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Use of Waste Cooking Oil in the Manufacture of Soaps

H. Sanaguano-Salguero[1], A. Tigre-León[2] and **I.F. Bayas-Morejón[2]**

[1] Centro de Investigación del Ambiente, Carrera de Ingeniería Agroindustrial, Departamento de Investigación, Universidad Estatal de Bolívar,
EC-020150, Guaranda-Ecuador.
E-mail : hrosario@hotmail.es

[2] Centro de Investigación y Desarrollo Biotecnológico, Carrera de Ingeniería Agroindustrial, Departamento de Investigación, Universidad Estatal de Bolívar,
EC-020150, Guaranda- Ecuador.
E-mails: roan_t@yahoo.es; fbayas@ueb.edu.ec

ABSTRACT

This research was conducted with the aim of recover waste cooking oil and its subsequent transformation into soaps using two endothermic and exothermic processes. The oils in admixture had acceptable saponification values to be processed into soap. Soaps obtained had acceptable TFM, moisture and pH values and were comparable to the control soaps (Palmolive, Dove and Protex). The treatment $A_2B_2C_1$ (Endothermic method + 15% NaOH + 12 h molding time) was considered the best of the treatments with 84.34% in performance and 5.47 cm^2 in fat removal area analysis. The use of waste cooking oils could be an alternative in the manufacture of soap, reducing in part the environmental contamination.

Keywords: Use; waste cooking oil; soap

Journal of Economic Literature (JEL) Classification : Q13, Q52

1. INTRODUCTION

Soap is a hydroxide base (Na or K) of naturally occurring fatty acids, that is produced by saponification or basic hydrolysis reaction of oils or fats (Betsy *et al*., 2013). The soap is perhaps the oldest detergent known to humans. For its chemical proprieties as anionic surface agent, and the presence of fatty acids as: lauric, stearic, myristic, palmitic and oleic acids contribute to the cleaning and washing properties of this (Onyango *et al*., 2014; Betsy *et al*., 2013). Nowadays, with increasing demands of cooking oil, the waste level has been increasing. The discharge of cooking oil residues into the water contaminates the flora and fauna of rivers and lakes, as this is floating on the surface and does not allow oxygenation, preventing the passage of sunlight and suffocating the photosynthesis, caused the death of aquatic animals and plants (Okafor, 2011; Omodanisi *et al*., 2011). A spill of used oil as tiny as 1 L can contaminate a million liters of fresh water. So that, the recycling of waste cooking oil is becoming a viable alternative in mitigating the environmental and ecological problems (Singh-Ackbarali *et al*., 2017; Sanaguano *et al*., 2017). In addition, the improper use of water has a high dispersion especially in the regions where the amounts

of water resources per capita is less than 3000 m^3 (Yagi *et al*., 2014). Animal fats and oils from Petroleum and vegetable oils share common physical properties producing similar environmental effects (EPA 2015, Rodewald, 2015).

Saponification of oils is the operation in which ethanolic KOH reacts with oil to form glycerol and fatty acids (Salimon et al., 2012), for which, in the soaps production is advisable to consider the amount of soda present in the oil or fat, so, a saponification value sample is previously performed. Saponification values are expressed by potassium hydroxide in mg required to saponify one gram of fat. It depends on the kind of fatty acid contained in the oil; the saponification reaction can be by endothermic or exothermic process (STM, 2012).

Cold process soap making (Exothermic). This reaction may occur spontaneously and result in higher randomness or entropy ($\Delta S > 0$) of the system. They are denoted by a negative heat flow (heat is lost to the surroundings) and decrease in enthalpy ($\Delta H < 0$), in the soap manufacturing, this process involves combining natural oils (coconut, palm, olive or butter), hydroxide and water. Typically, the soap is left to harden overnight (Helmenstine, 2017; Ruiz, 2008). After this process, the texture of soap could be being very smooth or fine, typically, only 95% of the oils are converted into soap; the other 5% of the oils remain in the soap to add to the excellent conditioning qualities of soap (Warra *et al*., 2011).

Hot process soap making (Endothermic). In endothermic reactions does not occur spontaneously, if a reaction absorb energy, a temperature drop occurs in the reaction, giving rise to a positive heat flux and an increase enthalpy ($+\Delta H$) (Helmenstine, 2017). In this sense, the process for hot soap elaboration is like the exothermic process up to the point where the mixture has an accepted consistency. When it cools down it hardens and can be used immediately without curing. The texture of endothermic soap is not quite as fine or smooth as soap made by the exothermic method, but it is still smooth (Ruiz, 2008).

