



PRODUCTION OF THE ANIONIC SURFACTANT FROM SOAPSTOCK OF THE SUNFLOWER OIL

Kozeta VASO¹, Mevlude DEMA¹ and Jozefita MARKU²

1 Chemistry Department, 2 Industrial Chemistry Department, Faculty of Natural Sciences, University of Tirana, Albania. E-mail: kozeta_v@yahoo.it

SYNOPSIS

Key words:

Soapstock, triglycerides, soap, anionic surfactant, detergents, free fatty acids, sunflower oil.

We report a simple method that efficiently saponifies completely all glycerides, free fatty acids and phosphoglycerides in the soapstock of sunflower oil. The saponification reaction was substantially complete within 2h at 90-95°C. We may use the soap that is prepared in this case as an anionic surfactant in detergents. The detergents, that have in their recipe anionic surfactant coming from soapstock of the sunflower oil, are more biodegradable and have a lower production cost. So all the available soapstock derived from sunflower oil can be put to beneficial use.

INTRODUCTION

The global consumption of edible oils has been increasing. In addition, consumers have become increasingly conscious of their diets, resulting in an ever-growing demand for higher-quality oils. To meet this requirement, the oils must be well refined. Some substances such as lecithin and free fatty acids present in the crude oil are responsible for rancidity. The oil-refining process usually results in a non-negligible amount of a by-product called soapstock (more than 25 tons soapstock of sunflower oil are produced annually in the Albania).

Soapstock, a by-product of the refining of vegetable oils is formed in the alkalizing operation during the oil-refining process, using either NaOH or a mixture of NaOH and Na₂CO₃. Soapstock as a lipid-rich by-product produced during vegetable oil refining process, especially sunflower soapstock is alkaline aqueous emulsion of lipids containing about 50% water, with free fatty acids, phosphatides, triglycerides, pigments and other minor non-polar compounds. Soapstock is generated at a rate of about 6% of the volume of crude oil refined. Its market value is about one-tenth the price of crude vegetable oil (Haas et al., 2001).

Although soapstock was underused and has found limited uses in the past, its applications are now expanding. Most soapstock goes into animal feedstuffs, and the use of acidulated soapstocks in poultry nutrition as an additional fat source (Daniels, 1997). Conversely a wide market currently exists for their methyl and ethyl esters for such uses as cosmetics, metalworking, and in the textile industry. Recently, conversion of the soybean soapstock into biodiesel, a less expensive diesel fuel substitute, has also been described (Haas et al., 2001). Soapstock of vegetable oils is a potential biodiesel feedstock is one of the most promising candidates for biodiesel production because of its easy collection (Park et al., 2008), (Wang et al., 2007). Acid oil is also a possible feedstock for biodiesel. Acid oil is prepared from typical industrial processing of soapstock by acidulation, wherein sulfuric acid and steam are employed to achieve partial acid hydrolysis or removal of the triglyceride and phosphatide ester bonds of soapstock.

This study, presents experimental results of the completely saponification of all glycerides, free fatty acids and phosphoglycerides in the soapstock of sunflower oil. From the saponification reaction the soap (anionic surfactant) is manufactured. The soap that is prepared in this case it's used as an anionic surfactant in powder detergents (as a partial replacement of the anionic surfactant of powder detergent), also the soapstock an environmental polluter for the refinery was reduced.

MATERIAL AND METHOD

1. Samples of sunflower soapstock are taken periodically within two years. The samples taking and their analyses are made according to the respective methods (Firestone, 2003; Pavia, 1994).

