



Original Research Article

Synthesis of Linear Alkyl-benzene Sulfonate Nanoparticle Using Green Promoter and High Efficiency

Meysam Rezaei^{*1}, Reza Tarvirdi-zadeh²

^{1*} MA of Organic Chemistry, Responsible for Prototyping and Formulation, Raysun Oil Company, Shams-Abad, Tehran, Iran

² MA of Analytical Chemistry, Quality Control Manager, Raysun Oil Company, Shams-Abad, Tehran, Iran

*Corresponding author Fax number: Tel.: +98 2156494659

*E-mail: rezaei_xy@yahoo.com

ABSTRACT

In this study, linear alkyl-benzene calcium sulfonate nanoparticles were made using linear alkylbenzene. Calcium sulfonate nanoparticles are widely used as an additive in a variety of engine oils and have cleansing, anti-wear and anti-oxidant properties and anti-corrosion properties. In this method, a sulfonation set up was constructed and sulfonation reaction was carried out both directly and indirectly with Oleum, which in the indirect method had better yield and the amount of acid used was much less. Sulfonation was carried out on two types of light and heavy alkylbenzene the calcification step was carried out with CaO, and then the supernatural stage and carbonation with CO₂ and CaO were performed for the first time with Ethanol green promoter, and The Total Base Number amount of for calcium was measured at different times. Carbonation time is very important and sensitive. In this research, residual sediments were reused in the carbonation reaction, and excellent results were obtained. It was also observed that the synthesis of linear calcium sulfonate nanoparticles with a high Total

Base Number and a stable structure can only be carried out with heavy alkylbenzene C26. In this work, linear calcium sulfonate alkylated benzene nanoparticles were made completely transparent. (and) The Total Base Number 470, and the weight percent of calcium also reached 17.4, and the nanoparticle stability was also tested using the standard ASTM D2273 method. This result compared with two commercially available linear calcium sulfonate nanoparticles.

Keywords: Sulfonation, alkylbenzene, overbased, linear alkylbenzene calcium sulfonate, Ethanol

1- Introduction

Linear alkylbenzenes (sometimes also referred as LABs) are a family(group) of organic compounds with the (general) formula $C_{10}H_{2n+8}$. Typically, n lies between 10 and (to) 16, although generally supplied as a tighter cut, such as C12-C15, C12-C13 and C10-C13, for detergent use. They are mainly produced as intermediate in the production of surfactants, for use in detergent. Since the 1960s, LABs have emerged as the dominant precursor of biodegradable detergents. Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). Therefore, a surfactant contains both a water-insoluble (or oil-soluble) component and a water-soluble component. Surfactants will diffuse in water and adsorb at interfaces between air and water or at the interface between oil and water, in the case where water is mixed with oil. A detergent is a surfactant or a mixture of surfactants with cleaning properties in dilute solutions [1]. These substances are usually alkyl-benzene sulfonates, a group of compounds that are similar to soap but are more soluble in hard water, because the polar sulfonate (of detergents) is less likely than the polar carboxylate (of soap) to bind to calcium and other ions found in hard water. Linear alkyl benzene sulfonate (LAS) is a highly biodegradable surfactant that has been used in the United States (U.S.) since 1965 as a replacement for branched alkyl benzene sulfonate. Linear alkyl benzene sulfonate represents a mixture of homo-logs having alkyl chain lengths ranging from 10 to 15 carbon units with isomers of varying phenyl position [2]. LAS is a conventional anionic detergent which is used in about 80% of household detergent and can be considerably found in greywater [3]. LAS can be very toxic for marine life and result in foam formation in water resources [4]. Aromatic sulfonation is a very important chemical transformation of organic compounds [5]. Because of the diversity of feed stocks, no single process fits all needs. An acceptable

