

REMOVAL OF SALTS IN THE MANUFACTURE OF PHENOLIC COMPOUND

The present invention relates to a process for separating products contained in an alkyl hydroperoxide cleavage mass, and in particular, to a process for the removal of salts of neutralisation present in a cleavage mass for the manufacture of phenol.

In general, phenol is manufactured by oxidising an alkyl substituted aromatic compound, such as cumene, to form the hydroperoxide derivative thereof, followed by cleavage of the hydroperoxide with a mineral acid such as sulphuric acid to form a cumene hydroperoxide cleavage mass. The cleavage mass generally contains species such as phenol, acetone, α -methyl styrene (AMS), cumene, cumyl phenol (CP), dimethylbenzyl alcohol (DMBA), acetophenone (AP), AMS dimers (AMSd), heavy by-products generally referred to as tars and heavies, and mineral acid such as sulphuric acid. Prior to separating out the different species and recovering acetone and phenol, the cleavage mass is neutralised with a caustic, such as sodium hydroxide, to prevent the acidic cleavage mass from corroding downstream equipment. Much of the salt is separated and removed from the process in a wash/phase separation step prior to feeding the partially or wholly neutralised cleavage mass to a splitter and further purification columns. However, a significant quantity of salt remains in the cleavage mass entering the splitter, and this quantity of salt becomes more concentrated as the stream passes from one purification column to the next.

In the course of making phenol, the fully or partially neutralised cleavage mass passes through

several distillation and purification columns to ultimately form a stream of heavy by-products. The heavy by-product stream may be subject to cracking, and the bottoms of the cracker are usually incinerated. The heavy hydrocarbon by-product stream feeding a cracker or furnace, however, contains a high concentration of the salts of neutralisation, typically sodium sulphate. The salts remaining after the wash/phase separation step are carried into the splitter, which separates out ketone as an overhead from phenol as a phenol bottoms stream, into the phenol bottoms stream and into further downstream equipment through the bottoms stream of each purification column, all the way to the cracker or furnace. It is in the cracker and furnace, and in the reboiler for the cracker, where the salts of neutralisation settle and are no longer carried through. The settling of the salts in the cracker, reboiler, and furnaces causes operating problems, requiring intermittent shut down to clean the equipment or replace parts. The salts also degrade the value of a tarry mass as fuel for burning. Therefore, it is highly desirable to remove as much salt as possible prior to feeding a cracker or furnace.

Many methods have been proposed for removing salts of neutralisation in the manufacture of phenol. One such method, disclosed in U.S. 4,328,377, involves feeding a neutralised cleavage mass to a multi-tray (20 or more) splitter, separating out the ketone as an overhead from a bottom fraction comprised of a crude phenol stream, and recovering the phenol, wherein a liquid layer located near or below the cleavage mass feed site but above the bottoms is withdrawn from the splitter column, phase separating the liquid layer into an oil layer and an aqueous layer containing the salts of neutralisation, and recycling the oil layer back to the splitter column at a site below the liquid layer withdrawal site. To enhance

the ability of the liquid layer to phase separate, a hydrocarbon having a lower boiling point than phenol and a specific gravity difference of at least 0.03 is added to the liquid layer.

5 A disadvantage of this process is that large quantities of liquid layer must be removed and processed to sufficiently reduce the amount of salt to the desired level. For example, for every 100 parts by weight per hour of cleavage mass fed to the multi-tray splitter,
10 over 127 parts by weight per hour of a liquid sidedraw was processed in a phase separator. Treating such large amount of liquid requires adding and processing correspondingly large quantities of water, and adding large quantities of lower specific gravity hydrocarbon,
15 processing large amounts of oil layer, and increasing the volume of the phase separation vessel. It would be desirable to discharge the salts of neutralisation from the process by feeding a phase separator with a small amount of hydrocarbon, discharging low amounts of water
20 containing the salts of neutralisation from the process while effectively removing at least 80% of the salts of neutralisation from the process, using low amounts of lower density hydrocarbon to enhance phase separation, concentrating the salt in a purge stream discharged from
25 a phase separator to high levels, and/or employing a smaller phase separation vessel. It would also be desirable to employ a process for manufacturing phenol where the amount of water or lower density hydrocarbon lost from the process is minimised or eliminated.

30 According to the invention, there is provided a process for the manufacture of phenolic compounds by oxidising an alkyl-substituted aromatic compound to form the hydroperoxide derivative thereof, followed by cleavage of the hydroperoxide to form an aralkyl (aryl
35 alkyl or alkyl aryl) hydroperoxide cleavage mass and

neutralisation of the aralkyl hydroperoxide cleavage mass to form a neutralised aralkyl hydroperoxide cleavage mass stream, comprising:

- a) separating the neutralised aralkyl hydroperoxide cleavage mass stream, containing salts of neutralisation into a crude ketone stream and a crude phenolic stream containing the salts of neutralisation;
 - b) separating the crude phenolic stream into a concentrated phenolic-rich stream, enriched in phenolic compounds, and a crude phenolic bottoms stream enriched in tars and alpha methyl styrene dimers, each compared to the crude phenolic stream, said crude phenolic bottoms stream containing salts of neutralisation;
 - c) to the crude phenolic bottoms stream, adding water and a diluent composition, thereby forming a phase separable crude phenolic bottoms stream, said diluent composition comprised of a hydrocarbon phase compatible with the crude phenolic bottoms stream and having a combined density lower than the density of the crude phenolic bottoms stream;
 - d) separating the separable crude phenolic bottoms stream into a hydrocarbon phase and an aqueous phase containing salts of neutralisation;
- whereby the amount of salts of neutralisation in the hydrocarbon phase is reduced compared to the amount of salts of neutralisation present prior to separation.

