

Alternative Synthesis of α -Naphthol for enhanced purity and yield.

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Abstract:

1-Naphthol or α -naphthol is produced by heating 1-naphthalene sulfonic acid with caustic or 1-naphthylamine with water under pressure and is used directly in the production of some dyes and in large quantities is converted to It ends up being a compound that is incorporated into other dyes. Growing research interest is focused on developing efficient systems using a variety of methodologies that are useful and provide stability.

Here, 1-naphthol was studied degradative. Specifically, we studied how reaction conditions affect reactivity and yield, and purity using alternative variations of the reaction regime. The present invention relates to a process for the production of sertraline, α -naphthyl ether of N-methyl carbamic acid, and α -naphthol used in the production of azo dyes. This work provided an efficient process and the experiment resulted in a method to synthesize α -naphthol with improved purity and yield.

Keywords: 1-naphthol, α -naphthol, sulphonation of naphthalene,

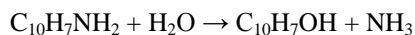
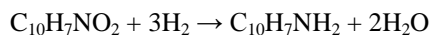
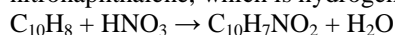
I. Introduction:

1-Naphthol or α -naphthol is a fluorescent organic compound with the formula C₁₀H₇OH. It is a white solid isomer of 2-naphthol distinguished by the position of the hydroxyl group on the naphthalene ring [1]. Naphthol is the naphthalene analogue of phenol, and the hydroxyl group is more reactive than phenol. Both isomers are soluble in simple alcohols, ethers, and chloroform [2]. They are precursors of various useful compounds. Naphthols (both mono- and di-isomers) are used as biomarkers in livestock and humans exposed to polycyclic aromatic hydrocarbons.

1-Naphthol is an important industrial raw material used in the production of pesticides, herbicides, pharmaceuticals and dyestuff intermediates.

1-Naphthol is a metabolite of the insecticides carbaryl and naphthalene. Along with TCPy, it has been shown to lower testosterone levels in adult men [3]. It biodegrades via the formation of 1-naphthol-3,4-oxide which is converted to 1,4-naphthoquinone.

1-naphthol is mainly produced by the two methods. In one method, naphthalene is nitrated to form 1-nitronaphthalene, which is hydrogenated to the amine, followed by hydrolysis.



Alternatively, naphthalene is hydrogenated to tetralin, which is oxidized to 1-tetralone and dehydrogenated[4].

Researchers are working on several ways to improve the environmental

performance of chemical processes, particularly the production of alpha-naphthol. The main challenges are:

- Development of baseline scenarios for alpha-naphthol production based on conventional chemical pathways, including process flow sheets, computer simulations, economic and environmental impact analyses.
- Development of alternative scenarios for the production of α -naphthol by biocatalytic pathways, including process flow diagrams, computer simulations, economic and environmental impact analyses.
- Comparison of two alternative scenarios based on performance, cost and environmental impact.

To achieve these set goals, flow charts are developed from technical information obtained from a thorough literature review.

There are 37 alpha-naphthol producers in the world. The Western world's production capacity was about 15,000 tonnes of α -naphthol per year [5]. α -Naphthol has historically been synthesized by three

different methods [6]. These include:

- a) Corrosive melting of naphthalene-1-sulfonic acid.
- b) I.G. Industrial Process Colors
- c) Union Carbide Process

The most important process in this work is the Union Carbide Process due to its relevance to modern industrial practice. The only difference is the raw material. Naphthalene is a raw material in conventional chemical processes, and tetralin is a raw material in the Union Carbide process. A detailed description of conventional chemical processes and alternative biocatalytic processes is described in more detail elsewhere [7].

