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(54) Title: SUSTAINABLE CHEMICAL PROCESS FOR ISOLATION OF NAPHTHALENE SULPHONIC ACID COMPOUNDS WITH INHERENT RECYCLE OF ALL ACIDIC STREAMS GENERATED DURING ISOLATION AND WASHING

(57) Abstract: Isolation of Naphthalene Sulphonic Acid Compounds is achieved with acidification of alkali fusion mixture with dilute sulphuric acid to precipitation at the predetermined conditions temperature, time and p H and Naphthalene Sulphonic Acid Compounds is separated as a partial alkali metal salt by precipitation and separated by filtration. The resulting filtrate after recycle treatment containing soluble Naphthalene Sulphonic Acid Compounds and/or a salt thereof after recycle treatment is used as a starting reaction medium, top up reaction medium, dilution reaction medium for said subsequent isolation of Naphthalene Sulphonic Acid Compounds. Isolation of Naphthalene Sulphonic Acids can be achieved by two methods viz. forward isolation and Reverse isolate.

**Sustainable chemical process for isolation of Naphthalene Sulphonic Acid Compounds with inherent recycle of all acidic streams generated during isolation and washing**

**Field of Invention:**

The present invention relates to a process for isolation of Naphthalene Sulphonic Acid Compounds as a partial alkali metal salt with inherent recycle all acidic streams generated.

More particularly, the invention pertains to a process for isolation of Naphthalene Sulphonic Acid Compounds by subjecting the alkali fusion mixture to precipitation by mixing the fusion mass with an acid to obtain H acid as a partial alkali metal salt (the precipitation by mixing the fusion mass with an acid being hereinafter referred to as "acidification precipitation" for brevity), characterized in that the acidification precipitation is performed by mixing said fusion mass with said dilute acid, the precipitated partial alkali metal salt of Naphthalene Sulphonic Acids is separated by filtration, and inherent recycle of the resulting filtrate containing soluble Naphthalene Sulphonic Acid Compound and/or a salt thereof is used as a reaction medium for said isolation process.

**Background of invention:**

Isolation, broadly defined as separation of product form alkaline mass by acidic solution after performing chemical process where the soluble product is separated

by known methods. Isolation is one of the important chemical processes extensively applied in the manufacture of many molecules.

Isolation of molecules finds applications in various groups of chemical including pharmaceuticals, dyes and pigents, agrochemicals, specialty chemicals, fine chemicals and explosives.

**Demerits of current isolation methods:**

Naphthalene Sulphonic Acid Compounds have long been manufactured and used as an intermediate for the production of dyes and pigents The general process for the isolation of Naphthalene Sulphonic Acid compounds comprises obtaining alkali fused Amine from naphthalene followed by acidification & precipitation with dilute acid.

Problems in the process are that the overall yield of Naphthalene Sulphonic Acid compounds from naphthalene is low and a large amount of acids and bases, etc. are required.

According to the process as described on pages 533 to 536 of Yutaka HOSODA, "Senryo Kagaku (Dye Chemistry)", the amount of caustic soda used for alkali fusion of 1 mole of Koch acid acid trisodium salt is 8.6 moles which corresponds to 4.3 times the theoretically required amount (2 moles). As a result, the amount of sulfuric acid required for obtaining H acid as its monosodium salt from the fusion mass reaches 5.8 moles for 1 mole of Koch acid.

Drawback of these methods is that, these methods generate large quantities of acidic liquid waste which is difficult to recycle. These methods require environmentally unsustainable reaction conditions in terms of pH, temperature, concentration, reaction agents and medium, and so on, and leave an unsustainable impact on the environment, specifically on our water bodies.

These methods suffer from drawbacks such as poor conversion rates and low yields, rendering these methods uneconomical and environmentally unsustainable.

Furthermore, other drawback of all methods described above is that undesirable organic and inorganic side products are always formed as a result of these methods. The type of side products formed and their quantities vary from process to process and from molecule to molecule. This difficulty during recycle of mother liquor results in generation of large quantities of liquid effluents.

Yet another drawback of the methods referred to above is that in some cases large quantity of inorganic solid wastes are also generated. These solid wastes are contaminated with organic compounds like starting material, product and side products and pose a serious pollution problem. Normally these wastes are sticky solids and are tedious to handle and are difficult to dispose off, and are known in the industry as non-green solid wastes.

There are still further drawbacks of the above methods. Because of generation of large quantities of liquid effluents and non-green solid wastes, above processes require a large facility for effluent treatment and disposal of solid wastes. These factors impose location related constraints making it mandatory for these

processes to be carried out only in designated industrial areas, suitable for handling special chemicals.

Thus, these methods are non-green, unsustainable, uneconomical, and harm the environment to a very large extent, which has worldwide become a major concern.

Hence there is a need for providing a process of green isolation of Naphthalene Sulphonic Acid Compounds with inherent recycle of acidic mother liquor, thereby avoiding above mentioned disadvantages and drawbacks, and providing an environmentally sustainable and economical recycling solution.

**Objects and advantages of invention:**

The inventors at have developed a novel process using commercially available customized formulations such as R-Cat 1 & R-Cat 2 for the isolation of Naphthalene Sulphonic Acid Compounds with inherent recycle of mother liquor and washings generated during the process.

According to the present inventors' follow-up, the use of such an excess of auxiliary material (e.g. acids) in the respective isolation step is unavoidable to a certain extent. It has been found that it is almost impossible to curtail sharply the amounts of these auxiliary materials used without impairing the other advantages of the process although there is some room for improvement in the process.

The use of an excess of auxiliary materials (for example, acids) in isolation step causes the use of a large amount of the other auxiliary materials (for example, bases) for neutralization liquid streams generated after Naphthalene Sulphonic Acid Compounds separation. As a result, most of the cost of raw and processed materials for the manufacture of Naphthalene Sulphonic Acid compounds is occupied by the cost of acids and bases. Also, a vast amount of waste acid or inorganic salt-containing drainage is produced and an economic burden for treating them is not negligible.

An object of the process of the present invention is to provide an environmentally friendly (green) process that overcomes the problem of generation of large quantities of acidic waste resulting from the conventional processes of Naphthalene Sulphonic Acid Compounds isolation.

It is, therefore, the principal object of the present invention to avoid the limitations encountered in the isolation of Naphthalene Sulphonic Acid compounds from the alkali fusion mass.

It is a further object to provide a green process for isolation of Naphthalene Sulphonic Acids which are not only inexpensive in operation but also produces a product of high quality.

Another object of the present invention is to provide an improved process for producing Naphthalene Sulphonic Acids with recycle of acidic streams generated during isolation, separation and washing of product resulting in zero liquid discharge.

Another object of the present invention is to provide economy by reducing consumption of auxiliary materials like acid with recycle of acidic streams generated during precipitation, separation and washing of product and base for neutralization of acidic liquid effluent streams.

Another object of the present invention is to provide a process, wherein the content of undesirable byproducts, organic as well as inorganic impurities are substantially reduced by the virtue of recycle ability of reaction medium which results in consistent purer product formation.

An advantage of the present invention is that since both the number and quantity of organic and inorganic impurities are comparatively less, the possibility of build of side products in acidic mother liquor during recycle is less due to use of proprietary formulation R-Cat-1 & R-Cat 2. This fact advantageously makes possible infinite number of acidic mother liquor recycles in our process.

A further advantage of the method of present invention is that the product separation processes disclosed herein ensure that the solid spent formed in the process of the present invention has surprisingly low levels of organic compounds and are thus green in nature. Consequently, the process described herein does not require any liquid effluent treatment facility or elaborate solid waste disposal facility. A further advantage of the process of the present invention over the prior art is that the process is not constrained in respect of plant location, in that it doesn't necessarily have to be carried out in industrial areas.

A yet further advantage of the present invention is that the method disclosed herein is carried out at milder reaction conditions and at atmospheric pressure, which makes it safer.

Another advantage of the present invention is that the use of the proprietary reaction formulations developed by the inventors, namely R-Cat 1 & R-Cat 2, or any other similar formulations used in the process of this invention makes it possible to recycle the acidic liquid streams completely.

A still further advantage of the process of the present invention is that its inherent thermodynamic conditions defined in terms of pressure, temperature, pH, concentrations of reaction components, and various reaction agents is close to respective conditions occurring in the nature, thereby making the process of the invention benign and environmentally friendly.

The process is carried out at such temperatures and pH values that it saves energy and therefore results in the process economy and also is greener since generation of energy mostly leads to lots of pollution.

**Summary of invention:**

Isolation of Naphthalene Sulphonic Acid Compounds is achieved with acidification of alkali fusion mixture with dilute sulphuric acid to precipitation at the predetermined conditions temperature, time & pH and Naphthalene Sulphonic Acid Compounds is separated as a partial alkali metal salt by precipitation and

separated by filtration. The resulting filtrate after recycle treatment containing soluble Naphthalene Sulphonic Acid Compounds and/or a salt thereof after recycle treatment is used as a starting reaction medium, top up reaction medium, dilution reaction medium for said subsequent isolation of Naphthalene Sulphonic Acid Compounds.

Isolation of Naphthalene Sulphonic Acids can be achieved by two methods viz. forward isolation and Reverse isolation. Detail process description of Forward and Reverse isolation is articulated in A & B respectively.

**Brief description of figures:**

Figure 1 shows the schematic representation of complete process of the present invention.

Figure 2 shows a reaction sequence of Forward Isolation part of the process

.Figure 3 shows a simplified schematic relationship between the isolation and recycle sequences of the present invention

Figure 4 shows the schematic representation of the complete process with the various streams and products that are generated during the process

Figure 5 shows a reaction sequence of Reverse Isolation individual cycles of the large number recycle loop.

Figure 6 shows a schematic of the recycle sequence

**Detailed description of the invention:**

We will begin by defining some key terms.

**Terminology used in description of the invention:**

In order to aid the understanding of the process described herein several terms are explicitly defined.

- **Forward isolation-** Forward isolation can be defined as "In the reaction sequence where Fresh water or reaction medium and sulphuric acid is taken as **Start-Up Reaction Medium** followed by the charging of Fusion mass **(Starting Material)** at the predetermined isolation conditions, charging of fusion mass is carried out in Continuous charging or Lot wise or by any other known method of charging.

- **Reverse isolation-** Reverse isolation can be defined as "The isolation reaction sequence in which Fresh water or reaction medium and Fusion mass **(Starting Material)** is taken as **Start-Up Reaction Medium** followed by the charging of sulphuric acid at the predetermined isolation conditions, the sulphuric acid solution charging is carried out in Continuous charging or Lot wise or by any other known method of charging.

- **Reaction medium** (RM) is mother liquor or diluted acid or acidic aqueous phase or a combination thereof used in the isolation process

- **Fresh reaction medium** (FRM) is the fresh water or fresh dilute acid or fresh acidic aqueous phase or a combination thereof used in the reaction.
- **Reaction medium factor** (RMF) is the ratio of the weight of FRM or RM with weight of Fusion Mass used in the process.
- **Mother liquor** (ML) is the liquid stream generated after performing a particular step. Mother liquor has been used as the reaction medium (RM) at various stages of the process of the invention in its cycles following the first cycle.
- **Separation RM** is the mixture of acidic pH in the specified range of H acid isolation which is aqueous phase and immiscible ready for phase separation.
- **Cooling curve** (CC) is profile of temperature verses time.
- **pH curve** is profile of pH verses quantity of sulphuric acid required for isolation of H acid
- **Seeding** – is the crystallization or isolation initiator to get desired result
- **Salting** – is the external input of salt to enhance rate of salt bleeding.

The process disclosed in the present invention is a sustainable chemical process for isolation of Naphthalene Sulphonic Acid compounds with inherent recycle of all acidic streams generated during isolation and washing.

Isolation of Naphthalene Sulphonic Acid Compounds can be carried out in two ways, namely:

**A: Forward isolation-** Forward isolation can be defined as "In the reaction sequence where Fresh water or reaction medium and sulphuric acid is taken as **Start-Up Reaction Medium** followed by the charging of Fusion mass **(Starting Material)** at the predetermined isolation conditions.

In forward isolation of Naphthalene Sulphonic Acid Compounds from Fusion mass, the fusion mass charging to the start up acid solution is carried out in two different methods namely – Continuous charging, Lot wise Charging.

**B: Reverse isolation-** Reverse isolation can be defined as "The isolation reaction sequence in which Fresh water or reaction medium and Fusion mass **(Starting Material)** is taken as **Start-Up Reaction Medium** followed by the charging of sulphuric acid at the predetermined isolation conditions.

In reverse isolation of Naphthalene Sulphonic Acid Compounds from Fusion mass, the sulphuric acid solution charging to the start up fusion mass solution is carried out in two different methods namely – Continuous charging, Lot wise Charging.

The process of the present invention uses proprietary chemical formulations namely R-Cat 1 & R-Cat 2 for Isolation & recycles. R-Cat 1 & R-Cat 2 are the multifunctional, chemical recycle formulations mainly comprising fine iron powder in the range of 0% (w/w) to 95% (w/w), tin, copper, titanium, and zinc,

or any combination thereof, depending on the Fusion mass to be acidified, in the range of 0% (w/w) to 10% (w/w). The purity of all components is in the range of 50% (w/w) to 100% (w/w). These proprietary catalysts are finalized and optimized after various studies with various R – Cats namely R – Cat A, A1, A2, A3, A4, A5, 1, 2 to remove the organic and inorganic impurities effectively.

