Preparation and Production of High Grade Sulfonic Acid

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Abstract: ***Sulfonic acid was prepared in laboratory by mixing Linear Alkyl Benzene, LAB (which produced by the Arabic Chemicals for Detergents at Beige / Iraq) with fumic Sulfuric acid at 55 – 60 C° for one minute residence time to know and to verify the practical conditions and requirements to be applied for mass production process flow sheet of high grade sulfonic acid production every pass which stimulates the construction of some fruitful plants locally. Samples of the prepared sulfonic acid were analyzed using Foot Print-IR Spectrometry showing that functional groups sites of the prepared compound are in coincidence with that of the standard Linear Alkyl benzene Sulfonic acid according to Colthup's tables for spectroscopic analytical data of standard compounds. The reaction is reliable, and almost of quantitative recovery within one minute residence time but it is highly exothermic ; therefore a high efficient heat exchanger recommended to supply urgent cooling and appropriate materials selection should be considered for the construction of plant units, such as its resistance to corrosion as well as their homogeneity characteristics for thermal flow to avoid the production of side products which result in the production of low quality product ; hence an auxiliary software should be constructed to control the process for high quality product insurance.***

Keywords: Sulfonic acid was prepared in laboratory by mixing Linear Alkyl Benzene

1. Introduction

Soaps and synthetic detergents are classified as" fine chemicals ", they were known during the past decades. Their growing use was erupted during the first and second World Wars due to increasingly consumption of animal fats and vegetable oils such as coconut oil, olive oil, sunflower oil and castor oil for human feed that leads to the development of industrial researches since 1940 to prepare *sulfonic acid* the basic raw material for synthetic detergent industry via *alkyl benzene* sulfonation with oleum. Therefore production of alkyl benzene is considered the front base for construction and development of detergents industry all over the World. *Sulfonic acid* mass production can be verified easily using petroleum cuts such as kerosene and benzene that initially produce alkyl benzenes which sulfonated by SO_3 gas or oleum to *sulfonic acid*, many well known companies were going in a race to produce *linear alkyl sulfonic acid, LAB* due to the increasing lack of detergents and to magnify petroleum investments. The global World production of *sulfonic acid* was 3,356 million tons more than59 % produced at Asia and Middle East Countries(Table-1)[1].

Table 1: Global Production of Sulfonic Acid for 2007*

	Site of Production	%
1	Asia	47
2	West Europe	14
3	Northern America	13
4	Middle East	12
5	Latin America	10
6	Eastern Europe	2
7	Africa	2

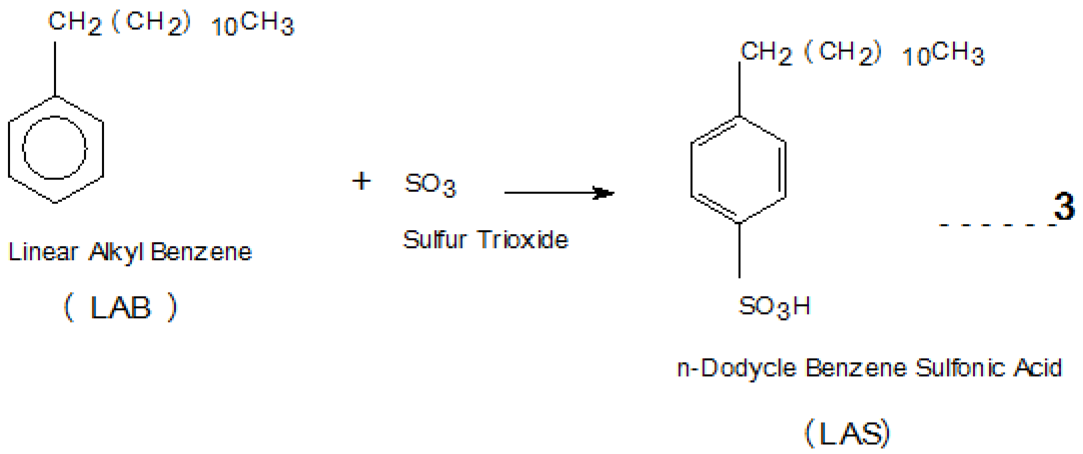
*Global production 3.356 million tons.