Conventional Process Fig. 1 shows a flow diagram for the process of synthesizing α -naphthol from naphthalene using the conventional chemical process. Naphthalene enters the hydrogenation reactor at 617°F and 1102 psia in the presence of $\text{COMO-Al}_2\text{O}_3$ catalyst where it is converted to tetralin [8]

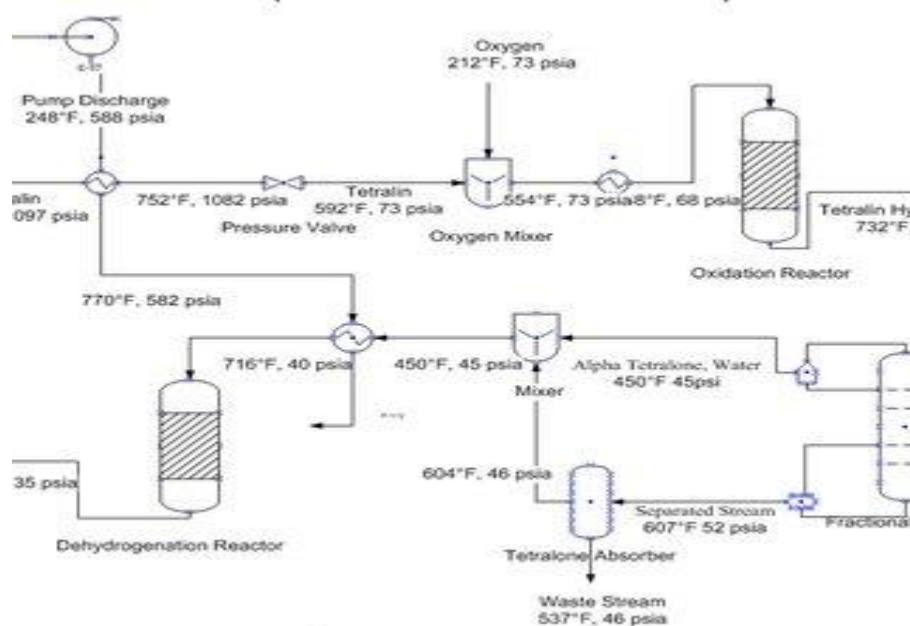


Fig 1 Flow Diagram of conventional α - Naphthol Production from Naphthalene.

The tetralin is then contacted with oxygen entering the oxidation reactor at 188°F and 68 psia where it is converted to the intermediate tetralin hydroperoxide. This immediately decomposed to α -tetralone and α -tetralol and was modeled in a decomposition reactor at 122°F and 58 psia. The dehydrogenation reaction takes place in the gas phase at 716°F and 40 psia in the presence of a catalyst to produce α -naphthol [9]. α -naphthol can be prepared by nitration of naphthalene under controlled conditions followed by reduction of the nitro compound to naphthylamine. The alpha and beta isomers are then separated and finally acid hydrolysis at elevated temperature gives α -naphthol. One of the major drawbacks of the alkaline fusion process used to create

alpha and beta. Naphthol is a requirement for thermodynamic control during the sulfonation of naphthalene, which yields the majority of isomeric naphthalene-1-sulfonic acids for α -naphthol and naphthalene-2-sulfonic acids for β -naphthol.

Another drawback is that the process is not "green". This involves hazardous steps such as sulfonation, alkaline smelting, hydrolysis of the sodium salt with acids, and ultimately the process produces by-products and expensive waste. Treatment of air and water pollution is required.

Other commercial processes for beta-naphthol from 2-isopropyl naphthalene disadvantageously involve hazardous reaction conditions such as the reaction of propylene with naphthalene at 1500-2400. It selectively produces 2-isopropyl naphthalene under pressure and hydroperoxide of 2-isopropyl naphthalene isomer at 110°. Further cleave the hydroperoxide with acid, with air or oxygen. Along with the by-products, this process also poses waste disposal problems [10-12]. Disadvantages of the α -Naphthol Process from Tetralon The main requirement for hydrogenation is that the naphthalene is sulfur free. A second drawback is the formation of hydroperoxides from tetralene to 1-tetralol and his two-step catalytic hydrogenation at temperatures ranging from 2000 to 4000 °C to produce α -naphthol. The steps involved are [13-14].