R-Cat 1 & R- Cat 2 also contain electrolyte salt of various metals such as sodium, magnesium, calcium, iron, nickel, cobalt, tin, zinc, titanium, copper, manganese, and any other metals with multiple valences in the range of 0% (w/w) to 50% (w/w). The purity of the salts is variable and in the range of 50% (w/w) to 100% (w/w). The R-Cat 1 & R- Cat 2 also contains customized grade of activated carbon in the range of 0% (w/w) to 5% (w/w); filter aid in the range of 0% - 95% and decolorizing agent in the range of 0% (w/w) to 5% (w/w).

R-Cat 1 & R-Cat 2 also contain hydroxides of calcium or alkali metals like magnesium, barium, sodium, potassium in the range of 0% (w/w) to 95% (w/w); customized grade of activated carbon in the range of 0.5% (w/w) to 5% (w/w); filter aid in the range of 5% (w/w) to 95% (w/w) and decolorizing agent in the range of 0.5% (w/w) to 5% (w/w) along with iron powder in the range of 5% (w/w) to 25 % (w/w).

R-Cat 1 & R- Cat 2 also contain specialty additives like polyelectrolyte, anti foaming agents, dispersing agents, emulsifying agents, mass transfer enhancing agents, anti caking agents, UV stabilizers, solubilising agents, and anti oxidants, and other such agents.

The process of the present invention also uses sodium salt of commercial grade in the range of 0% (w/w) to 95% (w/w), depending on the Fusion mass to be acidified, in the range of 0% (w/w) to 10% (w/w) for the salt bleeding from the Mother Liquor. The purity of bleed salt is in the range of 10% (w/w) to 90% (w/w), more accurately in the range of 30 – 60%. The sodium salt is bleeded out from the Mother Liquor at the predetermined period of time, at a predetermined temperature by a predetermined process. This bleed salt is recycled back in the process at a predetermined stage and at a predetermined process. This invention includes the sodium salt use in the range of 0% to 50% (w/w), more preferably in the range of 10 – 40 % (w/w).

The present application also discloses a sustainable chemical process for green isolation of Naphthalene Sulphonic Acid Compounds with inherent recycle of all acidic liquid streams generated in the same.

The chemical process of the present invention basically comprises inherent large number of recycles of processing the acidic mother liquor and all streams generated during any of the cycles. Each cycle further comprises two sequences Green Reaction Sequence and Green Isolation Sequence

One of the novel features of the process of present invention is regarding the reaction medium used in various stages of the process.

Referring to figure 1, In the very first cycle of the process, of the present invention FRM is used as the reaction medium in the start-up (Step 1.1) and

reaction (Step 1.2) steps, and for steps involving stirring & cooling, stirring & separation, filtration & washings (Steps 2.1, 2.2, 2.3, 2.4). As a key feature of the present invention, in the subsequent cycles, the liquid streams generated in various steps of recycling of the first cycle are used as the reaction medium. However, the use of these liquid streams as the reaction medium is optional and FRM can be used as the reaction medium in all cycles.

Streams generated at various stages of the invention are now defined. As shown in Figure 1, **Stream A** is generated after filtration in (step 2.3) that follows the reaction step. **Stream B** is generated after washing of product in step 2.4. Stream generated after collective treatment by R-Cat 1 to stream A & B is identified as **Stream C** and transferred to 2nd treatment. After 2nd treatment to Stream C the stream generated is stored in a storage tank and is defined as **Stream D**. Treated mother liquor stream D is used at various stages such as start – up, reaction, stirring & cooling, stirring & separation, isolation as **Stream E**.

Some quantity of FRM or any other appropriate liquid streams, or a combination thereof are used as make-up liquid in washing step to compensate for the various liquid losses through handling, evaporation, and so on.

Details of the steps involved in the two sequences that form a typical cycle of the process of the present invention are described below, with reference to figures 1, 2, 3, and 4.

The preferred embodiment of the present invention and various other embodiments are now described.

In another embodiment of present invention wherein the raw materials are added in different sequence described in embodiment A, at the same time generation and fate of all the steps in both the embodiments is same.

Change in the sequence of raw material charging is done to understand and optimize Naphthalene Sulphonic Acid Compounds isolation process parameters, to establish & maintain sustainability in process, to set inherent infinite recycle loop of reaction medium and consistency in quality of product.

**Sequence 1.0 - Green reaction sequence:**

The Green reaction sequence is performed in two different ways as (A) Forward Isolation (B) Reverse Isolation. Below is the detail description of process of invention. These two methods vary only in step Start Up (Step 1.1) and Reaction (Step 1.2), rest all other steps (1.3, 1.4, 2.1, 2.2, 2.3, 2.4, 3.1 & 3.2) are common in both the isolation methods.

***A: – Forward Isolation-***

As shown in Figure 2, this sequence comprises four steps, namely the start-up, reaction, isolation & separation. Each of these steps is described below.

One of the key features of this sequence is the reaction medium that is used in various steps. A predetermined quantity of reaction medium is added as

appropriate. The reaction medium along with the specific conditions generated as defined by the temperature, pressure, pH, agitation, and other such parameters lead to the unique inherent recyclability of the process of the present invention.

The total quantity of the reaction medium required in this sequence for a typical cycle (referred to hereafter as $Q_{RT}$) is dictated by the requirement of the conversion of fusion mass to Naphthalene Sulphonic Acid Compounds. $Q_{RT}$ is determined by a reaction medium's weight ratio, $(\text{Weight Ratio})_{RA}$, that is the ratio of the weight of the reaction medium required in a single cycle, $W_{RA}$ of the process of this invention to the weight of total amount of fusion mass to be converted in that single cycle, $W_N$. That is for a single cycle:

$$(\text{Weight Ratio})_{RA} = W_{RA}/ W_N \qquad \text{Equation 1}$$

The $Q_{RT}$ is such that its weight is equal to $W_{RA}$ which is determined from Equation 1.

In the preferred embodiment of the present invention, $(\text{Weight Ratio})_{RA}$ is preferably in the range of 0.25 to 25, the more preferable range being 0.5 to 2.5.

**Step 1.1 – Start-up:** This step is carried out in a reaction vessel that has an agitator and necessary attachments known to a person skilled in the art. As shown in figure 2, at the start of the first cycle of process of the present invention an RM is charged to the reaction vessel in suitable quantities.

In the preferred embodiment of the present invention FRM is used as the reaction medium. The total quantity of the reaction medium required for a typical cycle

(referred to hereafter $Q_{RMT}$) is dictated by the solubility of Naphthalene Sulphonic Acid Compounds. This quantity is determined by weight ratio of FRM or the reaction medium, denoted as $(\text{Weight Ratio})_{RM}$, that is the ratio of the weight of the FRM or the reaction medium required in a single cycle, $W_{RM}$, to the weight of total amount of Fusion mass to be converted in that single cycle, $W_N$. That is-

$$(\text{Weight Ratio})_{RM} = W_{RM}/ W_N \qquad \text{Equation 2}$$

The $Q_{RMT}$ is such that its weight is equal to $W_{RM}$ which is determined from Eq. 2.

The quantity of the FRM or the reaction medium used in Step 1.1, denoted as $Q_{RM1.1}$, is variable.

In the preferred embodiment, $(\text{Weight Ratio})_{RM}$ is preferably in the range of 5 to 100, the more preferable range being 10 to 75, and $Q_{RM1.1}$ is in the range of 0% (w/w) to 40% (w/w) of $Q_{RMT}$ used in this cycle.

A suitable acid is added in suitable quantity and suitable form while maintaining temperature of the reaction mixture in the reaction vessel in the range of 0 $^0$C to 200 $^0$C, preferable range 30°C to 100°C. In the preferred embodiment of the invention, sulfuric acid is used. In another embodiment of the present invention, the temperature at which the acid charged is in the range of 10 $^0$C to 100 $^0$C, more preferably 50 $^0$C to 100 $^0$C.

The mixture is agitated for a predetermined time that is in the range of 0 minutes to 5 hours, more preferably between 0.5 hours to 2.5 hours. In the agitation stage, the pH of the reaction mixture is maintained throughout at a predetermined level

that is in the range of 1 to 9, preferable range being 1 to 7 and most preferred being 1 to 2.

At the end of the agitation stage, a fusion mass is charged in suitable quantity. It is added either in its full required quantity or in any number of batches of any size, or continuously, or any combination thereof. The fusion mass is added over a predetermined period, at a predetermined temperature, and a predetermined pH. The period over which the fusion mass is added in the range of 0 minutes to 5 hours, more preferably between 0.5 hours to 2.5 hours. The temperature at which the fusion mass is added is in the range of 0 $^0$C to 200 $^0$C. The pH at which the fusion mass is added is in the range of 1 to 9, preferable range being 1 to 7 and most preferred being 1 to 2.

In the subsequent cycles of the process of the present invention, Stream E is used as a reaction medium instead of FRM in the start-up (step 1.1).

In another embodiment of the present invention, the temperature at which the reaction medium is charged is in the range of 10 $^0$C to 100 $^0$C, more preferably 30 $^0$C to 70 $^0$C.

In another embodiment of the present invention, the reaction medium and / or acid, and the fusion mass are added in any sequence.

**Step 1.2 – Reaction:** The Fusion Mass to be converted is added to the reaction vessel either Continuous in its full quantity or in any number of lots. The total amount of fusion mass to be converted is added over a period of 0 to 5 hours,

more preferably in 0.5 – 1.5 hrs at a suitable interval that depends on the molecule to be isolated.

A reaction medium is charged in suitable quantity to the reaction vessel while maintaining the temperature, and pH of the mixture in their respective predetermined ranges. The temperature at which the reaction medium is added is in the range of 0 $^0$C to 200 $^0$C, more preferably in the range of 50 - 100$^0$C. The pH at which the reaction medium is added is in the range of 1 to 9, preferable range being 2 to 5. In the preferred embodiment of the present invention, FRM is used as the reaction medium in step 1.2 of the first cycle of the process of the present invention. For subsequent cycle, stream E is used as the reaction medium for this step.

The quantity of the FRM or the reaction medium used in Step 1.2, denoted as $Q_{RM1.2}$, is variable in the range of 0% (w/w) to 40% (w/w) of the total quantity $Q_{RMT}$ used in this cycle.

A suitable acid is optionally added to the reaction vessel to achieve the desired pH level of the reaction mixture. The acid is added in a suitable form while maintaining temperature of the reaction mixture in the reaction vessel in the range of 0 $^o$C to 200 $^o$C.

Fusion mass is charged to the reaction mixture over a period of time at a predetermined temperature which is in the range of 0 $^0$C to 200 $^0$C, when the pH of the reaction mixture is at a predetermined value which is in the range of 1 to 9, preferable range being 1 to 2. The fusion mass required for Step 1.2 is added either in a single lot or in batches, or continuously, or any combination of these methods of addition.

The reaction mixture at all stages of this step is optionally stirred with agitators rotating at a rate between 0 to 500 RPM. The step can be successfully carried out even without stirring.

***B: – Reverse Isolation-***

In Reverse Isolation of Naphthalene Sulphonic Acid Compounds there is change in only Step No. 1.1 & 1.2 as shown in Figure 5, all other steps in Reaction Sequence 1.3 & 1.4 are same as in Forward Isolation. This sequence comprises four steps, namely the start-up, reaction, isolation & separation.

One of the key features of this sequence is the reaction medium that is used in various steps. A predetermined quantity of reaction medium is added as appropriate. The reaction medium along with the specific conditions generated as defined by the temperature, pressure, pH, agitation, and other such parameters lead to the unique inherent recyclability of the process of the present invention.

The total quantity of the reaction medium required in this sequence for a typical cycle (referred to hereafter as $Q_{RT}$) is dictated by the requirement of the conversion of fusion mass to Naphthalene Sulphonic Acid Compounds. $Q_{RT}$ is determined by a reaction medium's weight ratio, $(\text{Weight Ratio})_{RA}$, that is the ratio of the weight of the reaction medium required in a single cycle, $W_{RA}$ of the process of this invention to the weight of total amount of fusion mass to be converted in that single cycle, $W_N$. That is for a single cycle:

$(\text{Weight Ratio})_{RA} = W_{RA}/ W_N$ Equation 1

The $Q_{RT}$ is such that its weight is equal to $W_{RA}$ which is determined from Equation 1.

In the preferred embodiment of the present invention, $(\text{Weight Ratio})_{RA}$ is preferably in the range of 0.25 to 25, the more preferable range being 0.5 to 2.5.

**Step 1.1 – Start-up:** This step is carried out in a reaction vessel that has an agitator and necessary attachments known to a person skilled in the art. As shown in figure 5, at the start of the first cycle of process of the present invention an RM is charged to the reaction vessel in suitable quantities.

In the preferred embodiment of the present invention FRM is used as the reaction medium. The total quantity of the reaction medium required for a typical cycle (referred to hereafter $Q_{RMT}$) is dictated by the solubility of Naphthalene Sulphonic Acid Compounds. This quantity is determined by weight ratio of FRM or the reaction medium, denoted as $(\text{Weight Ratio})_{RM}$, that is the ratio of the weight of the FRM or the reaction medium required in a single cycle, $W_{RM}$, to the weight of total amount of Fusion mass to be converted in that single cycle, $W_N$. That is

$(\text{Weight Ratio})_{RM} = W_{RM}/ W_N$ Equation 2

The $Q_{RMT}$ is such that its weight is equal to $W_{RM}$ which is determined from Equation 2.

The quantity of the FRM or the reaction medium used in Step 1.1, denoted as $Q_{RM1.1}$, is variable.

In the preferred embodiment, $(\text{Weight Ratio})_{RM}$ is preferably in the range of 5 to 100, the more preferable range being 10 to 75, and $Q_{RM1.1}$ is in the range of 0% (w/w) to 40% (w/w) of $Q_{RMT}$ used in this cycle.

