Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249 - 261)
ISSN 1992 – 0849

Improvement of Industrial Linear Alkyl Benzene for Detergents Production

Omeed AL-Muhandis [1], Hussein Habeeb Mustafa [2], Thaer Abed Hallow [3]

[1,2] Department of Chemistry, College of Education for Pure Science, Kirkuk University, Kirkuk, Iraq.

[3] Department of Chemistry, College of Education for Girls, University of Mosul, Modul, Iraq.

[1]omeed27@gmail.com, [2]hu_1973@yahoo.com, [3]thhl@ymail.com

ABSTRACT

Standard and specifications of Linear Alkyl Benzene (LAB) compound are essential in the production of most good quality detergents. Pure LAB was obtained by purification of industrial LAB samples, followed by controlling/overcoming the problem of conversion of paraffinic materials to undesirable olefins. Concentrated sulfuric acid was used to remove the olefinic contaminants from the industrial LAB samples. The results were obtained using potentiometric method and color changes in Lovibond photometer. Evidently, significant improvement of the specifications was observed and thus, improved final products are industrially obtained. The new and modified reaction procedure has resulted in a superior quality LAB-based detergent product, compared to that obtained using LAB under the normal operating conditions.

Keywords: detergents, linear alkyl benzene, surfactants.

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

تحسين المواصفات الصناعية للألكيل بنزين الخطي لصناعة المنظفات

اوميد مجيد حميد المهندس [1]، حسين حبيب مصطفى [2]، ثائر عبد هلو [3]

[1، 2] قسم الكيمياء، كلية التربية للعلوم الصرفة، جامعة كركوك، كركوك، العراق.

[3] قسم الكيمياء، كلية التربية للبنات، جامعة الموصل، الموصل، العراق.

[1]omeed27@gmail.com, [2]hu_1973@yahoo.com, [3]thhl@ymail.com

الملخص

تستخدم مادة الالكيل بنزين الخطي ال (لاب) كمادة أولية في انتاج معظم المنظفات، ويشترط أن تكون نقاوتها ضمن المواصفات القياسية كمتطلب اساسي في انتاج منظفات فعالة. تم في هذه الدراسة تحضير مادة ال (لاب) القياسية من خلال تنقيتها بإتباع طريقة السيطرة على تفاعلات تحويل المواد البارافينية الى مواد أوليفينية غير مرغوب بها وذلك من خلال إزالتها والتخلص منها وذلك بإستخدام حامض الكبريتيك المركز والذي أظهر كفاءة عالية في ازالة الشوائب الأوليفينية من نماذج ال (لاب) الصناعية. أشارة النتائج التي تم الحصول عليها بأجهزة المطياف الجهدي ومطياف (Lovibond) اللوني، تحسنناً كبيراً في مواصفات ال (لاب) المستخدم والذين كان يمتلك صفات غير مرغوب بها تمثلت بزيادة في محتوى البرومين فيه حيث تم خفض نسبته من 15% الى الصفر وبشكل كلي، وهذا بدوره ينعكس على تحسين مواصفات المنظفات كناتج نهائي. إن بإستخدام هذه الطريقة الجديدة والمحورة أصبح بالأمكان أنتاج منظفات ذات مواصفات عالية مقارنة بتلك التي استخدمت فيها مادة ال (لاب) في الظروف الصناعية المعتادة.

الكلمات الدالة: detergents, linear alkyl benzene, surfactants.

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

1. Introduction:

Cleaning products like soaps and detergent play an essential role in our daily lives. In the beginning, soaps were used widely for cleaning purposes, washing, bathing, and other types of housekeeping. After that, and due to the increasing need for cleaning products, chemists have, therefore, been making extensive efforts to produce suitable alternatives to soaps. They are known now as detergents. Detergents are effective cleaning products because they contain one or more surfactants (surface active agents). Surfactants are organic chemicals that help to change the properties of water, depending on their ability to reduce surface tension when they exist in water solutions. In addition, detergents are resistant to hard water. There are many cleaning materials used in the market, for example, liquid soap, glass cleaning liquids, wood furniture cleaners, carpet cleaning mixtures, marble and tile cleaning mixtures, etc. In recent years, there have been several methods of obtaining simple chemical mixtures that can be used as industrial detergents, either from alkaline mixtures or from petroleum residues, without damaging the appearance and nature of the cleaned material, while ensuring maximum protection for the consumer [1].

