March 17, 1953 J. F. ADAMS ET AL 2,632,028

METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

Filed July 1, 1949 7 Sheets-Sheet 1

FIG. 1.

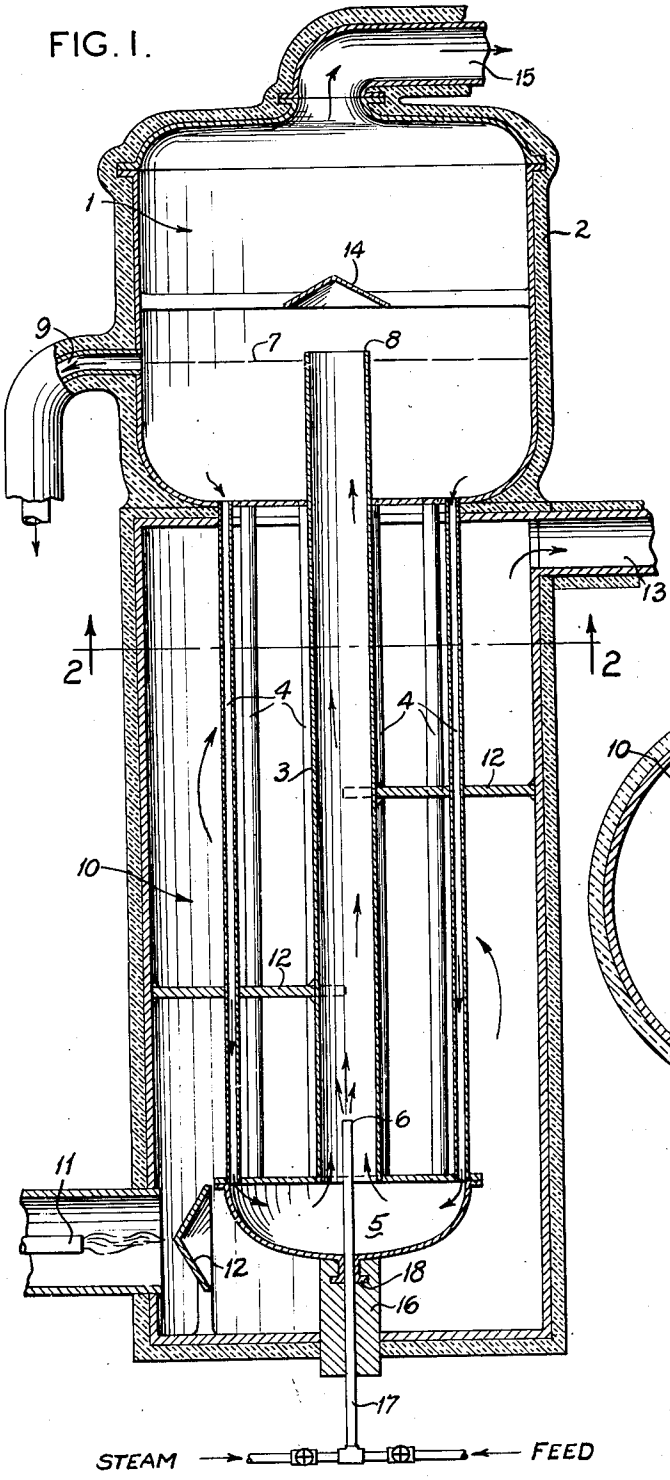
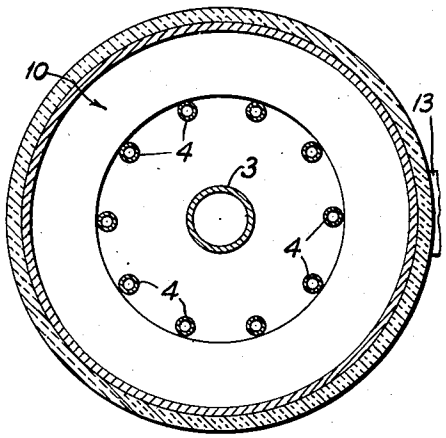


FIG. 2.



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METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

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FIG. 3.

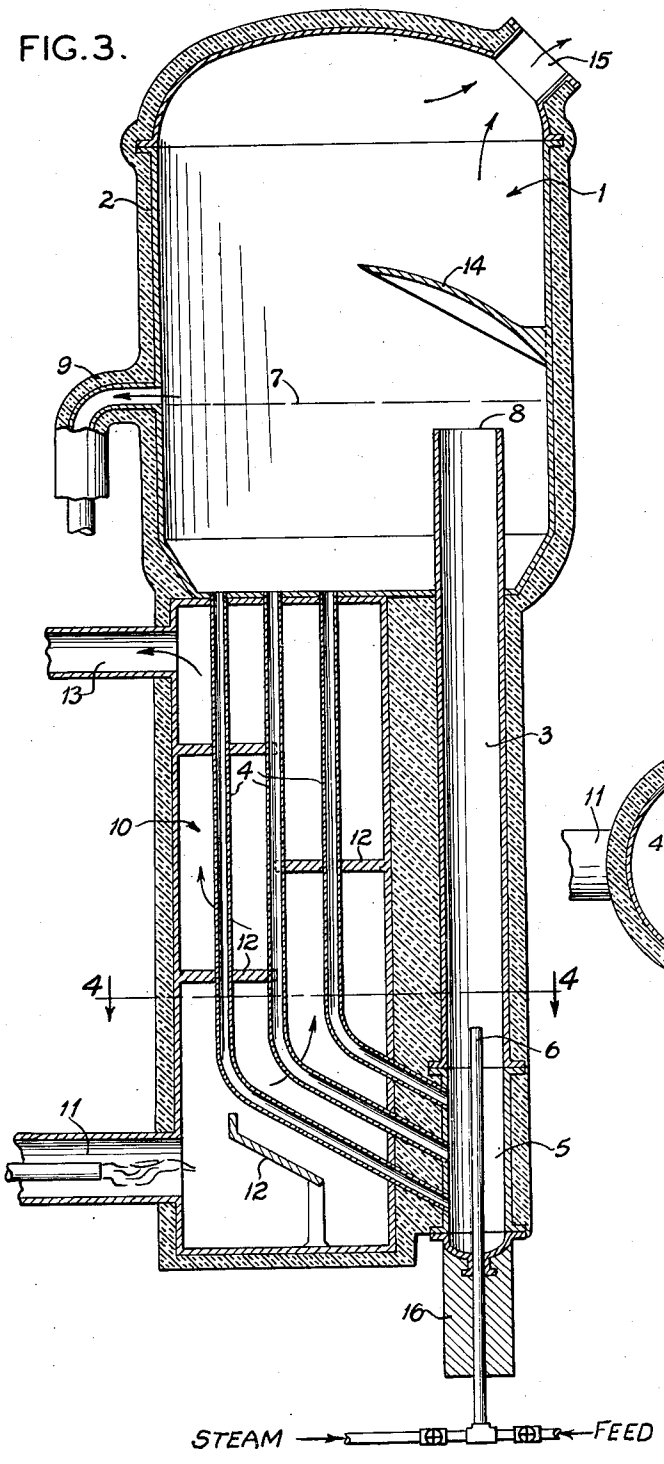
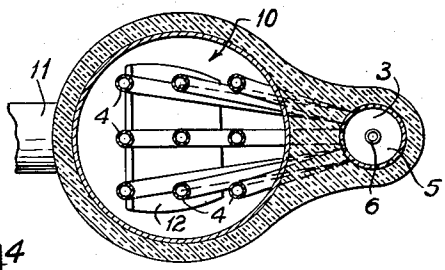


FIG. 4.



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METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

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FIG. 5.

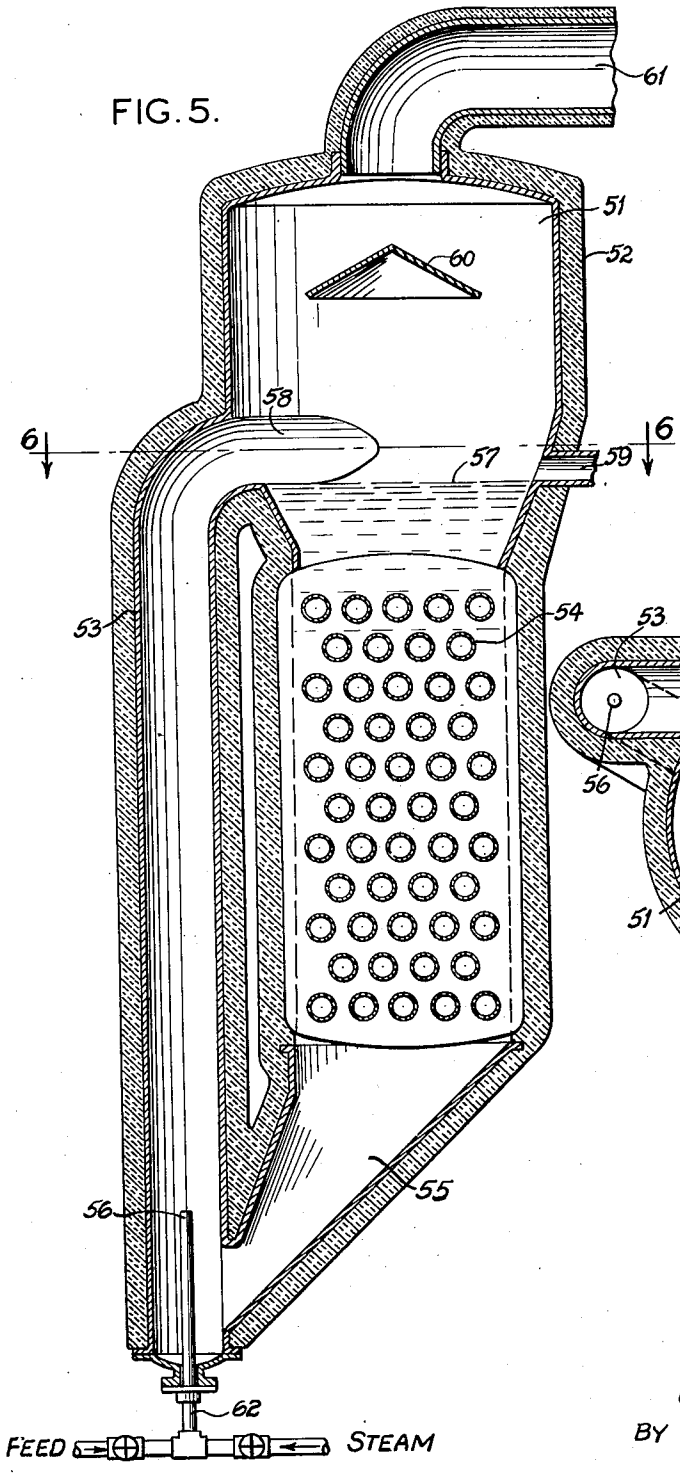
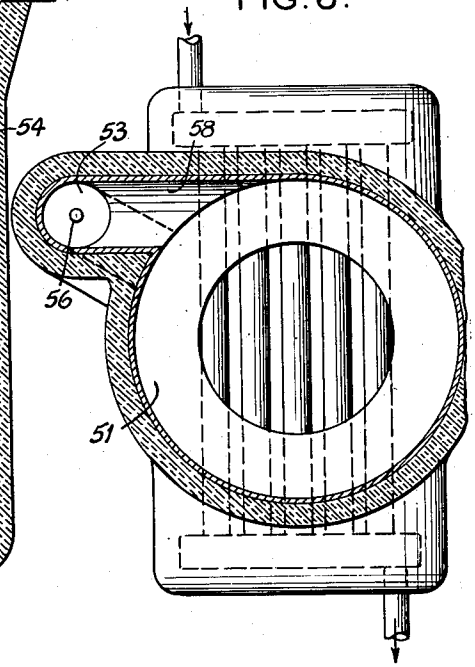


FIG. 6.



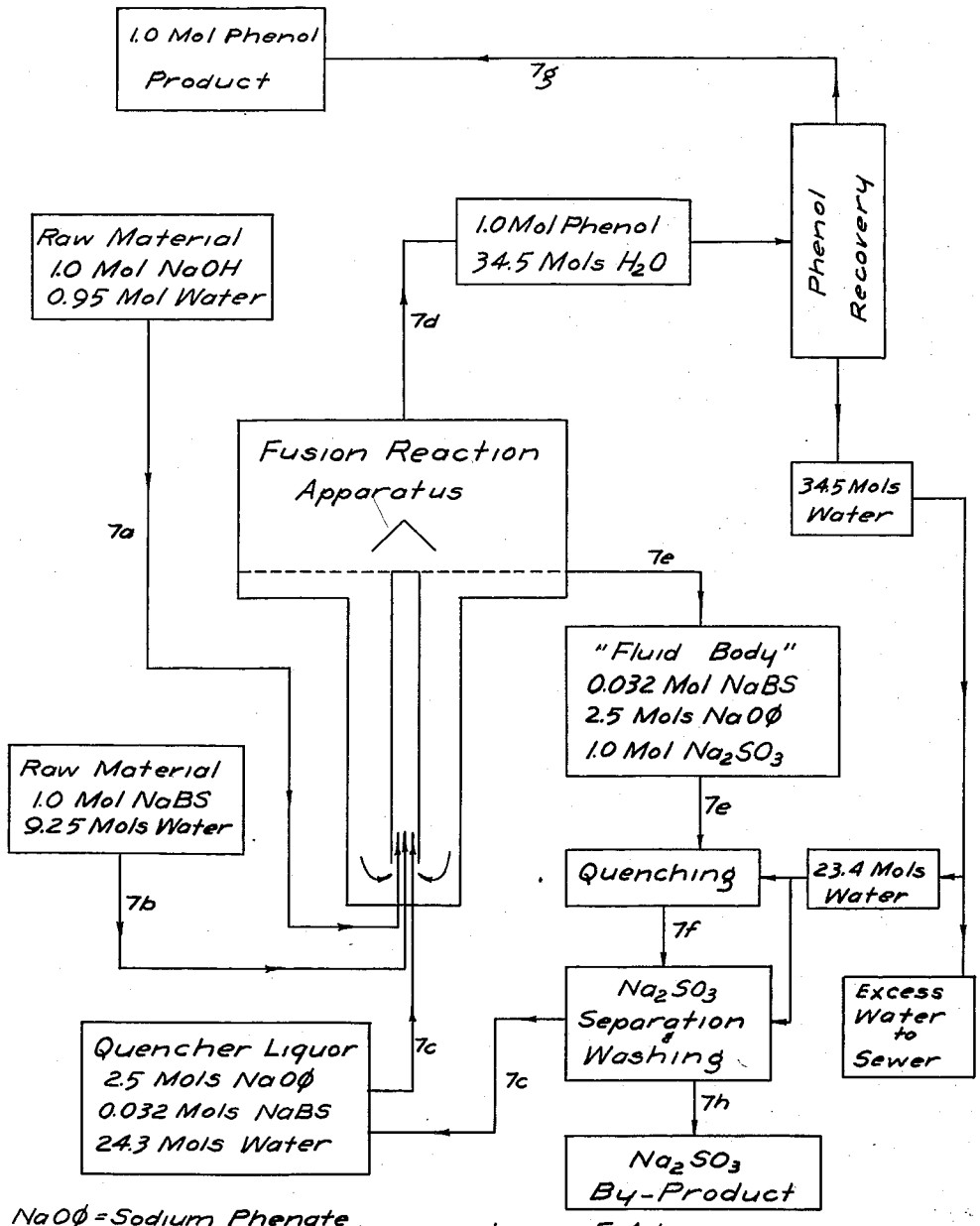
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March 17, 1953 J. F. ADAMS ET AL 2,632,028

METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

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FIG. 7



NaOϕ = Sodium Phenate

NaBS = Sodium Benzene Sulfonate

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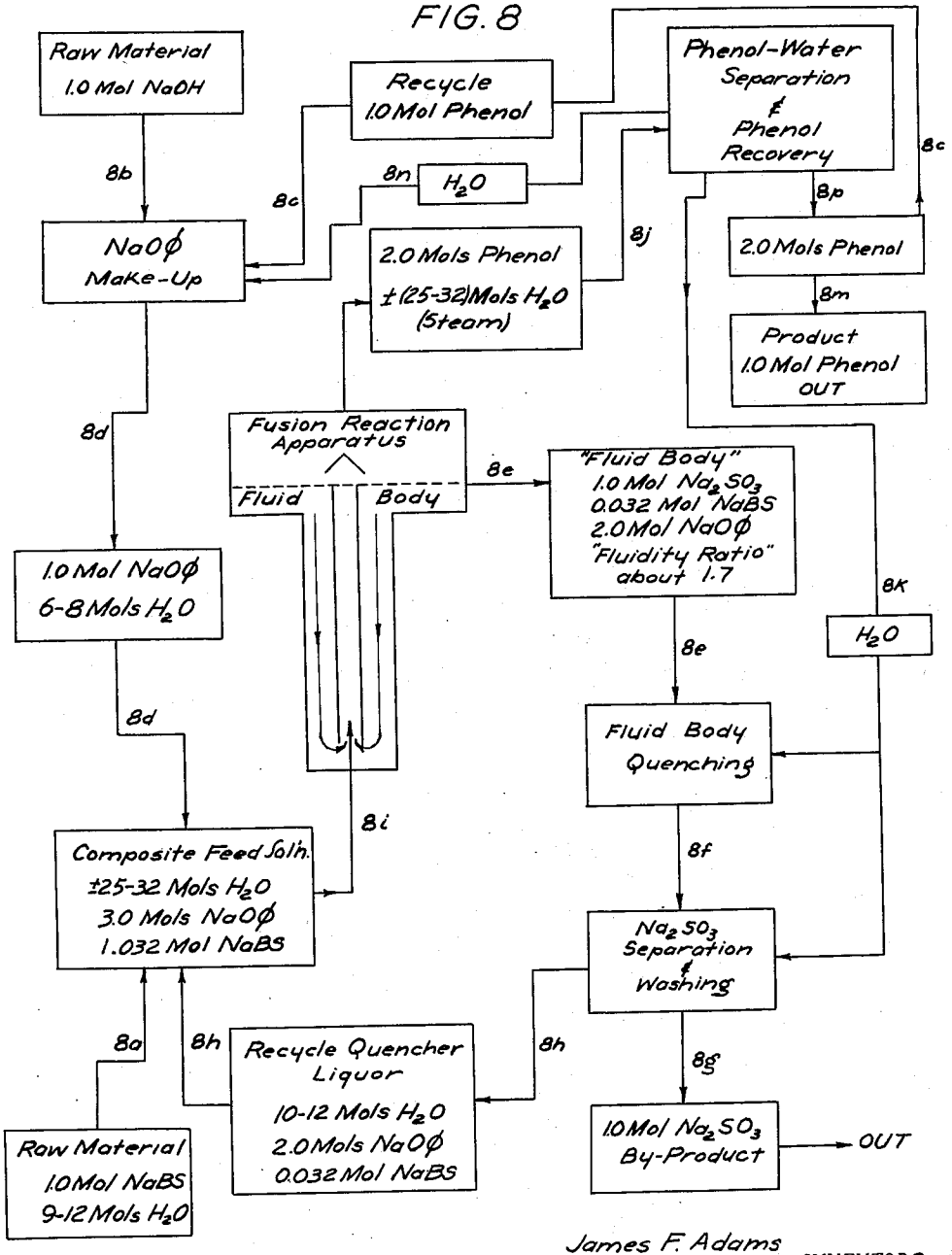
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METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

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FIG. 8



NaOϕ = Sodium Phenate
NaBS = Sodium Benzene Sulfonate

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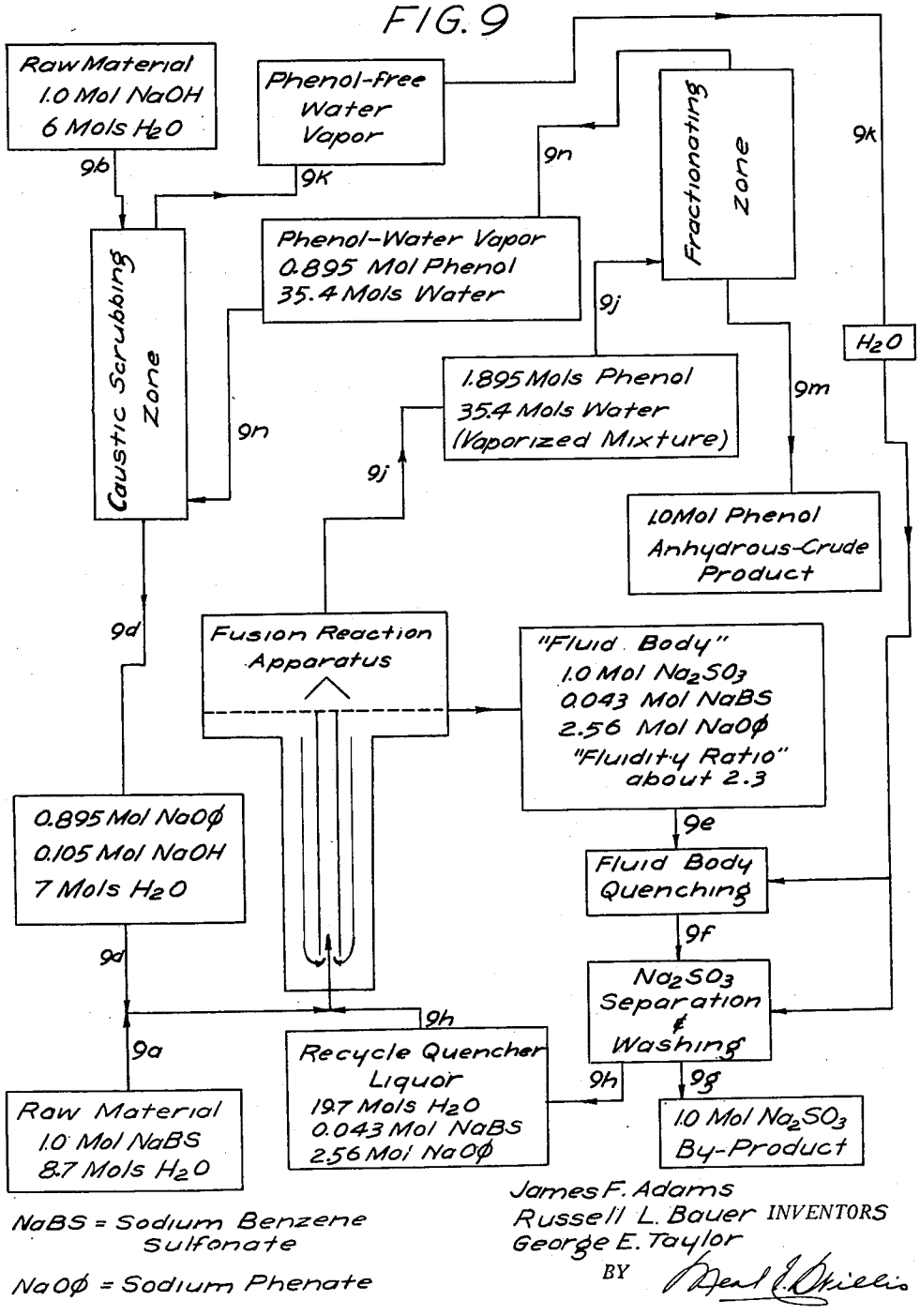
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March 17, 1953 J. F. ADAMS ET AL 2,632,028

METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

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FIG. 9



NaBS = Sodium Benzene Sulfonate

NaOϕ = Sodium Phenate

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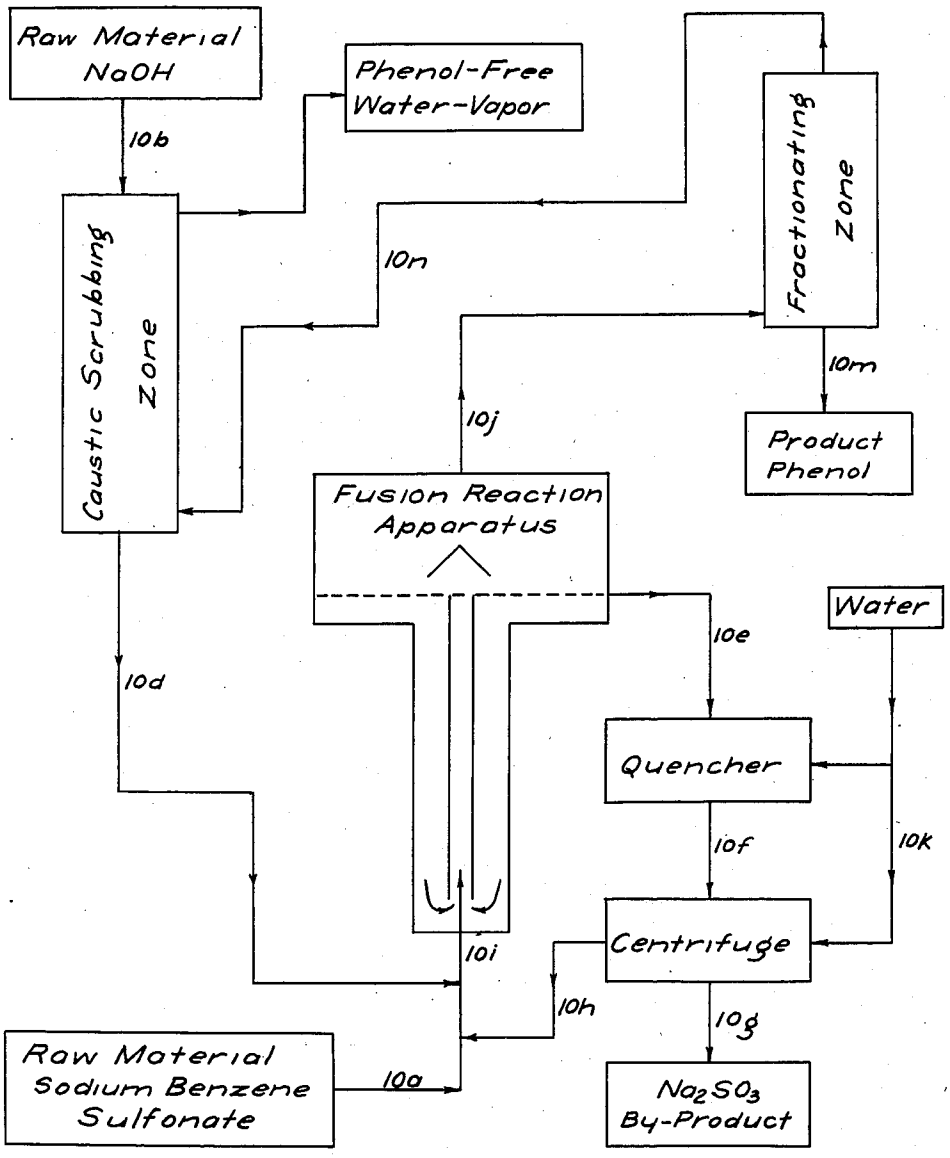
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March 17, 1953 J. F. ADAMS ET AL 2,632,028

METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

Filed July 1, 1949 7 Sheets-Sheet 7

FIG. 10



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Patented Mar. 17, 1953 2,632,028

UNITED STATES PATENT OFFICE

2,632,028

METHOD FOR FUSION REACTIONS, ESPECIALLY INCLUDING PRODUCTION OF PHENOLS

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Application July 1, 1949, Serial No. 102,512

7 Claims. (Cl. 260—628)

1

This invention relates to a new method for carrying out certain fusion reactions for organic chemical synthesis. The method of this invention may be applied to carry out those fusion reactions wherein at least one reactant is a fusible material and is maintained in a fused state during the reaction, or wherein the reactions produce fusible reaction products which are in the fused state in the reaction mixture, or wherein the fusion reaction produces fusible reaction products and also at least one reactant is a fusible material which is maintained in the fused state during the reaction. More particularly, this invention relates to a new method for carrying out those fusion reactions of organic chemical synthesis wherein steam is required as one reactant and wherein at least one other reactant or a reaction product is maintained in a fused or molten state; moreover, this invention also relates to a new method for carrying out those fusion reactions wherein at least one reactant or a reaction product is maintained in the fused and fluid state and wherein steam, although not a required reactant, does not adversely affect the desired course of the fusion reaction. The method of this invention may be applied, therefore, to those fusion reactions for the preparation of certain alkali metal arylates wherein, normally, an alkali metal hydroxide in the fused or molten state is reacted with an aryl sulfonic acid or an alkali metal salt of an aryl sulfonic acid.

The method of this invention may also be applied, for example, to those fusion reactions wherein a fusible metal arylate in the fused or molten state is reacted with steam; or wherein an aryl sulfonate salt is reacted with a fused metal arylate and steam; or wherein the fusion reaction mixture contains an aryl sulfonate salt, a fusible metal arylate, a fusible alkali metal hydroxide, and steam.

In particular, this invention also relates to a new and improved process for the manufacture of certain steam distillable phenols (or expressed otherwise, phenols volatile in steam) by a fusion reaction wherein the corresponding alkali metal aryl sulfonate is reacted with steam and the corresponding fused alkali metal arylate. This invention also relates to a new and improved process for the manufacture of certain steam distillable phenols by a fusion reaction wherein the corresponding alkali metal aryl sulfonate is reacted with an alkali metal hydroxide in the presence of steam, or wherein the fusion reaction mixture for the preparation of certain steam

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distillable phenols contains the corresponding alkali metal aryl sulfonate, the corresponding fused alkali metal arylate, a fused alkali metal hydroxide and steam.

Examples of those fusion reactions which the art in the past has normally effected by maintaining at least one reactant in a fused or molten state are the classical alkaline fusions whereby the sulfonic group of an aryl sulfonic acid or an aryl sulfonate salt is replaced by an alkali metal oxide group, such as NaO—, by a fusion reaction wherein the aryl sulfonic compound is reacted with a fused or molten caustic alkali such as fused sodium hydroxide or potassium hydroxide.