A suitable acid is added in suitable quantity and suitable form while maintaining temperature of the reaction mixture in the reaction vessel in the range of 0 $^0$C to 200 $^0$C, preferable range 30°C to 100°C. In the preferred embodiment of the invention, sulfuric acid is used. In another embodiment of the present invention, the temperature at which the acid charged is in the range of 10 $^0$C to 100 $^0$C, more preferably 50 $^0$C to 100 $^0$C.

The mixture is agitated for a predetermined time that is in the range of 0 minutes to 5 hours, more preferably between 0.5 hours to 2.5 hours. In the agitation stage, the pH of the reaction mixture is maintained throughout at a predetermined level that is in the range of 1 to 9, preferable range being 1 to 7 and most preferred being 1 to 2.

At the end of the agitation stage, a fusion mass is charged in suitable quantity. It is added either in its full required quantity or in any number of batches of any size, or continuously, or any combination thereof. The fusion mass is added over a predetermined period, at a predetermined temperature, and a predetermined pH. The period over which the fusion mass is added in the range of 0 minutes to 5 hours, more preferably between 0.5 hours to 2.5 hours. The temperature at which

the fusion mass is added is in the range of 0 $^0$C to 200 $^0$C. The pH at which the fusion mass is added is in the range of 1 to 9, preferable range being 1 to 7 and most preferred being 1 to 2.

In the subsequent cycles of the process of the present invention, Stream E is used as a reaction medium instead of FRM in the start-up (step 1.1).

In another embodiment of the present invention, the temperature at which the reaction medium is charged is in the range of 10 $^0$C to 100 $^0$C, more preferably 30 $^0$C to 70 $^0$C.

In another embodiment of the present invention, the reaction medium and / or acid, and the fusion mass are added in any sequence.

**Step 1.2 – Reaction:** The fusion mass to be converted is added to the reaction vessel either in its full quantity or in any number of lots. The total amount of fusion mass to be converted is added over a period of 0 to 5 hours, at a suitable interval that depends on the molecule to be isolated.

A reaction medium is charged in suitable quantity to the reaction vessel while maintaining the temperature, and pH of the mixture in their respective predetermined ranges. The temperature at which the reaction medium is added is in the range of 0 $^0$C to 200 $^0$C more preferably in the range of 50 -100 $^0$C. The pH at which the reaction medium is added is in the range of 1 to 9, preferable range being 1 to 2. In the preferred embodiment of the present invention, FRM is used as the reaction medium in step 1.2

of the first cycle of the process of the present invention. For subsequent cycle, Stream E is used as the reaction medium for this step.

The quantity of the FRM or the reaction medium used in Step 1.2, denoted as $Q_{RM1.2}$, is variable in the range of 0% (w/w) to 40% (w/w) of the total quantity $Q_{RMT}$ used in this cycle.

A suitable acid is optionally added to the reaction vessel to achieve the desired pH level of the reaction mixture. The acid is added in a suitable form while maintaining temperature of the reaction mixture in the reaction vessel in the range of 0 $^0$C to 200 $^0$C.

Fusion mass is charged to the reaction mixture over a period of time at a predetermined temperature which is in the range of 0 $^0$C to 200 $^0$C, when the pH of the reaction mixture is at a predetermined value which is in the range of 1 to 9, preferable range being 1 to 2. The fusion mass required for Step 1.2 is added either in a single lot or in batches, or continuously, or any combination of these methods of addition.

The reaction mixture at all stages of this step is optionally stirred with agitators rotating at a rate between 0 to 500 RPM. The step can be successfully carried out even without stirring.

***Forward and Reverse Isolation differs only in step 1.1 & 1.2 and rest of the processes carried out in step 1.3 (Isolation) and step 1.4 (Separation) are same in both the Isolation, refer fig 2 & 5.***

**Step 1.3 – Isolation:** After completion of charging of fusion mass at the end of Step 1.2, optionally a suitable reaction medium is charged in suitable quantity to the reaction vessel. The decision to add the reaction medium depends on the consistency of the solids. The quantity of the reaction medium used in Step 1.3, denoted as $Q_{RM1.3}$, is variable in the range of 0% (w/w) to 40% (w/w) of the total quantity $Q_{RMT}$ used in this cycle.

In the preferred embodiment of the invention, FRM is used as the reaction medium in the first cycle of this sequence, and for the subsequent cycles subject to the process of this invention, FRM is replaced by Stream E.

The reaction mixture at all stages of this step is optionally stirred with agitators rotating at a rate between 0 to 500 RPM. The step can be successfully carried out even without stirring.

In the preferred embodiment to remove completely the $SO_2$ (sulphur dioxide) gas generated during isolation reaction, the reaction is then heated under stirring to predetermined temperature in the range of 0 to 200°C, preferably 0 to 100°C, more preferably 70 to 100°C, to the predetermined time range 0 hrs to 10 hours, preferably 30 minutes to 8 hours, more preferably 30 minutes to 5 hours

**Step 1.4 – Separation:** In the preferred embodiment of the invention, FRM is used as the reaction medium in the first cycle of this sequence. The decision to add the reaction medium depends on the consistency of the product concentration & uniform crystal formation. The quantity of the reaction medium used in Step 1.4, denoted as $Q_{RM1.4}$, is variable in the range of 0% (w/w) to 40% (w/w) of the

total quantity $Q_{RMT}$ used in this cycle. The mixture thus formed is termed as the separation mixture.

In the preferred embodiment of the present invention, the separation temperature is in the range of 0 to 200, and the separation pH is in the range of 1 to 12, preferably 1to 2.

In the preferred embodiment pH and temperature conditions are maintained at predetermined level of pH and temperature for time that is in the range of 0 hours to 24 hours, preferably in the range of 30 minutes to 5 hours.

For the subsequent cycles subject to the process of this invention, FRM is replaced by **Stream E**.

In all of the above steps, that are steps 1.1 to 1.4, optionally sulfuric acid is used as the preferred suitable acid.

In another embodiment of the present invention, FRM is used as the reaction medium in the first cycle of the sequence. The quantity of the FRM or the reaction medium used in Step 1.4 $Q_{RM1.4}$ is variable in the range of 0% (w/w) to 40% (w/w) of QRMT used in this cycle.

The reaction mixture at all stages of this step is optionally stirred with agitators rotating at a rate between 0 to 500 RPM. The step can be successfully carried out even without stirring.

A single cycle of the green reaction sequence is complete at the end of step 1.4.

In another embodiment of the present invention, the separation temperature is preferably between $0^0$C to $100^0$C.

**Sequence 2.0 - Green separation sequence:**

As shown in Figure 3, this sequence comprises four steps, namely, a Stirring & Cooling, Stirring & Separation, Filtration and Washing step. Each of these steps is described in detail.

**Step 2.1 – Stirring & Cooling** : As shown in Figure 3, a reaction medium, referred to as the first settling RM, is optionally charged to the mixture obtained at the end of Step 1.4 in the reaction vessel in a suitable quantity and at suitable temperature and pH, the temperature being in the range of 0 to 200 and the pH being in the range of 1 to 11, preferably 2 to 5 and more preferably 1 to 2. The mixture thus formed is allowed to stir by maintaining it at a first stirring temperature for a stirring time.

In the preferred embodiment of the invention the first stirring pH is in the range of 1 to 11, preferably 2 to 5, more preferably 1 to 2; the first stirring temperature is in the range of 0°C and 200°C, preferably between 0°C to 100°C; and the first stirring time is for 1minute to 10 hours, preferably 30 minutes to 3 hours at a temperature range of 0°C to 100°C.

Liquid layer that forms as a result of the stirring process is cooled at a first cooling temperature, first cooling pH and first cooling time.

In the preferred embodiment of the invention FRM is used as the reaction medium in the first cycle, and for the subsequent cycles subject to the process of this invention, FRM is replaced by Stream E.

The quantity of the FRM or the reaction medium used in Step 2.1, denoted as $Q_{RM2.1}$ is variable in the range of 0% (w/w) to 60% (w/w) of the $Q_{RMT}$ used in this cycle.

**Step 2.2 – Stirring and Separation:** To the stirring & cooling mass at the end of step 2.1 of the first cycle is charged with a predetermined quantity of a reaction medium, referred to as a Stirring & Separation RM, at a predetermined first stirring temperature and a predetermined first stirring pH at a predetermined first stirring time. The mixture is stirred. Stirring is continued by maintaining the mixture at a predetermined first stirring continuation temperature, a predetermined first stirring continuation pH for a predetermined first stirring continuation time.

In the preferred embodiment of the invention, FRM is used in the first cycle as the stirring and separation RM, and for the subsequent cycles subject to the process of this invention, FRM is replaced by stream C; the values of the stirring temperature, are in the range of 0°C and 200°C, preferably between 0 $^0$C to 100 $^0$C; the values of the separation pH, 1 to 11, preferably between 2 to 5, more preferably 1 to 2; the values of the time and the separation time are in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours.

The quantity of the FRM or the reaction medium used in Step 2.2, denoted as $Q_{RM2.2\ is}$ variable in the range of 0% (w/w) to 40% (w/w) of $Q_{RMT}$ used in this cycle.

**Step 2.3 – Filtration:**

The separation mass formed at the end of step 2.2 of the first cycle is then filtered by the solid liquid separation methods known to the person skilled in the art; at a predetermined filtration temperature, a predetermined filtration pH for a predetermined filtration time. Liquid stream obtained at the end of Step 2.3 is charged as **Stream A** to the mother liquor storage tank.

In the preferred embodiment of the invention, the separation mass is filtered in the values of the filtration temperature range of 0 °C and 200 °C, preferably between 40 $^0$C to 100 $^0$C; in the filtration time are in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours.

**Step 2.4 – Washing and Filtration:** Total mass obtained from Step 2.3 at predetermined separation temperature and predetermined separation pH is then washed and filtered by methods known to the person skilled in the art with suitable quantity of FRM is defined as Stream B.

The liquid and washings together (**Stream A & B**) is stored in a storage tank that contains liquid from any of earlier cycles are then transferred to Recycle treatment Vessel for Treatment by R-Cat 1 followed by R-Cat 2.

In the preferred embodiment the separation temperature is between 0°C and 200°C, preferably between 40 $^0$C to 100 $^0$C, and pH between 1 to 11, preferably between 2 to 5.

A key advantageous feature of the present invention is that a part of the stored liquid, said part being defined as the stream E, in suitable quantity is recycled into various steps (Step 1.1 to 1.3 and 2.2) of the following cycles of the process of the invention.

The quantity of the FRM used in Step 2.2, denoted as $Q_{RM2.2}$ is variable in the range of 0% (w/w) to 40% (w/w) of $Q_{RMT}$ used in this cycle.

A typical cycle of the process of the present invention, that is a cycle consisting of a green reaction sequence and a green separation sequence, ends here. A key feature of the present invention is that all steps of a typical cycle are carried out at atmospheric pressure.

As a key advantageous feature of the present invention, the reaction medium used both the green reaction sequence and the green separation sequence, in the cycles after the first cycle is taken from the mother liquor and various streams generated during the process of this invention. In other words, the FRM used in the various

stages (Steps 1.1 to 1.4 and 2.1 to 2.4) of the first cycle is replaced by a suitable reaction medium in all subsequent cycles.

In steps 2.4 FRM is used in all cycles to make up the losses of previous cycles in the process of this invention.

The inventors of the present invention have found that the purity of product Naphthalene Sulphonic Acid Compounds so formed after drying in any cycle varies in the range of 75% to 100%, preferably 78% to 80%.

The mother liquor and washings comprising water obtained during various steps described above are stored for processing in further cycles, number of recycles being generally in the range of 5 to 100 and above.

The inventors have surprisingly found that the isolation of Naphthalene Sulphonic Acid Compounds from fusion mass carried out with the process described above generates inorganic by-product in any cycle in the ratio of weight in the range of 0.25 to 25 to the weight of fusion mass to be converted of the above sequence is crystalline and non-sticky in nature. Color of these by-product ranges from white to off white to pale yellow particularly off white. The pH of the inorganic by-product is in the range of 4.0 to 6.0. The moisture content of the inorganic byproduct is in the range of 5% to 50%, particular range being 10% to 30%.

**Recycle treatment to Naphthalene Sulphonic Acid Compounds mother liquor and washing**

The mother liquor and washings both are collected & mixed for recycle at source treatment. The combined mother liquor is then treated with a first treatment agent (R-Cat 1), and a second treatment agent (R-Cat 2) along with Sodium Sulphate as per process discussed here under. Refer figure 6 for the treatment cycle for the individual cycle of the invention.

**Step No.3.1 – Recycle treatment by R-Cat 1 –**

The filtrate Stream A & washing Stream B in step 2.3 & 2.4 respectively are combined and charged to R-Cat treatment vessel by the solid liquid separation methods known to the person skilled in the art; at a predetermined filtration temperature, a predetermined filtration pH for a predetermined filtration time as shown in fig 6.

In the preferred embodiment of the invention, the combine mother liquor is heated in a treatment vessel to a predetermined temperature range of 0 °C and 200 °C, preferably between 40 $^{0}$C to 100 $^{0}$C; in the predetermined treatment time are in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours. After reaching the desired temperature predetermined quantity of R-Cat 1 & salt is charged in predetermined charging time, at predetermined charging temperature either complete or lot wise under stirring.

The quantity of the R-Cat1 & salt used for recycle treatment in Step 3.1, denoted as $Q_{R\text{-}Cat\ 3.1}$ is variable in the range of 0% (w/v) to 40% (w/v), more preferably in the range of 0% (w/v) to 20% (w/v) of $Q_{RMT}$ used in this cycle.