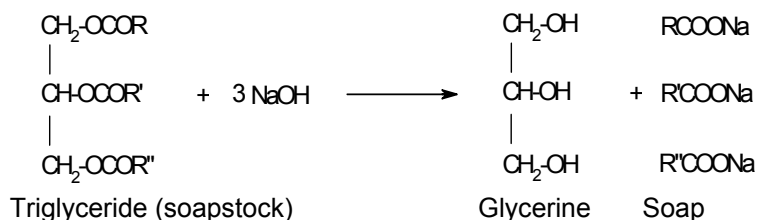
1.1 Experimental estimation of the saponification value (sv). Into a 250-mL round-bottomed flask equipped with a reflux condenser, 2 g of soapstock and 25 mL of 0.5 N ethanolic solution of KOH were charged. The mixture was stirred under reflux for 1 h. The excess of KOH was back-titrated with 0.5 N aqueous solution of HCl in the presence of 4% solution of phenolphthalein as indicator. The estimation of sv was provided by equation 1:

$$sv = (V_o - V) \times N \times M / w \quad (1)$$

Where: V_o is the volume in millilitres of the HCl solution (for the blank test); V is the volume in millilitres of the HCl solution (for the soapstock); N is the normality of the HCl solution; M is the molecular weight of KOH (56.1 g/mol); and w is the sample solution in grams.

The determination of the saponification value is essential in order to calculate the quantity of NaOH necessary for soapstock saponification. The saponification

value is referred to the dry mass (Moulay et al., 2005). The saponification reaction goes as follows:



Where the R, R', R'' are the different fatty acids radicals (Balestrini & Martinenghi, 1958). The average molecular weight of the triglyceride is taken 880 mg/mol while the soap molecular weight 908 mg all three moles. The saponification value is 220 mg KOH/g for a 100% oil content. The content of the free sunflower oil in the sunflower soapstock is 9%. The necessary weight of NaOH (56.1g KOH is equivalent with 40g NaOH) for saponification was calculated based on equation (2) and (3).

$$0.09\text{kg} \times 220\text{g KOH/kg} = 19.8\text{g KOH} \quad (2)$$

$$\text{And } 40/56.1 \times 19.8 = 14.14\text{g NaOH } 100\% \quad (3)$$

2. Saponification. Soapstock of sunflower was converted into soap (anionic surfactant). The soap production is carried out in simple equipment provided with stirrer and water bath. A quantity of sunflower soapstock is mixed with the stoichiometric quantity of NaOH. Because the soapstock has water content 60%, the NaOH is added in solid state gradually until the whole mass is dissolved. When the temperature reaches at 90°C the saponification is carried out for two hours, temperature interval 90-95°C. The saponification was controlled using phenolphthalein 1% as indicator. The reaction ends when the colour intensity of 1% phenolphthalein solution in small quantity of the mass doesn't change. The mass is taken away from the energy source and is treated with a solution of NaCl 25%. The mass stands still for the next 3 hours and after this time is put on a filter paper to dry up. The mass is further air dried up to 10% humidity. This process required three days. The yield of purified soap was 98.37% (w/w) based on the total fatty acids of the soapstock.

3. Fatty acids preparation. With a certain amount of the produced soap is carried out an experiment in order to transform it in fatty acids. The soap is dissolved in water. The water solution is further treated with the solution of H₂SO₄ at 90°C until the pH=6. Then they are rinsed with water until the pH of rinsed water reaches 7. These fatty acids are then dried. This scheme will be part of a study to produce fatty acids methyl esters FAME for biodiesel (Haas & Scott, 1996; Haas et al., 2000, 2003). At figure 1 is given the scheme of converted of soapstock in soap and fatty acids.

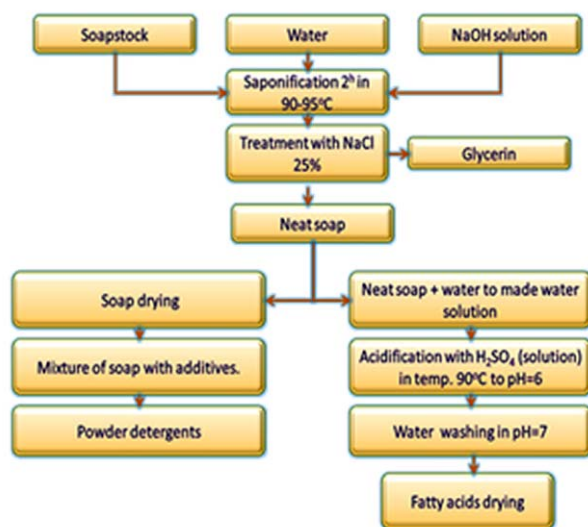


Figure 1: Scheme of converted of soapstock in soap and fatty acids.

