Process Design of Semi-Batch Sulfur Trioxide Sulphonator

Greeshma Nair	Avantika Bhargava	Nitika Sharma
Assistant Professor Chemical Engineering Department SAL College of Engineering Gujarat Technological University Gujarat	Technical Services Department Rashtriya Chemicals and Fertilizers Limited. Thal	Technical ServicesDepartment Rashtriya Chemicals and Fertilizers Limited. Chembur, Mumbai

ABSTRACT *The term SPENT ACID strikes a chord with most of the people associated to any form of chemical industries. A compilation on the problem of the generation of spent acid, mainly in the processes involving the use of oleum as a sulphonating agent is represented. The causes and the various methods of treating and curbing the spent acid so formed have been analyzed. On the basis of certain experiments conducted and literature surveys carried out, replacing the sulphonating agent from OLEUM to SO3 was zeroed in as the most appropriate solution. This paper is inclusive of the process design data of the proposed semi batch reactor for the sulphonation process involving sparging of the Sulfur trioxide gas in the slurry of the reactant material.*

1.Introduction

Generation of Spent Acid is a major problem encountered by almost all small scale industries manufacturing dyes and its intermediates,which not only is an environmental incursion but also a key economic pull-down for those firms.

A case study of production of a Dye intermediate Sulpho Tobias Acid has been discussed here to help develop a solution to this long standing problem.

2. Case Study- Sulpho Tobias Acid[3]

Oleum storage tank holds Oleum of 23% strength. 3 tonnes of Oleum from this tank is pumped into the reaction vessel. Thereafter 1 ton of Tobias Acid, 97% pure, is slowly hand charged into the reactor. An anchor type agitator in the vessel ensures a proper and efficient mixing of the raw materials in the reactor. The reaction being highly exothermic, chilled water having temperature of 10°C is circulated in a jacket around the vessel. Sulphonation of the T.A. takes about 18 hours to complete, the end of which is ensured by the TLC method. The sulphomass so obtained at the end of the reaction which constitutes of the mixture of Sulpho Tobias Acid + H_2SO_4 + H_2O is transferred to an open vessel (drowner) with the help of a compressor. It comprises of an agitator and cooling coils. The separation of Sulpho Tobias Acid from the sulphomass is conducted by means of precipitation of the former. Salt, a common and cheap medium is used as the precipitating agent. About 800-900 kg of salt is dumped into the vessel along with an additional 8 tonnes of water. At the end of about 12-15 hours Sulpho Tobias Acid precipitation gets completed. It is then drawn into the neutch filter. Herein the solid Sulpho Tobias Acid precipitates are recovered from the liquid content. This liquid contains the spent acid of 23% strength. Manual transfer of the filtered Sulpho Tobias Acid to the centrifuges is carried out for further removal of the liquid matter. The final product/ wet cake obtained at the end of centrifugation is then packed and sold.
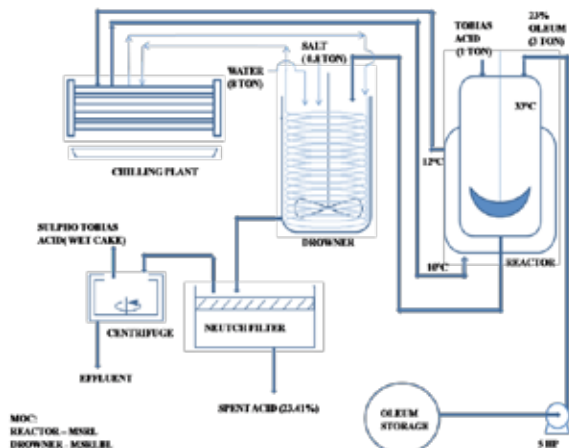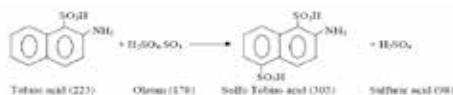
Chemical Reaction[3]:

Fig 1: Process Flow Sheet for manufacture of Sulpho Tobias Acid.

3. Major Issues Associated with the Conventional Process

3.1 Generation of Spent Acid[3]

The main and the most important issue we came across in the industry is the generation of Spent Acid in the manufacturing process of Sulpho Tobias Acid. The major portion of the Oleum being used in the reactor goes as the waste stream. The spent acid, so produced is in bulk and is colored, disposal of which is a problem. Presently, this spent acid is being neutralized with lime generating low quality Gypsum in bulk. This is not an economically and environmentally viable solution.