Conventional practice is the batch-wise slow addition of the aryl sulfonic compound to a fused caustic alkali or a highly concentrated solution of the caustic alkali (sodium hydroxide or potassium hydroxide) in a covered cast-iron fusion pot provided with a scraping stirrer and heated externally with steam, high temperature heat transfer media, or an open fire. As the water is evaporated on continued heating and stirring, the heated mass becomes substantially anhydrous and fuses and the reaction is sometimes considered essentially complete soon after the reaction mass fuses; on the other hand, the fusion reaction mass may be held in a substantially anhydrous fused state for one to several hours. The temperature of the fusion mass varies for different reactants, but generally the temperature falls within the range of 250–420° C.

Such a fusion reaction in daily industrial use is the step in the manufacture of phenol wherein sodium phenate is prepared by the reaction of sodium benzene sulfonate with fused or molten caustic soda. The operation is entirely batch-wise, and requires the slow addition of sodium benzene sulfonate to a molten body of substantially dehydrated caustic soda contained in huge oil or gas-fired fusion pots equipped with scraping stirrers, each of which commonly has a capacity of about 15 tons. The reaction mass is maintained within the temperature range of about 300–400° C. and the heating and stirring is continued until substantially all of the water is evaporated and the molten fusion reaction mass remains. The complete cycle of charging the fusion pots, heating and fusing, commonly takes 8 to 16 hours. The operation, although common in present industrial practice, has many attendant disadvantages, such as the long time cycle required, high heating costs due to inefficient heat transfer, large power require-

ments for stirring and the general disagreeableness of a cumbersome, batchwise process.

Another type of fusion reaction is known which is particularly adaptable to the manufacture of certain steam distillable phenols such as phenol, the cresols, the xylenols, and the naphthols. In this type of fusion reaction superheated steam is passed through a fusion mass containing a fused or molten metal arylate and a corresponding aryl sulfonate salt. As the phenols which are formed during the reaction distill with steam, the phenols are removed from the fusion reaction mass by a stream of excess superheated steam which is passed through the fusion mass. In this type of operation, the fusion mass is maintained in a fused state in the conventional direct-fired fusion pot equipped with a scraping stirrer and which is also equipped with a means for passing superheated steam through the fused reaction mass. In addition to the usual disadvantages inherent in the use of the conventional fusion pots, this type of fusion using superheated steam requires an independent source of supply of superheated steam, and in order to have even a semi-continuous process, the reactants such as the aryl sulfonate salt and the metal arylate have to be substantially anhydrous when added to the fusion reaction mass in the fusion pot. It is impractical to introduce the reactants as aqueous solutions due to the fact that the heat required to evaporate these large amounts of water in the feed solutions cause the temperature of the fusion mass to be lowered below the solidifying point due to the fact that it is impossible to obtain a high enough rate of heat transfer through the heat transfer areas of the fusion pot to supply the large additional heat requirements necessary in continuous operation for the evaporation of the water contained in an aqueous feed solution. Due to the magnitude and nature of the heat transfer problems, it has been considered that a continuous fusion process having an industrially practicable rate of production and utilizing aqueous feed solutions of reactants is almost impossible. As examples of some of these problems may be mentioned the fact that the temperature of many of the fusion reactions is of the order of 380–400° C. and the fusion reaction mixtures of these same reactants evidence an initial thermal decomposition with attendant carbonization at about 410–420° C. This means that excessive "skin" temperatures across the heat transfer areas of the conventional fusion pot must be avoided, otherwise the fusion mass will char or carbonize. In the conventional fusion pot batch-wise method, these excessive skin temperatures are avoided by stirring and maintaining a relatively low heat transfer rate through the heat transfer areas of the fusion pot. Aqueous feeds demand higher heat transfer rates through the heat transfer areas of the fusion pots and, of course, this can only be accomplished by increasing the furnace temperatures under the fusion pots. These increased furnace temperatures result in higher "skin" temperatures; and as the stirring does not provide a high velocity of the fusion mass across the heat transfer areas, those portions of the fusion mass in contact with these heat transfer areas are subjected to localized overheating and exceed the thermal decomposition temperatures, resulting in charring of the fusion mass.

Moreover, in this type of reaction a common by-product is an alkali metal sulfite which is an infusible material, and therefore, as the amount of this sulfite progressively increases throughout the course of the reaction, it becomes eventually necessary to stop the operation, remove the fusion mass containing the accumulated by-product sulfite from the fusion pot, and start the cycle over again. Therefore, this type of fusion reaction for the manufacture of steam distillable phenols has been limited to small batch-wise operation and has not been found to be adaptable to continuous operation on an industrial scale or to the use of reactants introduced in the form of aqueous solutions. Moreover, due to the requirements for an independent supply of superheated steam and the other disadvantage of this type of fusion pot operation, this method for the manufacture of steam distillable phenols has never been deemed to be industrially practicable.

It is an object of this invention, therefore, to provide a new continuous process for carrying out certain fusion reactions of organic chemical synthesis characterized by highly efficient mixing of the fusion reactants, efficient high rate of heat transfer to the fusion mass, rapid and uniform flow of the fusion mass across the high temperature heat transfer areas and substantial elimination of localized overheating.

It is a further object of this invention, also, to provide a new and industrially practicable continuous method for carrying out certain fusion reactions of organic chemical synthesis wherein at least one or all of the reactants may be introduced into the fusion reaction zone as aqueous solutions.

A still further object of this invention is to provide a new and industrially practicable process for carrying out continuously the preparation by the fusion reaction of certain arylates by the general reaction

(1) $ArSO_3M + 2MOH \rightarrow ArOM + M_2SO_3 + H_2O$

wherein ArOM represents a fusible metal arylate, $ArSO_3M$ represents an aryl sulfonate salt, and M_2SO_3 represents a metal sulfite. The equation as written represents the stoichiometric proportions when the aryl sulfonate salt and the metal arylate are mono-substituted aryl compounds and M is a mono-valent metal such as sodium or potassium. In other cases stoichiometric proportions for a particular fusion reaction will depend upon whether the metal aryl sulfonate is a mono- or poly-sulfonate; likewise the stoichiometric proportions will vary depending upon the valence of the metal as represented by M.

According to a more specific embodiment of this invention, there is also provided a new and industrially practicable continuous process for carrying out fusion reactions wherein certain steam distillable phenols, i. e., phenols volatile in steam, may be prepared and the net result of which fusion reactions may be represented by one of the following equations:

(2) $ArSO_3M + ArOM + H_2O \rightarrow 2ArOH + M_2SO_3$

(3) $ArSO_3M + MOH \rightarrow ArOH + M_2SO_3$

(4) $ArSO_3M + xMOH + (1-x)ArOM + (1-x)H_2O \rightarrow (2-x)ArOH + Na_2SO_3$

wherein x represents a fractional number greater than zero and less than one

wherein ArOH represents a steam distillable phenol such as phenol, a cresol, a xylenol or a naphthol; ArOM represents a fusible metal arylate such as potassium or sodium phenate, a

potassium or sodium cresylate, a potassium or sodium xylenolate, or a potassium or sodium naphtholate; $ArSO_3M$ represents a metal salt of an aryl sulfonic acid such as sodium benzene sulfonate, sodium toluene sulfonate, potassium xylene sulfonate, or sodium naphthlene sulfonate; and MOH represents a fusible caustic alkali such as sodium hydroxide or potassium hydroxide.

Other objects will be apparent from the following description and examples.

In general, the object of this invention are attained by the novel process of this invention for carrying out fusion reactions of organic chemical synthesis which comprises maintaining a fluid body containing at least one of the fusible reactants or a fusible fusion reaction product in a fused, fluid and molten state in an upper zone from which this fluid body may flow by gravity, or be otherwise passed, to the lower portion of a substantially vertical elongated zone, heating and increasing the temperature of this fluid body during its flow or passage from the upper zone to the lower portion of the elongated zone by indirect heat exchange with a higher temperature heat source, returning this heated fluid body from the lower portion of the elongated zone up through the length of the elongated zone to the upper zone by means of a stream of steam which is introduced into the fluid body near the lower portion of the elongated zone.

A further embodiment of this invention comprises maintaining a fluid body containing at least one of the fusible reactants or a fusible fusion reaction product in a fused, fluid and molten state in an upper zone from which this fluid body may flow by gravity or be otherwise passed to a heat transfer zone wherein the fluid body is further heated to a higher temperature by indirect heat exchange with a higher temperature heat source, passing this heated fluid body from the heat exchange zone, as by gravity, to the lower portion of a substantially vertical elongated zone, returning the fluid body to the upper zone from the lower portion of the elongated zone up through the length of the elongated zone by injecting at least one stream of an aqueous solution of one or more fusion reactants into the fluid body near the lower portion of the elongated zone, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to convert the water of the aqueous reactant solutions into superheated steam, thereby depositing and intimately dispersing the fusion reactants from the aqueous solution into the fluid body, thereby promoting substantially instantaneous fusion of the deposited reactants with the fluid body to form a fluid fusion mass and causing the rapid rise of the superheated steam through the upper portion of the elongated zone, returning the fluid fusion mass to the upper zone. In the case where the fusion reaction products are not volatile in, or are not carried out in the stream of superheated steam which returns the fluid fusion mass to the upper zone, the superheated steam is removed from the upper zone at some point above the level of the fluid body maintained in the upper zone. A portion of the fluid fusion mass in the upper zone is then removed from the upper zone for treatment to recover the fusion reaction products, and another portion of the fluid fusion mass is used to serve as the fluid body to circulate from the upper zone by gravity down through the heat exchange zone to the lower portion of the elongated zone, into which the aqueous solutions of the reactants are injected.

In some cases, however, a part of the fusion reaction products may be volatile in the stream of superheated steam and will be removed from the fluid fusion mass by the stream of steam. Therefore, a mixture of steam and the volatile fusion reaction products are removed from the upper zone at some point above the level of the fluid fusion mass. The non-volatile fusion reaction products remain in the fusion mass, a portion of which fusion mass may be removed from the upper zone for treatment to separate and recover fusion reaction products and another portion of the fluid fusion mass is used to serve as the fluid body, as described above, to be passed from the upper zone through a heat exchange zone and be thereby heated to a higher temperature, and then to be passed to the lower portion of the elongated reaction zone where the aqueous solutions of feed reactants are injected into the hot fluid body.

A still further embodiment of this invention which relates to the production of those steam distillable phenols comprises maintaining a fluid body containing a fusible metal arylate in a fluid and molten state in an upper zone from which this fluid body may flow by gravity or be otherwise passed through a heat transfer zone wherein the fluid body is heated to a higher temperature by indirect heat exchange with a higher temperature heat source, passing this heated fluid body from this heat exchange zone, preferably by gravity, to the lower portion of a substantially vertical elongated zone, returning the fluid body from the lower portion of the elongated zone to the upper zone through the length of the elongated zone by injecting one or more streams, substantially parallel to the longitudinal axis of the elongated zone, of aqueous solutions of the fusion reactants, as represented by Equations 2, 3 or 4 in substantially stoichiometric proportions into the fluid body near the lower portion of the elongated zone, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to convert the water of the aqueous reactant solutions into superheated steam, thereby depositing and intimately dispersing the aryl sulfonate and the other reactants from the aqueous solution into the fluid body, thereby promoting substantially instantaneous fusion of the deposited reactants with the fluid body to form a fluid fusion mass, and the rapid rise of the superheated steam up through the length or upper portion of the elongated zone returns the fluid fusion mass to the upper zone. The stream of superheated steam separating from the surface of the fluid fusion mass contained in the upper zone carries with it the steam distillable phenol which was formed during the passage of the fluid fusion mass and the steam through the elongated zone. A part of the fusion mass is removed from the upper zone for treatment to separate the sulfite byproduct and a part of the fusion mass is used to serve as the fluid body to be recirculated from the upper zone to the lower portion of the elongated zone through the heat exchange zone.

Other embodiments will be apparent from the description of the preparation of specific steam distillable phenols in the following examples.

Figures 1, 3 and 5 represent types of apparatus which may be used in performing the fusion reaction in accordance with the methods and processes of this invention.

Figure 1 is a vertical section through such an apparatus and Figure 2 is a cross-section of such an apparatus across line 2—2.

In Figure 1, an "upper zone" is represented by chamber 1, jacketed with an insulating material 2. A "heat transfer zone" to which a fluid material may flow, as by gravity, from the "upper zone" is represented by a plurality of substantially vertical elongated conduits 4 which are in direct heat exchange relationship with a high temperature heat source such as the hot combustion gases contained in the furnace chamber 10. The phrase "heat exchange tubes" will be used herein as descriptive of parts of an apparatus having the same function as the elongated conduits 4, namely the function of effecting heat transfer from the high temperature heat source to the fluid body.

An "elongated reaction zone" is represented by an elongated conduit 3 which is substantially vertical and located in the lower portion of chamber 1 and which has a substantially larger cross-sectional area than the total cross-sectional area of the heat exchange tubes 4. The lower extremities of the elongated heat exchange conduits 4 of the heat transfer zone and the lower extremity of the elongated reaction zone conduit 3 terminate in a common header chamber 5 whereby a fluid body may flow or pass from the heat transfer zone to the lower portion of the elongated reaction zone conduit 3. Circulatory liquid communication is therefore provided, under the proper conditions, whereby a liquid or fluid body contained in the lower portion of chamber 1 or "upper zone" may pass from chamber 1 down through the elongated heat exchange conduits 4 of the "heat transfer zone" and thence pass through the header chamber 5 to the lower portion of the elongated reaction zone conduit 3, up through the elongated reaction zone conduit 3 and thereby returning to the chamber 1 or "upper zone."

A fluid body containing an excess of at least one fusible reactant or fusible reaction product in the fused, fluid and molten state is maintained at a predetermined level 7 within chamber 1. The fluid body level 7 is shown as being maintained by means of an over-flow conduit 9, which also serves as a means for continuously withdrawing a portion of the fluid body containing non-volatile or non-steam distillable components of the fluid fusion-reaction mass. The fluid fusion-reaction mass is maintained at a predetermined level 7 within chamber 1. The preferred level 7 is shown as being substantially coincident with the upper extremity 8 of the elongated reaction zone conduit 3, although, in the alternative, the upper extremity of the elongated reaction zone conduit 3 may be maintained above or below the level 7. Under static conditions, when chamber 1 is full of the fluid body to the desired level 7, the heat exchange tubes 4 and the header chamber 5 are also filled with the fluid body and the elongated reaction zone conduit 3 is filled with the fluid body to a level corresponding to the level 7 in chamber 1.

The heat exchange tubes 4, the elongated reaction zone 3 and the connecting header chamber 5 are shown in Figure 1 as being in direct heat exchange relationship with a high temperature heat source such as the chamber forming means 10 containing a high temperature heat transfer medium, which high temperature heat source is represented in Figure 1 as being a furnace chamber 10 containing the hot combustion gases of a gas burner 11. The high temperature heat transfer medium is distributed throughout the chamber forming means 10 and around and in contact with heat exchange tubes 4 and the elongated reaction zone 3 by means of suitable baffling means 12. A stack 13 represents an exit for the combustion gases when such gases are used as the high temperature heat source.