sulfonation process requires [6] the proper reagent for the chemistry involved and the ability to obtain high product yields; [7] consistency with environmental regulations such that minimal and disposable by-products are formed; [8] an adequate cooling system to control the reaction and to remove significant heat of reaction; [9] intimate mixing or agitation of often highly viscous reactants to provide adequate contact time; products of satisfactory yields and marketable quality; and acceptable economics [10]. So far, several methods have been used for treatment of the greywater including physical approaches such as filtrations [11] as well as chemical methods including photochemical oxidation [12] and electrochemical process with iron oxides [13] and biological methods such as constructed wetlands [14], membrane bioreactors (MBR) [15], Sequencing Batch Reactor (SBR) [16] and Rotating Biological Contractors (RBC) [17]. For more than 100 years, for aromatics sulfonation with SO_3 in sulfuric acid or oleum or aprotic solvents a lot of experimental and theoretical researches has been done and has formed a consensus popular mechanism in organic chemistry textbooks [18]. Detergents are additives that are very important components of engine oils. Since the 1950s, nanosized colloidal inorganic particles have been widely used as detergents [19]. Detergent-dispersant agents consist, in different ratios, of high molecular-weighted calcium (or barium) sulfonate, colloidal calcium carbonate, and mineral oil (spindle oil) in accordance with the application area of lube oil [20] [21].

Sulfonates, well known for their high thermal stability, good detergency, rust inhibition, and anti-wear properties [22, 23], are the most widely used surfactant for nanodetergents followed by phenates, salicylates, phosphonates, and others [24] [25]. They are obtained from the neutralization of corresponding organic acidic molecules using various readily available alkaline or alkaline earth metals (sodium [Na], calcium [Ca], magnesium [Mg], and barium [Ba]). Detergents with acid/base neutralization close to the same equivalent are called “neutral” detergents. Ca salts are the most common detergent salts. Na salts are typically used in industrial oil as emulsifiers. Mg salts have less sulfated ash than Ca salts for the same alkaline reserve. This is desirable for low sulfated ash, phosphorous, sulfur (SAPS) engine oils. MgCO_3 is less basic and neutralizes acid slower than CaCO_3 , and Mg salts maintain the alkaline reserve better than Ca salts [20] Mg salts are usually used in combination with Ca salts as detergents in engine oils [26]. Mg salts are also used as fuel additives for corrosion control for vanadium-containing fuels in gas turbines [27].

2. Materials and methods

2.1 Chemicals and reagents

LAB (C18 & C26) Toluene, CaCl₂, CaO, Oleum 65 % (SO₃), Zero air cylinder. The chemicals applied(used) in this work were obtained from Merck & Sigma-Aldrich companies (and used) without further purification. Total Base Number of the products were recorded on a Metrohm Swiss made 848 Titrino Plus and are uncorrected. FT-IR spectra were recorded on a Perkin Elmer Model Spectrum Two. Elemental Analysis of the products were reported with Spectro Scientific Model Spectroil Q100 (ASTM D 6595).