Elimination of the generation of the waste acid is taken as a problem. If generation of waste acid is inevitable, then its treatment is taken as a problem

The observed problems can be summarized as following:

Generation of spent acid
As per the stoichiometric requirement of the reaction

shown above 1:0.5 molar ratio of the reactants (i.e. Tobias Acid: Oleum) is required. But in the industry 1:3 molar ratio of the reactants is in practice. Here the addition of excess Oleum must have been carried out for the following reasons[8]:

- For the initiation of reaction a certain pH of solution is needed to be maintained.
- To provide a medium for mixing of the reactants and also to facilitate efficient agitation.
- To provide the solution of the right viscosity at the end for the proper transfer of the resultant sulphomass into the drowner.

Be whatever the reason, the excess use of Oleum generates waste acid. Elimination of the usage of excess Oleum if possible preferably at this stage may reduce formation of waste acid and/or also replacement of Oleum by liquid SO_3 may prevent the formation of spent acid completely.

Treatment of the spent acid generated (if use of Oleum is inevitable)

The spent acid so generated at the end of the process has 23% strength and is of dark brown colour.

It consists of:-
1.37% STA, 6.8% salt, 68.33% H_2O and 23.41% of H_2SO_4

4. Tentative Solutions
The treatment for these problems becomes necessary which is then classified into the following:-

Decolourization of spent acid

The colour of the spent acid obtained in the process is Dark Brown. And this colour is needed to be removed.

Concentration of spent acid

The spent acid consists of 23.41% acid. For the reuse of acid we need its concentrated form. This necessitates the treatment of acid for removal of the excess water and other contaminants.

The tentative solutions for the aforementioned problems have been discussed here which will help reduce the colour problem as well help in the reduction of the spent acid formed.

4.1 Removal of Colour by use of Adsorbents
As defined in the problem statement the colour of the spent acid was to be removed. In that regards necessary adsorbents were researched upon.

The most common adsorbent-**Activated Carbon** was rejected due to lack of supporting literature regarding its past use or any possibilities for future for adsorption activities involving decolouration of spent acids or any acids in that regard.

Vermiculite, a natural mineral that possesses a property to absorb hazardous liquids for solid disposal was found out. Commercial vermiculite mines currently exist in Russia, South Africa, China, and Brazil, but limited resources of the same and its low economic feasibility in India has made it an inappropriate material to use. [12]

Certain experiments were carried out to check the reasons for the presence of the color in the spent acid formed.

4.1.1 Experiment – 1
Aim: To observe the change in colour in the given sample of dry Tobias Acid by,

Providing heat to the sample by means of a sand bath

Providing direct heat to the sample

Apparatus: Beaker, Test Tubes, Heating Mantle, Sand, Flask, Crucible, Burner

Chemicals: Tobias Acid

Procedure:
By means of heating by sand bath

Take 1 gm of Tobias Acid in a Crucible. Prepare a sand Bath on the heating mantle. Start the heating and simultaneously observe the colour change. Keep a note of the temperature.

By means of direct heating

Weigh 1 gm of Tobias Acid. Dry a test tube. Heat the weighed sample in a test tube directly on the burner. Observe the colour change and the fumes liberated.

Observations:
By means of heating by sand bath

Maximum temp till which the specimen was heated-165°C
Gradual colour change from pale skin colour to dark brown

By means of direct heating

Colour changed to black.
Yellow fumes emitted
Silver mirror obtained at the bottom of the tube.

4.1.2 Experiment – 2
Aim: To observe the colour change of solution of Tobias Acid before and after heating.

Apparatus: Beaker (500 ml), Magnetic Stirrer, Heating Mantle, Weigh Scale, Thermometer

Chemicals: Water, Tobias Acid

Procedure:
Take 1 gm of Tobias Acid and dissolve it in 200 ml of water in a 500 ml beaker. Heat the beaker on the mantle. Keep a watch on the temperature. Note down the colour change.
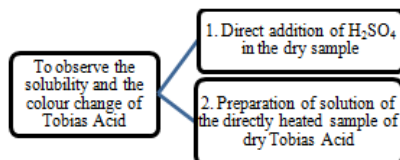
Observations:
There was no colour change.

The maximum temperature noted was 70°C

4.1.3 Experiment-3
Aim:

Apparatus: Beaker, Burner, Test Tube, Flasks, Test Tube Holder, Pipette

Chemicals: Tobias Acid, H_2SO_4, Water

Procedure:
(For 1st part of Experiment)

Take the sample obtained at the end of the exp-1b.Add about 30-40 ml of H_2SO_4 in order to provide a semi-solid state.Observe the solubility and colour change.