By means of feed inlet nozzle 6, a feed stream of an aqueous solution of the reactants is injected into the heated fluid body contained in the lower portion of the elongated reaction zone conduit 3. In the alternative, a plurality of feed inlet nozzles may be employed, each of which may inject one or more fusion reactants or other materials as liquids or as aqueous solutions. The feed inlet nozzles as represented by nozzle 6 may be designed in any number of fashions. The nozzle may be of the orifice type and each nozzle may eject a single or a plurality of streams of feed reactants or other materials. In many instances satisfactory injection of the feed stream has been accomplished by using a simple injection nozzle as the open end of a small diameter pipe. Nozzle 6 is preferably located in the lower portion of the elongated reaction zone conduit 3 and a short distance above the lower extremity of the elongated reaction zone conduit. When a single nozzle is used, the nozzle is preferably centrally located within the cross-section of the elongated reaction zone conduit; however, when more than one nozzle is employed, they are preferably symmetrically located within the cross-section of the elongated reaction zone conduit. The feed stream or streams are preferably injected into the fluid body contained in the lower portion of the elongated reaction zone conduit substantially parallel to the longitudinal axis of the elongated reaction zone conduit.

The water contained in the aqueous solutions flashes into superheated steam upon being injected into the hot fluid body contained in the lower portion of the elongated reaction zone conduit which fluid body has been previously heated during the passage of the fluid body through the heat exchange zone. This flashing action of the water of the aqueous solution deposits and intimately disperses the fusion reactants from the aqueous solution into the heated fluid body, thereby promoting substantially instantaneous fusion of the deposited reactants with the fluid body to form a fluid fusion mass. The rapid rise of the superheated steam through the length of the elongated reaction zone conduit 3, combined with the initial motion imparted to the fluid body due to the velocity of the aqueous streams injected from the inlet nozzle, results in a high velocity upward motion of the steam bubbles and the fluid fusion mass through the length of the elongated reaction zone conduit, thereby returning the fluid body to chamber 1. This rapid upward movement of the fluid body within the elongated reaction zone conduit 3 induces rapid circulation of the fluid body contained in the lower portion of chamber 1, down through the heat transfer tubes 4 into the header chamber 5 and thence into the lower portion of the elongated reaction zone conduit 3 and upwards through the elongated reaction zone conduit past nozzle 6, whereby the heated fluid body is continuously supplied immediately adjacent to the injection nozzle 6. During the passage of the fluid body through the heat transfer tubes 4, the fluid body acquires sufficient additional heat so that this

heated fluid body may serve as the high temperature heat transfer medium to supply the heat requirements for the conversion of the water of the aqueous feed solutions to superheated steam and also supply the heat requirements for the fusion reaction within the elongated reaction zone, without cooling the fluid body below its solidifying point.

The fluid body containing the non-volatile or non-steam distillable fusion reaction products, that is the fluid fusion mass, leaves the upper extremity 8 of the elongated fusion reaction zone conduit 3, together with a stream of superheated steam and any volatile or steam-distillable fusion reaction products, at a considerable velocity; and therefore, a suitable provision is made for disentraining the fluid fusion mass from the stream of vaporized materials. Any one of many conventional disentraining devices may be employed; however, the upper portion of chamber 1 is shown as being provided with a suitable baffing means 14 so as to function as a disengaging zone to disentrain the fluid fusion mass from the stream of steam and any other vaporized materials, and the steam together with any other vaporized materials are then removed from the apparatus by means of vapor outlet 15, and the disentrained fluid fusion mass falls back from the baffing into the lower portion of chamber 1 to maintain the level of the fluid body at the predetermined level 7 for recirculating through the heat exchange tubes 4, and the excess of the fluid body level 7 is continuously withdrawn through the over-flow outlet 9.

The design of the apparatus of Figure 1 may be modified so that the lower extremity of the elongated reaction zone terminates at about the floor level of the furnace chamber 10 and thereby placing the header chamber 5 outside of the furnace chamber. By placing the header chamber 5 below the floor of the furnace chamber, the header chamber is more readily accessible. One advantage of having the header chamber 5 within the furnace chamber is the fact that heat loss from the materials which are circulating through the header chamber 5 is materially reduced. However, if the alternative modification were desired wherein the header chamber 5 would be below the floor of the furnace chamber, the heat loss from header chamber 5 could be very effectively minimized by insulating the outside surface of header chamber 5.

In Figure 1, an insulation 16 is placed around that portion of the feed line 17 which passes in direct heat exchange relationship with the high temperature heat source, whereby excessive premature heating of the aqueous solutions within the feed line is avoided. Premature heating of this portion of the feed line to a high temperature may cause steam formation within the feed line which may result in improper functioning of the injection nozzle 6. This problem of premature heating of the feed line is, of course, not encountered when the lower surface of the header chamber is outside of the furnace chamber.

Figure 3 shows a further modification of the design of the apparatus of Figure 1, and Figure 3 is a vertical section through such an apparatus and Figure 4 is a cross-section view through line 4—4. In Figure 3 the elongated reaction zone conduit 3 and the header chamber 5 have been taken outside of the furnace chamber 10. In actual practice, very little, if any, heat transfer is made from the furnace chamber 10 to the fluid body through the elongated reaction zone conduit 3 or through the header chamber 5. The placing of the elongated reaction zone conduit 3 within the furnace chamber accomplishes the purpose of reducing the heat loss from the material within the elongated reaction zone conduit. However, the process of this invention may be carried out efficiently in an apparatus where the heat exchange tubes 4 are within the furnace chamber 10 and the elongated reaction zone conduit and the header chamber 5 are placed outside of the furnace chamber 10 and well insulated to prevent heat loss.

In Figure 1, the header chamber 5 was used to provide liquid communication between the lower extremities of the heat exchange tubes 4 and the lower portion of the elongated reaction zone conduit 3. However, in Figure 3, the lower extremities of the heat exchange tubes 4 actually terminate in the lower portion of the elongated reaction zone conduit 3, and header chamber 5 of Figure 3, therefore, may be considered as being the lower portion of the elongated reaction zone conduit 3 rather than as a separate and distinct chamber. For large scale operations, an apparatus to carry out the novel aspects of this invention may be designed having more than one elongated reaction zone conduit, and a plurality of several hundred heat exchange tubes 4.

In the types of apparatus as represented in Figures 1 and 3, instead of using combustion gases as the high temperature heat transfer medium, chamber 10 may be modified so as to receive high temperature vapors from some other source, as for example, the design of chamber 10 may be modified so as to receive mercury vapors from a mercury boiler and the mercury vapors passing in contact with the heat exchange tubes 4 would serve as the high temperature heat source to provide the additional heat to be transferred to the fluid body passing through the heat exchange tubes 4. On the other hand, the heat exchange tubes may be heated by radiant energy or a combination of radiant and convection heat if so desired.

Figure 5 is again a vertical section and represents another type of apparatus that may be used to carry out the process of this invention, and Figure 6 is a cross-section of the same apparatus across line 6—6. In Figure 5, the "upper zone" is represented by chamber 51, jacketed with an insulating material 52. The fluid body contained in the lower portion of chamber 51 may pass by gravity to a heat exchange zone wherein the fluid body passes around and in contact with a plurality of horizontal or inclined heat exchange tubes 54 through which may pass a high temperature heat transfer medium such as the mercury vapors from a mercury boiler, a molten mixture of sodium nitrate-sodium nitrite or one of the well known silicone polymer type of high temperature heat transfer fluids. The fluid body in passing around and in contact with the plurality of heat exchange tubes 54 is therefore heated to a higher temperature by indirect heat exchange with the high temperature heat transfer medium circulating through the heat transfer tubes. The heated fluid body then passes from the heat transfer zone by means of the connecting conduit 55 to the lower portion of an elongated reaction zone conduit 53. One or more streams of an aqueous feed solution are injected into the heated fluid body by means of one or more nozzles 56 and, as described hereinbefore, the water of the aqueous solution flash-

ing into superheated steam and rising through the elongated reaction zone conduit 53 returns the fluid body to the upper zone of chamber 51. Figure 5 illustrates a different method for disentraining the fluid body from the vaporized materials. In Figure 5 the elongated reaction zone conduit has a section 58 which enters the upper chamber 51 substantially tangentially to a wall of chamber 51. The fluid body and the vaporized materials, therefore, leave the upper extremity of conduit 53 at a rather high velocity and due to the tangential positioning of the upper extremity of conduit 53 with respect to the wall of chamber 51 these materials issue into chamber 51 with a circular motion providing a cyclonic effect to aid in the separation of the vaporized material from the fluid body. This cyclonic action coupled with suitable baffling means 60 in the upper portion of chamber 51 serves to disentrain the fluid body from the steam and other vaporized materials. The vaporized materials, including, of course, the steam, are then removed from chamber 51 through vapor outlet 61 and the disentrained fluid body falls back into the lower portion of chamber 51 to maintain the fluid body level 57 and the excess of the fluid body is removed through overflow out 59. The fusion reaction products may be therefore contained either in the vaporized materials leaving outlet 61 or contained in the fluid body which is removed from the outlet 59.

While the elongated reaction zone conduit 3 in Figures 1 and 3 and the elongated reaction zone conduit 53 in Figure 5 are shown as being vertical or substantially vertical, the design of the apparatus may be modified so that the elongated reaction zone conduits and/or the heat exchange tubes are inclined, as at an angle of 45° or any other convenient angle.

From the foregoing discussion of the types of apparatus and modifications which are suitable for carrying out the process of this invention, it is readily seen how the process of this invention may be applied for the purpose of carrying out fusion reactions on a continuous basis. The process of this invention, of course, has as one of its primary objectives the carrying out of the actual fusion reaction step on a continuous basis. The fusion reaction products will, of course, have to be recovered either from the vaporized materials which are removed from the upper zone or from the excess fluid body which is continuously removed from the chamber 1 as by outlet 9. These details will be evident and more clearly understood from the following examples of actual operation.

EXAMPLE I

Apparatus

An apparatus was constructed in a design substantially as shown in Figure 1, and this apparatus was used in the carrying out of the various fusion reactions which will be herein described. All of the metallic parts which were in contact with the fluid body and the fusion reaction mass, including the chamber 1, the elongated reaction zone conduit 3, the heat exchange tubes 4, the header chamber 5, the feed inlet nozzle 6 and the baffling 14 were fabricated from a nickel alloy stainless steel commonly known to the trade as Inconel. The entire fusion reaction apparatus was structurally designed to permit variations of pressures within the apparatus from 0 to 65 pounds per square inch absolute. The chamber 1 was substantially cylindrical with a diameter of about 4 feet and a height of about 10 feet. Centrally located with respect to the bottom of chamber 1 was an elongated reaction zone conduit 3, six inches inside diameter and approximately 25 feet in length. The elongated conduit 3 extended up into chamber 1 about 5 feet and depended into the furnace chamber 10 approximately 20 feet. Also fitted into the bottom of chamber 1, the bottom of chamber 1 functioning as a tube sheet, and equally spaced in a 9-inch circle around the elongated reaction zone conduit 3 (Figure 2 illustrates this arrangement) were ten 1½ inch heat exchange tubes 4 which were substantially 20 feet long. The lower extremity of the elongated reaction zone conduit 3 and the lower extremities of the heat exchange tubes 4 terminated in a common header chamber 5 such as is represented in Figure 1.

The elongated reaction zone conduit and the heat exchange tubes depending into the furnace chamber 10 were heated by hot gases, combustion gases plus secondary air, from a gas burner 11 capable of delivering up to 3,000,000 B. t. u. per hour and a maximum discharge temperature of 2000° F. By proper control of the natural gas and primary and secondary air supplies to the gas burner, it was possible to obtain discharged gases into the furnace chamber at any desired temperature from room temperature up to 2000° F. The temperatures of the discharged burner gases were controlled by means of an automatic temperature control system which continuously analyzed the temperature of the fluid body contained in the lower portion of chamber 1, the temperature of the fluid body leaving the heat exchange zone, and the temperature of the exit gases leaving chamber 10 through stack 13, and relayed this information to an automatic system which controlled the air and gas amounts and ratio to the burner 11 and thereby controlled the temperature of the discharge burner gases so as to maintain the fluid body in chamber 1 at a predetermined temperature. The furnace chamber was so baffled that none of the heat exchange surfaces could "see" the flame of the gas burner and the gases entering the lower portion of the furnace chamber were guided by means of suitable baffling so that the hot gases were suitably distributed over the heat exchange tubes.

The fluid body level within chamber 1 was maintained so that the upper extremity 8 of the elongated reaction zone conduit 3 terminated substantially at the fluid body level 7. Also, the upper portion of the chamber 1 contained the baffling so that the upper portion of chamber 1 acted as a disengaging zone to disentrain the fluid body from the vaporized materials, and the vaporized materials were removed by means of vapor line 15 connected to the top of chamber 1 and the fluid body comprising the fluid fusion reaction mass was removed by means of an over-flow pipe 9 arranged substantially as shown in Figure 1.

The lower surface of the header chamber 5 contained a flanged opening 18 to facilitate the positioning of the feed inlet nozzle 6 substantially centrally located within the cross-section of the lower extremity of the elongated reaction zone conduit 3 and the feed inlet nozzle extended substantially co-axially up into the elongated conduit 3 for a distance of about one foot. The feed inlet nozzle 6 was designed to provide for introducing a single stream of an aqueous feed solution substantially co-axially into the elongated conduit 3 at high velocities of the order of

50–150 feet per second to facilitate the injection of the aqueous feed solutions into the heated fluid body. The inlet nozzle was provided with piping and valving outside of the furnace chamber to facilitate the alternative admission of steam into the fluid body contained within the conduit 3 during the initial start-up periods and also to maintain circulation within the apparatus in the event that the supply of feed solution should fail.

The process of this invention may be used to carry out any of those fusion reactions of organic chemical synthesis which may be carried out in the presence of steam and wherein at least one reactant or a reaction product forms a fluid molten mass at the desired fusion-reaction temperature. However, present commercial requirements generally indicate the use of the process of this invention to be most highly advantageous in the manufacture of phenols, such as phenol, cresols, xylenols and naphthols through a fusion reaction wherein the raw materials are caustic soda and the sodium salt of the corresponding aryl sulfonic acid and the fusion reactants are steam, an alkali metal hydroxide, the corresponding sodium arylate, and the sodium salt of the corresponding aryl sulfonic acid. The presence of steam (H_2O) is required in the reaction. The sodium salts of these phenols fuse under the application of heat to form fluid, mobile fusion masses at the required fusion-reaction temperature and all of these phenols are volatile in the presence of superheated steam and can, therefore, be readily separated from the fusion masses by vaporization.

Preparation of phenol

In view of the fact that phenol is the most important chemical compound that may be produced by the method of this invention, a substantial portion of the following discussion and description will be directed toward the preparation of phenol by the method of this invention. However, it is here pointed out that those skilled in the art of fusion reactions and who have read and understood the following discussion relating to the preparation of phenol, may apply the teachings of the disclosure herein set forth to any similar fusion reaction utilizing different reactants and perform the fusion reaction realizing the benefits of this invention without departing from the spirit and scope of this invention.