4. In laboratory schale is experimented to produce powder detergent replacing the synthetic anionic surfactant with soap produced from sunflower soapstock. It is used the recipe of low foam forming powder detergent for washing machine. (DEKA company in Albania refines the sunflower and produces detergent as well). DEKA company imports a semi product (containing also the anionic surfactant) and carries out only the second part of the process that are mixing it with other active ingredients (additives). It is experimented in this way with the ingredients accompanying the imported semi product (**S**) from DEKA company is prepared the semi product (**P**) replacing the synthetic surfactant with the soap produced from the sunflower soapstock. The recipe of semi product for powder detergent with synthetic surfactant **S** imported from Deka Company is shown in Table 1, while table 2 gives the recipe **P** of semi product for powder detergent prepared with soap (anionic surfactant of soapstock) that has replaced the synthetic surfactant.

Table 1: Recipe of semi product for powder detergent with synthetic surfactant (**S**).

	Recipe of semi product for powder detergent S	Formulation in weight %
1	Anionic surfactant (sodium dodecylbenzene sulfonate)	12
2	Water content	5
3	Sodium tripolyphosphate STPP $\text{Na}_5\text{P}_3\text{O}_{10}$	17
4	Sodium silicate	7
5	Sodium carbonate	25
6	Sodium sulphate	33
7	CMC (60 %)	1

Table 2: Recipe of semi product for powder detergent with soap as surfactant (P).

	Recipe of semi product for powder detergent P	Formulation in weight %
1	Soap (anionic surfactant of soapstock)	12
2	Water content	5
3	Sodium tripolyphosphate STPP $\text{Na}_5\text{P}_3\text{O}_{10}$	17
4	Sodium silicate	7
5	Sodium carbonate	25
6	Sodium sulphate	33
7	CMC (60 %)	1

5. The semi product for powder detergent formulated with soap as surfactant P is analysed.

6. Mixing the semi product S and semi product P in different percentage according to table 3 the Ai formulations were prepared.

Table 3: The Ai formulations (mixing semi product S and semi product P).

Formulations	The Ai formulations %				
	A1	A2	A3	A4	A5
1/2 product for powder detergent with synthetic surfactant (S)	0	25	50	75	100
1/2 product for powder detergent with soap P	100	75	50	25	0

7. In order to prepare the whole recipe of the powder detergent, Ai formulations are mixed with some necessary additional ingredients (Meloan, 1976). At table 4 are summarized the percentage of additional ingredients. The powder detergents formulations Ai are analyzed.

Table 4: Additional ingredients for Ai formulations to prepare the whole recipe of powder detergent.

	Additional Ingredients	%
1	Sodium perborate	9
2	Defoamer	0.9
3	Perfume Zingaro 177.186	0.5

7.1 Foaming capacity. Volume of foam of powder detergents formulations Ai were estimated according (Moulay et al., 2003, 2005).

7.2 Wetting power (Moulay et al., 2005). The wetting capacities of powder detergents formulations A_i were estimated by the method depicted in figure 2. In this figure, a circular piece of cotton fabric (30mm in diameter) was allowed to sink through the detergent solution to the bottom of the beaker. The fabric was released from a point in the solution 2 cm beneath the solution surface, and the time was recorded starting from the release point (t_0) until it reached the bottom (t). The wetting capacity was estimated as the falling time $\Delta t = t - t_0$. The smaller the Δt , the better was the wetting.

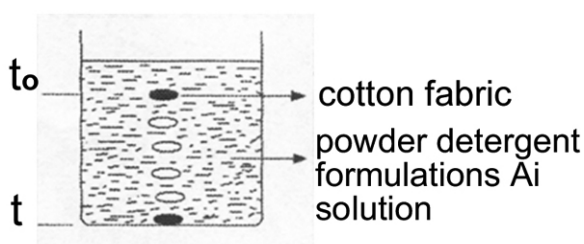


Figure 2: Device used for wetting capacity estimation.