In the preferred embodiment of the invention, fresh salt is used only in fresh cycle and in the following cycles the salt recovered from Step 3.2 i.e after R-Cat 2 treatment is recycled in both the treatment steps 3.1 & 3.2.

The whole treated mass is maintained under stirring at a predetermined temperature preferably in the range of 0 °C and 200 °C, preferably between 40 $^0$C to 100 $^0$C; for the predetermined treatment time in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours at a predetermined pH in the preferable range of 1 to 7, more preferable 2 to 5.

In the preferred embodiment of the invention the Baume of treated slurry is adjusted to the predetermined Baume range preferably 0 to 50, more preferably 10 to 35 in the preferable temperature range of 0 °C and 200 °C, preferably between 40 $^0$C to 100 $^0$C; at a predetermined pH in the preferable range of 1 to 7, more preferable 2 to 5.

In the preferred embodiment of the invention the total mother liquor is filtered by known methods of filtration at a predetermined filtration temperature preferably in the range of 0 °C and 200 °C, preferably between 40 $^0$C to 100 $^0$C; in the predetermined filtration time are in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours at a predetermined filtration pH in the preferable range of 1

to 7, more preferable 2 to 5. The spent R-Cat 1 separated as residue is kept aside for safe disposal.

The filtrate mother liquor stream after R-Cat 1 treatment is defined as Stream C is then transferred to R-Cat 2 treatment to another treatment vessel.

**Step No.3.2 – Recycle treatment by R-Cat 2 –**

The filtrate mother liquor Stream C received from first R-Cat treatment step 3.1 is charged to R-Cat 2 treatment vessel at a predetermined temperature, at a predetermined pH as shown in fig 6.

In the preferred embodiment of the invention, the Stream C is cooled to a predetermined temperature range of 0 °C and 50 °C, preferably between 10 $^0$C to 40 $^0$C; for the predetermined chilling time in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours. After reaching the desired temperature predetermined quantity of R-Cat 2 & salt is charged in predetermined charging time, at predetermined charging temperature either complete or lot wise under stirring.

The quantity of the R-Cat 2 and salt used in Step 3.2 denoted as $Q_{R\text{-}Cat\ 3.2}$ is variable in the range of 0% (w/v) to 20% (w/v) of $Q_{RMT}$ used in this cycle.

In the preferred embodiment of the invention, fresh salt is used only in fresh cycle and in the following cycles the salt recovered from same step i.e. Step 3.2 in fresh cycle & following cycle is recycled in treatment step 3.2.

The whole treatment mass is maintained at a predetermined temperature preferably in the range of 0 °C and 50 °C, preferably between 10 $^0$C to 40 $^0$C; in the predetermined treatment time are in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours at a predetermined pH in the preferable range of 1 to 7, more preferable 4 to 6.

In the preferred embodiment of the invention the Baume of treated slurry is adjusted to the predetermined Baume range preferably 0 to 50, more preferably 10 to 35 in the preferable temperature range of 0 °C and 50 °C, preferably between 10 $^0$C to 40 $^0$C; at a predetermined pH in the preferable range of 1 to 7, more preferable 4 to 6.

In the preferred embodiment of the invention the treated mother liquor is filtered by known methods of filtration at a predetermined filtration temperature preferably in the range of 0 °C and 50 °C, preferably between 10 $^0$C to 40 $^0$C; in the predetermined filtration time are in the range of 5 minutes to 5 hours; preferably 30 minutes to 3 hours at a predetermined filtration pH in the preferable range of 1 to 7, more preferable 4 to 6. The salt recovered along with spent R-Cat 2 is separated by known methods of filtration and stored for recycle treatment in next cycle.

The filtrate mother liquor Stream after R-Cat 2 treatment is defined as Stream D, is then transferred to mother liquor storage tank which is then recycled back in next cycle as Stream E.

**It is to be noted that** in the process as described above the fusion mass and/or acid is added to the step 1.2 in its entire quantity or in batches of any size at any interval.

It is to be further noted that in the process described above, said first and second treatment agents are selected from a group comprising hydroxides, carbonates, or bicarbonates of alkali metals, either individually or in any combination thereof; said hydroxides preferably being sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium hydroxide; said carbonates preferably being sodium carbonate, potassium carbonate, calcium carbonate, or lithium carbonate; said bicarbonates preferably being sodium bicarbonate, potassium bicarbonate, lithium bicarbonate.

It is also to be noted that the process described above is applicable to isolating similar kind of sulfonic acid products including 1, 8-Dihydroxynaphthalene-4-sulfonic acid, 1-Amino-8-naphthol-5,7- disulfonic acid, 1-Amino-8-naphthol-2,4-disulfonic acid (Chicago Acid), 2-Amino-8-naphthol-3,6-disulfonic acid (Gamma disulfonic acid), 2-Amino-5-naphthol -7-sulfonic acid (J-acid), 2-Naphthol-6-Sulfonic acid (Schaffer Acid), 2-Amino-5- naphthol-1,7-disulfonic acid (J-disulfomic acid), 2-Phenyl amino-5-naphthol-7-sulfonic acid (Phenyl J – acid), 1-Naphthylamine-8-sulfonic acid (Peri acid), 2-Aminonaphthalene-4,8-disulfonic acid (C-acid), 1-Amino-8-naphthol-4,6-disulfonic acid (K-acid), 1,8-Dihydroxynaphthalene-3,6-disulfonic acid (Chromotropic acid), 1-Naphthylamine-3,6,8-trisulfonic acid (Koch acid), 1-Naphthylamine-6-sulfonic

acid (Cleve Acid), 1-Naphthylamine-7-sulfonic acid (Cleve acid), R-acid, G-acid, Amino G-acid, 2-Amino-8-naphthol-6-sulfonic acid (Gamma Acid), 2-Amino-5-naphthol-7- sulfonic acid (iso gamma acid), M-acid, 1-Amino-8-naphthol-5-sulfonic acid, 1-Naphthylamine-4,7-disulfonic acid and all similar naphthalene sulfonic acid and beta-naphthol derivatives having functional groups like Animo, Nitro, Halo, Hydroxy, Sulfonic, Carboxylic, Benzyl, phenyl, ketone, aldehyde & thereof.

**The following examples illustrate some of the advantages mentioned herein.**

Many dyes & dyestuffs, specialty fine chemicals have **Naphthalene** Sulphonic acid salts as one of the building blocks and being currently used to manufacture various dyes & dyestuffs and Pharmaceutical Intermediates.

In the conventional H-acid manufacturing process, amount of caustic soda used for alkali fusion of 1 mole of Koch acid trisodium salt is 8.6 moles which corresponds to 4.3 times the theoretically required amount (2 moles). As a result, the amount of sulfuric acid required for obtaining H acid as its monosodium salt from the fusion mass reaches 5.8 moles for 1 mole of Koch acid.

To overcome above mentioned drawbacks of current process, the inventor has developed a process which is environmentally benign, safe & non-hazardous as illustrated in the examples that follow.

Example 1:

In this example a forward isolation reaction sequence of H-acid is described with recycle as follows.

**Fresh cycle:** In a 0.5-litre-4-neck round bottom flask equipped with stirrer, condenser, thermometer, addition port arranged in suitable heating/cooling system was charged 181 ml water and 50 g Sulphuric acid, heated to 60°C. 125 g Fusion mass was charged in the diluted acid slowly in 20 minutes with continuous stirring at 90°C. The reaction mass further heated to 95°C **to100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting the Baume of the mass to 25°Be.** The wet cake of H-acid was washed by 125 ml water. The H-acid was dried at 110°C to get on drying 17 g of Off white to pink H-acid with Nitrating Value (NV) 80%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**First Recycle (R1):** In the same set up as described above, 61ml fresh water, 120 ml treated mother liquor generated in fresh cycle and 48 g Sulphuric acid, heated to 60°C. 125 g Fusion mass was charged in the diluted acid slowly in 20 minutes with continuous stirring at 90°C. The reaction mass further heated to 95°C – **100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting the Baume of the mass to 28°Be.** The wet cake of H-acid was washed

by 125 ml water. The H-acid was dried at 110°C to get on drying 18.0 g of Off white to pink H-acid with Nitrating Value (NV) 79.40%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**Fifth Recycle (R5):** In the same set up as described above, 33 ml fresh water, 148 ml treated mother liquor and 76ml washing mother liquor generated in fourth recycle and 49g Sulphuric acid, heated to 60°C. 125 g Fusion mass was charged in the diluted acid slowly in 20 minutes with continuous stirring at 90°C. The reaction mass further heated to 95°C – **100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting Baume of the mass to 28°Be.** The wet cake of H-acid was washed by 125 ml water. The H-acid was dried at 110°C to get on drying 17.5 g of Dark pink H-acid with Nitrating Value (NV) 76.63%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**Tenth Recycle (R10):** In the same set up as described above, 26 ml fresh water, 155ml treated mother liquor generated in ninth recycle and 48 g Sulphuric acid, heated to 60°C. 125 g Fusion mass was charged in the diluted acid slowly in 20 minutes with continuous stirring at 90°C. The reaction mass further heated to 95°C – **100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting Baume of the mass to 28°Be.** The wet cake of H-acid was washed by 125 ml water. The H-acid was dried at 110°C to get on drying 22

g of L. Brown H-acid with Nitrating Value (NV) 76.3%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**Fifteenth Recycle (R15):** In the same set up as described above, 32 ml fresh water, 149 ml treated mother liquor generated in fourteenth recycle, and 48 g Sulphuric acid, heated to 60°C. 125 g Fusion mass was charged in the diluted acid slowly in 20 minutes with continuous stirring at 90°C. The reaction mass further heated to 95°C – **100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting Baume of the mass to 27°Be.** The wet cake of H-acid was washed by 125 ml water. The H-acid was dried at 110°C to get on drying 19.5 g of L. Brown H-acid with Nitrating Value (NV) 74.11%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**Twentieth Recycle (R20):** In the same set up as described above, 74 ml fresh water, 107 ml treated mother liquor generated in nineteenth recycle, 74 ml water and 48 g Sulphuric acid, heated to 60°C. 125 g Fusion mass was charged in the diluted acid slowly in 20 minutes with continuous stirring at 90°C. The reaction mass further heated to 95°C – **100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting Baume of the mass to 27°Be.** The wet cake of H-acid was washed by 125 ml water. The H-acid was dried at 110°C to get on drying 20.5 g of L. Brown H-acid with Nitrating Value (NV) 72.64%.

Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

The following table **(Table 01)** illustrates the savings in the quantities of fresh water used in the reaction of the present invention **Forward Isolation (Continuous charging of Fusion Mass)**

| Cycle | Basis | H2O & ML consumption & saving | | | H20 & Wash ML – Dilution | | Isolation Details | | |
|---|---|---|---|---|---|---|---|---|---|
| | [1] (g) | H2O (g) | Treated Wash ML (g) | From | H20 ml | Wash ML (ml) | Isolation Temp °C | Dry wt (g) | NV % |
| 0 | 125 | 181 | 0 | | 50 | 0 | 70 | 17 | 80 |
| 1 | 125 | 61 | 120 | Cycle 0 | 100 | 0 | 70 | 18 | 79.40 |
| 2 | 125 | 28 | 153 | Cycle 1 | 105 | 0 | 70 | 18 | 78.27 |
| 3 | 125 | 0 | 181 | Cycle 2 | 150 | 90 | 70 | 18 | 79.22 |
| 4 | 125 | 28 | 153 | Cycle 3 | 200 | 0 | 70 | 19 | 77.09 |
| 5 | 125 | 33 | 148 | Cycle 4 | 190 | 0 | 70 | 17.5 | 76.03 |
| 6 | 125 | 56 | 125 | Cycle 5 | 190 | 0 | 70 | 18.5 | 74 |
| 7 | 125 | 32 | 149 | Cycle 6 | 210 | 41 | 70 | 19 | 70.36 |
| 8 | 125 | 22 | 157 | Cycle 7 | 210 | 30 | 70 | 18 | 76.30 |
| 9 | 125 | 33 | 148 | Cycle 8 | 240 | 0 | 70 | 16.5 | 76.39 |
| 10 | 125 | 26 | 155 | Cycle 9 | 180 | 60 | 70 | 22 | 76.30 |
| 11 | 125 | 56 | 125 | Cycle 10 | 150 | 0 | 70 | 19 | 78.93 |
| 12 | 125 | 18 | 163 | Cycle 11 | 160 | 0 | 70 | 21 | 69.06 |
| 13 | 125 | 17 | 164 | Cycle 12 | 190 | 8 | 70 | 17.5 | 74.64 |
| 14 | 125 | 47 | 134 | Cycle 13 | 180 | 0 | 70 | 18.5 | 73.85 |
| 15 | 125 | 32 | 149 | Cycle 14 | 170 | 52 | 70 | 19.5 | 74.11 |
| 16 | 125 | 16 | 165 | Cycle 15 | 160 | 38 | 70 | 20.5 | 75.67 |
| 17 | 125 | 32 | 149 | Cycle 16 | 140 | 0 | 70 | 20.5 | 73.95 |
| 18 | 125 | 13 | 167 | Cycle 17 | 150 | 7 | 70 | 20 | 70.90 |
| 19 | 125 | 17 | 164 | Cycle 18 | 15 | 150 | 70 | 21.5 | 70.60 |
| 20 | 125 | 74 | 107 | Cycle 19 | 140 | 0 | 70 | 20.5 | 72.64 |

The mother liquor generated in each cycle of Forward Isolation sequence is treated with R-Cat 1 & Sodium Sulphate; the details of 1st treatment are mentioned in the following table 2.