In an embodiment of the invention, the aralkyl hydroperoxide cleavage mass feed has a pH of less than 6. The neutralised aralkyl hydroperoxide cleavage mass is suitably separated into an aqueous stream and a neutralised aralkyl hydroperoxide cleavage mass stream containing a smaller amount of salts than in the aqueous stream. The neutralised aralkyl hydroperoxide cleavage mass stream is subsequently advantageously separated into

a crude ketone stream and a crude phenolic stream containing the salts.

In the process of the invention the crude ketone stream is suitably separated into a concentrated ketone rich stream and a crude ketone bottoms stream, and the crude phenolic stream is suitably separated into a concentrated phenolic-rich stream and a crude phenolic bottoms stream. After conversion of the phenolic bottoms stream to the phase separable phenolic bottoms stream by the addition of water and diluent composition followed by phase separation, the hydrocarbon phase obtained is, advantageously, separated into a light ends stream, enriched in phenolic compounds, and a tarry stream having a reduced amount of salts of neutralisation, e.g., by at least 90%, relative to the crude phenolic bottoms stream.

Advantageously, at least a portion of the crude ketone bottoms stream is fed as said diluent composition to the crude phenolic bottoms stream. Suitably, at least a portion of said crude ketone bottoms stream is fed to the aralkyl hydroperoxide cleavage mass before neutralisation. A portion of the crude ketone bottoms stream may be fed to the neutralised aralkyl hydroperoxide cleavage mass, alone or also to the mass before neutralisation. Alternatively, at least a portion of said light ends stream is recycled as feeds to the aralkyl hydroperoxide cleavage mass, before or after neutralisation or both.

In another embodiment of the invention, there is provided a composition comprising at least 40 %wt water, less than 20 %wt phenolic compounds, alkali metal salts in an amount of at least 1.5 %wt, phenolic tars, and α -methyl styrene dimers, wherein the volume ratio of water to all ingredients in said composition other than water is between 1:1 to about 3:1.

The process of the invention provides for the removal of salts of neutralisation present in a neutralised aralkyl hydroperoxide cleavage mass by 80 %wt or more of said salts from said cleavage mass. The combined flow rate of all aqueous purge stream(s) containing the salts can be as low as less than 5 parts by weight per hour based on a flow rate of 100 parts by weight per hour of the neutralised aralkyl hydroperoxide cleavage mass that can be fed to a means for separating said cleavage mass into a crude ketone stream and a crude phenolic stream.

The neutralised aralkyl hydroperoxide cleavage mass containing salts of neutralisation may be fed to a splitter to separate ketone and phenolic compounds from said cleavage mass.

All or a portion of the crude phenolic compounds stream, comprising hydrocarbons, water, and salts of neutralisation, may be used as feed to the phase separation vessel, the total amount of hydrocarbon feed from any source to said separation vessel being less than 10 parts by weight per hour, based on 100 parts by weight per hour of said neutralised aralkyl hydroperoxide cleavage mass fed to the splitter.

In this process for removing salts of neutralisation from the aralkyl hydroperoxide cleavage mass the salts of neutralisation are suitably purged in an aqueous purge stream comprising at least 3 %wt of salts of neutralisation and at least 90 %wt water, based on the weight of the purge stream.

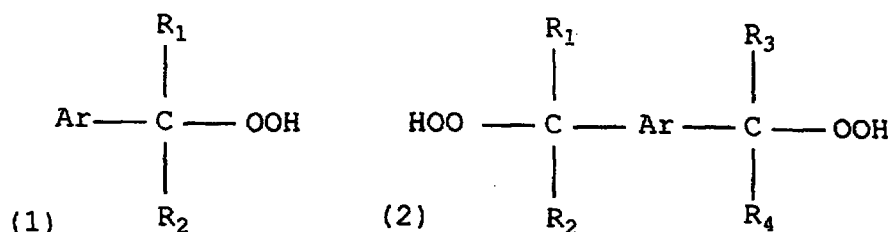
The phenolic compounds stream may, optionally, be concentrated by further distillation. The phenolic compounds stream may suitably be formed to a phase separable hydrocarbon stream by adding a net amount of water of 5 parts by weight per hour or less to the phenolic compounds stream, based on 100 parts by weight per hour of neutralised aralkyl hydroperoxide cleavage

mass. The phase separable hydrocarbon stream is advantageously separated into an aqueous stream and a hydrocarbon stream, and a portion or all of the aqueous stream is discharged from the process as an aqueous purge stream, wherein at least 80 %wt of the salts of neutralisation present in the neutralised aralkyl hydroperoxide cleavage mass are removed through said purge stream.

Figure 1 is a process flow diagram of that portion of the process for the separation of products contained in an aralkyl hydroperoxide cleavage mass.