7.3 Cleaning performance (Moulay et al., 2005). The cleaning tests for the different powder detergents formulations (A_i) using soiled white cotton fabrics (10 × 10cm) were carried out in a stainless steel drum (8.70 cm in diameter, 20.20 cm in height); the drum is fitted with an axle-arm by which it is rotated during the washing. The soils placed on the fabric were coffee soil and oil soil. The white fabric was immersed into this solution for a few minutes and dried overnight in a drying oven (temperature 50°C). The fabric specimen was inserted inside the drum containing 50 g every powder detergent formulations (A_i) with 500mL of distilled water, and the washing cycle consisted of rotating the drum for 15 min. The fabric was then removed, rinsed with cold water, air-dried for 10 min, and finally dried in a drying oven. The whiteness was determined using a digital refractometer with $BaSO_4$ as a reference. The whiteness of the cleaned fabrics was estimated against that of $BaSO_4$.

RESULTS AND DISCUSSION

Soapstock a by-product of the refining process of oilseeds to produce edible sunflower oil was converted into soap (anionic detergent). The physico-chemical characteristics of the soapstock samples were experimentally determined and are presented in Table 5.

Semi product (**P**) was prepared replacing the synthetic surfactant with the soap (anionic surfactant) produced from the sunflower soapstock table 2. Semi product P was analysed. The physico-chemical properties of semi product for powder detergent P are shown in table 6.

Table 5: Composition of soapstock samples.

Soapstock samples	Dry mass %	Free fatty acid %	Saponification value(sv) mgKOH/g	pH	Density kg/m ³ (25 °C)
Sample 1	43.9	7.9	215	8.4	912
Sample 2	30.76	10.63	227	8.2	912
Sample 3	54.76	9.8	230	8.9	913
Sample 4	54.1	7.8	208	8.4	912
Sample (final)	40	9	220	8.4	912

Table 6: Physico-chemical properties of semi product for powder detergent P.

	Description of property	Unit	Value
1	Surfactant	%	12
2	Density	g/cm ³	0.63
3	Water content	%	8
4	Phosphate	%	17
5	Active oxygen	%	8.9
6	Volume of foam	mL	260
7	Carbonate	%	24.9
8	Sodium sulphate	%	32.8

Mixing the semi product S and semi product P in different percentage according to table 3 the Ai formulations were prepared. The results of analyses of Ai formulations compared with standard are given at table 7.

Table 7: Physico-chemical properties of powder detergents formulations (Ai) and the comparison with standards.

	Description of property	A1	A2	A3	A4	A5	Standard
1	Density g/cm ³	0.63	0.65	0.64	0.65	0.64	0.6-0.7
2	Anionic surfactant %	12	12	12	12	12	10-14
3	Perborate %	8.2	8.2	8.2	8.2	8.2	6-8
5	Phosphate %	17	17	17	17	17	12-20
6	Carbonate %	24.8	25	25	25	25	25-30
7	Sulphate %	32.9	33	33	33	33	30-35
8	Water content %	8	8.1	8	8	8	10

The results for volume of foam produced from powder detergent Ai formulations are summarised at table 8.

Table 8: Volume of foam produced from powder detergents Ai formulations.

Time	Volume of foam produced mL				
	A1	A2	A3	A4	A5
0 s	260	260	180	100	130
30 s	250	250	300	310	360
180 s	220	230	245	280	310
300 s	190	200	225	230	265

A5 formulation is an anionic powder detergent 100%. These results from table 8 indicate that the A1, A2, A3 and A4 formulations foamed less than an anionic powder detergent. This low foaming suggests that these formulations may be used in washing-machine laundry applications. The best formulations are A3 and A4.

The results of wetting power of Ai formulations are shown in Table 9. It is well known that wetting power is a property that determines the efficacy of a surfactant solution in soil removal. Easier soil removal is partially a result of a good wetting of the substrate by the surfactant solution. The wetting capacities of the formulations A3 and A4 were generally better than that of the standard one, as shown in Table 9. In addition, it is not surprising to note that the higher the concentration of the formulation, the better is the wetting power.