In addition to the performance of the surfactant, acceptable market sustainability is affected by several factors: the starting materials local availability, reasonable cost, longer activity life, surface protection, and chemical / physical / thermal / color stability [2].The current trend is towards producing detergents based on linear alkyl benzene (LAB), for its biodegradability and ease of sulfonation [3,4].LAB material structure shown in Fig. (1) helps to make the detergent environmentally friendly as it decomposes in drainage water reducing its harmful pollution damage to the environment. LAB is normally produced by the reaction of benzene with linear paraffins C9-C15, which are produced from kerosene of crude oil in the presence of a solid catalyst or a liquid anhydrous aluminum chloride [5, 6, 7].

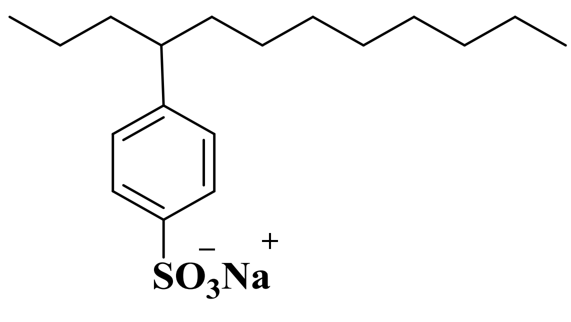


Fig. (1): Structural formula of linear alkyl benzene sulfonate.

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

Usually, 75% of the linear paraffin which is extracted from kerosene is used in production of LAB. The production process involves dehydration, conversion of paraffin to olefin using heat and platinum catalyst on alumina [8], as shown in the schematic representation Fig. (2) describing the production of LAB from kerosene (linear paraffin, C_9-C_{15}) [9].

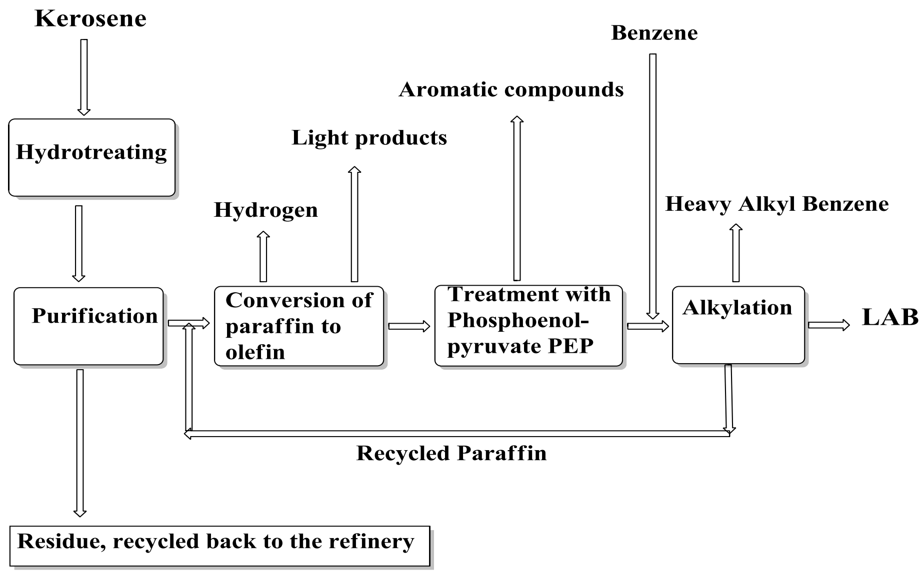


Fig. (2): Schematic representation of LAB production unit.

The remainder of linear paraffinic materials is used for the production of resins, dyes, lubricants, printer inks, polymers, etc [10].Alkyl benzene sulfonate is produced by the sulfonation of LAB process as shown in Fig. (1), where the sulfonation factor is the sulfur trioxides. This is produced by reacting sulfur with oxygen in the presence of vanadium pentoxide as an oxidizing agent. Sulfur trioxide is reacted with LAB at 50°C according to the following equation:

$$RC_6H_5 \rightarrow SO_3 \rightarrow RC_6H_4SO_3H \quad (1)$$

Upon the sulfonation process, the pure linear alkyl benzene colorless with good specifications, changes into undesirable light brown color due to the processes and reactions as shown in the Experiment Section. The changing color of the final product is as a result of two reasons: the contamination of kerosene with some undesirable olefinic impurities, and the effectiveness of the platinum catalyst used in the conversion process of paraffin to olefins [11, 12, 13].