(For 2nd part of Experiment)

Take the dry sample and crush it to fine powder. Weigh it. Add 30 ml of water to this finely powdered form. Divide it into 3 parts. Take 10 ml of each and subject it to the following mentioned conditions correspondingly:

- First heat and then add 25 ml H_2SO_4
- First add 2ml H_2SO_4 then heat.
- Add 30ml H_2SO_4 at room temperature(35C)

Observations:
(For 1st part of Experiment)

Dark Purple colour obtained.

Semi solid obtained. Not soluble.

(For 2nd part of Experiment)

Solutions behaved in the following manner:
- Very slightly soluble.
- High solubility obtained.
- Very slightly soluble.

The experimental outcome observed from exp-1 and exp-2 shows that the presence of this colour is due to intensive local heating of Tobias Acid in the initial steps of reaction in the reactor. No agreeable conclusionhighlighting the reason for the presence of the colour was derived from Experiment 3.

4.2Fractional Condensation [10]**:**

For the concentration of spent acid fractional condensation is considered as an alternative.
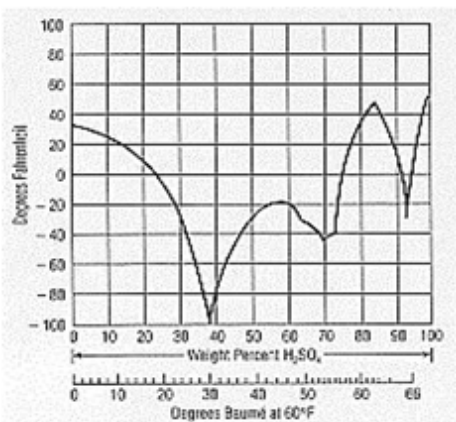
Fig2:Graph of Freezing Point Data of Sulphuric Acid v/s Weight Percent[10]

This method involves separation of components of vaporized liquid mixtures by condensing the vapours in stages (partial condensation); highest-boiling-point components condense in the first condenser stage, allowing the remainder of the vapours to pass on to subsequent condenser stages. But as seen from the graph above, fractional condensation for removal of spent acid is not supported by the data available as the temperatures to be attained for the condensation is quite low, achievement of which makes it an expensive means of separation thereby reducing its viability.

4.3Use of SO_3 Gas for Sulphonation:
This option would present us with a solution to both the problems viz. spent acid solution free from unwanted colour as well as reduction in the amount of spent acid.

On the basis of the experiments performed and the analysis of the relevant data thereof, we choose the 3rd option mentioned here as the **most optimum and feasible** solution comparatively.

Time of reaction is found and assuming that sulphonation using SO_3 would be three times faster than that using oleum, we will find out the time required for sulphonation of Tobias Acid using SO_3

5. Process Design for Sulphonation using Sulphur Trioxide
5.1 Find out the time required for sulphonation of Tobias Acid using SO_3

Assume Reaction temp for Tobias Acid and SO_3 is at 30

$$K = \frac{liters}{gmol.\sec}$$

Reaction temp = 30

Now,

K = (concentration) $^{1-n}$ (time)$^{-1}$

$$= \left(\frac{gmol}{liter}\right)^{-1}\left(\frac{1}{\sec}\right)^{-1}$$

Comparing 1-n = - 1

Thus, n = 2

So, order of reaction = 2nd order

Basis: 1000 kg of Tobias Acid

From the sulphonation mechanism, we can perceive the following:

SO_3 requirement   = 358.74 kg

Moles of Tobias Acid= 4.484kmol

5.1.1 Study of Tobias Acidand Oleum reaction
From the study it can be concluded that in terms of moles the requirement of Sulpho Tobias Acid is 4.484kmol.

5.1.2 Study of Tobias Acidand SO_3 reaction [5]

$$\frac{dc_A}{dt} \;==$$

$\alpha = 1$ $\beta = 1$, as it is unimolecular.