According to this invention, in the preparation of phenol, the fusion reactants in the form of aqueous solutions are injected into a fluid body maintained at a temperature within the range of 355–425° C. and preferably within the temperature range of 370–400° C., which fluid body is composed predominantly of molten sodium phenate and is contained in the lower portion of an elongated reaction zone such as has been described.

The fluid body serves two important purposes; namely that of a heat transfer medium to supply the heat requirements for the fusion reactions and the heat requirements for converting the water of the aqueous feed solutions to superheated steam, and a second purpose, that of a fluid vehicle to facilitate the removal of the insoluble, infusible and non-volatile fusion reaction products from the fusion reaction zone. Therefore, the fluid body will contain by-product sodium sulfite (see Equations 2, 3 and 4) and minor amounts of other components in addition to the predominant component sodium phenate. The minor amounts of the other components will include some unconverted sodium benzene sulfonate and other inorganic salts such as sodium sulfate, sodium chloride and sodium carbonate which salts are introduced into the system as impurities in the sodium benzene sulfonate and the caustic soda.

The fluid body must be fluid and mobile at all times. However, the by-product sodium sulfite and the other inorganic salts are infusible materials which in continuous operation must be continuously removed from the fusion reaction apparatus substantially at the same rate as they are formed. In the absence of a fluidizing vehicle, such as sodium phenate, this by-product sodium sulfite and the other inorganic salts would form a solid unmanageable, infusible mass within the fusion reactor. However, when a sufficient quantity of molten sodium phenate is present within the apparatus, the sodium sulfite can be kept in suspension in the molten sodium phenate to form a mobile and circulatable fluid body. "Fusion mass" is the term which is used herein to describe the fluid body in the manufacture of phenol composed of molten sodium phenate which has the by-product sodium sulfite in suspension and which issues from the elongated reaction zone. In addition to the sodium phenate and sodium sulfite, the fusion mass will principally contain the small quantity of unconverted NaBS (sodium benzene sulfonate), and any inorganic materials which are introduced into the process as impurities in the raw materials. The "fusion mass" may also contain a small amount of free alkali metal hydroxide due to equilibrium conditions; however, sodium hydroxide being a fusible material, contributes to the fluidity of the "fusion mass."

In view of the fact that the fusion mass or "fluid body" in the fusion reactor must remain fluid and mobile within the fusion reactor, there is a minimum critical ratio between the quantity of fusible and of infusible components of the fusion mass which can be tolerated and still maintain a fusion mass having the requisite fluidity for use in this process. The ratio of the quantity of fusible components to the quantity of infusible components of the fusion mass will herein be termed the "fluidity ratio," and will be defined as follows, all percentages being by weight:

$$\text{Fluidity ratio} = \frac{\text{Percent sodium phenate} + \text{percent NaOH}}{\text{The sum of the percentages of all the other components of the fusion mass (fluid body)}}$$

The fluidity ratio should be maintained as low as practicable in order to minimize the amount of sodium phenate which has to be recycled as vehicle. However, in order that the fusion mass will remain fluid and mobile at a minimum temperature of 355° C., the fluidity ratio must be maintained above 0.75. In other words, the fluid body must contain at least 0.82 mol of sodium phenate per mol of sodium sulfite present. It has been found that a fluidity ratio between about 1.5 and about 2.5 is preferred for an easily mobile fluid body at temperatures of 355° C. and above; that is, it is preferred that the fluid body contain about 1.5 to about 3.0 mols of sodium phenate per mol of sodium sulfite in suspension in the fluid body, although generally a fluid body containing from about one to about 6 mols of alkali-metal arylate per mol of alkali metal sulfite is satisfactory.

At the start-up of the fusion reaction process, the fluid body is practically entirely sodium phenate; therefore, the apparatus is first filled to the fluid body level 7 with fluid molten sodium phenate.

Start-up

The initial charging of the apparatus to level 7 with fluid molten sodium phenate may be accomplished in a number of ways. For example, the apparatus may be carefully preheated to a temperature above the solidifying point of sodium phenate and sodium phenate which has been carefully melted in another pot or piece of apparatus is then transferred to the fusion apparatus until the level 7 has been reached.

On the other hand, it is quite difficult to charge the apparatus to the level 7 with molten sodium phenate by the evaporation of an aqueous solution of sodium phenate within the apparatus. This is due to the fact that when an aqueous solution of sodium phenate is evaporated, a solid phase is encountered prior to the time that the dehydrated sodium phenate becomes a fused mass. Therefore, in attempting to dehydrate sodium phenate within the apparatus, there is danger of plugging the heat exchange tubes with a consequent reduction in circulation of the sodium phenate within the apparatus. This would normally be followed by charring of the sodium phenate within the heat exchange tubes because of localized overheating when it is attempted to heat the tubes hot enough to melt the sodium phenate. However, if the apparatus is carefully preheated to a temperature above the solidifying temperature of the sodium phenate, previously melted sodium phenate may then be charged to the reactor without danger of solidification or charring.

In view of the difficulty encountered in the dehydration of an aqueous sodium phenate solution and the fusion of the dehydrated sodium phenate within the apparatus, the following starting procedure is recommended when the process of this invention is used with the type of apparatus as has been herein described. This particular technique of starting up the process constitutes an important embodiment of this invention.

The fusion apparatus or "fusion reactor" is carefully preheated to 250° F. and filled with aqueous caustic soda solution (such as a 30–75% caustic soda solution) by pumping the caustic soda solution into the fusion reactor through the feed nozzle 6. By "aqueous" is meant any caustic solution that can be conveniently handled. The use of concentrated solutions, in the range of 70–75%, is desirable. After the reactor is filled to the operating level 7, as evidenced by the fact that the caustic soda solution has begun to flow from the chamber 1 through over-flow pipe 9, the temperature of the combustion gases from the gas burner 11 within the furnace chamber 10 is gradually raised. During this time the addition of aqueous caustic soda solution through the feed nozzle is continued and a small overflow from the reactor through the overflow pipe 9 is maintained.

After vaporization of water from the fusion reactor is observed, the temperature of the combustion gases is raised by 50° increments at 15 minute intervals until a top temperature level of 1250° F. is reached. As dehydration of the aqueous caustic soda solution proceeds, the boiling point of the caustic soda solution within the reactor is continuously observed and recorded until the temperature of the boiling caustic soda solution levels out at 390° C. At this point the fusion reactor is filled to level 7 with a concentrated, substantially anhydrous (i. e. less than 1% water) caustic soda at a temperature of 390° C.

At this point the feed is changed from aqueous caustic soda solution to 54% sodium phenate solution and the injection of this aqueous sodium phenate solution is maintained at a rate of 45 to 50 gallons per hour, while the automatic temperature control system is set to maintain the molten materials in the chamber 1 at 390° C. The material overflowing from outlet 9 is passed to a quenching tank wherein the hot materials removed from the fusion reactor are quenched with water. As the injection of the sodium phenate solution is continued, it will be noted that the overflow continues to show decreasing amounts of caustic soda and increasing amounts of sodium phenate. The injection of the sodium phenate solution is continued until substantially all of the caustic soda has been displaced from the fusion reactor by sodium phenate, as evidenced by the fact that the overflow materials contain almost entirely sodium phenate and very little (of the order of 1 to 2%) caustic soda. At this point the fusion reaction apparatus is filled with fluid molten sodium phenate at a temperature of 390° C.; and thereafter, the temperature control means may be set to maintain a temperature within the range of 355 to 420° C. and the apparatus is ready to begin continuous operation for the preparation of phenol.

Using this method of start-up, the transition is made from the fluid mobile molten caustic soda to a fluid mobile sodium phenate without going through any solid stages. In the use of this start-up procedure there is no evidence of burning, charring, localized overheating or any other decomposition of the sodium phenate.

EXAMPLE II

With an apparatus such as is shown and described in Example I filled to level 7 with a fluid body containing molten sodium phenate, phenol may be produced in accordance with the process of this invention by injecting an aqueous solution of sodium benzene sulfonate (NaBS) and an aqueous solution of sodium hydroxide (NaOH), as the raw materials, into the sodium phenate fluid body contained in the elongated reaction zone.

The overall fusion reaction may be represented as taking place step-wise according to the following reactions:

(5) $C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$

and

(6) $C_6H_5ONa + H_2O \rightleftharpoons C_6H_5OH + NaOH$

When free NaOH is introduced as a part of the feed reactants with NaBS, Equation 5 probably represents the first reaction taking place, however, as the NaOH is consumed within the fusion reaction zone due to the reaction of the NaOH with NaBS and the NaOH concentration is thereby reduced, Reaction 6 takes place favoring the formation of phenol, which phenol is removed from the fluid fusion mass together with the excess steam which is evolved within the elongated reaction zone. When the NaBS is substantially all reacted and converted to phenol, the free NaOH content due to the hydrolysis of the sodium phenate soon builds up to the point

where equilibrium conditions prevent further hydrolysis of sodium phenate. The Reactions 5 and 6 take place substantially instantaneously within the elongated reaction zone due to the intimate dispersion and contact of the reactants NaBS and NaOH with the fluid body containing the fluid fused sodium phenate and equilibrium conditions are substantially reached in the time it takes for the fusion mass to pass up through the elongated reaction zone and return to the upper zone. The net result of the reactions taking place in the elongated reaction zone may hence be represented by the chemical addition of Equations 5 and 6, namely

(7) $C_6H_5SO_3Na + NaOH \rightarrow C_6H_5OH + Na_2SO_3$

which is a specific reaction within the scope of Reaction 3. Therefore, for each mol of NaBS and each mol of free NaOH raw materials introduced into the elongated reaction zone, one mol of phenol is formed which is removed from the upper zone together with the excess steam which is formed from the water contained in the aqueous solutions of feed reactants.

Also, according to Reaction 7, 1 mol of by-product sodium sulfite is also formed for each mol of NaBS introduced into the elongated fusion reaction zone. As the sodium sulfite is a non-volatile and infusible material at these temperatures, it remains essentially in suspension in the molten sodium phenate. Under conditions of continuous operation, it is necessary to remove the sodium sulfite from the fusion process substantially at the same rate that it is formed in order to avoid an excessive build-up of sodium sulfite in the fluid body (which would reduce the fluidity ratio below the minimum ratio of 0.75). In continuous operation it is usually preferred not to allow the sodium sulfite content of the fluid body to build up over the ratio of 1 mol of sodium sulfite to about 2 mols of sodium phenate. This ratio of sodium sulfite to sodium phenate usually results in a preferred fluidity ratio of about 1.7 to 1.8, depending upon the amount of other inorganic salts introduced into the fluid body (fusion mass) as impurities in the raw material NaBS and NaOH. A fluid body containing fluid molten sodium phenate and sodium sulfite and having a fluidity ratio of about 1.7 to 1.8 is a very fluid and mobile fluid body at temperatures of 355–420° C. In continuous operation during the time that one mol of NaBS is injected into the elongated reaction zone, a portion of the fluid body containing substantially 1 mol of sodium sulfite is withdrawn from the upper zone. When the fluidity ratio is about 1.7 to 1.8 the portion of the fluid body containing substantially one mol of sodium sulfite also contains about two mols of sodium phenate. This quantity of sodium phenate must be replaced in the fluid body in order to maintain the desired fluidity ratio. Therefore, the portion of the fluid body removed from the upper zone is passed to a quencher wherein the hot fluid body is quenched in a sufficient amount of water to dissolve the sodium phenate, but not the sodium sulfite. The aqueous quencher mixture is then filtered or centrifuged to remove the insoluble sodium sulfite and other inorganic salts, and the quencher liquor containing the sodium phenate in solution is recycled and injected into the fluid body contained in the elongated reaction zone either through a separate nozzle as a separate stream; or, the quencher liquor may be combined with the aqueous NaOH and aqueous NaBS solutions to form one aqueous solution for injection into the elongated reaction zone through a feed injection nozzle. In this manner for each mol of NaBS and each mol of NaOH introduced into the elongated reaction zone, substantially 2 mols of sodium phenate are also introduced to replace the sodium phenate contained in the portion of the fluid body removed from the upper zone. Using this method of operation, the fluidity ratio of the fluid body is easily maintained and controlled at the desired value.

When the fluid body contained in the upper zone is maintained at a temperature within the range of 360–400° C. generally 94 to 98.5% of the NaBS passing through the elongated reaction zone is converted to phenol, and a conversion of about 97% can be consistently obtained when the fluid body is maintained at a temperature within the range of 370–390° C. After the initial start-up period and substantial equilibrium conditions have been established throughout the fusion reaction process, the fluid body will contain a small portion of unconverted NaBS. On the basis of 97% conversion, each time 1.032 mols of NaBS passes through the elongated reaction zone, 0.97 times 1.032 or 1.00 mol of NaBS is converted to phenol and 0.032 mol of unconverted NaBS remain in the fluid body. Under equilibrium conditions in the continuous process, that portion of the fluid body which is removed from the upper zone containing 1 mol of sodium sulfite and about 2 mols of sodium phenate will also contain about 0.032 mol of unconverted NaBS. This unconverted NaBS also goes into solution in the quenching step and is returned to the elongated reaction zone together with the recycled aqueous solution containing 2 mols of sodium phenate. Therefore, for each mol of raw material NaBS introduced into the process, 1.032 mols of NaBS pass through the elongated reaction zone, and at 97% conversion, 1.00 mol of NaBS is therefore converted to phenol. Also as the equilibrium conditions within the elongated reaction zone results in a small amount of free caustic being present in the fluid body, this free caustic soda also goes into solution in the quenching operation and is recycled to the elongated fusion reaction zone in the aqueous solution containing the sodium phenate and the unconverted NaBS.

Therefore, in continuous operation, after the initial start-up period has been passed, and a constant conversion ratio of NaBS to phenol has been established, the equilibrium conditions within the elongated reaction zone are such that for each mol of NaBS and each mol of NaOH introduced into the reaction zone as raw material feed reactants together with the recycled liquor from the quencher containing sodium phenate, the unconverted NaBS and NaOH, one mol of phenol may be removed from the process and Equation 7 is thereby realized.

The fusion process may be mode easily understood by reference to Figure 7 which is a diagrammatical representation of a period of time in the continuous operation of the process carried out according to this invention wherein 1 mol of product phenol is produced.

A fusion reaction apparatus substantially as described in Example I was filled with molten sodium phenate to the level 7 and the automatic temperature control system was set to maintain the fluid body contained in the lower portion of the upper zone at 370° C.

Into this hot fluid body contained in the lower

portion of the elongated reaction zone, were continuously and concurrently injected three streams of materials, so that during the same time interval that feed stream 7*a* containing 1.0 mol of NaOH and 0.95 mol of water was being injected, feed stream 7*b* containing 1.0 mol of NaBS and 9.25 mols of water and feed stream 7*c* representing a recycle stream of quencher liquor containing 2.5 mols of sodium phenate, 0.032 mol of NaBS and 24.3 mols of water were injected into the fluid body. The flow rates of each stream through the injection nozzles were maintained so that the reactants entered the elongated reaction zone in substantially stoichiometric proportions. The orifice in each nozzle was adjusted so that each stream was injected at a velocity of about 60 feet per second. The time period during which the amount of materials represented by lines 7*a*, 7*b* and 7*c* were injected was about 115 minutes.