2.2 Method

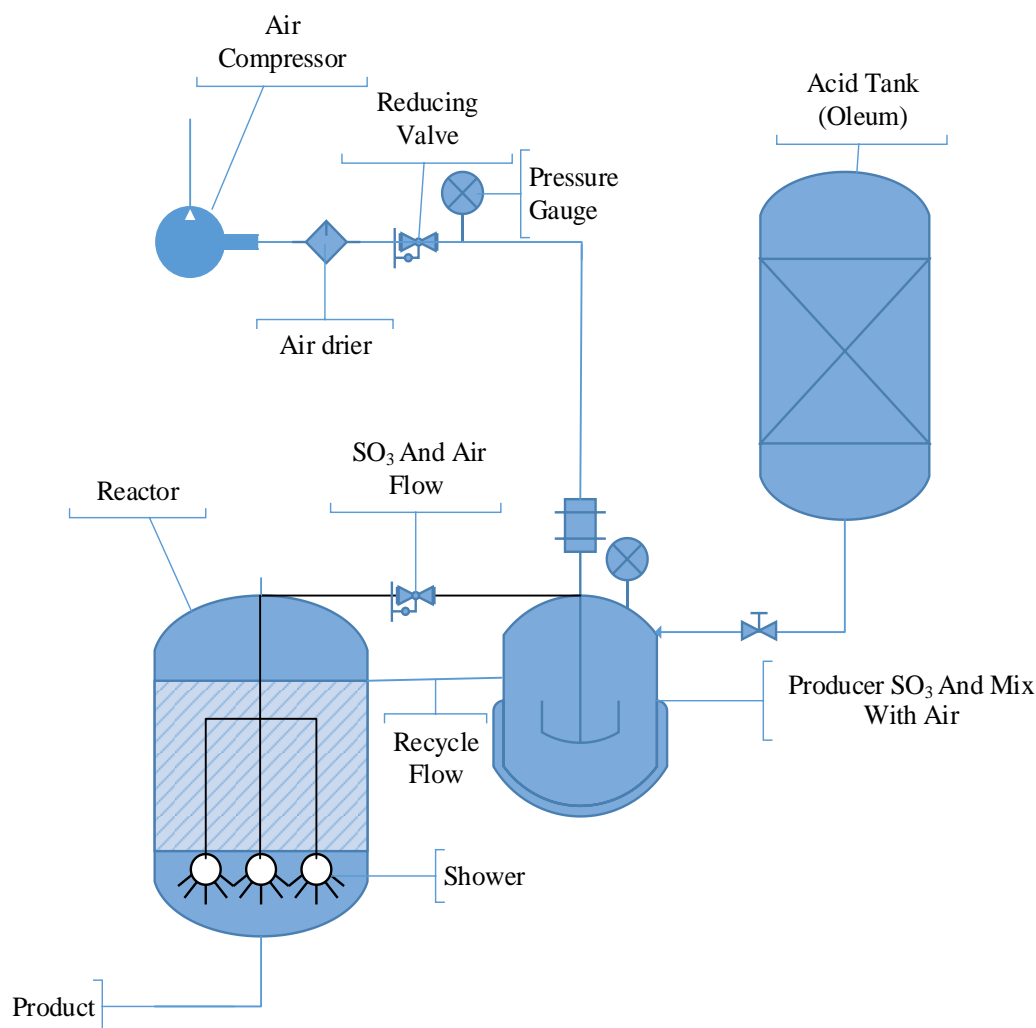
In this study, sulfonation was initially performed on two samples of alkyl-benzene with carbon-18 and 26 branches. The sulfonation process was initially performed with direct addition of oleum. The reaction time and the amounts consumed in Table 1 and 2 are presented. Elemental analysis of the samples before and after calcination and TBNs are listed in the following tables.

Table 1. results of sulfonation and calcination

(Table a. results of sulfonation and calcination LAB C26 and Table b. results of sulfonation and calcination LAB C18)

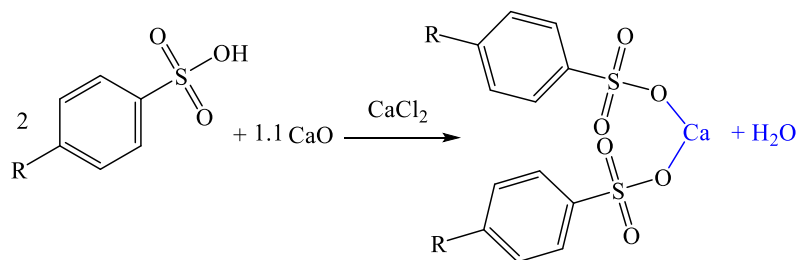
Table a					Table b				
Entry	Oleum%	ppm S	ppm Ca	TBN	Entry	Oleum%	ppm S	ppm Ca	TBN
1	6	3376	2100	0.4	1	5	3669	2301	0.61
2	10	4643	2907	0.59	2	10	4932	3079	0.73
3	15	5779	3618	1.05	3	15	6043	3762	1.07
4	30	11144	6948	2.6	4	20	11697	7301	1.89
5	40	22279	13900	4.7	5	25	23355	14600	3.78
6	50	41204	25706	9.01	6	40	44325	27695	5.74
7	60	60412	37680	13.43	7	50	64204	40108	6.83
8	70	60445	37504	13.45	8	55	64280	40104	6.65

As you can see, plenty of oleum is used to sulfone, and on the other hand it has a lot of waste. Also, a large amount of solvent has to be used to purify it, so we decided to make a small laboratory sulfonation set up, with a very low cost for it. All design and construction of this set up was carried out inside the Raysun Oil Company. You will see the schema below.



Scheme 1. Sulfonation set up

The body of the tanks is all made of steel, because the oleum is a very bad environmental substance. This set up was tested for sulfonation of LAB C26. In this study, SO₃ sulfonation method was used. The completion of the reaction was detected using TLC paper. As shown in Fig. 2, this method has very low losses and can be said to be close to zero. The resulting Calcination of LABS from this step was using CaO 10% higher than the stoichiometric value, which was done to ensure that all LABS were used up in reaction complete. To calcify in addition to CaO 1% CaCl₂ was also added Because calcium oxide always contains some impurities in the form of sodium magnesium and other metals that interfere with the reaction. The best way to remove them is to use calcium chloride, which is used in the calcination reaction.