The dark color of the sulfonated LAB will affect the appearance of the final cleaning product (detergent) that will reduce its performance and minimize its consumption in the market.

2. Experimental:

Several Tests are carried out on the LAB samples to ensure conformance with the required specifications and the possibility of their use in the production of detergents. Such tests included measurements of density, purity, molecular weight, percentage of carbon distribution, and bromine index (the weight of bromine consumed per 100 mg of the model). All measurements, chemicals and LAB sampling were coordinated and conducted by the Author, at his official workplace (The Arab Company for Detergent Chemicals, Mousol, Iraq).The high Bromine Index values of the tested samples before treatment were 15 mg/100g as indicated in Table 1. This significant value may negatively affect the LAB specification and, therefore, the quality of the final detergent.

Table (1): The specification of used linear alkyl benzene.

Test	Limits	Test Method
Appearance	Clear	
Density at 60 ^{o}F kg/L	0.8580 - 0.8605	ASTM D-4052
Paraffins Wt. %	0.5 Max	UOP 621
C9 & lighter Wt. %	0.5 Max	UOP 698
C10 - lab Wt. %	8- 15	UOP 698
C11 - lab Wt. %	35 - 40	UOP 698
C12 - lab Wt. %	26 - 32	UOP 698
C13 - lab Wt. %	10 - 20	UOP 698
C14 - lab Wt. %	0.5 Max	UOP 698
Total lab Wt. %	92 Min	UOP 698
2 - phenyl Wt. %	20 Max	UOP 673
Colour Saybolt	+29 Min	ASTM D-156
Br. Indx mg / 100g	15 Max	ASTM D- 1492
Biodegrability of Sodium Alkyl Benzene Sulfonate, pct	90 Min	ASTM D-2667
Completeness of Sulfonation, pct	98 Min	UOP - 429

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

The Bromine Index was determined using two methods:

2.1.1 Titration Technique: Measurement of Bromine Index was conducted using a Metrohm titration equipment, Swiss made, as shown in Fig. (3), (Available in Arab Company for Detergent Chemicals, Iraq) The titrant [KBr-$KBrO_3$] (0.5 N) solution was prepared by dissolving 51 g of KBr and 13.92 g of $KBrO_3$ using distilled water in a (1 L) volumetric flask, and completed to the mark with distilled water. While the titration consisted of a mixture of glacial acetic acid (714 ml), 1, 1, 1-trichloroethane (134 ml), methanol (134 ml), and sulfuric acid-20% (18 ml) [14,15,16].

Fig. (3): Metrohm titration equipment used measurement of Bromine Index.

2.1.2 The titration process involved the addition of precisely weighted sample to be measured (2 ml) to 100 ml of the solvent in the titration beaker. The mixture was cooled down to (0-5 °C) and titrated, automatically, with the titrant, bromide-bromate (0.5 N) using a double platinum wire pole where the End-Point of the reaction was determined. The Bromine Index was calculated by the following relationship:

$$\text{Bromine Index} = \left(\frac{\text{EP1} * 154.22}{\text{Wt of sample}}\right)/100$$

Where EP1 = The end point of the reaction; taken from the device reading;

Wt of sample = Weight of the sample in which the olefin compounds is to be estimated.

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

A

B

Fig. (4): Sulfonated LAB produced from: (A) good LAB and (B) from bad LAB

2.2 A second method, lovibond photometer, was also used for the determination of Bromine Index. This color method has been commonly used in industrial labs. After treating the LAB sample with the acid, the acid layer was taken and a relevant quantity was poured in a quartz cell and placed in the specified compartment of the photometer equipment (available in the Arab Company for Detergent Chemicals, Iraq), as shown in Fig. (5). The recorded color is then matched with the provided color tables, and accordingly the value of Bromine Index was determined.

Fig. (5): The Lovibond photometric equipment

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

The Bromine Index is very important in determining the specifications of the LAB, which is inversely correlated with the Bromine Index.

The LAB becomes off-specification when the Bromine Index exceeds the value 15 mg/100 g.After measuring the Bromine Index for the sample, it was treated with concentrated sulfuric acid at 1:1 ratio (w/w) in a separating funnel (250 mL) and shaken for one minute, giving rise to two distinct layers.

The upper layer is LAB material and the bottom layer is the acid of dark yellow color. After separation of the two layers from each other, a second amount of fresh acid was added to the remaining LAB layer, showing no change in color.

