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QUANTITATIVE ASPECTS IN THE SAPONIFICATION OF COCONUT OIL BY THE COLD PROCESS

Julian A. Banzon
Emeritus Professor of Food Science and Technology
University of the Philippines at Los Baños
College, Laguna, Philippines

ABSTRACT

In cold-process saponification of coconut oil (CNO), the quantity of soap desired is dependent largely on the selected weight of CNO. All quantities involved whether reactants or products are calculable in terms of CNO. In actual practice the alkali (NaOH), is always in solution of percentage concentration p. It is shown that proper selection of p leads to desired values of quality indices like anhydrous soap content, percentage moisture, fatty acid content, etc. When p=21.7, one unit of CNO yields 1.85 units of soap of moisture content 36% and anhydrous soap content of 56.4%; when p=17.8%, one unit of CNO yields 2.35 units of soap which can meet specs (36% H_2O; 40% FA) and can take in about 13% fillers.

Introduction

This study is about soap making, a process that goes back to antiquity (1). So what can be new?

It appears that making soap developed in countries where the oil/fat raw material is of animal origin: beef fat (tallow), pork fat (lard), kitchen grease, whale oil (5,7). The alkali came from wood ash leachings. The animal fats were not too reactive; they had to be boiled with the alkali solution. Even with the later availability of NaOH, the fats still required the boiling procedure. Refinements in the art came in the form of purification of the crude soap formed by "salting out". Thus, the so-called full-boil process developed. (7,8,10).

When coconut oil (CNO) reached the soap manufacturing countries, sometime around 1840 (10), it was discovered that to produce soap, there was no need to boil, not even to heat the mixture of coconut oil and alkali. Coconut oil has been cited as "the most valuable fat raw materials for soap making" (4,8). This process is the cold process and was used for special soaps (9).

But coconut oil is an alien oil of limited and undependable availability to those importing countries. The cold process was not therefore developed to as high an art as the full-boil process. It is likely, though, that much information about the cold process lie in the scientific files of European soap manufacturers unpublished and unavailable to us, late comers.

Because we possess the coconut oil upon which the cold process depends, it behooves us to explore the potential of this process. This is the objective of this study.

The Cold Process

At ambient tropical temperatures, a weighed amount of CNO is placed in a suitable container. The requisite amount of an alkali solution, usually NaOH is stirred in and stirring continued until the mixture starts to "thicken" where upon it is poured into molds and allowed to "ripen" for 2-3 weeks.

Stoichiometry and chemical factors. Michel Eugene Chevreul (1786-1889) elucidated the chemical basis of soap making (2).

The stoichiometry (based on an average saponification value of 257) is:

CNO	+ 3NaOH	= 3 Na-soap	+ glycerol
654.86	+ 120.0	= 682.86	+ 92.0

The chemical factors (weight relationships) are:

a) grams NaOH/gram CNO = 120/654.8 = 0.1833
b) grams dry Na-soap/gram CNO = 682.6/654.8 = 1.043
c) grams glycerol/gram CNO = 92.0/654.8 = 0.1405

Water in soap. In soap making, the NaOH is in the form of a solution. The water in the solution is the only source of "moisture" in the final soap produced. Since moisture or water content is limited by specifications for soap, e.g. not more than 36%, the importance of controlling the water content of NaOH solution is obvious. The weight (W/W) percentage concentration of NaOH in such solution, is

$$p = \frac{\text{grams NaOH}}{\text{grams NaOH} + \text{grams } H_2O}$$

$$\text{The weight of NaOH solution} = \frac{\text{grams NaOH}}{p}$$

$$\text{The weight of water in the solution} = \frac{1 - p}{p} \times \text{grams NaOH}$$