Fig. 1 is an illustration of a process directed towards separating the by-products contained in a cumene hydroperoxide cleavage mass into streams of acetone, phenol, α -methyl styrene (AMS), cumene, aqueous streams containing salts of neutralisation such as Na_2SO_4 , cumyl phenol (CP), dimethylbenzyl alcohol (DMBA), acetophenone (AP), AMS dimers (AMSd), and tars and heavies. Those of ordinary skill in the art will appreciate that other vessels not depicted in Fig. 1 may be included in the process of the invention, such as further distillation columns for additional purification, additional phase separators, coolers, heat exchangers, pumps, and storage vessels where desired. Thus, other purification columns may be introduced prior to or after each successive description where products contained in a particular stream are separated. For example, describing the separation of a light ends stream from a tarry stream in a crude phenol bottoms stream does not restrict the inclusion of any number of prior purification columns introduced to further purify the crude phenol bottoms stream prior to the point at which a tarry stream is extracted.

Turning to Fig. 1, while reference may be had to a cumene hydroperoxide cleavage mass flowing through line (2), the invention also includes processing an aralkyl hydroperoxide cleavage mass. The aralkyl hydroperoxide used in the process of this invention includes compounds represented by formulas 1 and 2 below:



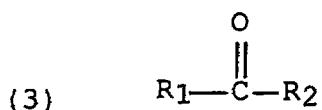
wherein Ar represents an aromatic ring, preferably a phenyl ring, that may contain substituents, such as alkyl groups with up to 6 carbon atoms, and R₁, R₂, R₃ and R₄ independently represent a lower linear or branched alkyl group having 1-4 carbon atoms. Specific examples of the aralkyl hydroperoxide are cumene hydroperoxide, p-methyl isopropylbenzene (p-cymene) hydroperoxide, m-methyl isopropylbenzene (m-cymene) hydroperoxide, sec-butylbenzene hydroperoxide, p-ethyl isopropylbenzene hydroperoxide, isopropylnaphthalene hydroperoxide, m-diisopropylbenzene dihydroperoxide and p-diisopropylbenzene dihydroperoxide. Cumene hydroperoxide, p-cymene hydroperoxide and m-cymene hydroperoxide are preferred. Cumene hydroperoxide is most preferred.

The cleavage mass is acidic due to the addition of an acid, suitably a mineral acid, such as sulphuric acid, to the aralkyl hydroperoxide to effect cleavage of the hydroperoxide into a ketone compound, such as acetone, and a phenolic compound, such as phenol, along with the other by-products noted above. Examples of the mineral acid used to cleave the hydroperoxide into a phenolic compound and a ketone compound include sulphuric acid,

hydrochloric acid, phosphoric acid and mixtures of these. Sulphuric acid is the most common agent used.

5 The phenolic compound, which is one of the desired acid cleavage products of the process, is represented by the formula Ar-OH or HO-Ar-OH corresponding to formula (1) or (2). Specific examples include phenol, p-cresol, m-cresol, ethylphenol, naphthol, hydroquinone and resorcinol. Phenol, p-cresol and m-cresol are preferred, and phenol is most preferred.

10 The ketone compound, another desirable acid cleavage product, is expressed by formula 3:



Examples include acetone and methyl ethyl ketone, preferably acetone.

15 Any known method can be employed to cleave the hydroperoxide with a mineral acid. Industrially, the cleavage reaction is usually performed in the presence of a hydrocarbon solvent. An aromatic hydrocarbon is preferred as the hydrocarbon solvent, and specific examples include benzene, toluene, xylene, cumene, cymene, ethylbenzene, phenol, diisopropylbenzene, butylbenzene, alpha-methylstyrene and isopropenyltoluene. The temperature of the acid cleavage is not particularly restricted. Advantageously, it is generally about 50 °C to about 100 °C, preferably about 70 °C to about 90 °C. 20 Generally, the amount of the mineral acid is 0.005 to 2 parts by weight, preferably 0.01 to 0.1 parts by weight, per 100 parts by weight of the hydroperoxide to be cleaved.

25 The mineral acid contained in the reaction mixture obtained by the acid cleavage of the hydroperoxide is then neutralised or removed. The particular method of neutralisation is not limited. The acidic cleavage mass 30

stream is fed through a line (1) to a neutraliser (10), where residual sulphuric acid is neutralised either partially or wholly by addition of a caustic through line (13). By a neutralised cleavage mass is meant a
5 cleavage mass which is partially or wholly neutralised. Neutralisation of the acid cleavage mixture of the hydroperoxide can be performed by any desired known method. The caustic may be added to line (1) prior to entry into neutraliser (10) as depicted, or directly to
10 the neutraliser (10) through a line (13). A typical caustic is an aqueous alkali metal hydroxide and/or phenolate stream, the alkali metal preferably being sodium.

The salt formed as a result of the neutralisation of
15 the acid cleavage needs not always to be separated and removed from the cleavage mass. However, it is common to remove a portion of the salts prior to feeding the cleavage mass to a splitter (30). Methods include contacting the acid cleavage mixture with an aqueous
20 solution of a strong alkali such as sodium hydroxide or sodium phenolate and then optionally removing the water layer in a phase separator; or contacting the acid cleavage mixture with an aqueous solution of a strong
25 alkali such as sodium hydroxide, removing the aqueous layer through phase separation, followed by washing the hydrocarbon oily layer with water to remove more salt; or a method where the neutralised cleavage mass is filtered to remove the salt precipitated in solid form.

