the type normally present therein, which impurity contains hydrogen and is characterized, under the conditions of the reaction zone defined below, by the property of being in the gaseous phase and by the property of being a better hydrogen donor than benzene, which comprises: passing a mixture of said crude benzol vapor and oxygen-containing gas under pressure through a heated reaction zone void of solid catalyst wherein a part of the benzene in said crude benzol is converted to phenol and other

oxidation products; separating unreacted benzene from said phenol and oxidation products of the reaction mixture so obtained; separating phenol from the reaction mixture substantially free of said unreacted benzene; removing part of said unreacted benzene, returning the remainder of said unreacted benzene to the reaction zone and adding fresh crude benzol to the said remainder of said unreacted benzene, prior to its admission to the reaction zone with oxygen-containing gas, the said removal of said unreacted benzene and the said addition of said fresh crude benzol being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

6. The method for the continuous manufacture of phenol from crude benzol containing at least one impurity of the type normally present therein selected from the group consisting of a paraffin, an olefin and cyclohexane, which comprises: passing a mixture of said crude benzol vapor and oxygen-containing gas through a reaction zone void of solid catalyst, under pressure, and at a temperature between about 650° F. and about 1225° F., wherein a part of the benzene in said crude benzol is converted to phenol and other oxidation products; separating unreacted benzene from the reaction mixture so formed and separating phenol from said reaction mixture substantially free of unreacted benzene; and recycling a substantial part only of said unreacted benzene with an excess of fresh crude benzol and with said oxygen-containing gas, the part of said unreacted benzene so recycled and the amount of said fresh crude benzol admixed therewith being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

7. In the method for the continuous purification of benzene wherein a mixture of crude benzol vapor and oxygen-containing gas is passed under pressure through a heated reaction zone void of solid catalyst to convert a part of the benzene in said crude benzol to phenol and other oxidation products, and wherein unreacted, substantially-pure benzene is separated from said phenol and other oxidation products and is returned for recycling in the reaction mixture; the improvement which comprises: continuously adding fresh crude benzol to the unreacted, substantially-pure benzene at a greater rate than that at which benzene is converted to phenol and other oxidation products and continuously removing excess, substantially-pure benzene prior to admixture of said substantially-pure benzene with said fresh crude benzol, the said fresh crude benzol containing at least one impurity of the type normally present therein selected from the group consisting of a paraffin, an olefin and cyclohexane, and the said addition of said fresh crude benzol and the said removal of said excess substantially-pure benzene being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

8. In the method for the continuous manufacture of valuable chemicals from crude benzol wherein a mixture of crude benzol vapor and oxygen-containing gas is passed under pressure through a heated reaction zone void of solid catalyst to concurrently convert a part of the benzene in said crude benzol to phenol and diphenyl, and wherein unreacted benzene is separated from said phenol and diphenyl and is returned for

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recycling in the reaction mixture; the improvement which comprises: continuously adding fresh crude benzol to the unreacted benzene at a greater rate than that at which benzene is converted and continuously removing excess unreacted benzene 5 prior to admixture of said unreacted benzene with said fresh crude benzol, the said fresh crude benzol containing at least one impurity of the type normally present therein selected from the group consisting of a paraffin, an olefin and cyclohexane, and the said addition of said fresh crude benzol and the said removal of said excess unreacted benzene being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said 15 mixture.

9. In the method for the continuous manufacture of diphenyl from crude benzol wherein a mixture of crude benzol vapor and oxygen-containing gas is passed under pressure through a 20 heated reaction zone void of solid catalyst to convert a part of the benzene in said crude benzol to diphenyl and oxidation products of benzene, and wherein unreacted benzene is separated from said diphenyl and oxidation products and is returned for recycling in the reaction mixture; 25

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the improvement which comprises: continuously adding fresh crude benzol to the unreacted benzene at a greater rate than that at which benzene is converted and continuously removing excess, unreacted benzene prior to admixture of the unreacted benzene with said fresh crude benzol, the said fresh crude benzol containing at least one impurity of the type normally present therein selected from the group consisting of a paraffin, an olefin and cyclohexane, and the said addition of said fresh crude benzol and the said removal of said unreacted benzene being so proportioned that a concentration, from about 0.25 per cent to about 5 per cent, of said impurity is maintained in said mixture.

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The following references are of record in the file of this patent:

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Number	Name	Date
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