The LAB layer was taken in another 250 ml separating funnel and shaken with a quantity of de-ionized water for the purpose of washing.

The mixture was left to settle for 15 minutes. The resulting two layers were separated from each other. A quantity of de-ionized water was added to the acid part and heated for the purpose of hydrolysis to produce alcohols and glycols.

After cooling, a sample was taken for examination.The hydrolysed acid seems to produce alcohols in addition to the recovery of sulfuric acid, which acts as a catalyst, indicating an economically successful process.

The overall industrial process Fig. (6) shows the purification of contaminated LAB and removal of undesirable olefinic compounds using sulfuric acid.

The overall industrial process is depicted in Fig. (6), showing the purification of the contaminated LAB and elimination of the undesirable olefinic compounds using sulfuric acid.

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

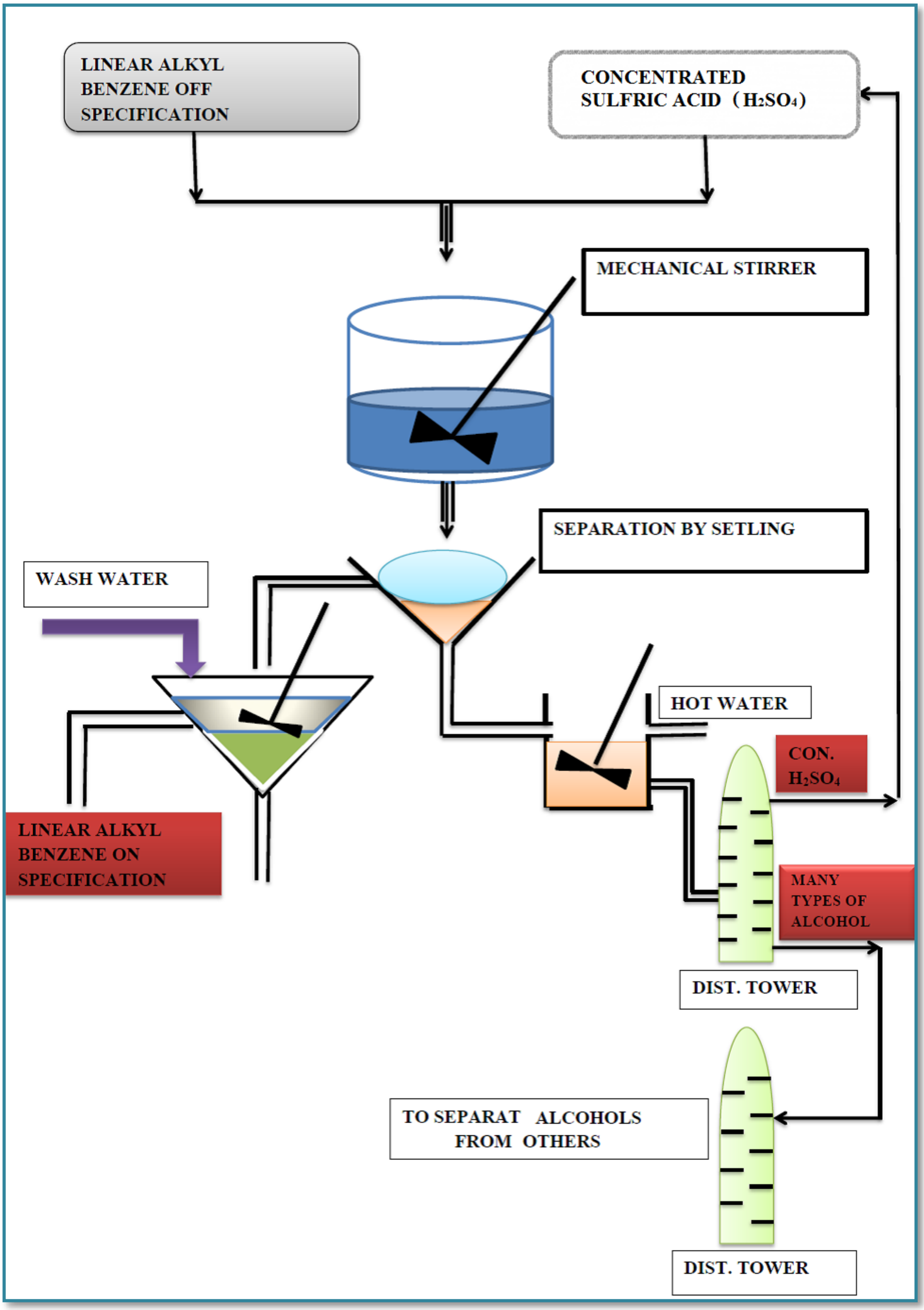


Fig. (6): The overall industrial process of purification of LAB with H_2SO_4

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

3. Results and Discussion:

The value of Bromine Index is used to assess the quality relevance of LAB as a raw material for the production of detergents. The lower Bromine Index, the better the specifications of the LAB material, and the higher the Bromine Index indicates poorer specifications. All samples taken from the industrially produced LAB material showed excessively high Bromine Index values of over 40 mg/100 g. For such reason the final products of the sulfonated detergents have a brown color and poor performance, which are negatively impacting its marketability. The desirable LAB material for industrial detergents production should have Bromine Index values of lower than 15 mg/100 g (ASTM D-1492). There are several reasons for the high values of Bromine Index of the industrial LAB material. Initially, the kerosene used in the production of linear paraffin seems usually contaminated with some cyclo olefins, which are difficult to separate