The temperature of the combustion gases from burner 11 was recorded at about an average of 1300° F. throughout the time period indicated and the temperature of the fluid body passing through the heat transfer zone was increased an average of about 5° C. The requisite high rate of heat transfer was obtained to permit continuous operation of the fusion reaction utilizing aqueous solutions of the reactants without any danger of localized overheating or thermal decomposition of the fluid body which begins at approximately 420° C. The water in these three feed streams is converted into superheated steam inside the elongated reaction zone and 34.5 mols of water in the form of superheated steam leaves the upper extremity of the elongated reaction zone carrying with it 1.0 mol of phenol by reason of Reaction 2. The phenol-steam vapors are passed along line 7*d* to a phenol-recovery zone consisting of an absorption tower in which tricresyl phosphate is circulated to scrub the phenol from the phenol-steam vapor, and thereafter the phenol is separated from the tricresyl phosphate by fractional distillation, and 1 mol of product phenol is removed from the process along line 7*g*.

During the time these three feed streams were being injected into the elongated reaction zone, a quantity of the fluid body was continuously and concurrently withdrawn through outlet 9 represented by line 7*e* of Figure 7, containing 0.032 mol NaBS, 1.0 mol Na_2SO_3 and 2.5 mols of sodium phenate (fluidity ratio about 2.2) and quenched in 23.4 mols of water at the quenching step. The resulting slurry from the quenching step was then passed along line 7*f* to the sulfite separation step and therein centrifuged to remove the solid sodium sulfite, the sulfite cake washed and removed from the process along line 7*h*, and the aqueous quencher liquor combined with the sulfite cake wash water and recycled to the fusion reaction zone via line 7*c*.

By this process, using aqueous solutions, free NaOH and NaBS in equimolecular proportions as the feed reactants, a conversion of 97% of the NaBS passing through the reaction zone (feed NaBS plus recycle NaBS) is realized, and a yield of 96% phenol is obtained, about 3% of the phenol having been converted to higher boiling phenols and ethers.

EXAMPLE III

With an apparatus such as is described in Example I, filled to level 7 with a fluid body containing molten sodium phenate, phenol may be produced in accordance with the process of this invention by injecting an aqueous solution of sodium benzene sulfonate (NaBS) and an aqueous solution of sodium phenate ($NaO\phi$), as the raw materials, into the fluid body contained in the elongated reaction zone.

Phenol is produced as a result of several intermediate reactions and the net result of the intermediate reactions may be represented by the reaction:

(8) $C_6H_5SO_3Na + C_6H_5ONa + H_2O \rightarrow 2C_6H_5OH + Na_2SO_3$

which is a specific reaction within the scope of the general Reaction 2.

This process of this example is distinguished from the process of Example I in that in Example I the aqueous solution of feed reactants contained free NaOH as one reactant, whereas, in this example, no free NaOH is introduced as a part of the feed, but rather only NaBS and sodium phenate. While in the process of this example, NaOH is required as a raw material in the overall process, free NaOH is not one of the principal reactants which are introduced into the fusion reaction zone such as was done in Example I.

Figure 8 is a diagrammatical representation of a time period in a continuous process carried out according to this invention wherein 1 mol of product phenol is produced.

One mol of raw material NaBS in the form of an aqueous solution containing 9 to 12 mols of water enters the process along line 8*a*. One mol of raw material caustic soda (NaOH) enters the process along line 8*b* and is reacted with 1 mol of phenol from line 8*c* to make up an aqueous solution containing 1 mol of sodium phenate ($NaO\phi$) and 6 to 8 mols of water which passes along line 8*d*.

The materials flowing along line 8*e* represents the portion of the fluid body withdrawn from the lower portion of the upper zone during the time period that 1 mol of raw material NaBS (from line 8*a*) is introduced into the elongated reaction zone. The portion of fluid body which is withdrawn is shown as containing 1.0 mol of by-product Na_2SO_3 (Reaction 8), 0.032 mol of NaBS (by reason of a 97% conversion of NaBS to phenol in the elongated reaction zone), and 2.0 mols of sodium phenate ($NaO\phi$), and having a fluidity ratio of about 1.7. This portion of the hot molten fluid body is quenched in sufficient water to dissolve the sodium phenate and the NaBS at the quenching step and this resulting quencher slurry is passed along line 8*f* to a centrifuge wherein the insoluble by-product Na_2SO_3 (and any other inorganic salts, such as Na_2SO_4, NaCl and Na_2CO_3 which are introduced into the process system as impurities in the commercial grade of raw material NaBS and NaOH used) is removed. The sodium sulfite removal is shown as line 8*g*. The centrifuge cake (Na_2SO_3) is washed free of $NaO\phi$ and NaBS with water and the wash water combined with the quencher liquor to make up the aqueous solution flowing along line 8*h*, whereby the 2.0 mols of sodium phenate are returned to the fluid body to maintain the desired fluidity ratio and the 0.032 mol of NaBS is returned to the elongated reaction zone so that the 1.0 mol of raw material NaBS plus the 0.032 mol of recycled NaBS make up 1.032 mol of NaBS passing through the elongated reaction zone. Therefore, at 97% conversion, $.97 \times 1.032 = 1.00$ mol of NaBS converted to phenol. Therefore, under continuous operation, and after

substantially equilibrium conditions have been established, 1 mol of phenol is actually produced for each mol of raw material NaBS introduced into the elongated reaction zone.

The materials moving along lines 8*a*, 8*d* and 8*h* may be injected into the fluid body contained in the elongated reaction zone by means of separate injection nozzles or these three streams may be combined to form one aqueous feed stream as represented by the composition of the aqueous solution passing along line 8*i*. The composite feed stream 8*i*, therefore, contains the 1 mol of the raw material NaBS from line 8*a* in addition to the 0.032 mol of NaBS recovered from the quenching of the fluid body for a total of 1.032 mols of NaBS. The composite feed stream 8*i* is also shown to contain 3.0 mols of NaOϕ, namely, the 1.0 mol of NaOϕ from line 8*d* plus 2.0 mols of NaOϕ recovered from the quenching of the fluid body, and passed along line 8*h*.

As all of the streams 8*a*, 8*d* and 8*h* are aqueous solutions, the water content of composite stream 8*i* will be the sum of the water content of the three streams 8*a*, 8*d* and 8*h* and it is preferred to maintain the water content of the composite feed stream 8*i* at about 45 to 50% by weight. The composite feed stream 8*i* is injected into the fluid body contained in the elongated reaction zone of a fusion reaction apparatus of one of the types as has been described and wherein the fluid body in the elongated reaction zone is maintained at a temperature within the range of 355 to 420° C. and preferably within the range of 370 to 400° C. During the time that an amount of feed solution of line 8*i* containing 1.032 mols of NaBS is injected into the fluid body, on the basis of a 97% conversion of the NaBS passing through the elongated reaction zone, 2 mols of phenol are formed according to Reaction 8 which are removed from the fusion reaction zone with the excess steam as represented by line 8*j*. This vaporized mixture of phenol and steam may be then passed to a recovery system wherein the phenol is scrubbed from the vaporized mixture by a suitable preferential solvent for the phenol, such as tricresyl phosphate, and the 2 mols of phenol separated from the preferential solvent by fractional distillation. A part of the scrubbed steam may then be condensed and recycled within the process along line 8*k* to furnish the water necessary for the quenching and sulfite cake washing operations.

Line 8*p* represents 2 mols of phenol being removed from the phenol recovery step, of which only one mol of phenol is removed from the process as product phenol along line 8*m*. The other mol of phenol is shown as being recycled along line 8*c* together with a part of the water along line 8*n* from the phenol recovery step and reacted with 1 mol of raw material NaOH passed along line 8*b* to form an aqueous NaOϕ solution which is then recycled along line 8*d* to become a part of the composite aqueous feed solution passed along line 8*i* to the fusion reaction apparatus.

The only source of aryl groups entering the process is the 1 mol of raw material NaBS, therefore, only 1 mol of phenol may be removed from the process for each mol of NaBS raw material entering the process. However, for each mol of NaBS which passes through the fusion reactor and is converted to phenol, according to Reaction 8 two mols of phenol leave the fusion reactor. This is due to the fact that the NaOϕ which enters into the Reaction 8 contains an aryl group which is also converted to phenol by the fusion reaction. However, as the NaOϕ is only a means of effecting the conversion of the NaBS to phenol, that part of the phenol which results from the destruction of the NaOϕ is reconverted to NaOϕ and recycled along line 8*d* to become a part of the aqueous feed solution for the fusion reaction. If this portion of the phenol were not reacted with NaOH and reconverted to NaOϕ and recycled as a part of the feed, the NaOϕ which serves as the fluidizing vehicle for the fusion mass would enter into the reaction with the fusion reactor and be depleted. However, by recycling the mol of phenol and converting it to a mol of NaOϕ and supplying to the reactor with the mol of NaBS raw material from line 8*a* as a part of the aqueous feed, the reactant requirements of Reaction 8 are satisfied and the fluidity ratio of the fusion mass remains substantially unchanged. Therefore, the continuous process may now be balanced and for each mol of raw material NaBS and each mol of raw material NaOH which enter the process, 1 mol of phenol and 1 mol of sodium sulfite may be removed and the net result of the overall process may again be represented by Reaction 7.

In carrying out the process of this invention the entire feed to the fusion reaction is supplied as aqueous solutions, which are preferred to be as concentrated as practicable without solids separation from the feed solution. The upper limit of concentration will be fixed by the temperatures at which the feed solution is maintained prior to being fed into the fusion reactor.

At about 80° C., 1 mol of NaBS raw material may be kept in solution with about 9 mols of water and this aqueous NaBS solution is suitable to form a part of the fusion reactor feed. The recycle NaOϕ liquor from the quenching and sodium sulfite separation and which is passed along line 8*h* may be kept in solution at 80° C. by maintaining a ratio of 5–6 mols of water per mol of recycled NaOϕ. The aqueous feed streams 8*a*, 8*d* and 8*h* may be led to a feed make up tank and composited to form a composite aqueous feed solution, as shown by line 8*i*, for injection into the fusion reactor by means of one or more injection nozzles. As an alternative, aqueous feed solutions as represented by 8*a*, 8*d*, and 8*k*, may be independently injected into the elongated fusion reaction zone through separate injection nozzles.

EXAMPLE IV

Phenol may also be produced in accordance with the process of this invention by injecting an aqueous solution of sodium benzene sulfonate (NaBS), an aqueous solution of caustic soda (NaOH) and an aqueous solution of sodium phenate (NaOϕ) into the fluid body containing sodium phenate, which is contained in the elongated reaction zone. An apparatus as described in Example I was used in carrying out this process for the preparation of phenol. The aqueous feed solutions injected into the sodium phenate fluid body will contain the reactants to satisfy the stoichiometric proportions of the following reaction:

(9) $C_6H_5SO_3Na + (1-x)C_6H_5ONa + (1-x)H_2O + xNaOH \rightarrow (2-x)C_6H_5OH + Na_2SO_3$

wherein x is a positive fraction greater than zero and less than one.

When x equals one, the feed conditions of Example II are realized, wherein free NaOH is in-

troduced as a reactant in the elongated fusion reaction zone, and the net result is represented by Reaction 7. When x is zero, the feed conditions of Example III are realized, wherein substantially no free NaOH is introduced as a reactant in the elongated fusion reaction zone, and the sum of the reactions taking place in the fusion reaction zone are represented by Reaction 8.

A process wherein NaBS, free NaOH, $NaO\phi$ and water are injected into the fluid body contained in the elongated reaction zone will now be described: The fluid body in the elongated reaction zone is maintained at a temperature within the the range of 355 to 420° C., and preferably within the range of 370 to 400° C. The fusion reaction apparatus may be operated at atmospheric pressure, or sub-atmospheric or super-atmospheric pressures. When equilibrium conditions have been reached under conditions of continuous operation, a conversion of 94 to 98.5% of the NaBS passing through the elongated reaction zone to phenol is generally obtained.

When the fluid body into which the aqueous solutions of feed reactants are injected was maintained at about 375° to 385° C., a conversion of about 96% of the NaBS ($C_6H_5SO_3Na$) passing through the elongated reaction zone was obtained.

The fluidity ratio of the fluid body must be maintained above 0.75, and in this example a fluidity ratio of about 2.3 was selected. With this fluidity ratio, the fluid body will have a composition of a ratio of about 2.56 mols of sodium phenate to 1 mol of by-product sodium sulfite, and on the basis of a 96% conversion of the NaBS to phenol, the fluid body will also contain 0.42 mol of NaBS per mol of sodium sulfite present.

For purposes of illustration in this example, x is 0.105, whereupon Reaction 9 may be rewritten.

(10) $1.000\ C_6H_5SO_3Na + 0.895\ C_6H_5ONa + 0.895\ H_2O + 0.105\ NaOH \rightarrow 1.895\ C_6H_5OH + 1.000\ Na_2SO_3$

The aqueous solution of feed reactants injected into the fluid body contained in the elongated reaction zone is made up of three streams, which are combined to make up a composite feed solution which is injected into the fluid body. In the alternative, each of these streams may be injected into the fluid body by means of separate nozzles, or these streams may be combined in any other desirable manner for injection into the fluid body through one or more injection nozzles, so long as the stoichiometric proportions of reactants as indicated by Reaction 10 are concurrently injected.

Reference may be made to Figure 9, as an aid in understanding this example.

One stream is represented by the aqueous solution of raw material NaBS flowing along line 9*a* which contains 1 mol of NaBS solution in about 9 mols (shown as 8.7 mols) of water. A second stream is represented by the aqueous solution containing 2.56 mols of sodium phenate and 0.043 mol of NaBS and about 19.7 mols of water flowing along line 9*h*. This second stream (line 9*h*) represents the aqueous quencher liquor from which the sodium sulfite has been separated. A third stream containing 0.105 mol of free NaOH and 0.895 mol of sodium phenate in solution in about 7 mols of water is represented as flowing along line 9*d*. These three streams are shown as being combined to form a composite feed stream flowing along line 9*i* to be injected into the fluid body contained in the fusion apparatus. During the time that an amount of feed stream 9*i* has been injected into the fluid body so that 1.0 mol of raw material NaBS has entered the elongated reaction zone, the water in this composite feed stream is converted into superheated steam within the elongated reaction zone and about 35.4 mols of water, as steam, is removed from the upper zone along line 9*j* carrying with it 1.895 mols of phenol, according to Reaction 10.

During the time that 1 mol of raw material NaBS (line 9*a*) plus 0.043 mol of recycled NaBS from line 9*i* was being injected into the fluid body within the fusion apparatus, a quantity of the fluid body was concurrently withdrawn, in a continuous manner along line 9*e* from the upper zone, containing 1.0 mol of sodium sulfite, 2.56 mols of sodium phenate and 0.043 mol of NaBS. This quantity of the fluid body was quenched in about 19.7 mols of water and the resulting quencher slurry was passed along line 9*f* to a centrifuge wherein the quencher slurry was centrifuged to separate the insoluble sodium sulfite which is removed from the system along line 9*g* and the aqueous liquor containing the sodium phenate and the NaBS was recycled along line 9*h* to replace the sodium phenate so that a substantially constant fluidity ratio of about 2.3 could be maintained.