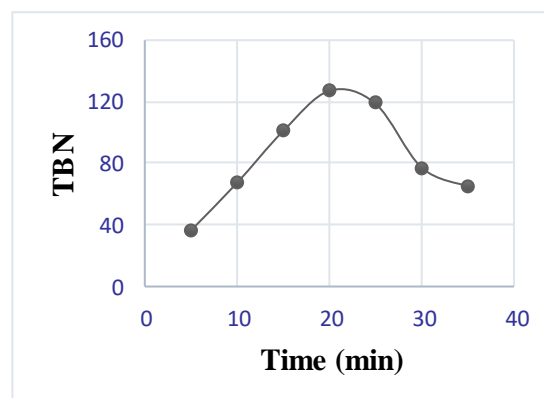
Scheme 2. Calcination of LABS

Times Roman, 12 font size, 1.5-spaced. Authors should be design manuscript in one-column and space between columns must be 0.5.

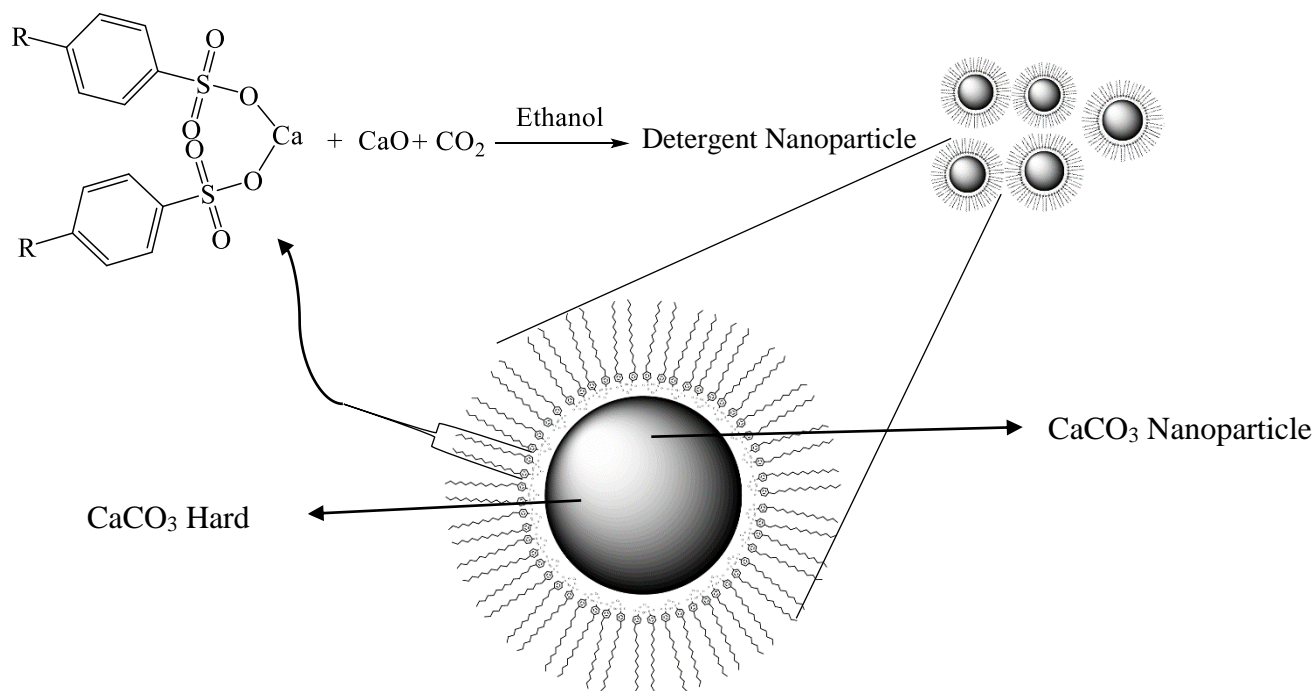
First of all, to prepare calcium sulfonate from above. A sample of 18-carbon alkyl-benzene was used and its calcium sulfonate content was 127.8 and which had the highest TBN in this study, but the resulting product was turbid and was not soluble in mineral and synthetic oils. The results are presented in the table.2 below.