Weight of finished soap. In the cold process, the reactants (CNO and NaOH solution) combine with no loss by evaporation or volatilization, to form soap. The weight of the reactants equal the weight of the products (soap). The weight of the "finished" soap is therefore:

$$\begin{aligned} \text{grams finished soap} &= \text{grams CNO} + \text{grams NaOH solution} \\ &= \text{CNO} + (\text{NaOH}/p) \\ &= \text{CNO} + (0.1833 \times \text{CNO})/p \\ &= \text{CNO}[1 + 0.1833/p] \end{aligned}$$

Percentage composition of the finished soap:

a) Percentage anhydrous soap

$$= \frac{1.043 \times CNO}{CNO\,[1 + \frac{0.1833}{p}]} = \frac{1.043}{1 + \frac{0.1833}{p}}$$

b) Percentage glycerol

$$= \frac{0.1405 \times CNO}{CNO\,[1 + \frac{0.1833}{p}]} = \frac{0.1405}{1 + \frac{0.1833}{p}}$$

c) Percentage of water

$$= \frac{\frac{1-p}{p} \times NaOH}{CNO\,[1 + \frac{0.18333}{p}]}$$

$$= \frac{\frac{1-p}{p} \times 0.1833 \times CNO}{CNO\,[1 + \frac{0.1833}{p}]}$$

$$= \frac{0.1833\,(1-p)}{p + 0.1833}$$

The fatty acids in the finished soap. One of the usual specifications for finished soap is that the fatty acid content should be at least 40%. The fatty acid (FA) component of soap comes from the coconut oil. The relation between FA and CNO is obtained from the chemical equation:

CNO	+ $3H_2O$	$\longrightarrow$	3 FA	+ glycerol
654.8	+ 54.0	=	(616.8)	+ 92.0

Or grams fatty acids/gram CNO = 0.942 that is, when soap is made from CNO grams of oil, the weight of FA involved is 0.942 x grams CNO and percentage of FA in such soap

$$= \frac{0.942 \times \text{grams CNO}}{\text{grams soap}}$$

$$= \frac{0.942 \times CNO}{CNO\,[1 + \frac{0.1833}{p}]} = \frac{0.942}{1 + \frac{0.1833}{p}}$$

An assumption is made here of complete saponification, that is, all the FA originally in the CNO, has been converted to soap.

A graphical presentation is given in Chart 1 of the relation of p (percentage concentration of the NaOH solution) and:

percentage of anhydrous soap in finished soap,
percentage of water in finished soap, and
percentage of FA in finished soap.

Practical aspects. Let us now consider making soap to meet the specifications that the FA content should be 40% or more and that the water (moisture) content should be 36% or less. What should be the concentration of the NaOH solution (value of p)? A fatty acid content of 40% is identical with an anhydrous soap content of 44.3% [(40 x 1.043)/0.942].

Solving for p in the equation:

$$\frac{1.043}{1 + \frac{0.1833}{p}} = 0.443, \text{ gives } p = 13.5$$

Using this value of p and solving for % H_2O in the equation

$$\%\ H_2O = \frac{0.1833\,(1 - p)}{p + .1833}, \text{ gives } \%\ H_2O = 49.86\%$$

These results show that while p = 13.5% would produce a product of 44.3% anhydrous soap (40% FA) the water content is 49.7% which is much higher than the desired limit of 36%.

To obtain % H_2O = 36, the value of p must be 21.6, then percentage anhydrous soap would be 56.4 which is higher than the 44.3% (40% FA) stipulated in specifications for soap.

To meet both requirements of 36% H_2O and 44.3% anhydrous soap, one way would be to use fillers to replace a part of the water; these will amount to 49.8 − 36.0 = 13.8g/100. Then 13.8g H_2O is removed by evaporation.