In a particular embodiment of the invention,
30 reference may be had to the design depicted in Fig. 1. In the neutraliser (10), the sulphuric acid present in the hydrocarbon phase of the cleavage mass forms a Na_2SO_4 salt in the aqueous phase which leaves the neutraliser through line (14). A portion of the salty aqueous stream

may be re-circulated back to the neutraliser through line (14), and a portion may be discharged through line (15). The conditions within the neutraliser (10) may vary depending upon the number of neutralisers, wash drums, and phase separators one may employ, but typical conditions are to maintain the pH between 5 and 8 at 1 or more bar (100 kPa) and at a temperature ranging from 35 °C to 55 °C. Other conditions and equipment, such as those specified in U.S. Patent Nos. 5,510,543; 3,931,339; 4,262,150; and 4,262,151 are also suitable, and each are herein incorporated by reference in full. For example, if desired, the cleavage mass may be only neutralised up to a pH within the range of 4-5. While the Figure depicts a sequence for the addition of various streams into line (1), it should be understood that the scope of the invention is not limited to a particular sequence, and that the streams flowing through lines (52A), (53), (13), (102), (14) and may be added into line (1) in any order.

The hydrocarbon phase leaves the neutraliser (10) through line (11) and is fed into a wash drum (20) through line (12). In addition to adjusting the pH back to a range of 5-7, the wash drum washes the residual Na_2SO_4 salts remaining in the hydrocarbon phase with water. An acid solution and fresh water can be added to the wash drum (20) directly or through line (12). The aqueous salty solution discharged from the wash drum (20) through line (22) may be re-circulated back to the wash drum by joining with line (11), and optionally, a portion of the salty aqueous stream may be purged from line (22) through line (23). The aqueous salty solution purged into line (23) may be purged from the process or may optionally, and preferably, be re-circulated back to the neutraliser (10) directly, or through lines (1) or (14) downstream of line (15).

In spite of the many efforts at effecting a substantially complete removal of salts, residual amounts of salts remain within the hydrocarbon stream. The amount of salt left in a composition of neutralised aralkyl hydroperoxide cleavage mass prior to entering the splitter will vary depending upon the degree of neutralisation and the efficiency of the separation techniques used to remove the salt in a phase separation and/or wash step. The process of the invention can be used to remove salt at any level. Typical amounts of salt in a neutralised cleavage mass range from 1000 ppm to 10,000 ppm. The amount of salt is generally reduced in a range of 300 ppm to several thousand ppm salt. In the process of the invention, the amount of salt can be reduced to even smaller quantities of salt, in the range of 25 ppm to 300 ppm, preferably from 25 ppm to 120 ppm.

The neutralised and optionally washed cumene hydroperoxide cleavage mass is fed to the splitter (30) through line (21) where the cleavage mass is separated through, for example, distillation, into a crude phenolic stream and a crude acetone stream. The crude acetone stream removed from the splitter at the overhead through line (31) is rich in acetone, meaning that acetone is the predominant species in the stream by weight. Small amounts of water and other higher boiling compounds such as AMS, cumene, some aldehydes, and un-neutralised organic acids may also be present in the crude acetone stream. Some of the lighter boiling impurities, such as other aldehydes, may optionally be removed from the composition by distillation and optionally recycled along with acetone caught up in the overhead to a cleavage zone where the aralkyl hydroperoxide is cleaved.

Whether or not distilled, the crude acetone stream is fed through line (31) ultimately to an acetone finishing column (40) where the crude acetone stream is separated

by distillation into a concentrated acetone stream enriched in acetone over the amount of acetone present in the crude acetone stream and into a crude acetone bottoms stream. The concentrated acetone stream is removed from the finishing column (40) through line (41), while the crude acetone bottoms stream is removed at the bottom of the column (40) through line (42). Optionally, caustic may be added to the finishing column (40) to react the aldehyde to heavier compounds, thereby facilitating removal by distillation.

The crude acetone bottoms stream comprises water, organic acids, AMS, and cumene. To separate water from the hydrocarbons in the crude acetone bottoms stream, it is useful to feed the stream to a phase separator (50) wherein water and the salts of the organic acid are separated and discharged as an aqueous phase through line (52) from the hydrocarbon phase, which leaves the separator (50) through line (51). Optionally, a portion of the aqueous phase discharged from separator (50) may be recycled to line (1) through line (52A) to reduce the amount of fresh water feed that is added to the phase separator/wash drum. The other portion is sent to treatment for dephenolation through line (52B).

The crude acetone bottoms stream in line (51) from which water has optionally been removed comprises AMS, cumene, and other hydrocarbon compounds having boiling points lower than phenol. Part of the crude acetone bottoms stream, whether processed through the phase separator (50) or not, is used to feed the neutraliser (10) through line (53) in order to facilitate phase separation between the cleavage mass and water. The amount of crude acetone bottoms stream fed to the neutraliser (10) through line (53) may range anywhere from 5 %wt to 40 %wt based on the weight of the cleavage mass stream. The crude acetone bottoms stream may be fed

and mixed into line (1) or may be fed directly into the neutraliser. Optionally, the crude acetone bottoms stream may be fed to the wash drum (20) as well.

Another portion of the crude acetone bottoms stream from the acetone finishing column (40) or from the phase separator (50) may be fed as a diluent to line (62) described further below in greater detail.

The crude phenol stream exits the bottom of the splitter (30) through line (32). The predominant species in the crude phenol stream is phenol, usually in amounts exceeding 85 %wt based on all ingredients in the crude phenol stream. The salts of neutralisation (Na_2SO_4) present in the neutralised cumene hydroperoxide cleavage stream in line (21) pass through the splitter (30) into the crude phenol stream. Accordingly, the amount of salts usually ranges from be 80-250 ppmw based on the weight of all ingredients in the crude phenol stream as measured at line (32), or from 0.05 to 0.3 %wt based on the weight of all ingredients in the crude phenol stream as measured at line (62). Other ingredients present in the crude phenol stream include AP, CP, AMSd, DMBA, and tars and heavies.