The chemical characteristics of soap depend of: the type of oil used, purity of alkali, capacity of saponification and age of the soap. Among the chemical characteristics, include moisture content, total fatty matter (TFM), pH, and others (Tarun *et al*., 2014; Betsy *et al*., 2013).

Considering the previously described, the objective of this work was to take advantage of waste cooking oils, manufacturing soap by saponification with the application of cold and hot process.

2. GENERATION OF THE DATA

2.1. Sampling

A total of 13 fast-food restaurants were sampled in the Guaranda, Ecuador between November 2012 and February 2013. The samples were stored in previously labeled tanks, and preserved under room temperature until to the analysis. Were used three commercial soaps as controls (Palmolive, Dove and Protex).

2.2. Determination of saponification value

The determination of saponification value was according to the methods AOAC, 1993 and ISO 3657, 2013. Approximately 2 to 5 g of oil sample were added into a 250 mL conical flask, then, were added 25.0 mL of 0.5 mol/L potassium hydroxide, and fix a cooling pipe to the flask. The flask was gently heat,

occasionally shaking while adjusting the heat so that backflow ethanol will not reach the top of cooling pipe. After heated for 30 minutes, immediately was cooled it, and titrated with 0.5 mol/L HCl before the test liquid is solidified. The saponification value was obtained with the formula:

$$SpV = \frac{56.1\ (RAB - RAS)\text{xN}}{Wo}$$

SpV= Saponification value, *RAB* = Required acid "HCl" by blank (mL), *RAS*= Required acid "HCl" by sample (mL), N= Normality of the standard HCl, *Wo*=weight of the oil (g).

2.3. Soap preparation

The soap was prepared according to the ingredients formulated from the block design with factorial arrangement AxBxC, where, A = Methods (A_1: Exothermic and A_2: Endothermic), B= Percentage of NaOH (B_1: 10%, B_2: 15% and B_3: 20%), C = Molding time (C_1: 12 h and C_2: 24 h). The soap from waste cooking oil was formulated using a mixture of oils, with additional ingredients by the saponification process. The methods from **Mak-Mensah and Firempong, (2011)** were modified and used for the soap preparation. The experimental design combination is shown in the following table.

Table 1. Experimental design combinations

Combinations	Description
$A_1B_1C_1$	Exothermic + 10% NaOH + 12 h
$A_1B_1C_2$	Exothermic + 10% NaOH + 24 h
$A_1B_2C_1$	Exothermic + 15% NaOH + 12 h
$A_1B_2C_2$	Exothermic + 15% NaOH + 24 h
$A_1B_3C_1$	Exothermic + 20% NaOH + 12 h
$A_1B_3C_2$	Exothermic + 20% NaOH + 24 h
$A_2B_1C_1$	Endothermic + 10% NaOH + 12 h
$A_2B_1C_2$	Endothermic + 10% NaOH + 24 h
$A_2B_2C_1$	Endothermic + 15% NaOH + 12 h
$A_2B_2C_2$	Endothermic + 15% NaOH + 24 h
$A_2B_3C_1$	Endothermic + 20% NaOH + 12 h
$A_2B_3C_2$	Endothermic + 20% NaOH + 24 h

The oils were weighed in a relation of 50% oil with 50% water and heated at 75°C for endothermic treatments with continuous stirring, using an overhead stirrer (IKA RW 20 Digital, Nara, Japan). The temperature of the soap mixture in the exothermic treatments was not below to 71°C.

The saponification reaction was initiated by adding the NaOH according the concentration of each treatment along with EDTA. NaOH pellets were added gradually while stirring until completion of saponification.

The temperature of the mixture cooled to 50°C, where other necessary ingredients were added such as glycerin, and the temperature was then further cooled to 40°C. After, the salt was added to separate the spent lye in the bottom, while saponification mass floats on the surface to reduce the soap viscosity and to separate the glycerol water in the bottom. The glycerol water was isolated by siphoning. Therewith, the soap paste was washed again by 5% of hot water at 80°C to reduce excess sodium hydroxide and any impurities found in the soap paste. The soap obtained was washed with 10 mL of

distilled water, filtered using a linen cloth, air-dried, then 50g of the soap paste was molded using a plastic mold and allowed to cool at room temperature (between 6ºC and 16ºC) at 12-24 h, according to the corresponding treatment before demolding. The finished molded soap samples were each cut to dimensions of 3 cm breadth, 5 cm length, and 1 cm height. The finished soap samples were air-dried on plastic trays and conditioned at ambient temperature (5-12°C) for 2 weeks before they were analyzed.