Another procedure, avoiding the evaporation step, may be possible considering the following:

When 100g of CNO is used for soap making and p = 13.5, the weight of the finished soap would be:

$$\begin{aligned} \text{grams soap} &= \text{CNO}\left[1 + \frac{0.1833}{p}\right] \\ &= 100\left[1 + 1.357\right] \\ &= 235.7 \end{aligned}$$

The weight of water in soap, of 36% moisture would be 0.36 x 235.7 = 84.85g/100. The value of p for this weight of water in a NaOH solution would be:

Table 1. Summary of quantitative relationship

P	CNO		NaOH		H_2O		Filler		Soap		Glycerol		H_2O		Filler		Product
13.5	1.00	+	0.1833	+	1.172	+	0	=	1.043 (44.3%)	+	0.140 (5.9%)	+	1.172 (4.98%)	+	0	=	2.355
17.8	1.00	+	0.1833	+	0.848	+	0.324	=	1.043 (44.3%)	+	0.140 (5.9%)	+	0.848 (36%)	+	0.324 (13.8%)	=	2.355
21.7	1.00	+	0.1833	+	0.665	+	0	=	1.043 (56.4%)	+	0.140 (7.60%)	+	0.665	+	0	=	1.85

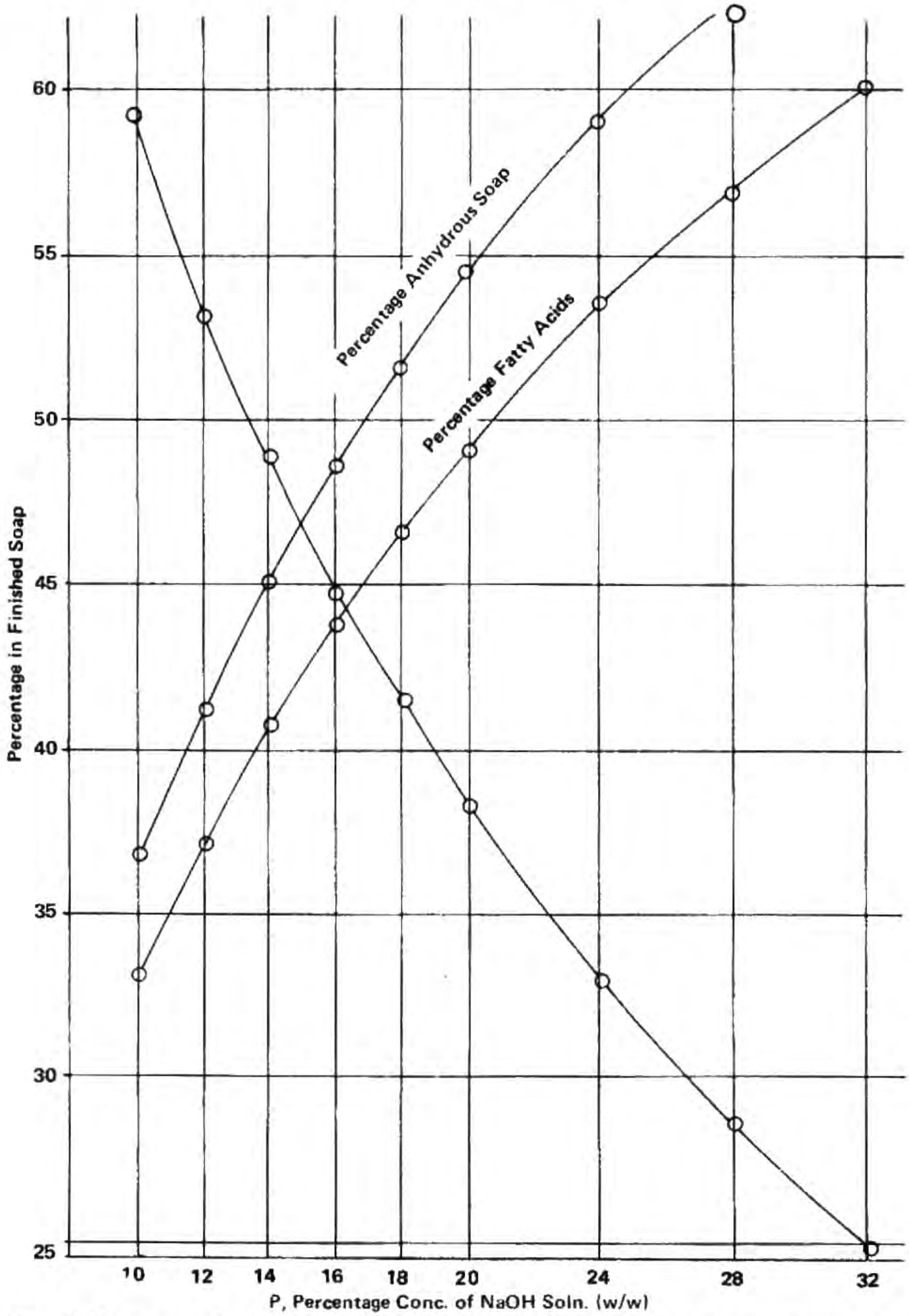

Chart 1. Percentage of anhydrous soap, fatty acids and water in relation to concentration of NaOH solution.

$$p = \frac{0.1833}{0.1833 + 0.8485} = 17.77$$

Therefore, if an NaOH solution of 17.77% (W/W) concentration is used for saponification, the resulting cold-processed soap will contain 36% H_2O, and 44.3% anhydrous soap. Note that glycerol is present and the percentage is:

$$\%\ \text{glycerol} = \frac{.1405}{2.357} = 5.96\%$$

To reach a total 100%, fillers are necessary, amounting to 13.8%.

Fillers. The fillers mentioned in publications are sodium phosphates, borax and sodium carbonate. The fillers are supposed to be used as an economy measure although they may contribute to lowering the hardness of washing water. In a country where CNO abounds and where these fillers are expensive, imported and hard to come by, the practice of using these fillers as an economy measure is of doubtful value.

Summary

One unit coconut oil yields upon saponification with NaOH of 13.5% solution concentration, 2.35 units of soap product; the moisture content is much higher than specification (49.7% when it should be no more than 36%). When p = 21.7%, one unit of CNO yields 1.85 units of soap; the moisture content is 36%, the anhydrous soap content is 56.4% (higher than specs).