A substantial amount of the phenol present in the crude phenol stream is removed by feeding the stream in line (32) into a crude phenol column (60) where phenol is separated by distillation into a concentrated phenol rich stream which is enriched in the weight percentage of phenol compared to the weight percentage of phenol present in the crude phenol stream, and into a crude phenolic bottoms stream enriched in tars and AMSd compared to the weight percent of tars and AMSd present in the crude phenol stream. The concentrated phenol rich stream exits the column (60) through line (61) for

finishing, while the crude phenolic bottoms stream exits the bottoms of the column (60) through line (62).

The typical composition of the crude phenolic bottoms stream is as follows:

5	Phenol	:	15-35 %wt
	AP	:	10-25 %wt
	DMBA	:	2-8 %wt
	CP	:	15-25 %wt
	AMSd	:	4-15 %wt
10	Tars/Heavies	:	12-25 %wt
	Salts	:	0.05-0.3 %wt

To the crude phenolic bottoms stream is added water and a diluent composition which is phase compatible with the crude phenolic bottoms stream in order to form a phase separable crude phenolic bottoms stream. A phase separable crude phenolic bottoms stream is one in which a hydrocarbon phase and an aqueous phase containing at least about 80 %wt of the salts of neutralisation, as measured by allowing the stream to stand without agitation, can be separated in less than one hour residence time.

The diluent composition suitably has a combined lower density than the density of the crude phenolic bottoms stream under the conditions existing in the bottoms phase separator (80). It suitably contains hydrocarbons, preferably aromatic hydrocarbons. While the diluent composition can be derived from any source, it is advantageous to recycle a portion of the crude acetone bottoms stream comprised of cumene and AMS through line (54) into the crude phenol bottoms stream in line (62). The hydrocarbons in the diluent composition in line (54) comprising cumene and AMS, flow through the process ultimately into line (102) from the distillation in the rectifier (100), and are fed to the neutraliser (10), thereby closing the loop on the flow of

the hydrocarbon diluent composition through the process with minimal discharge.

As an example, the density of the crude phenolic bottoms stream may be on the order of 0.86-0.93 g/ml (54-58 pcf) at temperatures ranging from 180-210 °C and at pressures sufficient to keep the stream in liquid state. Although phenol has a higher density than water, it is also readily miscible with water, rendering it difficult to obtain satisfactory phase separation between the hydrocarbon phase and the aqueous phase in a phase separation operation designed to remove the salts of neutralisation. Accordingly, a hydrocarbon diluent composition having a lower density than the density of the crude phenolic bottoms stream is added to enhance phase separation between the hydrocarbon and aqueous phase. This method of enhancing phase separation is more effective at removing salts than a method of increasing the salt concentration because by increasing the salt concentration, the amount of salt distributed into the hydrocarbon phase is increased and the effectiveness of the unit operation is reduced.

Diluents which are phase compatible and readily miscible with phenol, have a lower density than phenol, and which are phase incompatible with water under the operating conditions of the phase separator are preferred. Such diluents will attract solubilised phenol from the aqueous phase into the hydrocarbon phase. A diluent composition having a combined hydrocarbon density of 0.817-0.857 g/ml (51-53.5 pcf) comprised of 60-90 %wt cumene, 10-30 %wt of AMS, and optionally less than 10 %wt of other hydrocarbons and no water is but one example, but is a preferred composition because it is readily obtainable as an extract from the acetone finishing operation. Optionally, if desired, the diluent composition may be recycled directly from the acetone

finishing column (40) to line (62) without first removing water. Another example of a suitable diluent compositions include a stream of cumene or a stream of AMS, each as a fresh feed or derived from any source in the process.

While a hydrocarbon diluent composition having a lower density than the crude phenolic bottoms stream is preferably added to obtain satisfactory phase separation, the density difference need not be large. Although the invention is not restricted to a particular density difference, an advantage of the invention is that the hydrocarbon phase may be effectively separated from the aqueous phase in the phase separator (80) when the density difference between the two is only 0.016-0.032 g/ml (1-2 pcf). This advantage is achieved due to the low percentage of phenol present in the crude phenolic bottoms stream. A stream comprised of 85 %wt or more phenol would require the use of a diluent composition having a larger density delta to effectively phase separate the aqueous phase due to the ready miscibility between phenol and water.

An additional advantage to the invention is that the volume amount of diluent composition needed to provide a phase separable stream is low compared to the volume of diluent that would be needed if one attempted to create a phase separable stream from a stream exiting the splitter (30) as either a side-draw or from a bottoms, as in line (32). Since a large volume of compounds in the cleavage mass in line (21) is removed in the splitter (30) through line (31), and the volume of the crude phenol stream in line (32) is reduced further by removal of phenol through the crude phenol column (60) into line (61), the process provides the advantage of needing only low amounts of diluent composition to effect satisfactory phase separation.

Specifically, for every 100 part by weight per hour of cleavage mass fed through line (21) into the splitter (30), less than 3 parts by weight per hour of diluent composition is advantageously needed to make a phase separable crude phenolic bottoms stream, preferably less than 2, and even as little as 1.5 parts by weight per hour or less, each based on 100 parts by weight per hour of neutralised aralkyl hydroperoxide cleavage mass stream and discounting any water present in the phase separable crude phenolic bottoms.