The phenol-steam vapors recovered from the upper zone of the fusion apparatus were passed along line 9*j* to the phenol recovery step, wherein these phenol-steam vapors were first passed into a fractionating zone, from the bottom of which zone was withdrawn 1 mol of anhydrous product crude phenol which is removed from the process along line 9*m*. From the top of the fractionating zone is taken a mixture of phenol and water vapors, containing about 35.4 mols of water and 0.895 mol of phenol. These vapors are passed along line 9*n* into the lower portion of a caustic scrubbing (absorption) zone wherein these vapors pass upwards and countercurrent to a downwardly passing stream, on a continuous proportionate basis, containing 1.0 mol of raw material NaOH and 6 mols of water introduced to the top of the caustic scrubbing zone from line 9*b*, and therefore, from the bottom of the caustic scrubbing zone is withdrawn a solution made up of 0.105 mol of NaOH, 0.895 mol of sodium phenate and about 7 mols of water which makes up the feed stream 9*d*. The phenol-free water vapor leaving the caustic scrubber may be condensed and a part of the condensate recycled along line 9*k* to provide the water for the quencher.

As was pointed out in Example II, the only source of an aryl group entering the process is in the raw material NaBS. Reaction 10 shows 1.895 mols of phenol (1.895 aryl groups) being produced by the fusion reaction for each mol of raw material NaBS entering the fusion apparatus. Therefore, to prevent depletion of the sodium phenate contained in the fluid body, only one mole of phenol may be removed from the process as product and the other 0.895 mol of phenol must be recycled within the process. Caustic scrubbing of the phenol-water vapors from the fractionating zone is a convenient means of recovering the phenol to be recycled, as caustic soda is a required raw material, and this method of recovery may be preferred over solvent extraction of the azeotrope vapors with a preferential solvent such as tricresyl phosphate. Moreover, as this example

points out that the feed solution may contain free NaOH in addition to the sodium phenate, the effluent from the caustic scrubbing step may be used as a part of the aqueous solution of feed reactants without further treatment.

As has been pointed out hereinbefore, the actual water content of streams such as *9a*, *9d*, *9h* and *9i* may vary considerably, but it is preferred that the solutions carried along such streams be as concentrated as possible without having solids separation from such solutions.

EXAMPLE V

The operation described in this example was carried out in the apparatus described in Example I, and phenol was produced in accordance with the process of this invention. Figure 10 is a flow diagram which will be referred to in explaining this Example V. In any continuous operation, it oftentimes takes several hours of continuous operation following the initial start-up before substantial equilibrium conditions are reached. After substantial equilibrium conditions are obtained, the flow of materials entering and leaving the process may be balanced so as to maintain the further continuous operation of the process at or very close to equilibrium conditions.

The following discussion therefore, is directed to an "equilibrium run" of one hour's duration, that is, a period of one hour's operation of the process of this example after the process is operating continuously at or near equilibrium conditions and the flow of materials to and from the apparatus are substantially in balance.

A fluidity ratio of about 1.7 was selected for the fluid body for this operation, and therefore, during the "equilibrium run" the composition of the fluid body will be in the ratio of about 2.0 mols of sodium phenate to 1 mol of by-product sodium sulfite.

The aqueous solution of feed reactants to be injected into the fluid body will contain the reactants to substantially satisfy the stoichiometric requirements of the sum of the reactions taking place within the elongated reaction zone as represented by Equation 9 and in this example the value for x is selected as 0.704; therefore, for this example the reaction taking place within the elongated reaction zone, may be written

(11) $1.000\ C_6H_5SO_3Na + 0.704\ C_6H_5ONa + 0.296\ NaOH + 0.704\ H_2O \rightarrow 1.704\ C_6H_5OH + 1.000\ Na_2SO_3$

The composite aqueous feed solution delivered to the injection nozzle along line **10***i* will be made up in part of materials necessary to satisfy the proportions represented by the above Equation 11, and in addition, the composite feed solution will contain the recycled quencher liquor (from the quenching and separation of the sodium sulfite from the fluid body) containing an additional quantity of sodium phenate to replace the sodium phenate contained in the portion of the fluid body removed from the upper zone so that the fluidity ratio of the fluid body is maintained at a substantially constant figure.

The temperature control means was set to maintain the fluid body in the upper zone at about 375° C., and after the conditions of the equilibrium run were reached, the temperature of the fluid body in the upper zone was actually maintained within ±2° C. of 375° C. The combustion gases discharged from burner **11** were of a substantially constant temperature of 1350° F. and the stack gases left exit **13** at a temperature of about 435° C. During the equilibrium run the fluid body passed through the heat exchange tubes of the heat exchange zone at an average velocity of about 5 to 10 feet per second and the fluid body leaving the heat exchange zone and passing through header chamber **5** to the lower portion of the elongated reaction zone was maintained at an average temperature within the range of 379 to 383° C. The feed rate to the injection nozzle was kept substantially constant at the rate of 615 pounds of solution per hour and the injection nozzle was adjusted to inject the feed stream into the fluid body with a velocity of about 130 feet per second at this feed rate, and the mixture of steam, phenol and fusion mass was moving at a velocity of about 15 feet per second just as it emerged from the upper extremity of the elongated reaction tube.

During the course of the equilibrium run, a fluidity ratio of about 1.7 was maintained for the fluid body, and during one hour of the equilibrium run, 243.7 pounds of the fluid body was withdrawn from the upper zone by the overflow-level control outlet.

This portion of the fluid body is representative of the fluid body circulating within the fusion apparatus and was shown to have the following composition:

	Pounds	Percent by Wt.	Mols
Na_2SO_3	77.22	31.69	0.613
C_6H_5ONa	149.12	61.19	1.284
$C_6H_5SO_3Na$	3.41	1.40	.018
NaOH	3.34	1.37	.083
H_2O	2.44	1.00	
Na_2SO_4	3.63	1.49	
NaCl	2.95	1.21	
Na_2CO_3	1.60	0.65	
	243.71	100.00	

(Na_2SO_4, NaCl, Na_2CO_3 represent impurities contained in raw material NaBS and NaOH; the NaBS content indicates that 97% of the NaBS passing through the elongated reaction zone is converted to phenol.)

This amount of fluid body was passed in a continuous manner over the period of one hour along line **10***e* (Figure 10) to the quenching step and was quenched in a total of 169.9 pounds of water to form a slurry wherein the sodium phenate, the sodium benzene sulfonate and the caustic soda remained in solution and the by-product sodium sulfite and other inorganic salts were in suspension. This slurry was passed along line **10***f* to a centrifuge and upon centrifuging this quencher slurry, a sodium sulfite cake was removed from the process, along line **10***g*, having the following composition:

	Pounds	Mols
Na_2SO_3	77.22	0.613
$C_6H_5SO_3Na$	0.11	0.001
C_6H_5ONa	0.73	0.063
H_2O	8.34	
Na_2SO_4	3.39	
NaCl	0.05	
Na_2CO_3	1.01	

The quencher liquor, after the sodium sulfite separation, was then recycled along line **10***h* to become a part of the composite feed solution which is delivered along line **10***i* to the injection nozzle.

The recycled quencher stream passing along

line 10h carried the following materials during the one hour "equilibrium run":

	Pounds	Percent by Wt.	Mols
C_6H_5ONa	147.9	49.86	1.272
$C_6H_5SO_3Na$	3.3	1.11	0.0183
H_2O	138.2	46.59	7.67
NaOH	3.5	1.18	0.0875
Na_2SO_4	0.2	0.081	----
NaCl	2.9	0.98	----
Na_2CO_3	0.6	0.20	----

During the one hour equilibrium run, the solution passing along line 10a, containing the raw material sodium benzene sulfonate had the following composition:

	Pounds	Percent by Wt.	Mols
$C_6H_5SO_3Na$	110.5	52.0	.613
Na_2SO_4	3.4	1.6	----
H_2O	99.4	46.4	5.5

Also, during the same one hour equilibrium run, the solution passing along line 10d containing the raw material NaOH and the recycled phenol carried the following materials:

	Pounds	Percent by Wt.	Mols
C_6H_5ONa	50.79	48.1	.438
NaOH	7.26	6.9	.183
H_2O	46.4	44.0	2.58
NaCl	0.05	.05	----
Na_2CO_3	1.01	.9	----

These three feed streams flowing along lines 10a, 10d and 10h were continuously composited to form a composite aqueous feed solution and passed along line 10i to the injection nozzle.

During the one hour equilibrium run, the composite aqueous feed stream passing along line 10i carried the following materials into the fluid body contained in the lower portion of the elongated reaction zone:

	Pounds	Percent by Wt.	Mols
H_2O	282.6	46.11	15.8
$C_6H_5SO_3Na$	113.8	18.50	0.632
C_6H_5ONa	198.71	32.31	1.715
NaOH	10.76	1.75	.269
Na_2SO_4	3.63	0.59	----
NaCl	2.95	0.48	----
Na_2CO_3	1.60	0.26	----
	615.00	100.00	----

During the equilibrium run of one hour, a pressure of 25 pounds per square inch absolute was maintained within the upper chamber and a vaporized mixture of steam and crude phenol at 25 pounds per square inch absolute was removed from the upper zone through outlet 15 (Figure 1). This vaporized mixture is shown in Figure 10 as moving along line 10j from the fusion reaction apparatus to the fractionating zone and during the period of one hour, the following materials passed along line 10j:

	Pounds	Percent by Wt.
H_2O	273.5	73.65
Crude Phenol	97.8	26.35
	371.3	100.00

The following materials were removed from the upper portion of the fractionating zone and passed along line 10h to the countercurrent caustic scrubbing zone:

	Pounds	Mols
Water	273.5	----
Phenol	41.2	0.438

where the phenol was scrubbed from the vaporized mixture of steam and phenol, and the caustic scrubber effluent containing the 0.438 mol of phenol as sodium phenate was passed along line 10d to become a part of the aqueous feed solution as hereinbefore described.

Substantially anhydrous crude phenol was removed from the lower portion of the fractionating zone and was removed from the process along line 10m. During the one hour period, 56.6 pounds of crude phenol passed along line 10m. The crude phenol contained substantially 2% "high boilers" such as diphenyl ether and phenyl phenol. The crude phenol was fractionated in a refining fractionating zone and 55.5 pounds of pure phenol was recovered which represents the product of the one hour equilibrium run. The recovered pure phenol was of excellent quality and met all U. S. P. specifications.

Therefore, phenol was produced according to the process of this invention in substantially a 96% yield with a 97% conversion of the sodium benzene sulfonate to phenol per pass through the elongated reaction zone.

There was no evidence of any carbonization or thermal decomposition of the fusion mass at any time during the operation of the process even through a heat flux of 52,000 B. t. u./hr./sq. ft. was consistently maintained at the lower portion of the heat exchange zone. While an absolute pressure of 25 pounds per square inch was maintained within the upper zone, the process may have been carried out while maintaining a subatmospheric, atmospheric or a different superatmospheric pressure within the upper zone.

EXAMPLE VI

Sodium phenate may be prepared on a continuous basis in accordance with the process of this invention. An apparatus as shown in Figure 1 and described in Example I is filled to the level 7 with molten sodium phenate at a temperature within the range of 355–420° C. by the caustic soda displacement procedure as has been hereinbefore described. When the temperature of the molten sodium phenate has leveled out to a temperature, preferably within the range of 370–400° C., and with the automatic temperature control system set to maintain the sodium phenate in the upper zone at a temperature within this range, the introduction of an aqueous feed solution containing sodium benzene sulfonate and sodium hydroxide into the lower portion of the elongated reaction zone is begun. The aqueous feed solution contains sodium benzene sulfonate and sodium hydroxide in the ratio of one mole of sodium benzene sulfonate to substantially two mols of sodium hydroxide and sufficient water to keep these reactants in solution, and sodium phenate is produced in the elongated reaction zone by the fusion reaction

(5) $C_6H_5SO_3Na + 2NaOH \rightarrow C_6H_5ONa + Na_2SO_3 + H_2O$

which is a specific reaction within the broad Reaction 1.

The injection of the aqueous feed solution containing the sodium benzene sulfonate and the sodium hydroxide is continued, while the excess of the molten sodium phenate over that required to maintain the liquid level 7 in the upper zone is continuously removed from the upper zone by overflow outlet 9 and continuously passed to a quencher wherein the fused sodium phenate is quenched in water. Reaction 5 shows that sodium sulfite is a by-product of the reaction. Therefore, this sodium sulfite will accumulate in suspension in the molten sodium phenate circulating within the apparatus. The "fluidity ratio" of the fluid body, as hereinbefore defined, must be maintained above 0.75 and preferably within the range of 1.5 to 3.0. A very satisfactory fluidity ratio is about 1.7, at which figure the fluid body contains about two mols of molten sodium phenate per mol of sodium sulfite. The effluent from outlet 9 is periodically analyzed and the build up of the sodium sulfite content in the fluid body observed until the fluid body reaches the desired fluidity ratio. From this point on, in order to maintain substantially equilibrium operating conditions whereby the flow of materials entering and leaving the process may be balanced and the flows of materials maintained substantially constant for further continuous operation, it is necessary to maintain this fluidity ratio at substantially the same rate the sodium sulfite is formed in the elongated reaction zone.

The following description of the operation of the process of this invention is directed to a period of time in the continuous process under equilibrium conditions wherein one mol of product sodium phenate was produced according to Reaction 5 and during which time the fluidity ratio of the fluid body was maintained substantially constant at about 1.7.

The automatic temperature control system was set to maintain the fluid body in the upper zone at about 365° C. and one pound-mol of sodium phenate was prepared in a time period of about one and one-half hours of continuous operation. During this time period about 575 pounds of feed solution consisting of 180.2 pounds of sodium benzene sulfonate (one pound-mol), 80 pounds of sodium hydroxide (two pound-mols) in solution in about 315 pounds of water were introduced in a continuous manner over the time period into the elongated reaction zone containing the hot molten fluid body and substantially one pound-mol of sodium phenate was produced according to Reaction 5. During this 1½ hour time period, the fluidity ratio of the fluid body was maintained substantially constant at about 1.7, and about 460 pounds of the fluid body was removed from the upper zone through outlet 9. This portion of the fluid body was composed substantially entirely of sodium phenate and sodium sulfite in the ratio of two mols of sodium phenate per mol of sodium sulfite. This quantity of the fluid body was continuously quenched in a total of about 290 pounds of water to form a quencher slurry wherein the sodium sulfite was in suspension and the sodium phenate was in solution. The quencher slurry was continuously centrifuged to separate the insoluble sodium sulfite from the quencher liquor and the sodium sulfite cake resulting from this period of operation contained about 125 pounds of sodium sulfite on the dry basis. Six hundred fifteen pounds of quencher liquor was obtained from the centrifuging operations and contained 330 pounds of sodium phenate (substantially 2 pound-mols). Only one mol of sodium phenate was produced as a result of the fusion reaction (Reaction 5) whereas the quencher liquor contained substantially two mols of sodium phenate which were removed from the fusion reaction apparatus and passed to the quencher, therefore only one mol of the sodium phenate in the quencher liquor represents product material and the other mol of sodium phenate was returned to the apparatus to maintain the desired fluidity ratio. This was accomplished by continuously dividing the quencher liquor into two equal parts of about 307.5 pounds each by means of a continuous proportioning mechanism. Each portion of 307.5 pounds of quencher liquor contained about 115 pounds of sodium phenate in solution. One of these portions of 307.5 pounds was passed to a sodium phenate recovery system wherein the aqueous solution of sodium phenate was concentrated by evaporation and finally dehydrated by azeotropic distillation of the water with xylene as an azeotrope former. Other azeotrope-forming materials, such as benzene, toluene, kerosene could be used in place of the xylene for the azeotropic dehydration of the product sodium phenate.

