SULFONATION OF BY SO_3

Poonam Rathod[1], Prof S B Thakore[2]

[1] *Poonam Rathod, Masters Fallow, Chemical Engineering Department, L.D.C.E., Gujarat, India.*
[2] *S.B. Thakore, Assistant Professor, Chemical Engineering Department, L.D.C.E., Gujarat, India.*

ABSTRACT

Aromatic compound can be sulfonated directly with SO_3 in commercially available continuous and batch equipment. Conventionally sulfonation is done by sulphuric acid or oleum. But with SO_3 sulfonation process has the following advantages. It is more direct and considerably faster than the present process. It requires fewer man hours and, therefore, is more economical. Conditions can be varied to give a wide range of products having different solubility characteristics and combined SO_3 content. Since the reaction, batch or continuous, is stoichiometric, no waste products are formed, thus eliminating any pollution problems.
In sulfonation processes sulfur trioxide is vaporized and is brought into contact with the aromatic compound in the presence of a gaseous diluent such as air, nitrogen or an inert hydrocarbon. It has been thought necessary to utilize such diluent carrier gases to reduce the intensity of the reaction between the sulfur trioxide and the material being sulfated and thereby suppress unwanted side reactions. The purpose of admixing the sulfur trioxide vapour with a diluent gas is to reduce the partial pressure of the sulfur trioxide, so that the chance of a single molecule of the material being sulfated or sulfonated contacting several molecules of Sulfur trioxide is reduced. Aromatic compound is sulfonated by sulfur trioxide in sulfonation reactor.

Keyword: *sulfonation, sulfur trioxide, so_3.*

1. INTRODUCTION

The sulfonation process relates to the sulfur trioxide sulfonation of long chain and branched chain aliphatic alcohols such as fatty alcohols, and to the sulfonation of the aromatic nucleus of alkyl aromatic compounds. The reaction of sulfur trioxide is with an alkyl benzene whereby the sulfonated alkyl benzene is obtained. Such reactions are quite rapid and are accompanied by the evolution of heat; usually these reactions are so highly exothermic that the heat evolution may cause charring (i.e., discoloration and product impurities).
In vapour phase processes for the sulfur trioxide sulfation of organic compounds, for example in the sulfation of lauryl alcohol, sulfur trioxide is vaporized and is brought into contact with the alcohol in the presence of a gaseous diluent such as air, nitrogen or an inert hydrocarbon. It has been thought necessary to utilize such diluent carrier gases to reduce the intensity of the reaction between the sulfur trioxide and the material being sulfated and thereby suppress unwanted side reactions. The purpose of admixing the sulfur trioxide vapour with a diluent gas is to reduce the partial pressure of the sulfur trioxide, so that the chance of a single molecule of the material being sulfated or sulfonated contacting several molecules of Sulfur trioxide is reduced. Heretofore, in the absence of a gas diluent, the rate and intensity of reaction has been found to be excessive, with the result that undesirable side reactions tended to occur to a degree which impaired the quality of the sulfated or product.

1.1 Disadvantage in conventional sulfonation

A serious disadvantage inherent in conventional sulfation and sulfonation techniques using gaseous diluents is that substantial portions, e.g. as high as three to five percent, of the liquid products which are formed become entrained in the diluent gas stream and are lost or at least become uneconomical to recover. Moreover, the conventional technique requires the use of relatively expensive gas handling equipment and/ or equipment for separating entrained reactant materials from the air or gas stream.
A more serious objection to the conventional techniques has been that while undesirable side reactions are reduced by use of the diluent, they are not eliminated to the extent which might be desired, at least not without using extreme measures which defeat the economy of the vapour phase method of sulfation or sulfonation. The precise nature of all

of these side reactions is not known, but in general it may be said that secondary reaction products include water, which even in relatively small or trace quantities makes the sulfated product unstable, and various degradation products which impart an undesirable colour, odour or other undesirable physical properties to it. Such secondary reaction products are recognized as being detrimental to the purity of the sulfated product and substantially impair its commercial value. The same undesirable physical properties may be imparted to sulfonated product as well, except that product stability under reaction conditions is not nearly so sensitive to the presence of Water.

1.2 Advantages of sulfur trioxide

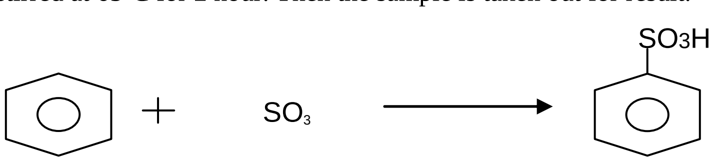
Use of sulfur trioxide as a sulfonating agent in place of oleum offers several advantages. It reduces reaction time from few hours to few seconds or minutes and avoids the problem of the disposal of spent acid. Thus it forms a part of green engineering.

2. EXPERIMENT

First distillation of 65% of oleum carried out at temperature starting from 48^{0}C and completed at 130^{0}C. Liquid SO3 collected in a flask. Reaction of benzene and SO3 is carried out. Benzene is charged drop wise in 3 hours. Here cooling of the reactant is required because the reaction is highly exothermic. After addition the mass become thick, which create load on stirring.