Table 2. Results of time Vs. TBN from carbonation reaction (LABSCa C18)

Entry	Time (min)	TBN	appearance
1	5	35.7	Opaque brown
2	10	67.1	Opaque brown
3	15	101.3	Opaque brown
4	20	127.8	Opaque brown
5	25	119.3	Opaque brown
6	30	77.1	Opaque brown
7	35	64.9	Opaque brown



Then, to obtain the desired product, 21 gr of LABSC26 was digested and supplemented with Nano Particle of alkylbenzene calcium sulfonate and again reacted with 3.5 gr CaO and CO₂ gas in the presence of Ethanol as a promoter. At this stage the amount of CO₂ injection is very important because if it is too much the excess amount of CO₂ will change the size of the nanoparticles and thus reduce the TBN and the amount of calcium as well, and that is why the color as become cloudy.

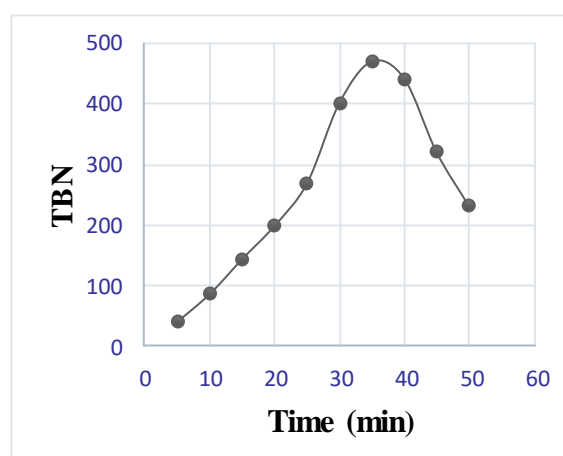


Scheme 3. Structure of linear alkyl-benzene calcium sulfonate nanoparticles

You can see in the table.3, the results of the above-mentioned reaction can be seen. This reaction was performed with constant CaO and CO₂ gas flow using a CO₂ capsule using a constant current flow meter of 6 NI / h. In this process, we tested the samples at different times and got the best time of 35 minutes.

Table 3. Results of time with total alkali by carbonation reaction (LABSCa C26)

Entry	Time	TBN	Appearance
1	5	40	Transparent red
2	10	86.1	Transparent red
3	15	143.7	Transparent red
4	20	198.6	Transparent red
5	25	268.7	Transparent brown red
6	30	401.4	Transparent brown red
7	35	469.8	Transparent brown red
8	40	441.7	Transparent brown red
9	45	320.3	Transparent brown red
10	50	231.1	Opaque brown



3. Results and Discussion

According to the results, it can be said that in alkylbenzene C18 is shorter than the length of the chain, and the polarity of the molecule is high, which causes it to become clouded and not mixed in the base oil, and also causes carbon dioxide injection the formation of the Micelle structure becomes smaller and more unstable. But in alkylbenzene C26 due to the bonding of the carbon chain and less polarity, there was no problem in the dissolution and instability of the Micelle in this study, high efficiency sulfonation was performed and this method has the least waste and good yield. There was no waste at the stage of making linear alkylbenzene calcium sulfonate nanoparticles, and in this reaction for the first time, Ethanol was used as a green promoter; in green chemistry, we are looking for ways to reduce and prevent pollution in the environment. Green chemistry tries to develop a pathway to design and modernize products and processes that eliminate or reduce environmental damage[38]. Research in Green Chemistry to reduce energy use to produce manufactured products The requirement for drugs, colors and other chemical products [29] or to reduce the damage to the materials and processes used in the production of these products, in the book Anastas & Warner, the 12 principles referred to the 12 principles of Green Chemistry and one of its most famous principles is the use of solvents and healthier reaction conditions [30] that the replacement of green solvents rather than toxic organic solvents and volatilization is very important among the Ethanol green promoters due to the cheap and easy to prepare and availability and non-renewable, and has no pollution for the environment.