from the kerosene bulk, so they get carried on with linear paraffin to the conversion unit (paraffin to olefin). Additionally, the over activity of the platinum catalyst used in the conversion process leads to the formation of compounds with dual double bonds, besides the presence of some unidentified olefinic compounds.

Concentrated sulfuric acid is known to react with olefins in the preparation process of alcohols through hydrolysis, so it was planned to use it for the removal of the undesirable olefinic contaminants from the LAB samples. During the treatment of the LAB samples, the concentrated sulfuric acid formed two layers. After separation, the LAB layer was washed using de-ionized water to remove all traces of the acid to carry out measurements of Bromine Index. As noted earlier, the Bromine Index was measured using two methods:

1. Titration method using a platinum pole - double wire.

Table (2): Measurements of Bromine Index using the titration method

No.	Samples	Bromine index mg/100g
1	Linear alkyl benzene before treatment with sulfuric acid	15 mg/100g
2	Linear alkyl benzene after treatment with sulfuric acid	0 mg/100g

Kirkuk University Journal /Scientific Studies (KUJSS)
Volume 13, Issue 1, March 2018, pp. (249-261)
ISSN 1992 – 0849

2. Photometric method using Lovibond devise.

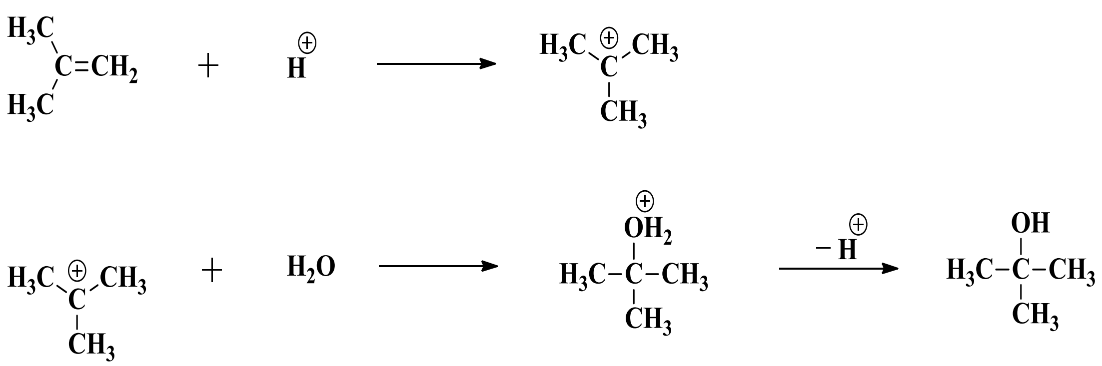
Table (3): Measurements of Bromine Index using the Lovibond photometric method

No.	Samples	Bromine index mg/100g
1	Linear alkyl benzene before treatment with sulfuric acid	15 mg/ 100g
2	Linear alkyl benzene after treatment with sulfuric acid	0 mg/ 100g

It is quite striking to observe, in both measurement methods, the dramatic decline of Bromine Index values for the LAB samples taken from industrial source. In fact, the high values of Bromine Index are characteristic in all LAB samples taken from the industrial source. Evidently, the decline in Bromine Index was due to the fact that the sulfuric acid withdrew all the non-colloidal olefinic contaminants, which were not consumed in the industrial process of alkylation during the production of the LAB.