Fig-1: Experiment setup

After completion of benzene addition, mass stirred at 45^{o}C for hour and slowly heated to 65^{0}C in 30 minutes. Now stirred at 65^{0}C for 2 hour. Then the sample is taken out for result.



Benzene

Benzene monosulfonic acid

3. RESULT AND DISCUSSION

In sulfonation process sulfonated sulfone formation is high. Mono benzene sulfonic acid and unreacted benzene is not present. Liquid SO_3 cannot be added directly to the organic material to be sulfonated because of safety and possible product due to high exothermic heat of reaction. SO3 is vaporized and diluted with dry air/nitrogen. The concentration of SO3 air concentration maintained 6-8%. In thin film sulfonation reactor SO3-air mixture is contacted with organic liquid inside the tubes in co current manner. Annnular flow should be obtained inside the tube in which liquid forms a thin film on inside of the tube wall and gas mixture travels down the centre of the tube. Cooling water or chilled water is circulated on shell side as a cooling medium.
One of the most widely used systems for reacting sulfur trioxide with organic compound is a tubular film sulfonation reactor.
In thin film sulfonation reactor SO3-air mixture is contacted with organic liquid inside the tubes in co current manner. Annnular flow should be obtained inside the tube in which liquid forms a thin film on inside of the tube wall and gas mixture travels down the centre of the tube. Cooling water or chilled water is circulated on shell side as a cooling medium.

Table-1: Product after sulfonation reaction

Component	Gram	Gmol	%
p-isomer	0.23	0.0014	18
MBSA	135.83	0.571	27.29
BDSA	135.83	0.57	70.84
Sulfonated sulfone	41.55	0.11	27.29

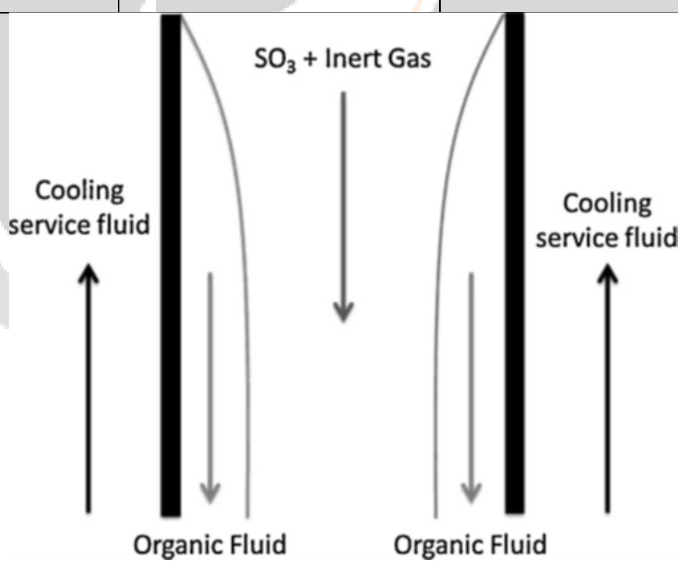


Fig -2: Sulfonation scheme in a falling film reactor (FFR)

4. CONCLUSIONS

In the process of sulfonation with sulfuric acid or oleum the reaction mixture contains a residue of sulfuric acid. Water is a by-product of the reaction so spent acid is inevitable. This spent acid is neutralized along with the sulfonated product when treated with a suitable base, usually sodium hydroxide. Use of sulfur trioxide for the sulfonation would be expected to overcome the difficulty since no water is formed and no residual acid would be expected. On the other hand, the neutralized products actually contain within the range of 2 to 5% sodium sulfate. Reaction time is also decreased. In any event, it is observed that the quality of the reaction is: improved, and in fact yield will usually be better than the yield obtained in known processes by reason of the elimination of losses of product through entrainment in the conventional diluent gas stream

REFERENCES

[1]. Mohammad R. Riazi “Modeling of gas absorption into turbulent films with chemical reaction” Vol. IO. No. 1, pp. 41-46, 1996, Chemical Engineering Department, Kuwait University, PO Box 5969, Safat 13060, Kuwait

[2]. Noel Andrés Gómez Mendozaa,b, Izabela Dobrosz-Gómeza,c, MiguelÁngel Gómez García, “Modeling and simulation of an industrial falling film reactor using the method of lines with adaptive mesh. Study case: Industrial sulfonation of tridecylbenzene”, 2014. Vol. IO. No. 1, pp. 41-46, 1996

[3]. Akanksha, K.K. Pant, V.K. Srivastava, “Modelling of sulphonation of tridecylbenzene in a falling film reactor” Department of Chemical Engineering, Indian Institute of Technology, 2007. Mathematical and Computer Modelling 46 (2007) 1332–1344

[4]. T. Ahmed Zaid, K. Benmaza, C.E. Chitour, “Sulfonation of linear alkyl benzene (LAB) in a corrugated wall falling film reactor”, Département de GénieChimique, Algeria, 1999.

[5]. Journal of the American Oil Chemists’ Society, July 1971, Volume 48, Issue 7, pp 314-317, “The sulfonation of castor oil with sulfur trioxide”