2.4. Soap analysis obtained (all treatments)

Determination of total fatty matter (TFM)

A modified method from **Roila *et al.* (2001)** was used. The total fatty matter in the soaps was calculated using the relation.

$$TFM\ (\%) = \frac{(PDS - PDE)}{ISS * 100}$$

Where: TFM= total fatty matter, PDS= weight of the porcelain dish + soap (g) after drying; PDE= weight of the porcelain dish empty (g); ISS= weight of the initial sample of soap (g).

Moisture Content

Approximately 5 g of samples was accurately weighed using analytical balance (sensitivity 0.1 mg) into dried, the moisture was determined in an infrared analyzer (Mettler Toledo, HE53, Switzerland).

Determination of pH

Ten grams of the crushed soap was weighed and dissolved in distilled water in a 100mL volumetric flask. This was made up to prepare 10% soap solution. The pH of the soap solution was determined using a pH meter (Metrohm Herisau, Mod. Y-510, Switzerland).

Determination of fat removal area

Three grams of soup was weighed and dissolved in 300 mL of distilled water at 25-30ºC, and then a slide greased was submerged into the soap solution for 10 minutes, according to the methods descripted by **Kozlik and Diebold, (1943)**. Finally, the fat removal area was measured with a caliper.

Determining % foaming

This analysis was developed using the method **(Mishra, 2010)**. Sixteen mL of water was deposited in a flask and 8 g of soap were dissolved in the mixture. Then, was warmed the contents to get a solution. One mL of soap solution was deposited into a test tube with 3 mL of water, was closed the mouth of the test tube and was shaken vigorously for a minute. Finally, was activated the timer immediately and notice the rate of disappearance of 2 mm of froth, also was measured the initial and final volume of the froth.

Performance analysis

The performance of soap was carried out by the application of the formula:

$$P = \frac{MOx100}{ME}$$

Where: P = Performance; MO= Matter out; ME= Matter enter

2.5. Statistics analysis

INFOSTAT program was applied to the variance analyzes comparison of means according to Tukey. Values show a 95% of values trust **(Hsieh *et al.*, 2013)**.

3. RESULTS

3.1. Determination of saponification value

The saponification value (Sv) carried out on the waste cooking oil showed a value of 187.5 mg NaOH/g oil.

3.2. Analysis of soap obtained

TFM, moisture and pH analysis

The results of chemical analysis reflecting the characteristics of the soap are shown in the table 2. These results were compared with parameters of 3 toilet soaps.

Table 2. Chemical characteristics of the prepared soap

	Soap from waste cooking oil		
Tratamientos	TFM	Moisture	pH
$A_1B_1C_1$	63.45 a	43.24 f	11.20 a
$A_1B_1C_2$	65.12 a	24.90 a	11.00 a
$A_1B_2C_1$	63.25 a	42.51 f	11.30 a
$A_1B_2C_2$	65.14 a	33.34 d	11.00 a
$A_1B_3C_1$	65.54 a	34.87 e	11.00 a
$A_1B_3C_2$	64.03 a	26.77 bc	10.98 a
$A_2B_1C_1$	63.18 a	27.08 bc	10.20 a
$A_2B_1C_2$	65.01 a	26.93 bc	10.40 a
$A_2B_2C_1$	63.82 a	27.50 c	10.00 a
$A_2B_2C_2$	63.58 a	27.90 c	9.96 a
$A_2B_3C_1$	64.13 a	26.73 bc	10.00 a
$A_2B_3C_2$	65.05 a	25.73 ab	10.00 a
Dove	64.12	32.23	7.42
Palmolive	63.51	34.11	8.90
Protex	63.22	29.55	7.30
Norm	76 (INEN 823)	20-35 (INEN 0841)	------

Means with common letter are not significantly different (p < = 0.05)

In the table 2, the total fatty matter values (TFM) were between 63.18 and 65.54 %. From the results, the pH values ranged between 9.0 and 11.