Table 9: Results of wetting power of powder detergents Ai formulations.

Concentration g/L	Δt (s)					
	A1	A2	A3	A4	A5	Standard
5	10	10	9.5	8	6	≤ 10
4.5	11.5	11.5	10	9	7	≤ 11.5
3.5	13	12.5	12	11	9	≤ 13
3	13.5	13	12.5	12	11	≤ 13.5

The different powder detergents formulations (Ai) were tested for the cleaning performance. The results of cleaning performance of powder detergent Ai formulations are shown in Table 10

The powder detergents Ai formulations were subjected to a washing performance the results are given in Table 10 and are expressed as the degree of whiteness of the soiled cotton fabric.

The washing performance of powder detergents Ai formulations was less than moderate, and they were lower than that of a powder detergent formulation.

Table 10: Results of cleaning performance of powder detergent Ai formulations.

	A1	A2	A3	A4	A5 Anionic detergent powder
Whiteness of the soiled fabric (%)	36.80	34.40	33.10	31.62	30.22
Whiteness of the washed fabric (%)	47.20	46.20	48.60	51.52	57.62
Washing performance (%)	10.40	11.80	15.50	19.90	27.40

For the detergents series cost account is made too. Comparing the price of the semi product it is possible to find the price of synthetic surfactant. The price of the semi product S corresponds to the best quality. The price of the soap prepared from the soapstock is also accounted. (Anionic surfactant) The values are given in the table 11 and fig. 3. In addition, it is not surprising to note that the higher the concentration of the soap prepared from soapstock in formulation, the cheaper is the price of powder detergent, but the best quality detergent will be that which has the standard parameters.

Table 11: Price for synthetic anionic surfactant and soap (anionic surfactant prepared from soapstocs).

	KINDS OF ANIONIC SURFACTANT	Price (Euro/kg)
1	Soap (anionic surfactant prepared from soapstock, our product)	0.093
2	Synthetic anionic surfactant (market)	0.478

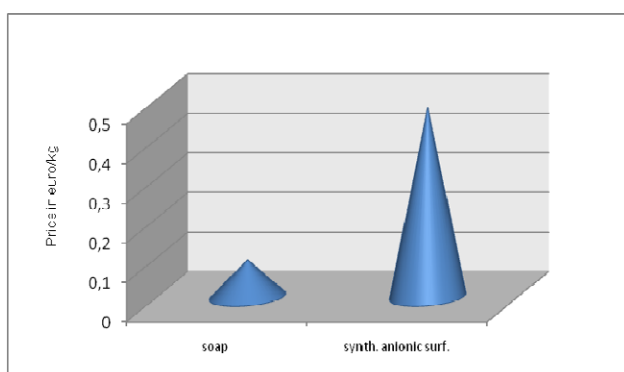


Figure 3: Price for synthetic anionic surfactant and soap.

CONCLUSIONS

The results of the present investigation have shown the possibility of converting of the soapstock in soap. The use of sunflower soapstock to produce

anionic surfactant and than its use as partial replacement in powder detergents was theoretically supported and practically confirmed.

The soapstock of vegetable oils is an environmental polluter especially for the refinery. This study is very important to eliminate the pollution around the refinery. Its disposition is essential to the continuous operation of the refinery.

To produce soap (an anionic surfactant) from sunflower soapstock the optimal processing conditions are:

- Saponification temperature 90-95°C.
- Saponification time 2 hours.
- The quantity of NaOH used for saponification must be equal to the reaction stoichiometric in order to avoid the presence of an excess of NaOH which may damage the fabrics during washing.
- The process scheme is simple and realizable.

The Na soap may substitute the anionic surfactant at the detergents. The powder detergent formulations A_i with the best washing characteristics is that in which 50% and 25% of anionic surfactant is replaced by soap (A₃ and A₄ formulations)

The use of soap as a component in detergents has an economical effect since it reduces the expenses of raw material. The synthetic anionic surfactant is 5 time more expensive than soap prepared from soapstock.