The following **Table 02** illustrates bleed of impurities in 1st recycle at source treatment by R-Cat 1 & Sodium Sulphate in the reaction of present invention of Forward Isolation.

| Cycle | Basis (g) | Input mother liquor (ml) | | 1st Recycle treatment input | | Recovered mother liquor forward to 2nd treatment |
|---|---|---|---|---|---|---|
| | | Filtrate | Wash | R-Cat-1 (g) | Na2SO4 (g) | (ml) |
| 0 | 125 | 210 | 130 | 4 | 34 | 310 |
| 1 | 125 | 210 | 132 | 4 | 34 | 312 |
| 2 | 125 | 210 | 127 | 4 | 34 | 310 |
| 3 | 125 | 195 | 130 | 4 | 34 | 308 |
| 4 | 125 | 200 | 118 | 4 | 34 | 300 |
| 5 | 125 | 205 | 120 | 4 | 34 | 315 |
| 6 | 125 | 195 | 130 | 4 | 34 | 310 |
| 7 | 125 | 200 | 125 | 4 | 34 | 310 |
| 8 | 125 | 200 | 130 | 4 | 34 | 318 |
| 9 | 125 | 205 | 125 | 4 | 34 | 305 |
| 10 | 125 | 210 | 125 | 4 | 34 | 300 |
| 11 | 125 | 210 | 130 | 4 | 34 | 310 |
| 12 | 125 | 205 | 118 | 4 | 34 | 305 |
| 13 | 125 | 200 | 125 | 4 | 34 | 315 |
| 14 | 125 | 200 | 125 | 4 | 34 | 310 |
| 15 | 125 | 210 | 130 | 4 | 34 | 310 |
| 16 | 125 | 205 | 130 | 4 | 34 | 310 |
| 17 | 125 | 210 | 125 | 4 | 34 | 310 |
| 18 | 125 | 210 | 125 | 4 | 34 | 305 |
| 19 | 125 | 210 | 129 | 4 | 34 | 308 |
| 20 | 125 | 210 | 130 | 4 | 34 | 315 |

Mother liquor generated after 1st treatment is then treated with R-Cat 2 & Sodium Sulphate before recycle in further cycles of the present invention. The details of the same are mentioned in table 3.

The following **Table 03** illustrates bleed of impurities in 2nd recycle at source treatment by R-Cat 2 and the savings in the quantities of fresh water used in the reaction of the present invention of Forward Isolation

| Cycle | Basis | Input 1st treated mother liquor | 2nd Recycle at Source Treatment input | | Recovered salt | Recovered mother liquor used in next cycle |
|---|---|---|---|---|---|---|
| | | (ml) | R-Cat 2 (g) | Na2SO4 (g) | (g) | (ml) |
| 0 | 125 | 310 | 4 | 45 | 175 | 120 |
| 1 | 125 | 312 | 4 | 45 | 195 | 153 |
| 2 | 125 | 310 | 4 | 45 | 225 | 181 |
| 3 | 125 | 308 | 4 | 45 | 189 | 153 |
| 4 | 125 | 300 | 4 | 45 | 185 | 148 |
| 5 | 125 | 315 | 4 | 45 | 170 | 125 |
| 6 | 125 | 310 | 4 | 45 | 190 | 149 |
| 7 | 125 | 310 | 4 | 45 | 205 | 157 |
| 8 | 125 | 318 | 4 | 45 | 190 | 148 |
| 9 | 125 | 305 | 4 | 45 | 220 | 155 |
| 10 | 125 | 300 | 4 | 45 | 215 | 125 |
| 11 | 125 | 310 | 4 | 45 | 220 | 163 |
| 12 | 125 | 305 | 4 | 45 | 240 | 164 |
| 13 | 125 | 315 | 4 | 45 | 250 | 134 |
| 14 | 125 | 310 | 4 | 45 | 250 | 149 |
| 15 | 125 | 310 | 4 | 45 | 230 | 165 |
| 16 | 125 | 310 | 4 | 45 | 225 | 149 |
| 17 | 125 | 310 | 4 | 45 | 245 | 167 |
| 18 | 125 | 305 | 4 | 45 | 220 | 164 |
| 19 | 125 | 308 | 4 | 45 | 215 | 107 |
| 20 | 125 | 315 | 4 | 45 | 220 | 124 |

**Example 2:**

In this example a reverse isolation reaction sequence of H-acid is described with recycle as follows.

**Fresh cycle**: The total water 1086 g was divided into two equal parts of 543 ml each. 200.0g 98% sulphuric acid was diluted with one part of water of 543ml

which made 640ml volume. 500.0 g Fusion mass was diluted with remaining part of water which made 840ml volume.

In a 2.0-litre-4-neck round bottom flask equipped with stirrer, condenser, thermometer and addition port arranged in suitable heating/cooling system was charged diluted Fusion mass, heated to 90°C. The dilute acid slurry was then charged in 10 equal lots comprising 64 ml each, every lot added in 5 mins. The reaction mass further heated to 95°C **to100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting the Baume of the mass to 30°Be by further evaporating the mass.** The wet cake of H-acid was washed by 500 ml water. The H-acid was dried at 110°C to get on drying 86 g of Off white to pink H-acid with Nitrating Value (NV) 77.03%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**First Recycle (R1):** To 386.4 g treated Mother liquor generated in Fresh cycle, 699.6 g water was topped up to make 1086g total mass. This volume made 1045ml was divided in two equal lots of 522.5ml. 194.77 g 98% sulphuric acid was diluted with one part of ML of 522.5ml which made 610ml volume. 500.0 g Fusion mass was diluted with remaining part of ML which made 830ml volume.

In the same set up as described above, was charged diluted Fusion mass, heated to 90°C. The dilute acid slurry was then charged in 10 equal lots comprising 61 ml each, every lot added in 5 mins. The reaction mass further heated to 95°C **to100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was

checked by Congo red test. Reaction mass was cooled to 70°C and filtered **after adjusting the Baume of the mass to 30°Be by further evaporating the mass.** The wet cake of H-acid was washed by 500 ml water. The H-acid was dried at 110°C to get on drying 88 g of Off white to pink H-acid with Nitrating Value (NV) 76.36%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

**Fifth Recycle (R5):** To 489.3 g treated Mother liquor generated in third recycle, 596.7 g water was topped up to make 1086g total mass. This volume made 1000ml was divided in two equal lots of 500ml. 189.92 g 98% sulphuric acid was diluted with one part of ML of 500ml which made 600ml volume. 500.0 g Fusion mass was diluted with remaining part of ML which made 850ml volume.

In the same set up as described above, was charged diluted Fusion mass, heated to 90°C. The dilute acid slurry was then charged in 10 equal lots comprising 60 ml each, every lot added in 5 mins. The reaction mass further heated to 95°C **to100°C** for SO2 gas evolution and confirmed. Completion of SO2 evolution was checked by Congo red test. Reaction mass was cooled to 70°C and filtered **at the Baume of the mass to 30°Be.** The wet cake of H-acid was washed by 500 ml water. The H-acid was dried at 110°C to get on drying 94 g of Off white to pink H-acid with Nitrating Value (NV) 74.70%. Total filtrate i.e. reaction medium and washings were collected and recycled in subsequent batches after treatment.

The following **Table 04** illustrates the savings in the quantities of fresh water used in the reaction of the present invention of Reverse Isolation

| Cycle | Basis | | H2O & ML consumption & saving | | H20 & Wash ML – Dilution | | Isolation Details | |
|---|---|---|---|---|---|---|---|---|
| | [1] G | H2O (g) | Recovered ML (g) | Treated ML (W) g From | H20 ml | Wash ML (ml) | Dry wt (g) | % Purity by HPLC |
| 0 | 500 | 1086 | 0 | Fresh | 543 | 543 | 86 | 99.84 |
| 1 | 500 | 699.6 | 386.4 | Cycle 0 | 522.5 | 522.5 | 88 | |
| 2 | 500 | 512.7 | 573.3 | Cycle 1 | 505 | 505 | 90 | 99.65 |
| 3 | 500 | 547.2 | 538.2 | Cycle 2 | 500 | 500 | 88 | |
| 4 | 500 | 281 | 805 | Cycle 3 | 500 | 500 | 92 | 99.59 |
| 5 | 500 | 489.3 | 596.7 | Cycle 4 | 500 | 500 | 94 | |

The mother liquor generated in each cycle of Reverse Isolation sequence is treated with R-Cat 1 & Sodium Sulphate; the details of 1st treatment are mentioned in the following table 5.

The following **Table 05** illustrates bleed of impurities in 1st recycle at source treatment by R-Cat 1 in the reaction of present invention of Reverse Isolation.

| Cycle | Basis | Input mother liquor | 1st Recycle at treatment input | | Recovered mother liquor | Recovered salt |
|---|---|---|---|---|---|---|
| | | (ml) | R-Cat-1 (g) | Na2SO4 (g) | (ml) | (g) |
| 0 | 500 | 1180 | 16 | 118 | 735 | 515 |
| 1 | 500 | 1260 | 16 | 126 | 960 | 480 |
| 2 | 500 | 1315 | 16 | 131.5 | 1070 | 328 |
| 3 | 500 | 1540 | 16 | 154 | 1130 | 299 |
| 4 | 500 | 1490 | 16 | 149 | 1210 | 455 |
| 5 | 500 | 1470 | 16 | 147 | 1050 | 594 |

Mother liquor generated after 1st treatment is then treated with R-Cat 2 & Sodium Sulphate before recycle in further cycles of the present invention. The details of the same are mentioned in table 6.

The following **Table 06** illustrates bleed of impurities in 2nd recycle at source treatment by R-Cat 2 and the savings in the quantities of fresh water used in the reaction of the present invention of Reverse Isolation

| Cycle | Basis | Input mother liquor | 1st Recycle at treatment input | | Recovered salt | Recycle mother liquor |
|---|---|---|---|---|---|---|
| | | (ml) | R-Cat-2 (g) | Na2SO4 (g) | (g) | (ml) |
| 0 | 500 | 725 | 16 | 108.75 | 552 | 345 |
| 1 | 500 | 950 | 16 | 142.5 | 630 | 490 |
| 2 | 500 | 1060 | 16 | 159 | 845 | 460 |
| 3 | 500 | 1320 | 16 | 198 | 896 | 700 |
| 4 | 500 | 1200 | 16 | 180 | 898 | 510 |
| 5 | 500 | 1040 | 16 | 156 | 540 | 720 |

Based on the foregoing discussion it is clear that the present invention comprises the following items:

1. A chemical process of isolation of a naphthalene sulphonic acid from fusion mass, characterised in that it is a sustainable process comprising a reaction sequence, wherein the fusion mass is reacted with acid, followed by an isolation sequence, wherein isolation of the reaction product is completed, followed by a recycle treatment sequence, wherein the impure mother liquor is treated for further recycling in said reaction and isolation sequences, and further wherein said reaction sequence and said isolation sequence are carried out in a steady state closed loop circuit capable of inherently and intrinsically recycling at source level of all mother liquor

generated, with plurality of cycles, wherein fresh water is added only to make up for systemic losses such as by evaporation, said mother liquor being any of the reaction medium, extraction medium, or wash medium, or any combination thereof, used in said process, as shown in fig 4.

2. A process as described in item 1, wherein the number of said plurality of cycles is preferably greater than 3, more preferably greater than 15, even more preferably greater than 30.

3. A process as claimed in claim 1, characterised in that said naphthalene sulphonic acid in said fusion mass is an H-acid.

4. A process as described in items 1 to 3, wherein for any single cycle said reaction sequence are carried out the stages of preparing separately diluted fusion mass and diluted acid, mixing together diluted fusion mass and diluted acid, characterised in that said stages are carried out in following steps:

step 1.1a – charging a first start up reaction medium to a first vessel with an agitator and charging to it an acid, preferably sulfuric acid, while maintaining the temperature of said acid up to 200 $^{o}$C and pH between 1 and 7, wherein the quantity of first start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the first start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times, the total fusion mass to be isolated in the current cycle,

step 1.1b – charging a second start up reaction medium to a second reaction vessel with an agitator and charging to it fusion mass in a quantity such that the pH of the mixture in said second reaction vessel is between 8 and 14, preferably between 9 and 13, and wherein the quantity of second start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the second start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times the total fusion mass to be isolated in the current cycle,

step 1.1c – agitating mixtures of first and second reaction vessels for a duration up to 5 hours, preferably between 30 minutes to 2.5 hours, while maintaining the temperatures of the respective mixtures at up to 200 $^{o}$C,

step 1.2 – charging the diluted fusion mass of said second reaction vessel to said diluted acid of said first reaction vessel over a period of up to 5 hours, and optionally charging a first reduction reaction medium and maintaining the temperature of the mixture to up to 200 $^{o}$C and a pH between 1 to 9, characterized in that for all cycles beginning with the second cycle of the process, the said first and second start up reaction mediums are drawn from a mother liquor storage tank where the mother liquor recycled from the recycle treatment sequence is stored, and

the reaction mixture obtained at the end of step 1.2 is taken to a completion of the reaction sequence, followed by isolation of the product

resulting from the reaction further followed by the recycle treatment of the mother liquor generated.