After the second World War synthetic alkyl naphthalene 's detergents of short carbon chains were prepared by reaction of propyl or butyl alcohols with naphthalene,then sulfonated to produce the detergents, among those was the well known Nekal of powerful foam, high wetting and fast humidifying, for such properties it is still used in textile industry. During 1920-1930 long chain alcohol sodium sulfonates and branched alkyl benzene sodium sulfonates,BABSS were produced at United States of America. Tide the novel detergent was a mixture of both of them as well as some additives. Shampoo, Teepol,Igepon T, and Mesolate were produced by secondary long chain alcohols produced either by Zeigler Synthesis (produce 50 % of detergents) or petroleum cuts[2-7]. Branched Alkyl Benzene was prepared by the reaction of propylene- tetramer and benzene as in the following equations (1&2):

$$4CH_2 = CH - CH_3 \xrightarrow{H_3PO_4} CH_3(CH_2)_{10}CH_3 \quad ....\ 1$$

1-Propene — Propylene Tetramer

The branched alkyl benzene treated with oleum yielding Tetra Propylene Benzene Sulfonic Acid, TPBS, then neutralized with sodium hydroxide forming the branched alkyl benzene sodium sulfonate BABSS, of environmental draw bags due to its long biological degradation time, foam stability upon the surfaces of rivers and lakes assists growth of algae colonies clusters and blockage of plant drainages, for such reasons linear alkyl benzene sulfonic acid, LAS, was produced by reaction of linear alkyl benzene, LAB with SO_3 gas or oleum (eq.-3).LAB is synthesized by alkylation of benzene and normal olefins produced brought by petroleum cuts.



Hydrofluoric acid was used as alkylation catalyst since 1960(UOP-process),such process has many problems related to high corrosive ability of the catalyst which restrict materials selection to the valuable inconieal, monieal and histalloy-c for construction of plant units, as well as its harm for human beings and environment [8-12], soon a new modified process using a solid fixed bed catalyst (DETAL) was developed as a real revolution in synthetic detergents industry due to the ease of plants construction using this process. The properties of sulfonic acid differs due to petroleum cuts raw materials, table-2 depicts the properties of *Iraqi sulfonic acid* for its straight chain alkyl radicals.

Table 2: Guaranteed specifications of Iraqi- LAB

Property	Value	Test Method
Molecular Weight	240±2	UOP-673
Normal Alkyl Benzene Wt. pct.	92.0Min..	UOP-698
2-Phenylalkane Wt. pct.	20.0Max.	UOP-673
Bromine Color	40Max.	ASTM D-1492
Saybolt Color	29min.	ASTM D-156
Doctor Test	Negative	UOP-41
Paraffin Content,Wt.pct.	0.5Max.	UOP-621
Biodegradability of Sodium Alkyl Benzene Sulfonate, Wt. pct.	90Minute	ASTM D-2667
Completeness of sulfonation,Wt.pct.	98	UOP-429

Raw materials for linear alkyl benzene production are benzene and kerosene that comes out of fractionation distillation towers along temperature range 190-250 C° (20% of kerosene production) which contains normal paraffins of 11-18 carbon atoms suitable for detergents industry. Kerosene is initially thermally treated to expel polar compounds such as water which deactivate the molecular sieves that separate normal paraffins out of branched ones, then normal paraffins converted to α- olefins by dehydrogenation process [3-12]. Olefins are found in petroleum and natural gas by small proportions due to their chemical reactivity therefore it could be produced by heavy oils cracking processes.

