Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science Second Year (S. Y. B. Sc.)

Subject: Industrial Chemistry

Paper Code: CHC153

Paper Title: General Industrial Chemistry

Unit: IX – Sulphonation

Module Name: Commercial Sulphonation of Naphthalene and Alkyl benzene, Batch v/s Continuous Sulphonation

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Notes:

<u>Commercial Sulphonation of Naphthalene</u>:

•The hydrocarbon is reacted with Sulphuric acid; in addition to the desired isomer, about 15% of the alpha isomer is also formed.

•Naphthalene (3,350 1b -26.2 1b moles) is charged to a cast iron Sulphonation kettle, 500 gal capacity, equipped with propeller or anchor agitator and heated either directly with generator gas or by high-pressure (100 lb) jacket steam.

•It is melted by heating to 90-110°C. Sulphuric acid (3,350 lb. of 96% strength -32.8 lb. moles) is then added with agitation, the temperature being allowed to rise to about 160 °C.

•The batch is held at 160 -165°C for about 2hrs to complete reaction, during which time water (approx. 400 lb-22.2 lb. moles) and naphthalene (approx. 350 lb. -2.7 lb. moles) distill off and are collected by condensation.

- **The reaction products contains mainly monosulphonic acids (85 % beta and 15% alphas) plus some sulphone, free Sulphuric acid, disulphonic acids and tar.**

- **The undesired α-sulphonate is now removed by blowing dry steam into the charge to effect hydrolytic desulphonation, the liberated naphthalene being distilled and recovered.**
- **It is essential to employ dry steam to avoid foaming and to maintain a temperature in the range 160-165˚C to ensure rapid reaction.**
- **About 16% or 540 lb. of the original naphthalene employed is recovered, leaving the β-sulphonate contaminated with only about 0.1% alpha isomer.**
- **The hydrolyzed Sulphonation mixture is discharged into the water with good agitation and the resulting solution is run into the brine to form the sodium sulphonate salt.**
- **The slurry so obtained is agitated for 10 hr. as it cooled to 30 ˚C this yields an easily filterable precipitate.**
- **The filtration is accomplished by pumping or blowing the sodium sulphonate suspension into a pressure filter containing wooden plate filters and rubber-coated frames.**
- **The shell of the filter is coated with tar to minimize corrosion.**
- **The filtrate is permit to stand and more salt added if necessary and then it is refiltered to collect any additional sulphonate that has crystallized out.**
- **The second crop of sodium sulphonate is not as pure as the first.**
- **The filter cakes are washed with a minimum of water and these washings are employed to advantage as part of the liquor in the Sulphonation dilution tank.**
- **The filter cake of sodium sulphonate containing about 70 % water is pressed hydraulically to a water content of about 30%.**
- **The press cakes are dried to moisture content of about 5%, disintegrated and delivered to the caustic fusion kettles for conversion to β -Naphthol.**
- **The yield is about 90% of theory on the basis of naphthalene consumed.**

<u>Commercial Sulphonation of Alkyl Benzene (Dodecylbenzene):</u>

- **Dodecylbenzene (Detergent Alkylate) is treated with 20% Oleum.**
- **The Hydrocarbon (1000 lb – 1500 gal.) is pumped into the glass lined sulphonation kettle, 2500 gal capacity, equipped with 10-hp turbo type mixer, and external heat exchanger of about 1000 sq. ft. of cooling capacity.**
- **Circulation of the Alkylate through the external heat exchanger is begun.**
- **The mixer is turned on and 20% Oleum (13750 lb) is added as fast as possible, not exceeding a temperature of 30°c which usually required 1.5 - 2 hrs.**
- **Following the addition, the batch is digested for about 2 hrs. at about 30°c to complete the reaction**
- **At this point the spent acid has a strength of 98.2% and is mixed with the sulphonic acid.**
- **To effect layer separation, water (2650 lb) is added with full agitation and cooling at not over 60°c to yield a spent acid of approximately 78%.**
- **Layer separation occurs upon standing for about 4 hours at 60°c, the lower layer comprising 10800 lb of 78% spent acid is removed.**
- **The upper sulphonic acid layer is neutralised by addition of aqueous caustic soda (3000 lb as 20% soln.) at not over 55°c at a final pH of 7.5 - 8 to yield a sodium salt slurry which can be processed further as appropriated, depending upon the final formulation required.**
- **Approximately 99% of the hydrocarbon charge is sulphonated; the product loss by solution in the spent acid is very small.**

<u>Batch v/s Continuous Sulphonation:</u>

- **Under optimum condition, the reaction time for this process has been calculated at 1.5 hr. at 180°C using a seven-stage reactor.**
- **Continuous process uses 10 moles of benzene per mole of Sulphuric acid required.**
- **In contrast, the same process when operated in batches at 160-180°C would require 14 hr. and 6-8 moles of benzene per mole sulphuric acid.**

- **Thus the continuous method increases by nearly ten times the capacity of the batch method.**
- **It is further estimated that the ratio of benzene used, to benzene reacted could be reduced as low as 3 :1 by doubling the time of reaction.**
- **The efficiency of the process can be further increased by using 10% Oleum instead of sulfuric acid, thereby reducing the required water removal without substantially raising by product sulphone formation.**