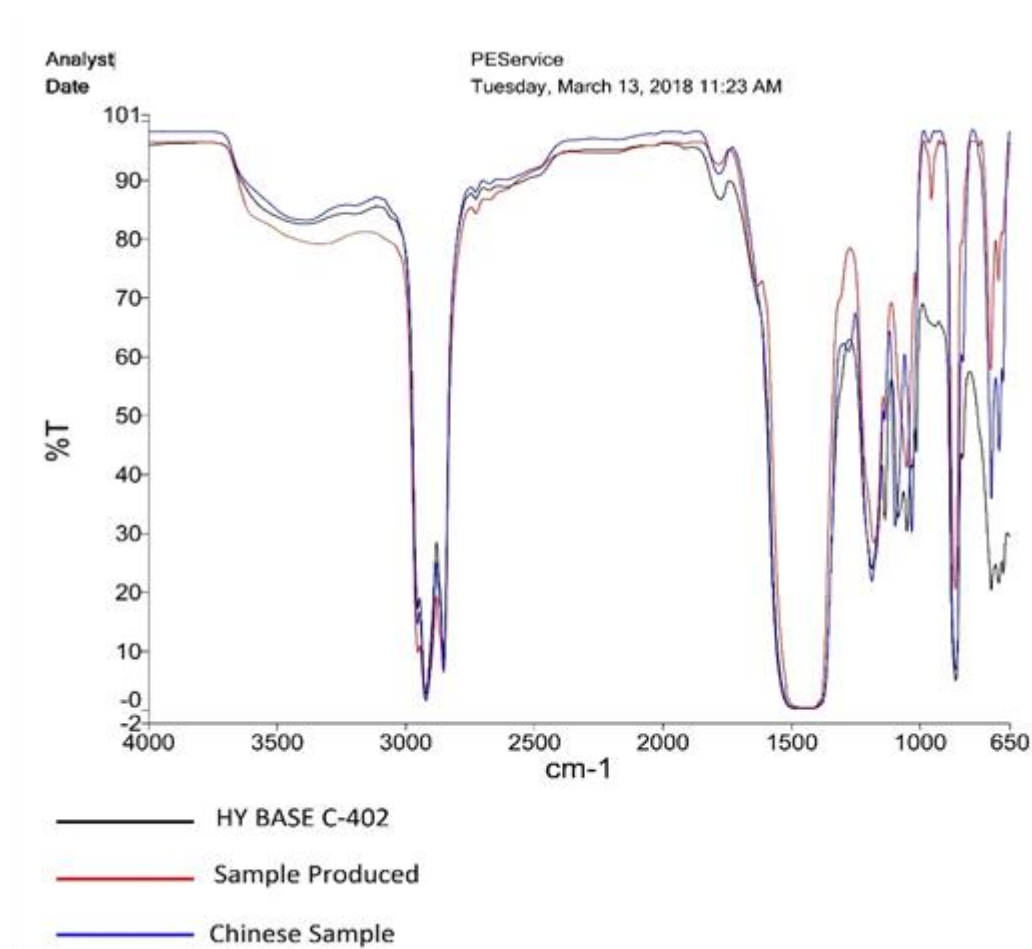
In this method, the TBN for the final product was 469.8 and the percentage of calcium was also determined by elemental analysis (17.4%). As you can see in Table 4, the results of this study are compared with several other studies.

Table 4: Comparison of several examples of research done

TBN (mg KOH/g)	% Ca (w/w)	€Solvent	reference
274	30.4	Monoethanolamine	[31]
from 300 to 420	--	n-Butanol	[32]
416	about 15.5	(NH4)2CO3	[33]
400	---	Methanol	[34]
469.8	17.4	Ethanol	In this study

The product was compared using a FT-IR device with two commercial samples (HY BASE C-402) and (Chinese Sample, and it was found that the sample was made both in terms of color and in terms of the spectrum given completely with the sample HY BASE C-402 (Chemtura) is the same. The product was also tested for stability. This test was carried out using standard ASTM D2273 method, which showed no sediment.

Also, FT-IR spectrum was taken from them and compared with each other. Which shows that the sample made with the Chemtura sample is very similar



Scheme 4. FT-IR spectrum

In this study, high efficiency sulfonation was performed and this method has the least waste and good yield. There was no waste at the stage of making linear alkyl-benzene calcium sulfonate nanoparticles, and the Ethanol was used as a green promoter, following the twelve principles of green chemistry. In this study, we collected all waste deposits and placed them in a furnace at 500 °C to remove water and organic compounds, and again used it for the

reaction, and did not cause any disturbance in the final results and was like a pure CaO sample.