5. A process as described in items 1 to 3, wherein for any single cycle said reaction sequence are carried out the stages of preparing separately diluted fusion mass and diluted acid, mixing together diluted fusion mass and diluted acid, characterised in that said stages are carried out in following steps:

step 1.1a – charging a first start up reaction medium to a first reaction vessel with an agitator and charging to it fusion mass in a quantity such that the pH of the mixture in said second reaction vessel is between 8 and 14, preferably between 9 and 13, and wherein the quantity of first start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the second start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times the total fusion mass to be isolated in the current cycle,

step 1.1b – charging a second start up reaction medium to a second vessel with an agitator and charging to it an acid, preferably sulfuric acid, while maintaining the temperature of said acid up to 200 $^{o}$C and pH between 1 and 7, wherein the quantity of second start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the first start up reaction medium used in the

entire cycle is between 5 to 100 times, preferably 10 to 75 times the total fusion mass to be isolated in the current cycle,

step 1.1c – agitating mixtures of first and second reaction vessels for a duration up to 5 hours, preferably between 30 minutes to 2.5 hours, while maintaining the temperatures of the respective mixtures at up to 200 $^{o}$C,

step 1.2 – charging the diluted acid of said second reaction vessel to said fusion mass of said first reaction vessel over a period of up to 5 hours, and optionally charging a first reduction reaction medium and maintaining the temperature of the mixture to up to 200 $^{o}$C and a pH between 1 to 9, characterized in that for all cycles beginning with the second cycle of the process, the said first and second start up reaction mediums are drawn from a mother liquor storage tank where the mother liquor recycled from the recycle treatment sequence is stored, and

the reaction mixture obtained at the end of step 1.2 is taken to a completion of the reaction sequence, followed by isolation of the product resulting from the reaction further followed by the recycle treatment of the mother liquor generated.

6. A process as described in items 4 to 5 wherein for any cycle of the process the reaction mixture obtained at the end of said step 1.2 is taken to completion of reaction sequence as follows:

Step 1.3 – optionally adding to said first reaction vessel a second reaction medium in a quantity up to 40% (w/w) of the total amount of reaction medium used for this entire cycle while optionally stirring the mixture at

up to 500 RPM and by maintaining the temperature of the reaction mixture at up to 200 °C, preferably up to 100 °C, and carrying out the stirring for up to 10 hours, preferably between 30 minutes to 8 hours so that complete removal of sulfur dioxide generated during the reaction takes place, and the Baume value is between 10 to 50,

Step1.4 – in the first cycle a third reaction medium in the form of fresh reaction medium is added to said first reaction vessel in a quantity not exceeding 40% (w/w) of the total amount of reaction medium used in the entire current cycle to form a separation mixture, while maintaining the temperature of the separation mixture up to 200 °C, preferably up to 100 °C, and the pH between 1 and 7 while stirring the separation mixture for up to 24 hours, preferably up to 5 hours, characterized in that said third reaction medium used for all following cycles is selected from said mother liquor storage tank.

7. A process as described in items 1 to 6 wherein for any cycle of the process the isolation sequence comprises the following steps:

Step 2.1 – a first stirring reaction medium in the form of a fresh reaction medium is charged to said first reaction vessel in a quantity not exceeding 60% (w/w) of the total quantity of reaction medium used in the current cycle, while allowing the mixture to cool to a temperature of 70 °C, and by maintaining its pH between 1 and 7, while continuously stirring the mixture for up to 10 hours, characterized in that for all following cycles

the said first stirring reaction medium is taken from said mother liquor storage tank,

Step 2.2 – maintaining the temperature of the reaction mixture at 70 oC and pH at 1 to 7 by optionally adding a fourth reaction medium in the form of a fresh reaction medium in the first cycle, while stirring the reaction mixture for a duration of up to 24 hours, preferably up to 5 hours, characterized in that characterized in that for all following cycles the said first stirring reaction medium is taken from said mother liquor storage tank,

Step 2.3 – filtering the separation mass formed at the end of step 2.2 at a temperature of about 70 $^{o}$C and pH at 1 to 7, and generating a first filtrate stream A as a result of the filtration process, said process of filtration taking place over a period of up to 5 hours,

Step 2.4 – washing the total mass obtained at the end of step 2.3 using fresh reaction medium at a temperature of 70 $^{o}$C and a pH of 1 to 7, and generating the washing stream B.

8. A process as described in items 1 to 7 wherein for any cycle of the process the first filtrate stream A and the washing stream B and combined and subjected to a catalytic treatment as follows:

Step 3.1 – heating in a first treatment vessel the combined streams A and B to a temperature up to 100 $^{o}$C, preferably 70 $^{o}$C, for up to 5 hours, followed by adding a first treatment agent and a first sulfate salt, wherein the quantity of said first treatment agent is up to 40% (w/v) of the total

quantity of the reaction medium used in the current cycle, such that the Baume value of the mixture is maintained at up to 50 while maintaining the temperature of said mixture after addition of the agent maintained at up to 50 $^{o}$C, and pH between 1 and 7, whereby a second filtrate in the form of mother liquor stream C is generated as well as spent material which needs disposing of, characterized in that fresh sulphate salt is used only in the first cycle of this step and in the following cycles, the salt generated from step 3.2 is used,

Step 3.2 – charging said second filtrate stream C to a second treatment vessel wherein said second filtrate is cooled to a temperature of up to 25 $^{o}$C for up to 5 hours followed by charging of a second treatment agent and sulphate salt, wherein said second treatment agent and sulphate salt is in a quantity up to 20% (w/v) of the total quantity of reaction medium used in the current cycle, while maintaining the Baume value of the mixture up to 50, and the pH between 1 to 7, preferably 4 to 6, characterized in that in the first cycle of the process, fresh salt is used and in all following cycles the salt recovered at the end of step 3.2 is used, wherein .

9. A process as described in any of items 2 to 8, wherein said acid is sulphuric acid.
10. A process as described in item 9 wherein said first and second treatment agents are any proprietary agents.

11. A process as described in any of items 2 to 10, wherein the fusion mass and/or acid is added to the step 1.2 in its entire quantity or in batches of any size at any interval.
12. A process as described in any of items 2 to 11, wherein said first and second treatment agents of steps 3.1 & 3.2 are selected from a group comprising hydroxides, carbonates, or bicarbonates of alkali metals, either individually or in any combination thereof; said hydroxides preferably being sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium hydroxide; said carbonates preferably being sodium carbonate, potassium carbonate, calcium carbonate, or lithium carbonate; said bicarbonates preferably being sodium bicarbonate, potassium bicarbonate, lithium bicarbonate.
13. A process as described in any of items 1 to 12 can also be applied for isolation similar kind of sulfonic acid products like1, 8-Dihydroxynaphthalene-4-sulfonic acid, 1-Amino-8-naphthol-5,7-disulfonic acid, 1-Amino-8-naphthol-2,4-disulfonic acid (Chicago Acid), 2-Amino-8-naphthol-3,6-disulfonic acid (Gamma disulfonic acid), 2-Amino-5-naphthol -7-sulfonic acid (J-acid), 2-Naphthol-6-Sulfonic acid (Schaffer Acid), 2-Amino-5- naphthol-1,7-disulfonic acid (J-disulfomic acid), 2-Phenyl amino-5-naphthol-7-sulfonic acid (Phenyl J –acid), 1-Naphthylamine-8-sulfonic acid (Peri acid), 2-Aminonaphthalene-4,8-disulfonic acid (C-acid), 1-Amino-8-naphthol-4,6-disulfonic acid (K-acid), 1,8-Dihydroxynaphthalene-3,6-disulfonic acid (Chromotropic acid), 1-

Naphthylamine-3,6,8-trisulfonic acid (Koch acid), 1-Naphthylamine-6-sulfonic acid (Cleve Acid), 1-Naphthylamine-7-sulfonic acid (Cleve acid), R-acid, G-acid, Amino G-acid, 2-Amino-8-naphthol-6-sulfonic acid (Gamma Acid), 2-Amino-5-naphthol-7- sulfonic acid (iso gamma acid), M-acid, 1-Amino-8-naphthol-5-sulfonic acid, 1-Naphthylamine-4,7-disulfonic acid and all similar naphthalene sulfonic acid and beta-naphthol derivatives having functional groups like Animo, Nitro, Halo, Hydroxy, Sulfonic, Carboxylic, Benzyl, phenyl, ketone, aldehyde & thereof.

14. A process as claimed in any of items 1-6 and 6-12 wherein said number of cycles is greater than 100.
15. A process as described in any of items 8 to 14, wherein said first and second treatment agents are either added together in small lots till the temperature of the reaction mixture reaches 0 $^{o}$C 100 $^{o}$C, preferably 70 to 20 $^{o}$C, or alternatively both agents are added together once the temperature has reached 0 $^{o}$C 100 $^{o}$C, preferably 70 to 20 $^{o}$C.

While the above description contains much specificity, these should not be construed as limitation in the scope of the invention, but rather as an exemplification of the preferred embodiments thereof. It must be realized that modifications and variations are possible based on the disclosure given above without departing from the spirit and scope of the invention. Accordingly, the scope of the invention should be determined not by the embodiments illustrated, but by the appended claims and their legal equivalents.

**Claims**:

1. A chemical process of isolation of a naphthalene sulphonic acid from fusion mass containing salts of said naphthalene sulphonic acid, characterised in that it is a sustainable process comprising a reaction sequence, wherein the fusion mass is reacted with acid, followed by an isolation sequence, wherein isolation of the reaction product is completed, followed by a recycle treatment sequence, wherein the impure mother liquor is treated for further recycling in said reaction and isolation sequences, and further wherein said reaction sequence and said isolation sequence are carried out in a steady state closed loop circuit capable of inherently and intrinsically recycling at source level of all mother liquor generated, with plurality of cycles, wherein fresh water is added only to make up for systemic losses such as by evaporation, said mother liquor being any of the reaction medium, extraction medium, or wash medium, or any combination thereof, used in said process, as shown in fig 4.
2. A process as claimed in claim 1, characterised in that said fusion mass is an the number of said plurality of cycles is preferably greater than 3, more preferably greater than 15, even more preferably greater than 30.
3. A process as claimed in claim 1, characterised in that said naphthalene sulphonic acid in said fusion mass is an H-acid.
4. A process as claimed in claims 1 to 3, wherein for any single cycle said reaction sequence are carried out the stages of preparing separately diluted fusion mass and diluted acid, mixing together diluted fusion mass and diluted acid, characterised in that said stages are carried out in following stages:

stage 1.1a – charging a first start up reaction medium to a first vessel with an agitator and charging to it an acid, preferably sulfuric acid, while maintaining the temperature of said acid up to 200 °C and pH between 1 and 7, wherein the quantity of first start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the first start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times, the total fusion mass to be isolated in the current cycle,

stage 1.1b – charging a second start up reaction medium to a second reaction vessel with an agitator and charging to it fusion mass in a quantity such that the pH of the mixture in said second reaction vessel is between 8 and 14, preferably between 9 and 13, and wherein the quantity of second start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the second start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times the total fusion mass to be isolated in the current cycle,

stage 1.1c – agitating mixtures of first and second reaction vessels for a duration up to 5 hours, preferably between 30 minutes to 2.5 hours, while maintaining the temperatures of the respective mixtures at up to 200 °C,

step 1.2 – charging the diluted fusion mass of said second reaction vessel to said diluted acid of said first reaction vessel over a period of up to 5 hours, and optionally charging a first reduction reaction medium and

maintaining the temperature of the mixture to up to 200 $^{o}$C and a pH between 1 to 9, characterized in that for all cycles beginning with the second cycle of the process, the said first and second start up reaction mediums are drawn from a mother liquor storage tank where the mother liquor recycled from the recycle treatment sequence is stored, and

the reaction mixture obtained at the end of step 1.2 is taken to a completion of the reaction sequence, followed by isolation of the product resulting from the reaction further followed by the recycle treatment of the mother liquor generated.

5. A process as claimed in claims 1 to 3, wherein for any single cycle said reaction sequence are carried out the stages of preparing separately diluted fusion mass and diluted acid, mixing together diluted fusion mass and diluted acid, characterised in that said stages are carried out in following steps:

stage 1.1a – charging a first start up reaction medium to a first reaction vessel with an agitator and charging to it fusion mass in a quantity such that the pH of the mixture in said second reaction vessel is between 8 and 14, preferably between 9 and 13, and wherein the quantity of first start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the second start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times the total fusion mass to be isolated in the current cycle,

stage 1.1b – charging a second start up reaction medium to a second vessel with an agitator and charging to it an acid, preferably sulfuric acid, while maintaining the temperature of said acid up to 200 °C and pH between 1 and 7, wherein the quantity of second start up reaction medium is up to 40% (w/w) of the total amount of reaction medium used for this entire cycle, and the total amount of the first start up reaction medium used in the entire cycle is between 5 to 100 times, preferably 10 to 75 times the total fusion mass to be isolated in the current cycle,

stage 1.1c – agitating mixtures of first and second reaction vessels for a duration up to 5 hours, preferably between 30 minutes to 2.5 hours, while maintaining the temperatures of the respective mixtures at up to 200 °C,

step 1.2 – charging the diluted acid of said second reaction vessel to said fusion mass of said first reaction vessel over a period of up to 5 hours, and optionally charging a first reduction reaction medium and maintaining the temperature of the mixture to up to 200 °C and a pH between 1 to 9, characterized in that for all cycles beginning with the second cycle of the process, the said first and second start up reaction mediums are drawn from a mother liquor storage tank where the mother liquor recycled from the recycle treatment sequence is stored, and

the reaction mixture obtained at the end of step 1.2 is taken to a completion of the reaction sequence, followed by isolation of the product resulting from the reaction further followed by the recycle treatment of the mother liquor generated.