The soap produced by the soapstock used as a substitute of the anionic surfactant at the detergents is biodegradable. Biodegradation describes how organic (carbon-containing) detergent ingredients, like surfactants, enzymes and fragrances, are broken down into carbon dioxide, water and minerals by the action of microorganisms such as bacteria. This process reduces the amount of detergent ingredients discharged into the environment to such levels that are harmless to fish or other aquatic life.

As soap (soap produced from soapstock) can not be used because of its objectionable smell. The fragrances and other ingredients in powder detergents remove this smell.

Soapstock from vegetable oils is also a possible feedstock for biodiesel, in the manufacture of liquid soap etc. This study must be carry on further. The acid oil produced would be as a source of industrial fatty acid.

ACKNOWLEDGMENTS

The authors thank DEKA company and its laboratory staff for their help in providing us with the basic raw materials, for technical assistance.

REFERENCES:

- BALESTRINI, G. & MARTINENGI, B.G. 1958: Caratteri Specifici, Dei Principali Oli Vegetali Del Comercio. - *Verlag Tipografia U. Allegretti di Campi*, Milano, 71 pp.
- DANIELS, S.R. 1997: Soapstock Utilization, An Environmental-Agricultural Breakthrough. - *AGROTECH, INC.* Sherman, Texas USA. Presented at the American Oil Chemists' Society Annual Meeting Seattle, Washington 12 May, pp: 112-114.
- FIRESTONE D. 2003: Official methods and recommended Practices of the AOCS, 5th Edition - *American Oil Chemists' Society*, 1200pp.
- HAAS, M.J. & SCOTT, K.M. 1996: Combined Nonenzymatic-Enzymatic Method for the Synthesis of Simple Alkyl Fatty Acid Esters from Soapstock. - *Journal of the American Oil Chemists' Society*, 73: 1393-1401.
- HAAS, M.J., BLOOMERB, S. & SCOTT. K.M. 2000: Simple, High-Efficiency Synthesis of Fatty Acid Methyl Esters from Soapstock. - *Journal of the American Oil Chemists' Society*, 77 (4): 373-379.
- HAAS, M.J., SCOTT, K.M., ALLEMAN, T.L. & McCORMICK, R.L. 2001: Engine Performance of Biodiesel Fuel Prepared from Soybean Soapstocks: A High Quality Renewable Fuel Produced from a Waste Feedstock. - *Energy Fuels*, 15: 1207.
- HAAS, M.J., MICHALSKIA, P.J., RUNYONB, S., NUNEZA, A. & SCOTT. K.M. 2003: Production of FAME from Acid Oil, a By-product of Vegetable Oil Refining. - *Journal of the American Oil Chemists' Society*, 80 (1): 97-102.
- MELOAN, C.E. 1976: Detergents-Soaps and Syndets. - *Journal of The American College of Toxicology*, 49(7): 6-10.
- MOULAY, S., HALIM, B. & MOHAMED, A. 2003: Algerian Montmorillonite as a Builder in a Detergent Powder. - *Journal of Surfactants and Detergent*, 6: 113-118.
- MOULAY, S., ZENIMI, A. & DIB, M. 2005: Rosin/Acid Oil-Based Liquid Soap. - *Journal of surfactant and detergents*, 8 (2): 169-174.
- PAVIA, L.D. 1994: Introduction to Organic Laboratory Techniques. - *Edizioni SORBONA* Milano, Sr.I., pp: 106-117.
- PARK, Ji-Y., KIM, D-K., WANG, Zh-M., LEE, J-P., PARK, S-Ch. & LEE, J-S. 2008: Production of biodiesel from soapstock using an ion-exchange resin catalyst. - *Korean Journal of Chemical Engineering*, 25(6): 1350-1354.
- WANG, Zh-M., LE, J-S., PARK, Ji-Y., WU, Ch-Zh. & YUAN, Zh-H. 2007: Novel biodiesel production technology from soybean soapstock. - *Korean Journal of Chemical Engineering*, 24 (6): 1027-1030.

Original research article

Received:31 July 2010.