The drawbacks of other hydroxylation processes mentioned in the literature are the dangerous reaction conditions of the process, the use of expensive corrosive liquid catalysts such as HF, CF_3COOH , HF

complexes, and the use of harsh conditions. React at -10°C . From C to -700 C , the final conversion to the hydroxylated product is poor [15].

It is therefore necessary to develop a process for the hydroxylation of naphthalene to β -naphthol and α -naphthol in appreciable yields, use solid recyclable catalysts and operate at sufficiently low temperatures (below 1000°C). It is clear that there is Minimize the formation of by-products while avoiding hazardous reaction conditions [16-17].

An aromatic peroxygenase was constructed to synthesize 1-naphthol. Altering the ratio of peroxidation and peroxygenase activity resulted in an evolved enzyme with a total turnover number of 50 000 and high selectivity. This biocatalyst is a promising one-pot alternative to replace currently dominant polluting chemical processes to meet the industrial demand for 1-naphthol synthesis.[18]

C-centered radicals under electrochemical conditions. Cyclization is a viable strategy for building cyclic structures. Herein, we report the electrochemical synthesis of highly functionalized 1-naphthols using alkynes and 1,3-dicarbonyl compounds for the cyclization of the (4+2)-C-centred radical. Electrolysis was performed using $\text{Cp}^*\text{2Fe}$ as the redox catalyst, eliminating the use of oxidants and transition metal catalysts. The synthesized 1-naphthol compounds exhibited excellent anti-tumor activity in vitro and further studies showed induced apoptosis of tumor cells [19-20]. It is possible to increase the yield of α -naphthol and at the same time increase its purity.

This object is achieved by a process for the production of alpha-naphthol.

Current Work:

According to the invention, an equimolar amount of sulfuric acid is taken for sulfonation, the process is carried out for 60-120 minutes, after which the naphthalene- α -sulfonic acid thus produced is heated to a temperature in the range of $180\text{-}285^{\circ}\text{C}$. melted at temperature.

Here, the alkali metal is added in an amount of 3 to 4 mol per 1 mol of naphthalene- α -sulfonic acid and water. The resulting melt consisting of alkali metal α -naphtholate and alkali metal sulfite is mixed with a polar solvent, the resulting mixture is acidified with an equivalent amount of mineral acid based on the amount of alkali metal α -naphtholate, and then the obtained α -Naphthol is recovered from the resulting suspension. Carbonic acid is used to acidify the melt to minimize corrosive activity in process media and to form carbonates from alkali metals (such as potash).

Experimental:

The method is carried out as follows. Sulfonation of naphthalene is carried out using an equimolar amount of concentrated sulfuric acid at temperatures ranging from 30 to 85°C . 60 to 120 minutes.

Reaction products are naphthalene- α -sulfonic acid and acetic acid, essentially free of impurities (naphthalene, disulfonic acid, sulfone, gums). The content of naphthalene- β -sulfonic acid in the reaction mixture does not exceed 1% by weight. An equimolar ratio between naphthalene and sulfuric acid results in substantially complete conversion of the reactants and maximizes the yield of naphthalene- α -sulfonic acid. The sulfonation of naphthalene by the process according to the invention takes place in a homogeneous phase from the beginning to the end of the reaction. For naphthalene- α -sulfonic acid with a purity of 98-99.5%. The naphthalene- α -sulfonic acid obtained is further melted with 3-4 mol of alkali metal hydroxide, preferably lithium hydroxide, at a temperature of $180\text{-}285^{\circ}\text{C}$. for 10-30 minutes. The melting process within this temperature range also takes place in a homogeneous phase.

When the melting is complete, the melt consists of alkali metal α -phenolates, alkali metal sulfites, impurities (alkali metal hydroxides and alkali metal β -phenolates), mono- or dihydric alcohols. The weight ratio of melt to polar solvent is in each case 1:1 to 3.