1.1 Catalytic Cracking

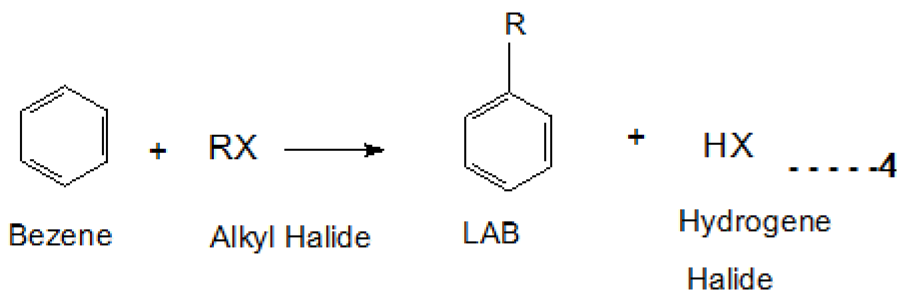
Process converts heavy oil cuts of petroleum to paraffins, cyclo paraffins, naphthenes, and aromatic compounds using Fluid bed Cracking Catalyst, FCC, and Thermal Cracking Catalyst, TCC, such as Zeolites, Aluminum Silicates, Chromium Dioxide and Manganese Oxide. Cracking occurred at 400-500 C°. Addition of Platinum and Lanthanides to catalyst increases its activity by reducing charring phenomena to minimum due to conversion Carbon and Carbon Monoxide to Carbon Dioxide

1.2 Hydro-Cracking

Process converts Liquefied Petroleum Gas, LPG, with hydrogen to isobutylene, gasoline and naphtha using zeolites, Al-silicates, Pt,Pd, and Co-Mo catalysts at temperatures 220-450 C° / 80-200 bar. The process consumes 300-500 m^3 of Hydrogen gas / 1ton heavy oil. This process is too costly and too dangerous to be used in a petroleum refinery.

1.3 Thermal Cracking

Practical cracking process occurred at 400-500 C°, it is carried out by free radical mechanism within 0.5 second, produces olefins and aromatic compounds needed for linear alkyl benzene production according to Fridel-Crafts synthesis (eq-4) [3-12].



Sulfonic acid is called " the jewels of the crown " for its vast uses, e.g. an active ingredient in synthetic detergents, an additive to white and blue dyes for plastic, rubber and synthetic fibers, emulsifying and wetting agent, admixture with other soap types to improve their specifications, LAS used with cationic exchangers for chromatographic analysis (HPLC) [13] and as anti scaling agent in steam boilers[14]. The physical properties of LAS are shown in (Table-3)as well ease of bio degradation, efficient, economic, high thermal and light stability(up to350C$^{\circ}$). It is clear that novel companies such as UOP, DETAL, Petresa, Tecsaco, Exxon-Kellogy and Stone&Webster design and construct detergent plants according to the available raw materials and product specifications satisfying people needs of area under plan.

Table 3: Physical Properties of Linear Alkyl Benzene Sulfonate

1	Physical State	Brown Liquid
2	Melting Point	10 C$^{\circ}$
3	Boiling Point	315 C$^{\circ}$
4	Specific Gravity	1.2
5	Molecular Weight	346.49 gm
6	Solubility	Partially Soluble
7	NEPA Ratings	Health 2, Flammability 0, Reactivity 0
8	Toxicity	Oral rat LD_{50}=650 mg/kg
9	Flash Point	149 C$^{\circ}$
10	Stability	Stable under ordinary conditions
11	Active Matter	96 %
12	Free Oil	1.5 % Max.
13	Water	1%

Industrial development authorities consider that the availability of raw materials such as sulfur and petroleum are basic encouraging factors for construction and proliferation of different industries, therefore the aim of this research is to enhance construction some detergent plants locally on basis of optimized annual production capacity (70000-100000 tons/year) estimated upon the global amounts of imported detergents as well as the increasing future demands. Mass production of *sulfonic acid* using *Thin Film Tube Reactor*, *TFTR* controlled by digital computers is a typical, efficient, reliable and environmentally safe process using heterogeneous phase reaction of SO_3 gas and linear alkyl benzene over inert surface media.

Our aim in this project is to determine the conditions responsible for the production of low grades sulfonic acid with variable properties for every pass which produced by the locally constructed domestic sulfonic acid plants plants.