C_A = Concentration of Tobias Acid

C_B = Concentration of Oleum (23% and 65% oleum)

$$\frac{dc_A}{dt} =$$

For, Volume of Tobias Acid= 665.77 lt

Evaluation of Initial concentration $= Ao$ = 0.0067351 kmol/lt

Assuming 80% conversion of Tobias Acid to Sulpho Tobias Acid, we get the value of C_A as 0.0019282 gmol/lt Now, for Oleum concentration

For 23% Oleum

$$C_{B1} = \frac{N_{B1}}{V} = 6.31 \frac{gmol}{l}$$

For 65% Oleum

$$CB_2 = \frac{NB_2}{V} = 8.7253 \frac{gmol}{l}$$

Thus, C_{BO}= 15.25 gmol / l

The amount of A and B which have reacted at any time t is equal and given by

$X_A C_{A0} = X_B C_{B0}$

$= C_{A0} (M-1) K t$

$M = \dfrac{C_{B0}}{C_{A0}}$

Assuming t= 6 hrs.

Therefore k = 6.525 * 10^{-6}lt/gmol.sec

For Tobias Acid and SO$_3$ reaction

Take K = 2-3 times of k of Tobias Acid and Oleum= 1.9575* 10^{-5} $\dfrac{l}{gmol\,\sec}$

5.2 Kinetic study of sulphonation in Semi batch reaction operation [5], [8], [9]
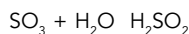
$$-r_A = k \cdot C_A \cdot C_B$$

Here C_A is the concentration of SO$_3$

C_B is the concentration of Tobias Acid.

$$t = \frac{1}{kC_A} \ln \frac{C_{BO}}{C_B}$$

C_A = concentration of SO$_3$

Consider,

SO$_3$ + H$_2$O H$_2$SO$_2$

Solubility of SO$_3$ $= \dfrac{4.44}{1} = \dfrac{444}{100}$ gm Tobias Acid

Solution of SO$_3$ in Tobias Acid= 0.004484305

Therefore as per the calculations according to the kinetic studies, time required for production is evaluated which for one batch of Sulpho Tobias Acid equals 5 hr.

5.2.1 Calculation of flow rate of SO$_3$
For a batch time of 6 hr, the flow rate evaluated is approximately equals 0.8 litre/hr.

6. Conclusions
The technical assessment based on an outline design of process requirements in terms of input, procedure and output was carried out in order to estimate whether the new system will perform adequately or not and whether the technical aspects for the development of the proposed project are feasible.

Excess Oleum used in sulphonation leads to colossal amount of sludge. This can be curbed by the use of SO$_3$ instead of Oleum for sulphonation purpose. This process is useful as;

- SO$_3$ used instead of oleum, drastically decreases the amount of sludge formation and spent acid generation.
- Implementation of SO$_3$ converts batch process into semi batch process, in turn increasing the rate of conversion of product from same reactant.
- It increases the yields of product and gives best quality of it.

The use of the proposed technology has certain risk. As stated, the use of SO$_3$ gas leads to increase in the intensity of risk faced in the process.

The anticipated modification does not hinder the ability of the process to produce the desired product. Instead a better quality product can be obtained with reduced investment and greener surroundings.

REFERENCE 1. Norman C. Foster, Ph.D., P.E., Sulfonation and Sulfation Processes, West Marginal Way SW Seattle, WA 98106–USA 1997 | 2. K Falk et. al, Milan, Process of Reacting Organic Compounds With Sulfur Trioxide, Patent No.: US 2,923,728, Date of Patent :Feb 2, 1960 | 3. Centre for Environment Education and Naroda Industries Association (October 2003) Working Paper titled 'Options for improving sulphonation – A Technical Intervention Supporting Eco Industrial Development'. | 4. Robert H. Perry, Don W. Green, James O. Maloney ,Perry's Chemical Engineers' Handbook,8th Edition | 5. Octave Levenspiel, Chemical Reaction Engineering, 3rd edition | 6. P.H.Groggins, Unit Process in Organic Synthesis,5th edition | 7. Kirk Othmer Encyclopedia of Chemical Technology (R), New York, vol.22. Interscience Pub | 8. S.B.Thakore, D.A.Shah , Illustrated Process Equipment Design,2nd edition | 9. M.V. Joshi, Process Equipment Design, 3rd edition,(2003) | 10. Freezing Point graph for Sulphuric Acid at various concentrations http://www.resistoflex.com/sulfuricgraphs.htm | 11. Process for the isolation of 2-naphthylamine-1,5-disulphonic acid from-www.freepatentsonline.com | 12. Properties and Occurrence of Vermiculite-http://en.wikipedia.org/wiki/Vermiculite | 13. http://www.iitsrl.it/sulfonation_sulfation_sulphation.html | 14. http://www.chem.ucla.edu | 15. http://www.standardbase.com |