When the melt is diluted with water, an aqueous solution of alkali metal alpha-naphtholate and alkali metal sulfite is formed. The resulting solution is mixed with a mineral acid taken in an equivalent amount based on the alkali metal α -naphtholate. Cool the mixture to a temperature between 10° and 25°C the resulting α -naphthol precipitates while the inorganic salt of the alkali metal remains in the form of an aqueous solution. From the suspension so formed, the precipitated α -naphthol is recovered by conventional means such as filtration, centrifugation or decantation. The obtained α -naphthol is repeatedly washed with 2 to 3 times its weight of water in order to remove impurities (inorganic salt of alkali metal dissolved in water). The yield of 99.5% pure crystalline α -naphthol is 0.55-0.57 mol per mol of reacted naphthalene. The content of β -naphthol in the α -naphthol obtained does not exceed 0.5% by weight. Other impurities are essentially absent. The filtrate containing water, inorganic salts of alkali metals, unprecipitated α -naphthol and β -naphthol is treated with an organic solvent such as carbon tetrachloride (volume ratio of filtrate to carbon tetrachloride is 1:0.25). After settling, the organic layer containing naphthol is separated from the aqueous layer containing

the above salts. another 0.15-0

By distilling off the organic solvent, 27 moles of α -naphthol with a purity of 95-98% are obtained. The content of β -naphthol in the additionally produced α -naphthol is 2 to 5% by weight. No other impurities. The overall yield of α -naphthol is 0.55 - 0.57.5 mol (55 - 57.5% of theory) per mol of naphthalene used.

A mixture of inorganic salts containing alkali metals, preferably potassium, which is produced as a cation from the aqueous layer by distilling off the water.

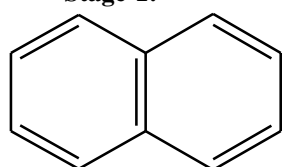
This mixture is used in mineral fertilizer compositions after suitable processing.

Distilled water is returned to the dissolution process of the melting product of naphthalene- α -sulfonic acid and alkali (melt melt).

When the product of the alkali metal melt of naphthalene- α -sulfonic acid is diluted with water, preferably water, the alkali metal α -phenolate contained in the melt dissolves in water, the amount of alkali α -naphthol, equivalent to A mineral acid, preferably carbonic acid, acidified at a temperature in the range 20-60°C. Precipitated α -naphtholate, lithium carbonate and other inorganic salts of alkaline acids are recovered in pure form by filtration or centrifugation. All solids are slurried in toluene and solids are filtered to obtain α -naphtholate m1s in toluene and compound extracted with toluene from filter m1s. Pure alkali metal sulfites are obtained from suspensions obtained by filtration or centrifugation The resulting toluene solution of α -naphthol is distilled. It is then isolated with water to obtain α -naphthol with a purity of 98-99%. The total yield of α -naphthol is 0.55-0.57 mol per mol of naphthalene used, equal to 55-57.5% of theory. In order to provide a better understanding of the invention, some specific illustrations are set forth below.

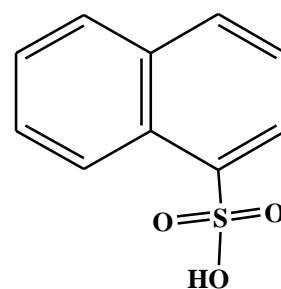
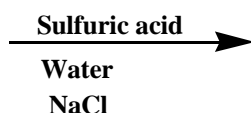
1-NAPHTHOL- ROS