2. Procedure

Alkyl benzene is sulfonated in laboratory by mixing LAB with fumic sulfuric acid (96 %) i,e it contains 3-4 % SO_3 gas in equilibrium with the acid (10 milliliters LAB with 50 milliliters fumic sulfuric acid) is mixed into a reaction vessel for different time intervals using a variable speed mechanical stirrer, at the end of every time interval samples were withdrawn out of the reaction vessel using a glass dropper for chemical and physical analysis.. The reaction vessel is a round bottom flask (500 ml.) made of Pyrex glass with three neck ports, the middle port used for mechanical stirrer, the second for a quick fit thermometer and the third one for reactants addition and sampling, the reaction vessel containing reactants is immersed into water of thermostatic circulator at fixed temperature degree, the procedure could be summarized as follows :

2.1Determination of Residence Time

Experiments to determine the best residence time of the reaction 0.5, 1.0, 2.0, 3.0, 5.0. 10.0, 15.0 and 30 minutes(fig.-1).

2.2 Determination of Reaction Temperature

Experiments to determine the best reaction temperature 50, 55, 60 and 65 Cº (Table- 4).

2.3Analysis

Laboratory experiments were analyzed by neutralization of sulfuric acid during the course of each experiment using Potentiograph E- 536 and Dosimat E-536 (± 0.01 ml.).

2.4 FTIR- Spectroscopy

The final samples were analyzed using Foot Print IR-Spectrometry.

3. Results and Discussion

Sulfonic acid was prepared in laboratory using linear alkyl benzene produced by the Arab Chemicals Company for Detergents at Beige / Iraq proved that 3 minute is the best residence time for sulfonation reaction as seen in fig.-1(98.5 % recovery).

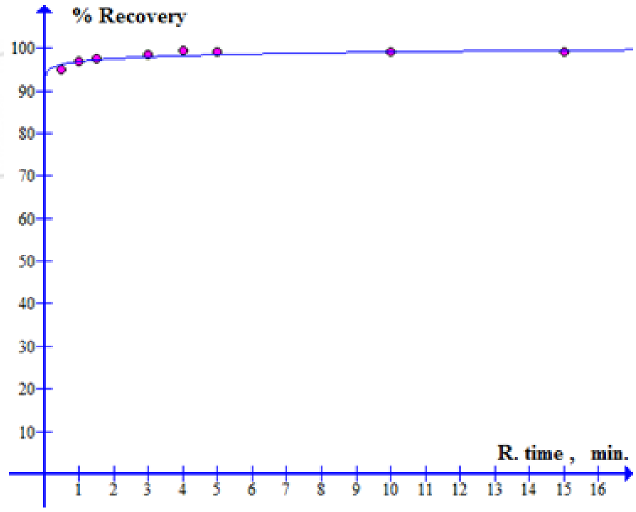
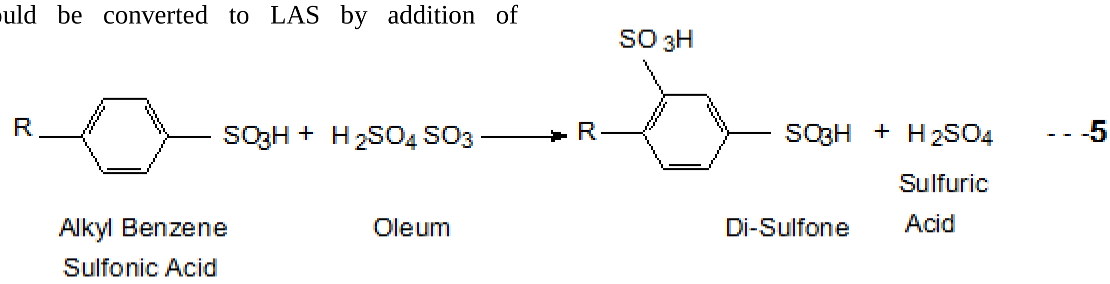


Figure 1: Residence Time of Sulfonation Reaction

Sulfonation is a highly exothermic reversible reaction as seen in eq.-3 (Δ G = - 40 Kcal./ mole) confirms the essential role of heat control ought to be applied verified using efficient heat exchangers to maintain reaction temperature within 50-60 C$^{\circ}$ in order to avoid LAB over sulfonation to di- sulfone,

sulfone and anhydrous sulfone eqs. (5 & 6) which add bad properties to LAS, then to the produced detergents, Di-sulfone could be converted to LAS by addition of equivalent amounts of LAB, more over sulfone and anhydrous sulfone hydrated to LAS during reaction course.