By using NaOH solution of 17.8%, one unit of CNO yields 2.35 units of soap which contains 36% H_2O and 44.3% anhydrous soap (equivalent to 40% fatty acids). These situations are summarized in Table 1.

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Leopoldo S. Castillo, Discussant

For the 54 million Filipinos, the maximal utilization of coconut products and by-products of the coconut industry is vital to its existence. Statistics shows that about one-third of the population is directly/indirectly dependent on the coconut industry. This is farther bolstered by the fact that about one million small hold farmers are raising coconut trees.

In an Egyptian fable, the phoenix, a miraculous bird which lived up to 500 years is then consumed by fire to rise again in youthful freshness from its own ashes. In a similar manner is the study reported by the Academician on the cold process in the manufacture of soap from coconut oil. He retraces and explains further what has been done in over a century. His paper also added more insights into the stoichiometry of CNO in the cold process.

An advantage of the cold process over that of heating the mixture of CNO and alkali is the savings in energy. But the drawback of the former is the need for a longer time of 2-3 weeks "ripening" process. Perhaps the process could be hastened with the use of catalysts to make it attractive to the commercial sectors.

The stoichiometry shown in this study is almost perfect except for a very minor omission of 100 as a multiplier in changing to percentages the equations in anhydrous soap, glycerol, water, and fatty acids (equations 6, 7, 8 and 9, respectively).

In addition to catalysts, perhaps there could be room for detergents in small quantities as a part of the filler to improve the cleaning power of the soap. Furthermore, herbal perfumes may be considered. The proliferation of brands of laundry and bath soaps attests to the desire of Filipinos to smell clean and "sweet".

And for the coconut industry, the first priority is to maximize the use of CNO, hence to increase CNO by about 5% rather than decreasing NaOH by about 5-6% for better quality and quantity of soap. Also for KOH, others.

This study has contributed much to the present knowledge of CNO by the cold process. It deserves commercial application.

Congratulations!