Stage-1:



naphthalene

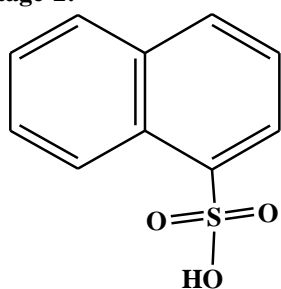
$C_{10}H_8$
Mol. Wt.: 128.17



naphthalene-1-sulfonic acid

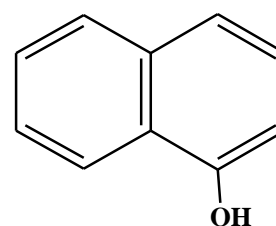
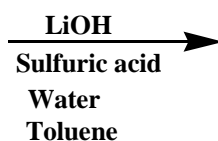
$C_{10}H_8O_3S$
Mol. Wt.: 208.23

Stage-2:



naphthalene-1-sulfonic acid

$C_{10}H_8O_3S$
Mol. Wt.: 208.23



naphthalen-1-ol

$C_{10}H_8O$
Mol. Wt.: 144.17

1-NAPHTHOL- Process

Step 1:

A homogeneous mixture of 100.0 g (0.78 mol) of naphthane, 183.0 g (1.86 mol) of 100% sulfuric acid is continuously added to the supplied reaction mass at 25-30 °C. Add. Then heat to 45-50°C. The reaction mass is stirred at 45-50° C. for 4-5 hours. Add water and sodium chloride and heat to 60-70°C. Cooling to 20-25° C. gave naphthalene- α -sulfonic acid (158.0 g; 97%).

Step-2:

Melt 173.6 g (3.1 mol) of lithium hydroxide in water (16.4 mL) at 170-175 °C. and slowly added (164.0g; 0.788 mol) naphthalene- α -sulfonic acid. The temperature of the reaction mixture rises to 250°C and to 265°C at the outlet. Stir the reaction mixture at 250°C for 60 minutes. Then slowly add water at 40-50°C, adjust the reaction mass to pH 6.5-7.0 with sulfuric acid solution at 5-10°C, then filter the solid to obtain a solid. The solid was dissolved in toluene, filtered and distilled to give α -naphthol. This is 65.0 g (57.7%) of the calculated theoretical value for naphthalene charged.

Sulphuric acid is continuously fed into a reaction mass at 25-30°C. and then heated to 45-50°C. stir the reaction mass for 4-5 hours at 45-50°C. and then added water and sodium chloride heat to 60-70°C. then cooled to 20-25°C filter the solid to get a naphthalene- α -sulphonic acid (158.0g; 97%).

Stage-2:

Water(16.4ml), 173.6 g (3.1 moles) of lithium hydroxide is melted at 170-175°C. And then slowly added (164.0g; 0.788 moles) of naphthalene- α -sulphonic acid. The reaction mixture temperature rises to 250°C., at the outlet 265°C.; the reaction mixture Stir for 60 minutes at 250°C. then slowly added water at 40-50°C. and adjust the reaction mass pH 6.5-7.0 with Sulfuric acid solution at 5-10°C then filter the solid to get solid. Solid dissolved in Toluene and filter filtrate was distilled to get a α -naphthol, is 65.0 g (57.7%) of the theoretical value) as calculated for the employed naphthalene.

Spectral data:

ASPEN BIO PHARMA
 PAN-II-0010122
 (NAPHTHOL)
 1H, DMSO
 SBTIC/AACR/2022/11/0054
 21-11-2022

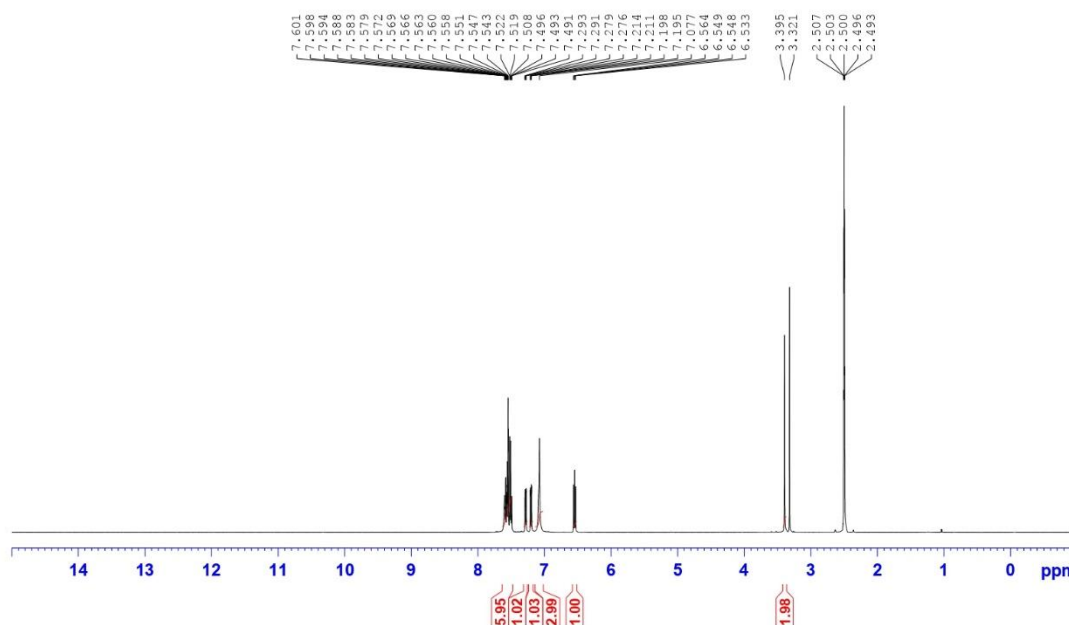


Fig-2 NMR Spectra of 1-Naphthol.

Spectral Analysis:

¹H NMR (400 MHz, DMSO): δ = 8.24 – 8.16 (m, 1H), 7.87 – 7.80 (m, 1H), 7.55 – 7.44 (m, 3H), 7.32 (t, J = 7.9 Hz, 1H), 6.82 (dd, J = 7.4, 1.0 Hz, 1H), 5.26 (s, 1H) ppm;
 MS (EI): m/z calculated for C₁₀H₈O [M-1H]⁺: 142.8; found 142.8;

The spectral analysis was in accordance of the recorded data.