The process of hydrolysis of the separated acid layer will lead to the production of alcohols and the recovery of the sulfuric acid, used in the process of withdrawing the olefinic contaminants, for the re-usage in the second and third batches.

The acid gets separated from the formed alcohol compounds by distillation under vacuum to avoid crashing of these alcohols into corresponding olefins at the elevated temperatures of 150 °C. The reaction undergoes the following mechanism (isobutene is taken as an example only).



The presence of alcohols was detected by adding a drop of CrO_3 solution and sulfuric acid (5 N) to the applied sample. Upon heating, the color changes from orange to bluish green, indicating the presence of primary and secondary alcohols.

4. Conclusion:

Linear alkyl benzene (LAB) compounds are the raw materials used in the production of detergents. Upon sulfonation of LAB compounds, which is normally conducted over platinum catalyst, some resulting detergents fail to meet the globally required specifications. Evidently, such industrially produced out-of-spec LAB is due to some olefinic contaminants, as a byproduct, derived from the lack of control over the operating conditions in the LAB production. It appears that during the process of LAB sulfonation using aluminum catalyst, the paraffinic LAB tends to get converted into olefins of dark brown color, which eventually, causes the out-of-spec detergent products. Therefore, this industrial research work successfully improved the specifications of Linear Alkyl Benzene (LAB) compounds using a simple and cost effective method.

References

[1] http://goldbook.iupac.org/html/D/D01643.html, "***IUPAC Gold Book-detergent***", Goldbook.iupac.org. 2012-08-19, Retrieved (2013).

[2] Thomas H. V., Anton V., **"*Properties of Detergent Solutions*"**, Industrial and Engineering Chemistry, 35(10), 1094 (1943).

[3] Al-Dubooni A. A., Ali L. H, **"*Industrial Chemistry*"**, Mosul University Press, Iraq, (1987).

[4] Frederic′ L., Michael B., **"*A short primer on benzene, toluene, ethylbenzene in the environment and in hydraulic fracturing fluids, Smart water res*"**, BTEX in the environment, Griffith University – Smart Water Research center, (2010).

[5] Adam A. K., "***Industrial Chemistry***", Basrah University Press, Iraq, (1985).

[6] Eadsforth, C.V., Dirkzwager, H. and Maase B., "*Compositional Analysis and Environmental Performance of LAS Produced from GTL Normal Paraffin and Different Alkylation Routes. Tenside Surfactants Detergents*", Submit Article in hanser-elibrary.com, 45, Issue 4, 194 (2008).

[7] Samimi, A., ***"Normal Paraffin Production Process of Kerosene in Oil Refinery Company"***, International Journal of Basic and Applied Science, 1, Issue 3, 540 (2013).

[8] Buyanov, R. A., Pakhomov, N. A., **"*Catalysts and processes for paraffin and olefin dehydrogenation*"**, *Kinetics and Catalysis*, 42, Issue 1, 64, (2001).

[9] Padmavathi, G, Ghandhurit, K., ***"Kinetics of n-dodecane dehydrogenation on promoted platinum catalyst ",*** *Chemical Engineering Science*, 60, 4119 (2005).

[10] UOP 4522-21, **"*UOP Linear alkyl benzene (LAB) Complex*"**, Des Plaines 60017-5016, USA، https://www.honeywell-uop.cn/wp-content/, (2007). .

[11] Thomas, R. L., **"*Process chemistry of lubricant base stocks*"**. CRC press, tuylor and Francis group, Ontario, Canada, (2008).

[12] Roberts, D.W.**,"*Sulfonation Technology for Anionic Surfactant Manufacture*"**, Journal Organic Process Research & Development, 2(3), 194, (1998).

[13] Roberts, D.W., **"*Optimisation of the Linear Alkyl Benzene Sulfonation*** Process ***for Surfactant Manufacture "***, Journal Organic Process Research & Development, 7(2), 172 (2003).

[14] Mieure, J. P., Waters, J., Holt, M.S., Matthijs, E., **"*Terrestrial Safety Assessment of Linear Alkylbenzene Sulfonate"***, Chemosphere, 21, 251 (1990).

[15] Chorkendroff, J. W., **"*Concepts of modern catalysis and kinetic, 2nd edition. Niemantsverdriet copyright*"**, Wiley-VCH. Verlag Gmb (2007).

[16] www.metrohm.com/Lab_Instruments ،**"*Application Bulletin Automatic determination of the bromine index and/or the bromine number in petroleum products*",** *Metrohm* no. 177/4, 2000.