The amount of diluent composition added relative to the amount of crude phenolic bottoms stream is sufficient to phase separate the hydrocarbon phase from the aqueous phase. While there is no upper limit, the more diluent composition added, the higher the loading of material through downstream equipment which must be processed and handled. Suitable weight ratios of diluent composition to crude phenolic bottoms composition are at least 0.15:1, more preferably 0.3:1, most preferably from 0.45-0.6:1. The specific amount of diluent composition is balanced between keeping the loading factor low while providing sufficient diluent to efficiently phase separate.

A diluted crude phenolic bottoms stream composition may comprise:

AMS	:	3-10 %wt
Cumene	:	10-40 %wt
Phenol	:	5-25 %wt
AP	:	7-20 %wt
DMBA	:	1-5 %wt
CP	:	7-20 %wt
AMSd	:	3-10 %wt
Tars/Heavies	:	6-20 %wt
Salts	:	0.05-0.25 %wt

Since relatively small amounts of feed to the phase separator are effective to remove 80 %wt or more of salts of neutralisation, the overall volumetric hydrocarbon flow to the phase separator (80) is also very low. By hydrocarbon is meant any compound in a stream other than water. In particular, the flow rate of all hydrocarbons to the phase separator from any source need only be on the order of less than 10, preferably less than 7, more preferably 6, most preferably 5 or less parts by weight per hour based on 100 parts by weight per hour of total neutralised aralkyl hydroperoxide cleavage mass fed to the splitter (30), to effectively separate and discharge at least 80 %wt, more preferably at least 90 %wt of the salts of neutralisation from the phase separator into a salty aqueous purge stream.

In addition to a diluent composition, water is added to the crude phenolic bottoms stream as an additional ingredient to further enhance the ability of the crude phenolic bottoms stream to phase separate. As depicted in Fig. 1, water is added to the diluted crude phenolic bottoms stream in line (63) through line (82) after the diluent composition has been added, to make the phase separable crude phenolic bottoms stream. The amount of water should be kept as low as possible to concentrate the salts and avoid loading the system with excess water and avoid loss of phenol to the aqueous phase due to the miscibility of phenol and water, while on the other hand, a higher amount may be facilitating removal of salts from the hydrocarbon phase by increasing the difference in density between the phases. It is within the ordinary skill to acquire an optimal range of water balanced between enhancing phase separation and avoiding an excessive loss of phenol into the aqueous stream. In general, the amount of water by volume is in excess over the amount of hydrocarbon in the phase separable phenolic

bottoms stream. A volume ratio of water to hydrocarbon in the phase separable crude phenolic bottoms stream is suitably at least 1:1, preferably ranging from 1.1:1 to 3:1, with a ratio of about 1.5:1 to 2.5:1 being more preferred, and a ratio of about 2:1 being most preferred.

Water can be added as a liquid or vapour, preferably as a liquid. Water can also be added as a fresh stream or as a recycle stream originating from the bottoms phase separator (80), preferably the latter. Water may be added before, simultaneous to, or after the diluent composition is added. In one embodiment, water is added to the diluted crude phenolic bottoms stream through line (82) originating from a bottoms phase separator (80). A typical non-limiting example of the water stream composition comprises 90-95 %wt water, 3-7 %wt salts of neutralisation, and 0.5-3 %wt of phenol.

Suitably, the phase separable phenolic bottom stream is formed by adding water at a net amount of 5 parts by weight per hour or less to the phenolic bottoms stream, that may optionally be concentrated, e.g., by further distillation. While more water can be added, as mentioned above, the net addition of water should be kept low to avoid treating larger amounts of water downstream. More preferably, only 2 net parts by weight per hour or less, most preferably 1 part by weight per hour or less, and even 0.5 net parts by weight per hour, or less, of water needs to be added to make a phase separable hydrocarbon phenolic bottoms stream, each based on a flow of 100 parts by weight per hour of all ingredients in the neutralised aralkyl hydroperoxide cleavage mass fed to the splitter (30).

Once water and the diluent are added to the crude phenolic bottoms stream to form a phase separable crude phenolic bottoms stream, the ingredients are optionally but preferably thoroughly mixed. Any means of mixing is

suitable, including static mixing, turbulent in-line mixing, or agitation through a variable speed mixer, depicted in Fig. 1 as the bottoms mixer (70). As shown in Fig. 1, the phase separable crude phenolic bottoms stream enters the bottoms mixer (70) through line (64) to provide sufficient mixing to contact the diluent composition with as much water as possible, thereby transferring phenol solubilised in the water phase into the hydrocarbon phase. If desired, the stream may be micro-emulsified. The well mixed stream then enters the bottoms phase separator (80) through line (71).

In one embodiment of the invention, the composition of the phase separable crude phenolic bottoms stream entering the separator (80) comprises at least 40 %wt water, less than 20 %wt phenolic compounds, alkali metal salts in an amount of at least 1.5 %wt, phenolic tars, and α -methyl styrene dimers, wherein the volume ratio of water to all ingredients in the composition other than water is 3:1 or less. In a more preferred embodiment, the composition of the phase separable crude phenolic bottoms stream comprises 50 %wt or more of water, greater than 5 %wt cumene, greater than 0.5 %wt AMS, less than 10 %wt phenol, phenolic tars present in an amount of less than 8 %wt, and AMSd present in an amount of less than 5 %wt. In a most preferred embodiment, the weight range of ingredients in the phase separable crude phenolic bottoms composition is as follows:

AMS	:	0.5-8 %wt
Cumene	:	5-15 %wt
Phenol	:	3-10 %wt
AP	:	3-10 %wt
DMBA	:	0.2-4 %wt
CP	:	3-10 %wt
AMSd	:	1-5 %wt

Tars/Heavies : 3-8 %wt
Salts : 2-5 %wt
Water : 50-75 %wt

Any means of phase separating the hydrocarbon phase from the aqueous phase in the phase separable crude phenolic bottoms stream is suitable. As depicted in Fig. 1, there is provided a bottoms phase separator vessel (80) wherein the phase separable crude phenolic bottoms stream is injected as a spray into one end of the vessel and allowed to phase separate by settling and flotation over time without agitation into the hydrocarbon phase and aqueous phase.