ASPEN BIO PHARMA
AAN-II-0010122
(NAPHTHOL)
1H, DMSO
SBTIC/AACR/2022/11/0054
21-11-2022

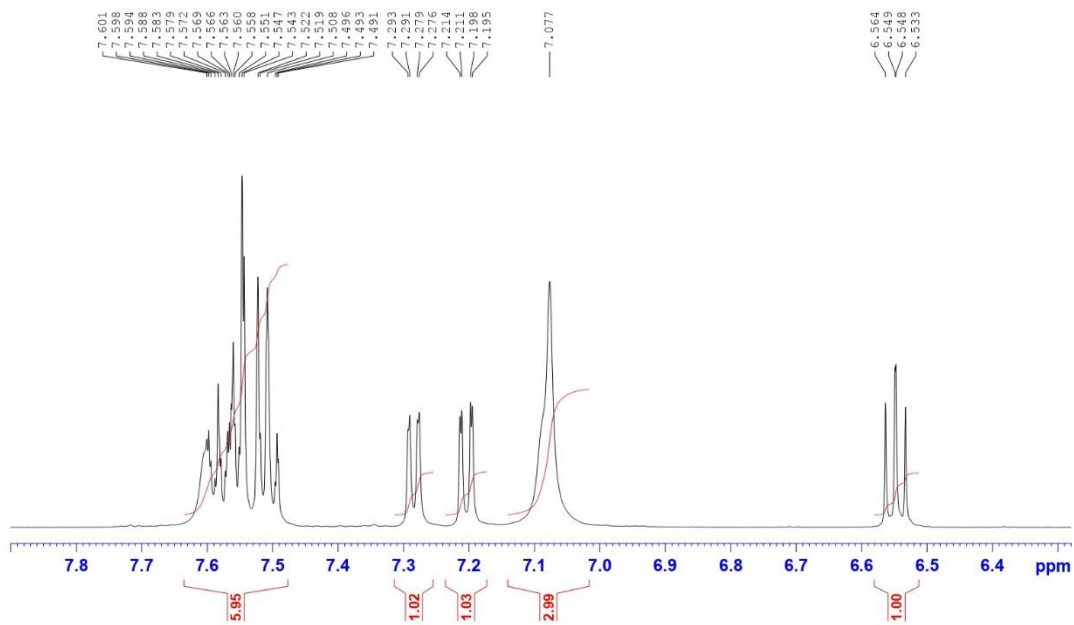


Fig-3 NMR Spectra of 1-Naphthol.



MASS REPORT

Sample details

Sample name:	AAN-II-0010122	Location:	92
Sequence Name:	23-11-2022019	Inj. volume:	10.000
Instrument:	SA/AD/INS/013		
Acquired on:	11/23/2022 1:49:27 PM		

MS Spectrum

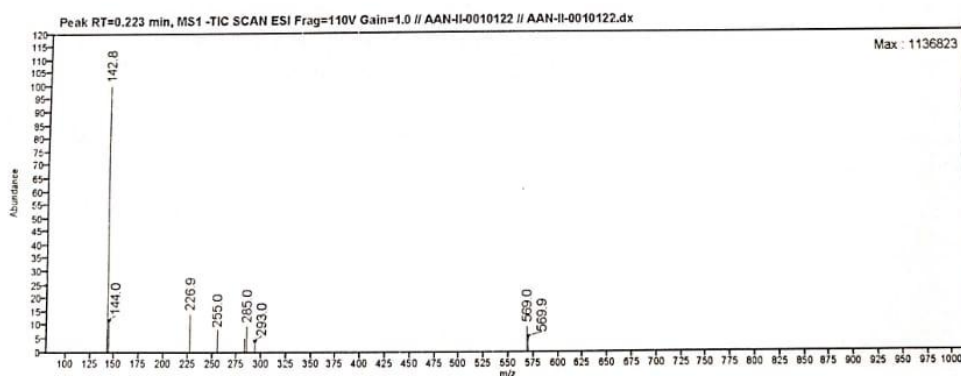
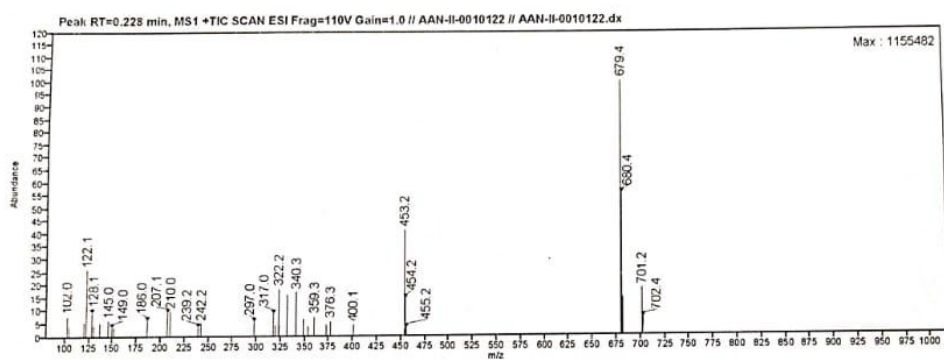


Fig-4 Mass Spectra of 1-Naphthol.

II. Conclusion:

According to the invention, the current study indicates that the advantages of the current process are increased yields and better purity of α -naphthol, all process steps using a to reduce acid and sulfuric acid consumption. Free of alkalis, almost unusable by-products, waste and polluted wastewater. Spectra were simulated for all compounds investigated and are in agreement with the literature. According to the invention, the main advantage of the process lies in the separate production of alkali metal sulfites and alkali metal carbonates, which ensures their efficient use in the production of cellulose and alkali metal cyanates, thus, the whole process.

Data availability

Data sets generated and/or analyzed during the current study are available upon reasonable request from the corresponding author.

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