Acknowledgments

In this research, we thank Mr. Seyed Ali Shahmoradi, CEO of Raysun Oil Co., for financial support. We also appreciate the of the unit of repair and maintenance that helped us in construction of sulfonation set up.

References

- [1] Kosswig, K., *Surfactants, Ullmann's Encyclopedia of Industrial Chemistry, Electronic Release*. 2000, Wiley-VCH, Weinheim.
- [2] Rapaport, R. Eckhoff, W. *Environ. Toxicol. Chem.*, **9**, 1245 (1990).
- [3] Belanger, S. E., et al., *Chemosphere.*, **155**, 18 (2016).
- [4] Asok, A.K. and M. Jisha, *Water. Air. Soil. Pollut.*, **223**, 5039 (2012).
- [5] Smith, M.B. and J. March, *March's advanced organic chemistry: reactions, mechanisms, and structure*. 2007: John Wiley & Sons.
- [6] Dado, G.P., E.A. Knaggs, and M.J. Nepras, *Sulfonation and sulfation*. Kirk-Othmer Encyclopedia of Chemical Technology, 2006.
- [7] Appel, R. Senkpiel, W. *Chem. Ber.*, **91**, 1195 (1958).
- [8] Spitz, L., *Soaps and Detergents. A Theoretical and Practical Review*. 1996, AOCS.
- [9] Farmer, D.E., et al., *Sulfonation process for viscous sulfonic acid*. 1992, Google Patents.
- [10] Adami, I., *Tenside. Surfact. Det.*, **41**, 240 (2004).
- [11] Katukiza, A., et al., *J. environ. manage.*, **146**, 131 (2014).
- [12] Sanchez, M. Rivero, M. Ortiz, I. *Desalin.*, **262**, 141 (2010).
- [13] Barışçı, S. et al., *Desalin. Water. Treat.*, **57**, 11375 (2016).
- [14] Saumya, S., et al., *J. Clean. Prod.*, **91**, 235 (2015).
- [15] Santasmasas, C., et al., *conserv. recycl.*, **72**, 102 (2013).
- [16] Gabarró, J., et al., *Environ. technol.*, **34**, 1385 (2013).
- [17] Eriksson, E., *Ecol. eng.*, **35**, 661 (2009).
- [18] Carey, F.A. and R.J. Sundberg, *Advanced organic chemistry: part A: structure and mechanisms*. 2007: Springer Science & Business Media.
- [19] Carvalho, J. M. F. *HOLOS*, **33**, 116 (2017).
- [20] Hudson, L., Eastoe, J. Dowding, P. *Adv. colloid. interface. sci.*, **123**, 425 (2006).

- [21] A. Sharifi, L. Hajiaghababaei, S. Suzangarzadeh, M. R. Jalali Sarvestani, *Anal. Bioanal. Electrochem.*, **9**, 888 (2017).
- [22] Best, R.D. and J.F. Brument, *Coating compositions*. 1994, Google Patents.
- [23] Cizaire, L. *Tribol. Lett.*, **17**, 715 (2004).
- [24] Topolovec-Miklozic, K. Forbus, T. R. Spikes, H. *Tribol. Lett.*, **29**, 33 (2008).
- [25] Galsworthy, J. Hammond, S. Hone, D. *Curr. Opin. Colloid. Interface.*, **5**, 274 (2000).
- [26] Van Dam, W., et al., *TBN Retention-Are We Missing the Point?* 1997, SAE Technical Paper.
- [27] Redmore, D. Welge, F. T. *Magnesium carboxylate-sulfonate complexes*. 1977, Google Patents.
- [28] Dua, R., *Middle East. J. Sci. Res.*, **11**, 846 (2012).
- [29] R. Ahmadi, M. R. Jalali Sarvestani, *Iran. Chem. Commun.*, **7**, 344 (2019).
- [30] Anastas, P. N. Eghbali, *Chem. Soc. Rev.*, **39**, 301 (2010).
- [31] Beşergil, B., A. Akın, S. Çelik, *Ind. Eng. Chem. Res.*, **46**, 1867 (2007).
- [32] Du, L., *Ind. Eng. Chem. Res.*, **52**, 10699 (2013).
- [33] Pu, Y., *A. I. Ch. E. J.*, **63**, 3663 (2017).
- [34] Chen, Z. *J. Colloid. Interface. Sci.*, **359**, 56 (2011).