The second portion of quencher liquor also containing about one mol of sodium phenate was continuously recycled and combined with the aqueous feed solution so that the 307.5 pounds of quencher liquor was also introduced into the elongated reaction zone substantially concurrently with the 575 pounds of feed solution injected into the elongated reaction zone, whereby substantially one mol of sodium phenate was returned to the apparatus during the same time period that one mol of sodium benzene sulfonate was introduced into the elongated reaction zone; therefore, one mol of sodium sulfite is produced by Reaction 5 along with one mol of sodium phenate, and as one mol of sodium phenate was concurrently returned to the apparatus there was always present in the fluid body 2 mols of sodium phenate per mol of sodium sulfite and the fluidity ratio of the fluid body was maintained substantially constant.

The steam removed from outlet 15 of the upper zone 2 will contain a small quantity of phenol as some sodium phenate will be hydrolyzed to phenol by the superheated steam formed in the elongated reaction zone. However, as the ratio of 2 mols of NaOH per mol of sodium benzene sulfonate are introduced in the feed solution, this high NaOH concentration largely suppresses the hydrolysis of the sodium phenate to phenol. Moreover, if an additional quantity of free caustic can be tolerated in the product sodium phenate, the ratio of NaOH to sodium benzene sulfonate can be increased such as 2.2 to 2.5 mols of NaOH per mol of sodium benzene sulfonate and thereby even further suppressing the tendency of the sodium phenate in the fluid body to hydrolyze. However, any phenol carried out in the steam leaving the upper zone can be easily recovered from the steam by caustic scrubbing vaporized effluent from outlet 15, and the recovered phenol (as sodium phenate) from the caustic scrubbing zone combined with the feed solution and introduced into the elongated reaction zone thereby preventing any actual loss of sodium phenate due to hydrolysis.

The injection nozzle 6 for this run was designed to inject the combined aqueous feed solution and recycled quencher liquor into the elongated reaction zone at a velocity of about 90 feet per second at the above described feed rate. The

hot combustion gases entered the heat exchange zone at an average of about 1300° F., and the temperature of the fluid body circulating through the heat exchange tubes at a velocity of about 5–7 feet per second was increased to a temperature of about 370–375° C. and the circulating fluid body entered the lower portion of the elongated reaction zone at a temperature within this range. Throughout the entire run there was no evidence of any thermal decomposition of the fluid body even though the high rate of heat transfer was achieved within the heat exchange zone.

The conversion of sodium benzene sulfonate to sodium phenate reached 98.5% during this run.

While all of the above specific examples describe the preparation of only phenol and sodium phenate, the process of this invention may be applied equally well to the production of other fusion reaction products such as a cresol or a sodium cresylate by substituting a sodium toluene sulfonate for the sodium benzene sulfonate and sodium cresylate for sodium phenate in the above examples and the feed solution injected into a fluid body composed predominantly of sodium cresylate. The naphthols and the alkali metal naphthanates or the xylols and the alkali metal xylylates may also be prepared in a similar manner. With the above detailed examples, the adoption of the process of this invention for use in other fusion reactions is obvious and requires only the exercise of ordinary technical skill.

What is claimed is:

1. In a process for carrying out fusion reactions, the steps comprising maintaining within an upper zone the upper level of a fluid body comprising in the molten state at least one material selected from the group consisting of fused reactants and fused reaction products, passing a portion of said fluid body contained in the upper zone from the upper zone to the lower portion of an elongated zone, heating the said fluid body in a defined zone separate from said elongated zone during its passage from the upper zone to the lower portion of the elongated zone by indirect heat exchange with a higher temperature heat source, introducing an aqueous solution containing at least one reactant into the heated fluid body passing into the lower portion of the elongated zone whereby the additional heat acquired by the fluid body during its passage from the upper zone to the lower portion of the elongated zone is used to convert the water of the aqueous solution to superheated steam and effect the fusion reaction whereby the rapid rise of the superheated steam up through the elongated zone causes the fluid body to pass through the elongated zone and return to the upper zone.

2. In a continuous process for carrying out fusion reactions, the steps comprising maintaining within an upper zone the upper level of a fluid body comprising in the molten state at least one material selected from the group consisting of fused reactants and fused reaction products passing by gravity a portion of the said fluid body contained in the upper zone to a heat exchange zone and therein increasing the temperature of the fluid body by indirect heat exchange with a higher temperature heat source, passing the thus heated fluid body by gravity from the heat exchange zone into the lower portion of a substantially vertical elongated zone which is a defined zone separate from said heat exchange zone and concurrently injecting fusion reactants in aqueous solution into the said heated fluid body passing into the lower portion of the elongated zone, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to effect the fusion reaction and to convert the water of the aqueous solution to superheated steam whereby the rapid rise of the superheated steam through the elongated zone effects the passage of the fluid up through the upper portion of the elongated zone and thereby returning the fluid body to the upper zone, removing steam and volatile reaction products from the upper zone at a point above the level of the fluid body maintained within the upper zone, and withdrawing a portion of the fluid body from the upper zone while maintaining a level of the fluid body within said upper zone.

3. In a continuous process for the manufacture of a phenol volatile in steam, the steps comprising maintaining a fluid body comprising a molten alkali-metal arylate and an alkali-metal sulfite in the ratio of 1 to 6 mols of the alkali metal arylate per mol of the alkali metal sulfite at a temperature within the range of about 350° C. to about 420° C. and maintaining the upper level of said fluid body in an upper zone, passing a portion of the fluid body from the upper zone to a heat exchange zone and therein increasing the temperature of the fluid body to a temperature above 350° C. but not exceeding about 420° C. by indirect heat exchange with a heat source of higher temperature, passing the fluid body of increased temperature from the heat exchange zone to the lower portion of an elongated zone, which is separate from said heat exchange zone, concurrently injecting into the heated fluid body passing into the lower portion of the elongated zone an aqueous solution containing the reactants sufficient to satisfy the stoichiometric requirements of the reaction

$$ArSO_3M + xMOH + (1-x)\,ArOM + (1-x)\,H_2O \rightarrow (2-x)\,ArOH + M_2SO_3$$

wherein Ar represents an aryl radical, M represents an alkali metal and wherein the value of x is selected from values of zero, one and intermediate positive fractions greater than zero and less than one, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to effect the fusion reaction and to convert the water of the aqueous solution to superheated steam and whereby the rapid rise of the superheated steam through the upper portion of the elongated zone returns the fluid body to the upper zone.

4. In a continuous process for the manufacture of phenol, the steps comprising maintaining a fluid body comprising molten sodium phenate and sodium sulfite in the ratio of about 1 to 6 mols of sodium phenate per mol of sodium sulfite at a temperature within the range of about 355° C. to about 420° C. and maintaining the upper level of said fluid body in an upper zone, passing a portion of the fluid body from the upper zone to a heat exchange zone and therein increasing the temperature of the fluid body to a temperature above 355° C. but not exceeding about 420° C., by indirect heat exchange with a heat source of higher temperature, passing the fluid body of increased temperature from the heat exchange zone into the lower portion of a substantially vertical elongated zone which is separate from said heat exchange zone and concurrently injecting into the heated fluid body passing into the lower portion of the elongated zone an aqueous solution containing the reactants sufficient to satis-

fy the stoichiometric requirements of the reaction

$$C_6H_5SO_3Na+xNaOH+(1-x)C_6H_5ONa+(1-x)H_2O\rightarrow(2-x)C_6H_5OH+Na_2SO_3$$

wherein the value of x is selected from values of zero, one and intermediate positive fractions greater than zero and less than one, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to effect the fusion reaction and to convert the water of the aqueous solution to superheated steam and whereby the rapid rise of the superheated steam through the upper portion of the elongated zone returns the fluid body to the upper zone.

5. In a continuous process for the manufacture of phenol, the steps comprising maintaining a fluid body comprising molten sodium phenate and sodium sulfite in the ratio of about 1 to 6 moles of sodium phenate per mol of sodium sulfite at a temperature within the range of about 355 to 420° C. and maintaining the upper level of said fluid body in an upper zone, passing a portion of said fluid body from the upper zone to a heat exchange zone and therein increasing the temperature of said portion of the fluid body to a temperature not exceeding about 420° C. by indirect heat exchange with a heat source of higher temperature, passing said portion of the fluid body of increased temperature from the heat exchange zone into the lower portion of a substantially vertical elongated reaction zone, which is a separate zone from said heat exchange zone, withdrawing a second portion of the fluid body from said upper zone while maintaining the upper level of the fluid body in said upper zone, quenching said second portion of fluid body in a sufficient quantity of water to form a quencher slurry wherein the sodium sulfite remains in suspension and the sodium phenate is in solution, separating the sodium sulfite from the solution of sodium phenate and introducing this aqueous solution of sodium phenate into the lower portion of the elongated reaction zone concurrently with the said portion of fluid body of increased temperature passing into the lower portion of said elongated reaction zone, also concurrently injecting into the lower portion of said elongated zone an aqueous feed solution containing the reactants sufficient to satisfy the stoichiometric requirements of reaction

$$C_6H_5SO_3Na+xNaOH+(1-x)C_6H_5ONa+(1-x)H_2O\rightarrow(2-x)C_6H_5OH+Na_2SO_3$$

wherein the value of x is selected from the values of 0, 1 and intermediate positive fractions greater than 0 and less than 1, permitting the additional heat acquired by the portion of fluid body during its passage through the heat exchange zone to effect the fusion reaction and to convert the water of the aqueous solutions to superheated steam and to rise rapidly up through the elongated zone, thereby effecting the circulation of the fluid body from the lower portion of the elongated reaction zone to the upper portion of the elongated reaction zone and into the upper zone, removing steam and vaporized phenol from the upper zone at a point above the level of the fluid body maintained within the upper zone; in effecting the operation of the continuous process, the first portion of the fluid body is circulated through the heat exchange zone at a high rate to provide sufficient heat in the elongated reaction zone to effect the fusion reaction as shown by the above equation and to convert the water of the aqueous solutions to superheated steam, the second portion of the fluid body is withdrawn from the upper zone at a rate such that the amount of sodium sulfite contained in said second portion of the fluid body will result in sodium sulfite being removed from the upper zone at a rate which will correspond substantially to the rate at which the sodium sulfite is formed in the elongated reaction zone.

6. In a continuous process for the manufacture of phenol, the steps comprising maintaining a fluid body comprising molten sodium phenate and sodium sulfite in the ratio of about 1.5 to 3.0 mols of sodium phenate per mol of sodium sulfite at a temperature within the range of about 370 to about 400° C. and maintaining the upper level of said fluid body in an upper zone, passing a portion of the fluid body from the upper zone to a heat exchange zone and therein increasing the temperature of said portion of fluid body to a temperature above 370° C. but not exceeding about 420° C., by indirect heat exchange with a heat source of higher temperature, passing said portion of fluid body of increased temperature from the heat exchange zone into the lower portion of a substantially vertical elongated zone, which is a zone separate from said heat exchange zone, and concurrently injecting into the lower portion of said elongated zone an aqueous solution containing the reactants sufficient to satisfy the stoichiometric requirements of the reaction

$$C_6H_5SO_3Na+xNaOH+(1-x)C_6H_5ONa+(1-x)H_2O\rightarrow(2-x)C_6H_5OH+Na_2SO_3$$

wherein the value of x is selected from values of zero, one and intermediate positive fractions greater than zero and less than one, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to effect the fusion reaction and to convert the water of the aqueous solutions to superheated steam and whereby the rapid rise of the superheated steam through the elongated zone returns the fluid body to the upper zone, during substantially the same time period that one mol of $C_6H_5SO_3Na$ is injected into the lower portion of said elongated reaction zone concurrently and on a substantially proportionate basis withdrawing a second portion of the fluid body from the upper zone containing substantially one mol of sodium sulfite in suspension in molten sodium phenate while maintaining the upper level of the fluid body in said upper zone and at a rate such that the amount of sodium sulfite withdrawn will result in sodium sulfite being removed from the upper zone at a rate which will correspond substantially to the rate at which sodium sulfite is being formed in the elongated reaction zone, quenching this quantity of the fluid body in a sufficient quantity of water to form a quencher slurry wherein the sodium sulfite remains in suspension and the sodium phenate is in solution, separating the sodium sulfite from the quencher slurry to form a quencher liquor comprised of an aqueous solution of sodium phenate and introducing this quencher liquor into the elongated reaction zone concurrently and on a substantially proportionate basis with the aqueous solutions of reactants, concurrently removing during said time period steam and substantially $(2-x)$ mols of vaporized phenol from the upper zone at a point above the level of the fluid body maintained

within the upper zone, separating the phenol from the vaporized mixture of steam and phenol, removing substantially one mol of product phenol from the process, reacting substantially $(1-x)$ mols of the recovered phenol with one mol of sodium hydroxide to form a mixture containing $(1-x)$ mols of sodium phenate and x mols of sodium hydroxide and using this mixture to make up a part of said aqueous solutions of reactants for injection into the elongated reaction zone.

7. In a continuous process for the manufacture of cresol, the steps comprising maintaining a fluid body comprising molten sodium cresylate and sodium sulfite in the ratio of about 1 to 6 mols of sodium cresylate per mol of sodium sulfite at a temperature within the range of about 355° C. to about 420° C. and maintaining the upper level of said fluid body in an upper zone, passing a portion of the fluid body from the upper zone to a heat exchange zone and therein increasing the temperature of the fluid body to a temperature above 355° C. but not exceeding about 420° C., by indirect heat exchange with a heat source of higher temperature, passing the fluid body of increased temperature from the heat exchange zone into the lower portion of a substantially vertical elongated zone which is a defined zone separate from said heat exchange zone and concurrently injecting into the heated fluid body passing into the lower portion of the elongated zone an aqueous solution containing the reactants sufficient to satisfy the stoichiometric requirements of the reaction

$$CH_3C_6H_4SO_3Na + xNaOH + (1-x)\,CH_3C_6H_4ONa + (1-x)\,H_2O \rightarrow (2-x)\,CH_3C_6H_4OH + Na_2SO_3$$

wherein the value of x is selected from values of zero, one and intermediate positive fractions greater than zero and less than one, whereby the additional heat acquired by the fluid body during its passage through the heat exchange zone is used to effect the fusion reaction and to convert the water of the aqueous solution to superheated steam and whereby the rapid rise of the superheated steam through the upper portion of the elongated zone returns the fluid body to the upper zone.

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