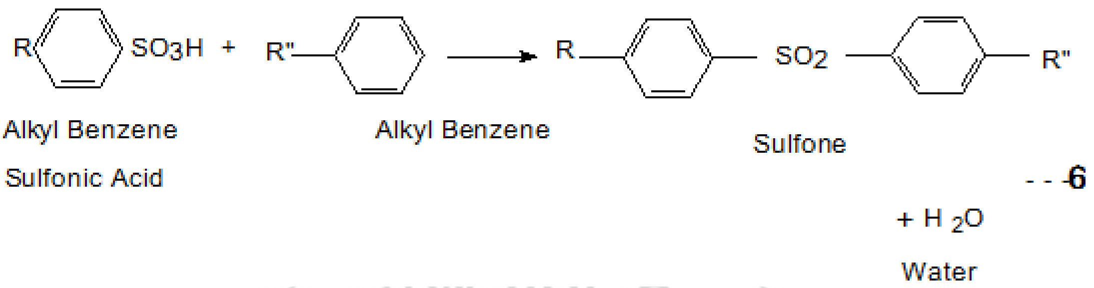


Table- 4 illustrates the vital role degree of temperature for sulfonation reactions, at 50 C° lower yield of product was attained, when as at 60-65 C° LAS product is contaminated with the pre mentioned by products noticed by the dark brown color of the prepared LAS, **but at 55-60 C° is considered the best reaction temperature because of high purity LAS prepared (light brown color, resemble to pure honey color), this narrow temperature range is because of the sensitivity of sulfonation reaction for it is highly exothermic reaction ; therefore such conditions necessitates the role of the auxiliary equipment such as efficient heat exchanger systems recommended to supply urgent cooling and appropriate materials selection should be considered for the construction of plant units, such as their resistance to corrosion as well as their homogeneity characteristics for dynamic homogenous thermal flow to avoid the production of unwanted side products by locally heat concentration points inside the tube reactor which result in the production of low quality LAS product ; moreover an auxiliary software should be constructed to control the process for reliable high quality product insurance for every pass. The locally constructed domestic sulfonation plants did not aware for such control auxiliary equipment on behalves of cost investments rather than product quality.**

Table 4: Effect of Temperature on LAS Properties*

Temp. Deg. C°	Color	%Yield
50	Light Brown	90
55	Light Brown	98
60	Light Brown	98
65	Dark Brown	98

*Residence time of the reaction is 1 minute

Fig.-2 showing the *FTIR* analytical profile of the prepared sulfonic acid by Foot Print IR-Spectrometry reflects excellent coincidence of functional groups' sites according to LAS standard compound on basis of Culthup's tables for standard chemicals [15-16], the double bonds of benzene ring for the compound appeared at 1598.9, 1450 Cm $^{-1}$ where as for LAS standard compound appear at 1600, 1580 &1450 Cm^{-1} respectively, γ C –H of benzene ring appeared at 2858.9 Cm^{-1} but for LAS appears at 3000 Cm^{-1}, meanwhile C-H $_{rock}$ at (665.5 Cm^{-1}) & C-C $_{stretch}$ at (835.1 Cm^{-1}) when as for LAS standard appear at 600-900 Cm^{-1}, 800- 1200 Cm^{-1} respectively, proving that the prepared compound is Linear Alkyl Benzene Sulfonic Acid.