6. A process as claimed in claims 4 to 5 wherein for any cycle of the process the reaction mixture obtained at the end of said step 1.2 is taken to completion of reaction sequence as follows:

step 1.3 – optionally adding to said first reaction vessel a second reaction medium in a quantity up to 40% (w/w) of the total amount of reaction medium used for this entire cycle while optionally stirring the mixture at up to 500 RPM and by maintaining the temperature of the reaction mixture at up to 200 $^{o}$C, preferably up to 100 $^{o}$C, and carrying out the stirring for up to 10 hours, preferably between 30 minutes to 8 hours so that complete removal of sulfur dioxide generated during the reaction takes place, and the Baume value is between 10 to 50,

step1.4 – adding in the first cycle a third reaction medium in the form of fresh reaction medium to said first reaction vessel in a quantity not exceeding 40% (w/w) of the total amount of reaction medium used in the entire current cycle to form a separation mixture, while maintaining the temperature of the separation mixture up to 200 $^{o}$C, preferably up to 100 oC, and the pH between 1 and 7 while stirring the separation mixture for up to 24 hours, preferably up to 5 hours, characterized in that said third reaction medium used for all following cycles is selected from said mother liquor storage tank.

7. A process as claimed in claims 1 to 6 wherein for any cycle of the process the isolation sequence comprises the following steps:

step 2.1 – a first stirring reaction medium in the form of a fresh reaction medium is charged to said first reaction vessel in a quantity not exceeding 60% (w/w) of the total quantity of reaction medium used in the current cycle, while allowing the mixture to cool to a temperature of 70 °C, and by maintaining its pH between 1 and 7, while continuously stirring the mixture for up to 10 hours, characterized in that for all following cycles the said first stirring reaction medium is taken from said mother liquor storage tank,

step 2.2 – maintaining the temperature of the reaction mixture at 70 °C and pH at 1 to 7 by optionally adding a fourth reaction medium in the form of a fresh reaction medium in the first cycle, while stirring the reaction mixture for a duration of up to 24 hours, preferably up to 5 hours, characterized in that characterized in that for all following cycles the said first stirring reaction medium is taken from said mother liquor storage tank,

step 2.3 – filtering the separation mass formed at the end of step 2.2 at a temperature of about 70 °C and pH at 1 to 7, and generating a first filtrate stream A as a result of the filtration process, said process of filtration taking place over a period of up to 5 hours,

step 2.4 – washing the total mass obtained at the end of step 2.3 using fresh reaction medium at a temperature of 70 oC and a pH of 1 to 7, and generating the washing stream B.

8. A process as claimed in claims 1 to 7 wherein for any cycle of the process the first filtrate stream A and the washing stream B and combined and subjected to a catalytic treatment as follows:

step 3.1 – heating in a first treatment vessel the combined streams A and B to a temperature up to 100 °C, preferably 70 °C, for up to 5 hours, followed by adding a first treatment agent and a first sulfate salt, wherein the quantity of said first treatment agent is up to 40% (w/v) of the total quantity of the reaction medium used in the current cycle, such that the Baume value of the mixture is maintained at up to 50 while maintaining the temperature of said mixture after addition of the agent maintained at up to 50 °C, and pH between 1 and 7, whereby a second filtrate in the form of mother liquor stream C is generated as well as spent material which needs disposing of, characterized in that fresh sulphate salt is used only in the first cycle of this step and in the following cycles, the salt generated from step 3.2 is used,

step 3.2 – charging said second filtrate stream C to a second treatment vessel wherein said second filtrate is cooled to a temperature of up to 25 °C for up to 5 hours followed by charging of a second treatment agent and sulphate salt, wherein said second treatment agent and sulphate salt is in a quantity up to 20% (w/v) of the total quantity of reaction medium used in the current cycle, while maintaining the Baume value of the mixture up to 50, and the pH between 1 to 7, preferably 4 to 6, characterized in that in

the first cycle of the process, fresh salt is used and in all following cycles the salt recovered at the end of step 3.2 is used.

9. A process as claimed in any of claims 2 to 8, wherein said acid is sulphuric acid.

10. A process as claimed claim 9 wherein said first and second treatment agents are any proprietary agents.

11. A process as claimed in any of claims 2 to 10, wherein the fusion mass and/or acid is added to the step 1.2 in its entire quantity or in batches of any size at any interval.

12. A process as claimed in any of claims 2 to 11, wherein said first and second treatment agents of steps 3.1 & 3.2 are selected from a group comprising hydroxides, carbonates, or bicarbonates of alkali metals, either individually or in any combination thereof; said hydroxides preferably being sodium hydroxide, potassium hydroxide, calcium hydroxide, lithium hydroxide; said carbonates preferably being sodium carbonate, potassium carbonate, calcium carbonate, or lithium carbonate; said bicarbonates preferably being sodium bicarbonate, potassium bicarbonate, lithium bicarbonate.

13. A process as claimed in any of claims 1 to 12 can also be applied for isolation similar kind of sulfonic acid products like1, 8-Dihydroxynaphthalene-4-sulfonic acid, 1-Amino-8-naphthol-5,7-disulfonic acid, 1-Amino-8-naphthol-2,4-disulfonic acid (Chicago Acid), 2-Amino-8-naphthol-3,6-disulfonic acid (Gamma disulfonic acid), 2-Amino-5-naphthol -7-sulfonic acid (J-acid), 2-Naphthol-6-Sulfonic acid (Schaffer Acid), 2-Amino-5- naphthol-1,7-disulfonic acid (J-disulfomic acid), 2-Phenyl amino-

5-naphthol-7-sulfonic acid (Phenyl J –acid), 1-Naphthylamine-8-sulfonic acid (Peri acid), 2-Aminonaphthalene-4,8-disulfonic acid (C-acid), 1-Amino-8-naphthol-4,6-disulfonic acid (K-acid), 1,8-Dihydroxynaphthalene-3,6-disulfonic acid (Chromotropic acid), 1-Naphthylamine-3,6,8-trisulfonic acid (Koch acid), 1-Naphthylamine-6-sulfonic acid (Cleve Acid), 1-Naphthylamine-7-sulfonic acid (Cleve acid), R-acid, G-acid, Amino G-acid, 2-Amino-8-naphthol-6-sulfonic acid (Gamma Acid), 2-Amino-5-naphthol-7- sulfonic acid (iso gamma acid), M-acid, 1-Amino-8-naphthol-5-sulfonic acid, 1-Naphthylamine-4,7-disulfonic acid and all similar naphthalene sulfonic acid and beta-naphthol derivatives having functional groups like Animo, Nitro, Halo, Hydroxy, Sulfonic, Carboxylic, Benzyl, phenyl, ketone, aldehyde & thereof.

14. A process as claimed in any of claims 1-6 and 7-12 wherein said number of cycles is greater than 100.
15. A process as claimed in claims 8 to 14, wherein said first and second treatment agents are either added together in small lots till the temperature of the reaction mixture reaches 0 $^{o}$C 100 $^{o}$C, preferably 70 to 20 $^{o}$C, or alternatively both agents are added together once the temperature has reached 0 $^{o}$C 100 $^{o}$C, preferably 70 to 20 $^{o}$C.

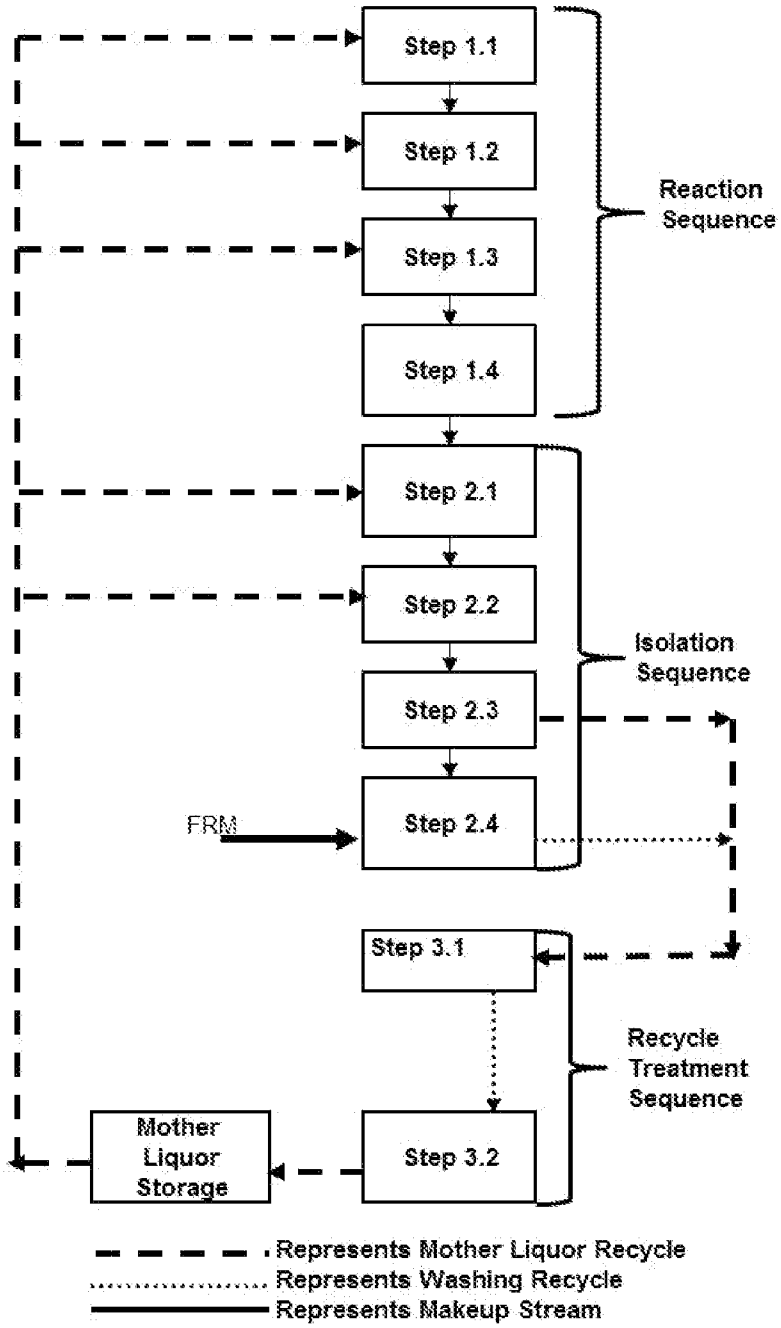

Step 1.1
Step 1.2
Step 1.3
Step 1.4
Reaction Sequence
Step 2.1
Step 2.2
Step 2.3
Step 2.4
Isolation Sequence
FRM
Step 3.1
Recycle Treatment Sequence
Mother Liquor Storage
Step 3.2
Represents Mother Liquor Recycle
Represents Washing Recycle
Represents Makeup Stream

**Figure 1**

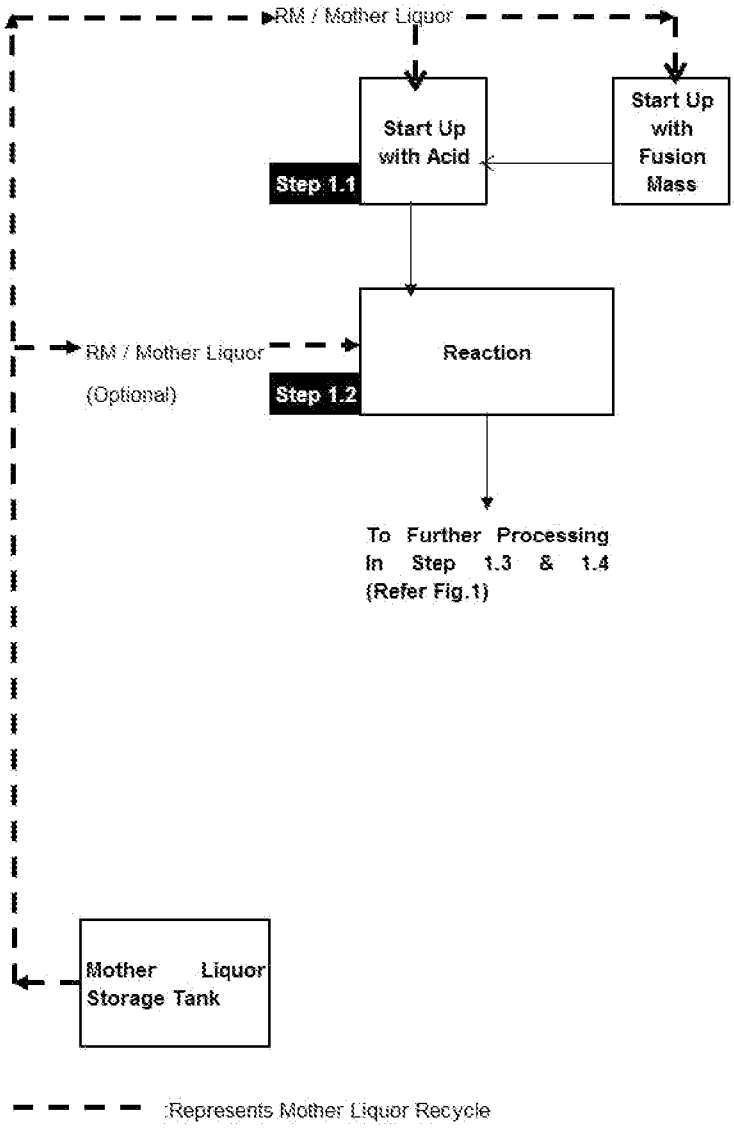

RM / Mother Liquor
Start Up with Acid
Step 1.1
Start Up with Fusion Mass
RM / Mother Liquor
(Optional)
Step 1.2
Reaction
To Further Processing In Step 1.3 & 1.4 (Refer Fig.1)
Mother Liquor Storage Tank
:Represents Mother Liquor Recycle