While the temperature and pressure within the bottoms phase separator (80) may be advantageously lowered compared to the up-stream temperature and pressure conditions in order to promote phase separation, the temperature desirably remains above 100 °C to keep the viscosity of the liquid composition low and preferably to provide an optimal density gradient between the hydrocarbon phase and the aqueous phase. Thus, temperatures exceeding the boiling point of water are preferred, especially temperatures above 110 °C, most preferably from 115 °C to 140 °C. The pressure inside the vessel should be kept sufficiently high to retain the composition in a liquid phase when the temperatures exceed the boiling point of any ingredient at atmospheric pressure. Preferably, the pressure is set from 13.8 kPa-0.69 mPa excess (2-100 psig), most preferably from 0.24-0.48 mPa excess (35-70 psig). The residence time within the separator depends upon the composition of the stream and the conditions inside the separator. In general, a residence time of 5 to 60 minutes is sufficient to effectuate phase separation.

Since the process of the invention does not require a phase separator to process large quantities of feed to

separate and discharge 80 %wt or more of the salts of neutralisation from the phase separator as a salty aqueous purge stream, the vessel can be advantageously sized.

5 Once the aqueous phase is separated from the hydrocarbon phase, it is withdrawn as a bottoms stream through line (82), and the less dense upper layer hydrocarbon stream is withdrawn from the bottoms phase separator through line (81) to the heavy ends cracker
10 (90). Through phase separation, the amount of salts of neutralisation present in the hydrocarbon phase is reduced compared to the amount of salts of neutralisation present prior to phase separation, or the amount of salts present in the neutralised aralkyl hydroperoxide cleavage
15 mass stream or the crude phenolic stream. In one embodiment, at least 80%, more preferably at least 90 %wt, of the salts present in the crude phenolic bottoms stream are removed from the hydrocarbon phase and transferred to the aqueous phase. As much as 94 %wt or
20 more of the salts of neutralisation are removed from the process of the invention as a salty aqueous purge stream.

 At least a portion of the aqueous stream separated from the hydrocarbon phase is purged from the process as a waste stream for treatment if necessary. Preferably, a
25 portion of the aqueous phase is re-circulated through line (82) to line (62) or (63) and used as the water source, along with a fresh feed of water in line (84) to make up for water lost through the salt water purge, for addition to the crude phenolic bottoms stream, and
30 another portion of the aqueous phase is purged as a salt water purge through line (83).

 An advantage of the process of the invention is that the amount of water containing salts of neutralisation discharged at any step downstream from the stripping
35 column is low while simultaneously removing substantial

amounts of salts of neutralisation from the process. In particular, the process of the invention enables one to discharge and purge a net amount of an aqueous phase containing salts of neutralisation at a rate of less than 5 parts by weight per hour based on 100 parts by weight per hour of the aralkyl hydroperoxide cleavage mass stream. Even at this low discharge rate, at least 80 %wt, preferably 90 %wt or more, of the salts of neutralisation present at any stage from the neutralised aralkyl hydroperoxide cleavage mass immediately prior to entry into the splitter are removed. In a more preferred embodiment, the net amount of aqueous phase discharged is less than 1.5 parts by weight per hour, and even less than 1, more preferably less than 0.5, and most preferably less than 0.3 parts by weight per hour each based on 100 parts by weight per hour of the neutralised aralkyl hydroperoxide cleavage mass immediately prior to entry into the splitter. Accordingly, the process consumes only small quantities of waste water, leading to other advantages including a reduction in the amount of water that must be treated and a reduction in the amount of phenol lost to a water purge. The removal of salts of neutralisation in the process of the invention is also not dependent on the stability of the composition profile throughout the splitter.

The process according to the invention also concentrates the amount of salt in the salty aqueous purge stream (83). The process according to the invention can achieve salt concentrations of at least 3 %wt in at least 90 %wt water, more preferably at least 4 or even at least 5 %wt of salts of neutralisation based on the weight of the salty aqueous purge stream. A typical composition of the purge aqueous stream in line (83) comprises 90-95 %wt water, 3-7 %wt salts of

neutralisation, and 0.5-3 %wt of phenol, based on these three components.

5 The hydrocarbon stream in line (81) is introduced into a heavy ends cracker (90) where the hydrocarbon stream is separated into a light ends stream enriched in phenolic compounds over the phase separated hydrocarbon stream, and a tarry stream enriched in tars over the phase separated hydrocarbon stream, wherein the tarry stream has a reduced amount of salts of neutralisation
10 relative to the crude phenolic stream. The cracker may optionally generate light ends which are included in the light ends stream enriched in phenolic compounds.