Fat removal area, foaming, and performance analysis

Table 3. Determination of fat removal area

	Soap from waste cooking oil		
Treatments	Fat removal area (cm^2)	Foaming (%)	Performance (%)
$A_1B_1C_1$	2.80	51.34 a	71.82
$A_1B_1C_2$	5.07	41.64 bc	71.82
$A_1B_2C_1$	2.20	39.12 c	74.31
$A_1B_2C_2$	4.60	33.83 c	74.31
$A_1B_3C_1$	3.07	47.98 ab	78.25
$A_1B_3C_2$	3.80	37.00 c	48.25
$A_2B_1C_1$	2.33	36.10 c	78.20
$A_2B_1C_2$	1.93	35.98 c	80.03
$A_2B_2C_1$	5.47 a*	35.11 c	84.32 *
$A_2B_2C_2$	4.43	37.61 c	83.78
$A_2B_3C_1$	5.17	36.70 c	83.75
$A_2B_3C_2$	4.80	36.70 c	81.89
Dove	3.20	42.13	82.15
Palmolive	3.80	39.92	82.74
Protex	3.00	45.12	82.86

Values with common letters are not significantly different (p <= 0.05)
** Best treatment*

By analyzing fat removal was found that treatment ($A_2B_2C_1$) showed the larger area of fat removal with 5.47 cm^2, followed by treatment ($A_2B_3C_1$) with 5.17 cm^2; ($A_1B_1C_2$) with 5.07 cm^2; ($A_2B_3C_2$) with 4.80 cm^2; ($A_2B_2C_2$) with 4.43 cm^2, in these treatments no significant statistical difference, while the other treatments were less than 4 cm^2.

In the analysis of percentage of foam generated the treatment ($A_1B_1C_1$) was the best with 51.34% fat removed, followed by treatment ($A_1B_3C_1$) with 47.98%, there was significant statistical difference in these two treatments.

The performance analysis showed that the treatment $A_2B_2C_1$ (Endothermic method + 15% NaOH + 12 h molding time) was the best with 84.32%, followed by treatments $A_2B_2C_2$ and $A_2B_3C_1$ with 83.78% and 83.75% respectively.

It is of great importance to know; the fat removal area and performance were the parameters that prioritize the best method to obtain soap.

4. DISCUSION AND CONCLUSION

Saponification value was similar to others obtained from sunflower oil (188.7) and olive oil (192), but high than that of beewax (93.0) (**Mabrouk, 2005**), value of 153.8 in Sv of corn oil was obtained by **Zahir *et al*., (2014),** which are commonly used in soap manufacturing. Saponification value is within the established parameters this indicates that the oil could be used in soap making. It could also substantially be used in the preparation of cosmetic products **(Warra *et al*., 2010)**.

According to the norm INEN 823 (1982) between 63 and 66 are the recommended values to TFM. Statistically there is no difference between the treatments, our results were found to be similar than the controls and to those obtained by **Betsy *et al*. (2013)** (60% in lux soap and 65% in Breeze soap) other similar value was obtained by **Mak-Mensah *et al*. (2011)** with 63.75 ±0.07%, but our results were lower to the result obtained by **Taiwo *et al*. (2008**) (70%). These differences in the TFM are due to high

moisture concentrations and the kinds and quantities of the used fatty materials and perhaps to the difference in the saponification method.

The moisture content was similar to the recommended by the norm INEN 0841 (20-35%), statistically have been different. The moisture content of the soap found in the current work was similar to the controls, and was higher than that (12.63±0.04%) **Mak-Mensah *et al*. (2011)**. This value may be due to the difference in the soap preparing methods.

Vales of pH are consistent with the normal pH range for soap 9-10 **(Tarun *et al*., 2014)**, a pH value of 10.4 ±0.04 was obtained by **Mak-Mensah *et al*. (2011**), and the values are slightly higher than controls. This high value is due to incomplete alkali hydrolysis resulting from the saponification process. It can be overcome by the addition of excess fat or oil or any other super fatting agent to reduce the harshness of the soap **(Warra *et al*., 2011)**.

In conclusion, in this study the chemical characteristics of obtained soap showed values according to the norms and soap controls; the treatment $A_2B_2C_1$ was the best treatment in performance and fat removal area parameters. This work shows that the waste cooking oil could be used to make soaps with favorable characteristics to industries, as an alternative to use of this waste to partially mitigate the negative effects on environment.

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