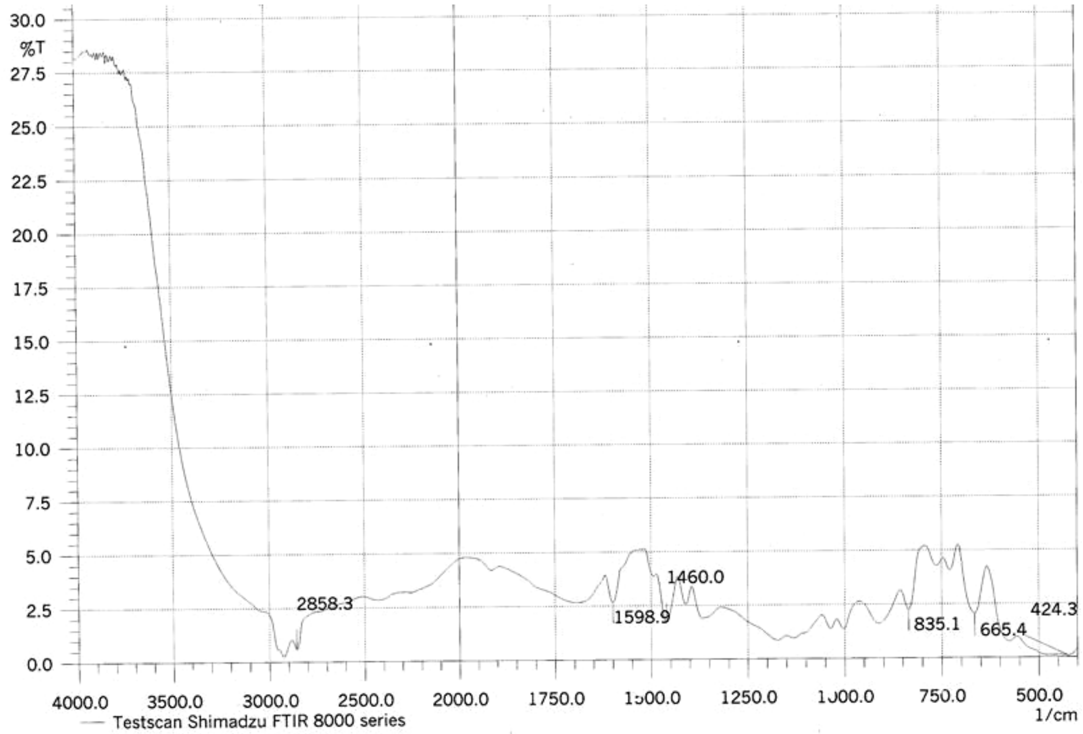


Figure 2: FTIR - Spectrum for the Prepared Sulfonic Acid.

Iraqi – LAB has many advantages(over the previously mentioned, BAB) due to straight Carbon chain of its alkyl group, therefore it is easily bio degraded by bacteria within 90 minutes (Table-2) hence it is safe with regards to environmental considerations.The chemical structure of alkyl benzene affects the properties of the prepared detergent such as dissolution ability and foaming power that increases as branching of the alkyl group increases meanwhile the time of bio degradability increases too approaching unacceptable values so recent researches trying to approach a hygiene alkyl benzene of most practical properties using new processes depend upon Fisher Tropsch synthesis [8, 17 -20].

Table-5 explains the wide spread of newly constructed detergent plants in our area [21-30] especially for Arabian Gulf countries who were participating in planning and construction of the Arab Chemical Detergents Company a Beige / Iraq which work now at 2.2 % of its annual capacity.

Table 5: Some LAB Companies in our Area

	Company	Site	LAB Tons/year	Date of Operation
1	Saief Co. Ltd. (Qatar petroleum Co.)	Qatar	100000#	2006
2	Al-Faraby (of Al-Ragihy group)	Saudia Arabia Kingdom (Al-Gubail)	70000	2006
3	Group of Indian Companies for New Detergents+	India (New Delhi)	80000	1986
4	Arab for Chemical Detergents Co.*	Republic of Iraq (Beige)	1091	1980

Plus 3600 tons HAB (highly alkylated alkyl benzene) used for LUB- oils. + Three plants.
*Of 50000 tones/year (annual capacity).

4. Results and Suggestions

The aim of this research is to verify the requirements of Beige-LAB sulfonation process in order to encourage construction some plants of optimized annual capacities (70000-100000 tons / year) estimated on basis of our needs for detergents. Such plants increase work chances for our people, establish better market to our pure sulfur and petroleum resources capable to increases investments 7-8 folds for the raw materials consumed by detergent industry.

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