The hydrocarbon phase exiting as a stream through line (81) has a typical composition comprising:

15	AMS	:	3-10 %wt
	Cumene	:	10-40 %wt
	Phenol	:	5-25 %wt
	AP	:	7-20 %wt
	DMBA	:	1-5 %wt
20	CP	:	7-20 %wt
	AMSd	:	3-10 %wt
	Tars/Heavies	:	6-20 %wt
	Salts	:	0.005-0.02 %wt

25 Heavy ends such as un-cracked AP, CP, AMSd, and tars/heavies, and a very small amount of phenol are removed from the bottoms of the heavy ends cracker (90). Since the amount of salts are low, fouling of bottoms of the heavy ends cracker is substantially reduced. Further, fouling of the reboilers which re-circulate a
30 portion of the heavy ends cracker bottoms stream to the heavy ends cracker, as well as fouling of other equipment for treating the heavy bottoms tar stream exiting through line (92), is substantially reduced. Accordingly, the heavy ends bottom stream exiting the heavy ends cracker
35 is usable as fuel for boilers. Lighter ends in the

hydrocarbon stream such as AMS, cumene, phenol, water, and the cracked products of DMBA, CP, AMSd, and tars/heavy oligomers, exit the heavy ends cracker as an overhead through line (91).

5 In another embodiment of the invention, at least a portion of the light ends stream is re-circulated back to the neutralisation zone where the aralkyl hydroperoxide cleavage mass is neutralised. This is preferably accomplished by first purifying the lighter ends stream.

10 The lighter ends composition is fed through line (91) to a rectifier (100). Very light ingredients such as benzene, propane, and water are removed from the overhead of the rectifier through line (101), while higher boiling compounds such as phenol, cumene, and AMS, and minor

15 amounts of ethyl benzene exit the bottoms of the rectifier through line (102), at least a portion or all of which is recycled to the neutraliser (10) through line (1). This will further enhance the ability of the composition in line (1) to phase separate in vessel (20)

20 once neutralised, partially or wholly, in neutraliser (10).

C L A I M S

1. A process for the manufacture of phenolic compounds comprising by oxidising an alkyl-substituted aromatic compound to form the hydroperoxide derivative thereof, followed by cleavage of the hydroperoxide to form an
- 5 aralkyl hydroperoxide cleavage mass and neutralisation of the aralkyl hydroperoxide cleavage mass to form a neutralised aralkyl hydroperoxide cleavage mass stream, comprising:
- a) separating the neutralised aralkyl hydroperoxide
- 10 cleavage mass stream containing salts of neutralisation into a crude ketone stream and a crude phenolic stream containing the salts of neutralisation;
- b) separating the crude phenolic stream into a concentrated phenolic-rich stream, enriched in phenolic
- 15 compounds, and a crude phenolic bottoms stream enriched in tars and alpha methyl styrene dimers, each compared to the crude phenolic stream, said crude phenolic bottoms stream containing salts of neutralisation;
- c) to the crude phenolic bottoms stream, adding water
- 20 and a diluent composition, thereby forming a phase separable crude phenolic bottoms stream, said diluent composition comprised of hydrocarbons phase compatible with the crude phenolic bottoms stream and having a combined density lower than the density of the crude
- 25 phenolic bottoms stream;
- d) separating the phase separable crude phenolic bottoms stream into a hydrocarbon phase and an aqueous phase containing salts of neutralisation;
- whereby the amount of salts of neutralisation in the
- 30 hydrocarbon phase is reduced compared to the amount of salts of neutralisation present prior to separation.

2. The process of claim 1, wherein the weight ratio of diluent composition to crude phenolic bottoms stream is at least 0.15:1.

3. The process of claim 1 or 2, wherein the volume ratio of water to crude phenolic bottoms stream is at least 1:1.

4. The process of any one of claims 1-3, wherein the diluent composition comprises less than 20 %wt of phenolic compounds.

5. The process of claim 4, wherein the diluent composition comprises cumene and α -methyl styrene.

6. The process of any one of claims 1-5, further comprising:

(i) separating said crude ketone stream into a concentrated ketone-rich stream, enriched in ketone over the crude ketone stream, and a crude ketone bottoms stream;

(ii) feeding at least a portion of the crude ketone bottoms stream as said diluent composition to the crude phenolic bottoms stream in step c).

7. The process of claim 6, further comprising feeding a portion of said crude ketone bottoms stream to the aralkyl hydroperoxide cleavage mass before neutralisation.

8. The process of any one of claims 1 to 7 in which the hydrocarbon phase is separated into a light ends stream, enriched in phenolic compounds, and a tarry stream enriched in tars, said tarry stream having a reduced amount of salts of neutralisation relative to the crude phenolic stream.

9. A composition comprising at least 40 %wt water, less than 20 %wt phenolic compounds, alkali metal salts in an amount of at least 1.5 %wt, phenolic tars, and α -methyl styrene dimers, wherein the volume ratio of water to all



* C L M S *

ingredients in said composition other than water is between 1:1 and about 3:1, and the percentages are based on the total of water, phenolic compounds, alkali metal salts phenolic tars and α -methyl styrene dimers.

- 5 10. The composition of claim 9, comprising 50 %wt or more of water, greater than 5 %wt cumene, greater than 1 %wt α -methyl styrene, less than 10 %wt phenol, phenolic tars present in an amount of less than 6 %wt, and α -methyl styrene dimers present in an amount of less than 4 %wt,
- 10 the percentages being based on the total of water, cumene, α -methyl styrene, phenol, phenolic tars and α -methyl styrene dimers.