**Figure 2**

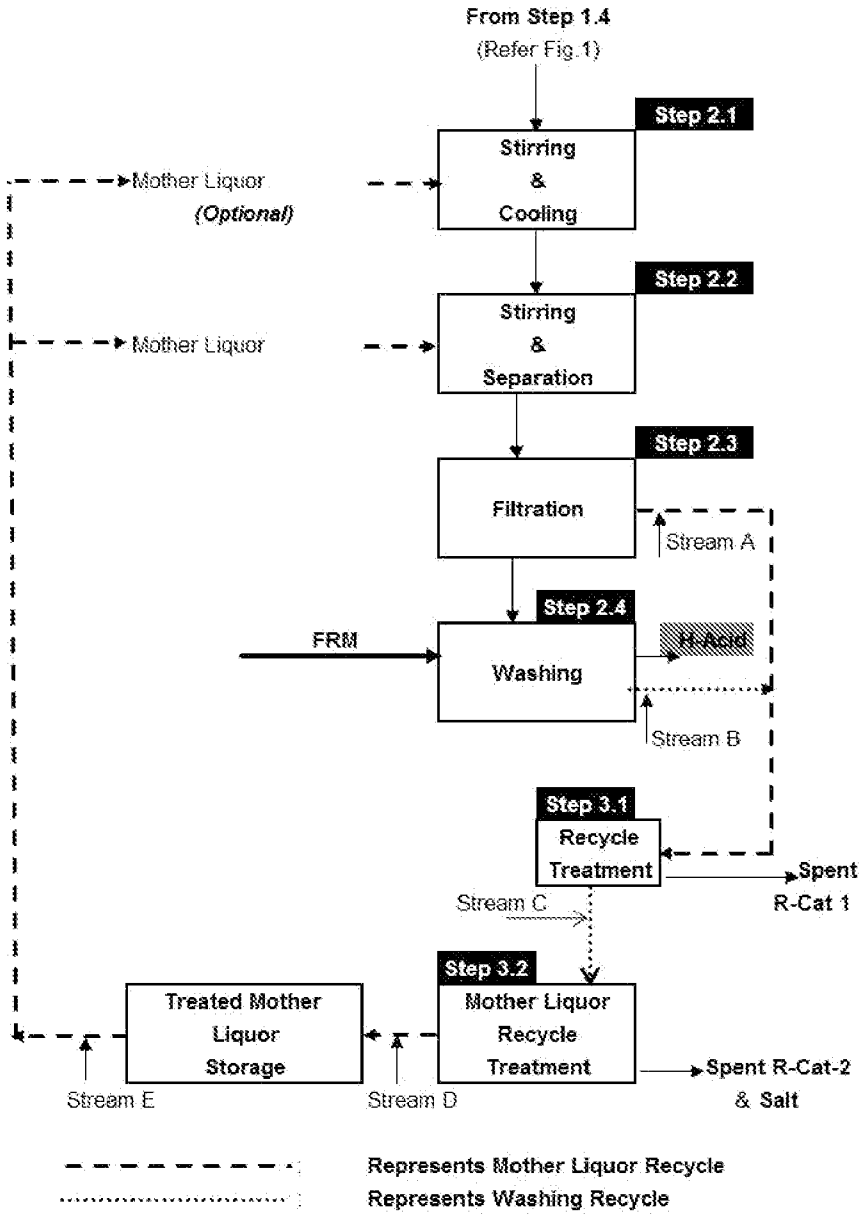

From Step 1.4
(Refer Fig.1)
Step 2.1
Stirring
&
Cooling
Mother Liquor
(Optional)
Step 2.2
Stirring
&
Separation
Mother Liquor
Step 2.3
Filtration
Stream A
Step 2.4
FRM
Washing
H Acid
Stream B
Step 3.1
Recycle
Treatment
Spent
R-Cat 1
Stream C
Step 3.2
Mother Liquor
Recycle
Treatment
Spent R-Cat-2
& Salt
Treated Mother
Liquor
Storage
Stream E
Stream D
Represents Mother Liquor Recycle
Represents Washing Recycle

**Figure 3**

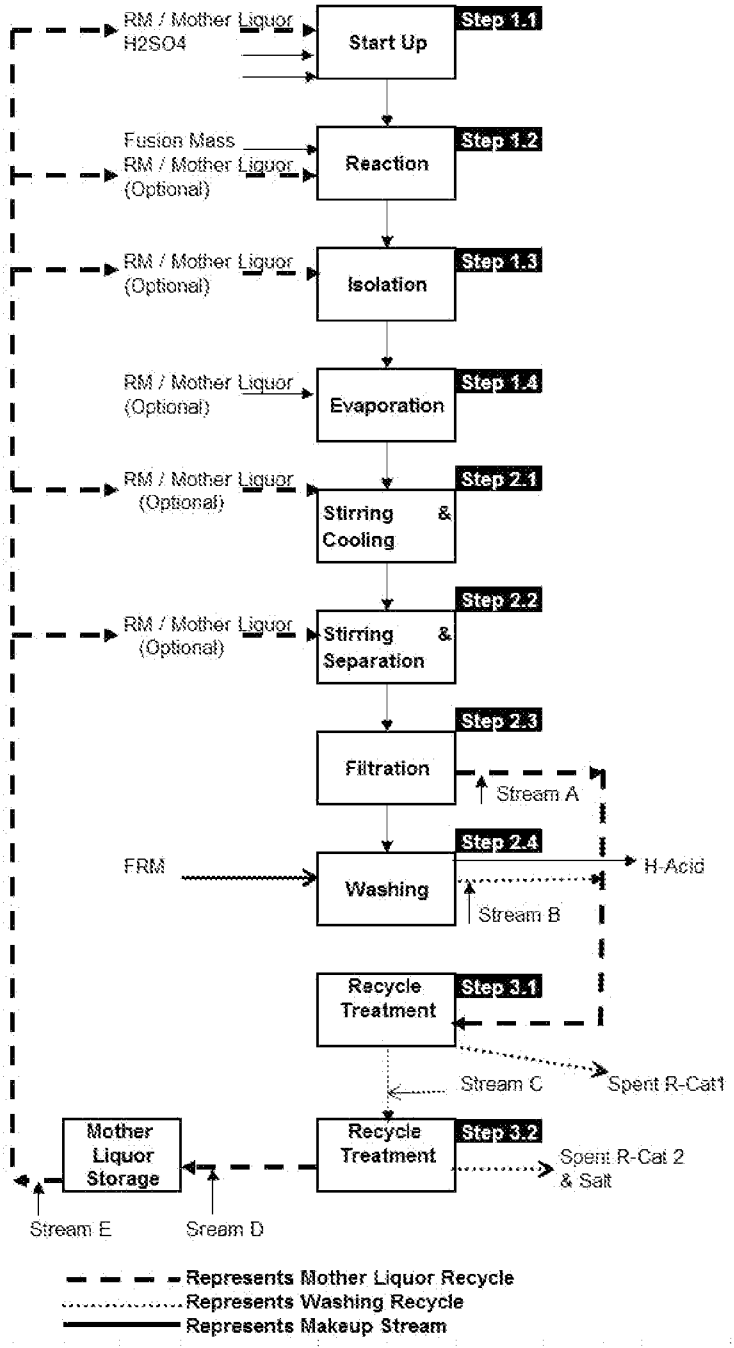

RM / Mother Liquor
H2SO4
Start Up
Step 1.1
Fusion Mass
RM / Mother Liquor
(Optional)
Reaction
Step 1.2
RM / Mother Liquor
(Optional)
Isolation
Step 1.3
RM / Mother Liquor
(Optional)
Evaporation
Step 1.4
RM / Mother Liquor
(Optional)
Stirring & Cooling
Step 2.1
RM / Mother Liquor
(Optional)
Stirring & Separation
Step 2.2
Filtration
Step 2.3
Stream A
FRM
Washing
Step 2.4
H-Acid
Stream B
Recycle Treatment
Step 3.1
Stream C
Spent R-Cat1
Mother Liquor Storage
Recycle Treatment
Step 3.2
Spent R-Cat 2 & Salt
Stream E
Sream D
Represents Mother Liquor Recycle
Represents Washing Recycle
Represents Makeup Stream

**Figure 4**

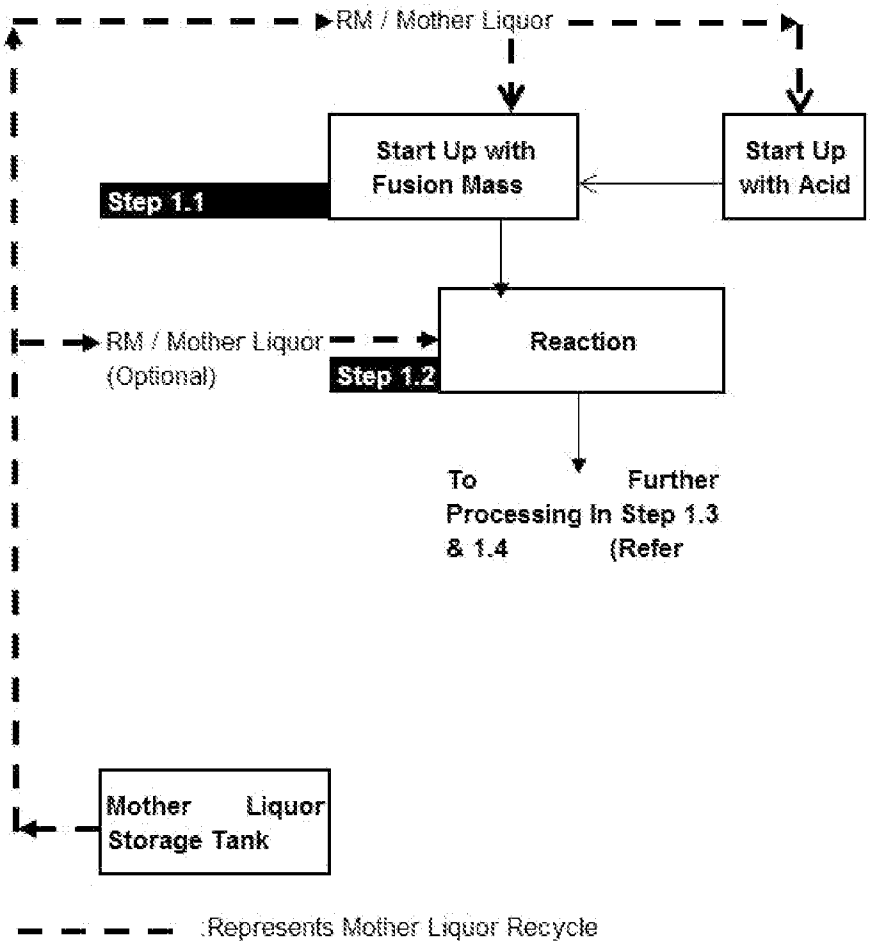

RM / Mother Liquor
Start Up with Fusion Mass
Start Up with Acid
Step 1.1
RM / Mother Liquor (Optional)
Step 1.2
Reaction
To Further Processing In Step 1.3 & 1.4 (Refer
Mother Liquor Storage Tank
:Represents Mother Liquor Recycle

**Figure 5**

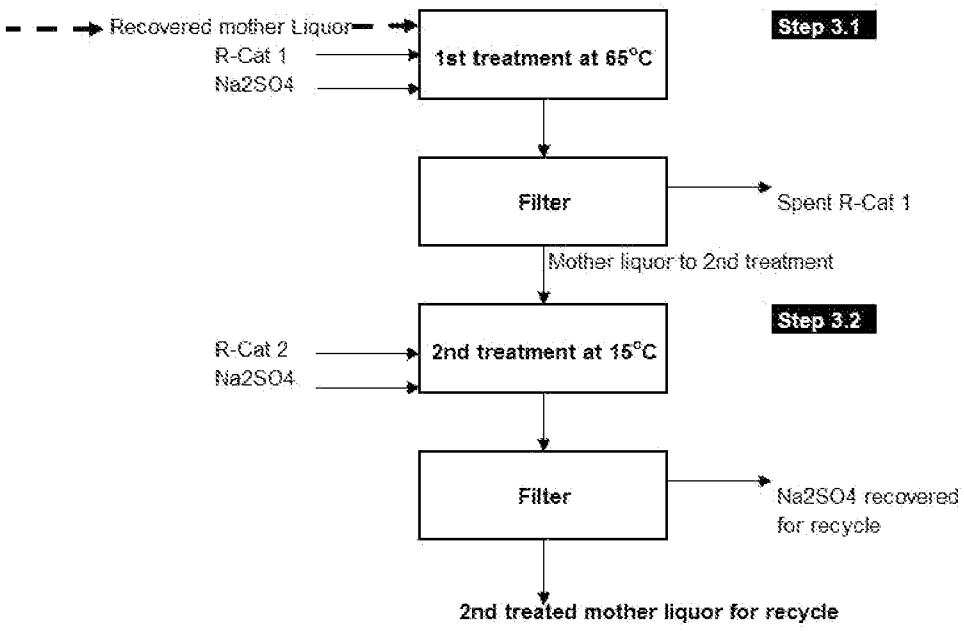

Recovered mother Liquor
R-Cat 1
Na2SO4
1st treatment at 65°C
Step 3.1
Filter
Spent R-Cat 1
Mother liquor to 2nd treatment
R-Cat 2
Na2SO4
2nd treatment at 15°C
Step 3.2
Filter
Na2SO4 recovered for recycle
2nd treated mother liquor for recycle

**Figure 6**