

SAPONIFICATION CATALYSTS

Part I. Organic Catalytic Activity of Carvacrol and Chlorophenol

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A simple and rapid method for saponification has been studied, using carvacrol and *p*-chlorophenol as catalysts under ambient conditions.

Key words: Saponification, Catalytic activity, Carvacrol, Chlorophenol.

INTRODUCTION

Soaps, the alkali salts of higher fatty acids are obtained by the hydrolysis of oils and fats with sodium and/or potassium hydroxides. The reaction of soap formation is very slow and does not start spontaneously. It is generally carried out at an elevated temperature thus consuming a substantial amount of heat energy. It has been reported that the boiling of the fat charge with caustic alkalies is conducted for at least 8 hours in soap kettles and it takes 85 lbs of steam [1]. In other words 42687×10^3 BTU of heat energy (at 100° of steam temperature) for 100 lbs. of fat charge are consumed for the saponification. The economics of soap making are thus dependent not only on the cost of the raw materials but also that of the energy.

In recent years the energy costs have shown an upward trend and consequently the price of soap has also risen considerably. Because of this reason it was of interest to search for new methods of saponification that would require less energy.

Catalysts normally accelerate the speed of the reaction and it is known that cresol and thymol catalyse the fat hydrolysis or saponification [2]. In the present studies, efforts were made to study such catalysts as would help in achieving complete saponification without using any additional energy inputs.

It has been found that carvacrol and *p*-chlorophenol have such catalytic activity for the saponification reaction. It has further been observed that these compounds, when added in the fat charge in small amounts (@ 1 %), shorten the reaction time. The present findings thus offer a simple and rapid method of obtaining soaps without the use of any elevated temperatures and at ordinary pressure.

EXPERIMENTAL

Saponification was carried out at room temperature (30°). All extracts were dried over anhydrous sodium sulphate.

Samples of cotton seed oil and coconut oil (100 ml. each) were separately taken in two beakers (250 ml. capacity). To each sample the catalyst (1 ml.) (1 % v/v) was added with stirring and followed by the addition of 34 % sodium hydroxide solution (50 ml.) in the blank experiment 34 % Sodium hydroxide (50 ml.) alone was used. It was observed that the sample mixture thickened within ten minutes.

The extent/rate of saponification was followed by withdrawing samples (10 g) from the reaction mixture at regular intervals (20 minutes). The non saponified matter was extracted with *n*-hexane (B.P. $60-70^\circ$) and its percentage determined as usual after recovering the dried solvent. The data relating to the rate of reaction is given in Table 1.

The temperature increase, both for cottonseed and coconut oils, during the catalytic saponification was observed and is recorded in Tables 2A and 2B respectively.

DISCUSSION

Catalytic saponification of cotton seed oil and coconut oil, as exemplified in the present studies, suggests that the process is accelerated and complete in a short time (60 minutes) than usual (480 minutes). Using *p*-chlorophenol as saponification catalyst, 99 % coconut oil is saponified in 60 minutes and 97.5 % cotton seed oil in 120 minutes. With carvacrol as the catalyst 98 % coconut oil is saponified in 60 minutes and 96 % cottonseed oil in 120 minutes. Without using the catalysts only 64.93 % coconut oil and 52.90 % cotton seed oil is saponified in 180 minutes.

From these facts it is inferred that the saponification time depends upon the nature of both the oil and the

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Table 1. Extent of saponification with and without catalyst at ambient temperature.

| Oil/catalyst used | Oil % reacted after (minutes) | | | | | | | | |
|---|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| | 10 | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 180 |
| Coconut oil (alone) | 46.50 | 48.75 | 51.45 | 53.33 | 55.90 | 56.27 | 60.54 | 64.50 | 64.93 |
| Coconut oil + 1 % carvacrol | 89.50 | 93.5 | 98.0 | — | — | — | — | — | — |
| Coconut oil + 1 % <i>p</i> -chlorophenol | 97.0 | 98.5 | 99.0 | — | — | — | — | — | — |
| Cottonseed oil (alone) | 35.52 | 38.42 | 46.37 | 50.40 | 51.30 | 51.65 | 51.76 | 52.01 | 52.90 |
| Cottonseed oil 1 % carvacrol | 74.0 | 86.0 | 94.5 | 95.0 | 95.70 | 96.0 | — | — | — |
| Cottonseed oil + 1 % <i>p</i> -chlorophenol | 76.0 | 89.5 | 96.0 | 96.5 | 97.20 | 97.5 | — | — | — |

Table 2(A). Increase of temperature °C during the catalytic saponification of cottonseed oil.

Temperature of cotton seed oil before adding catalyst = 30°C.

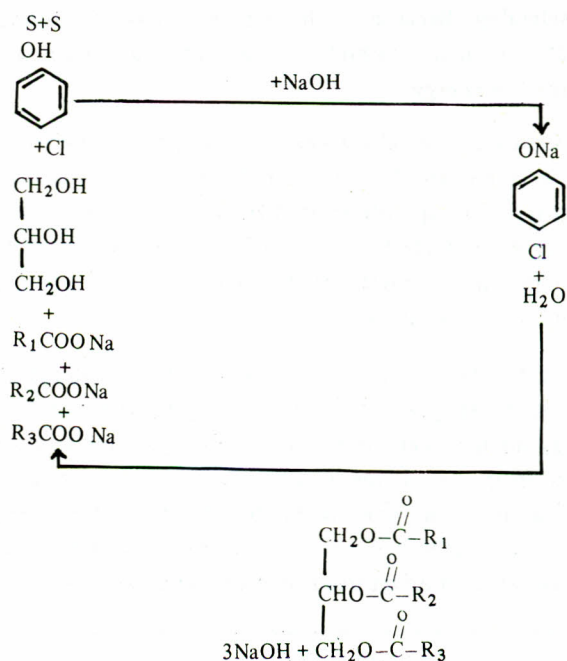
| + 1% <i>p</i> -Chlorophenol | | + 1% Carvacrol | |
|-----------------------------|---------|----------------|----------|
| Time (min) | Temp °C | Time (min.) | Temp. °C |
| After 0 | 40 | After 0 | 39 |
| 10 | 39 | 10 | 38 |
| 20 | 38 | 20 | 37 |
| 30 | 35 | 30 | 35 |
| 40 | 34.5 | 40 | 34.5 |
| 50 | 34.0 | 50 | 34.5 |
| 60 | 34.0 | 60 | 34.0 |

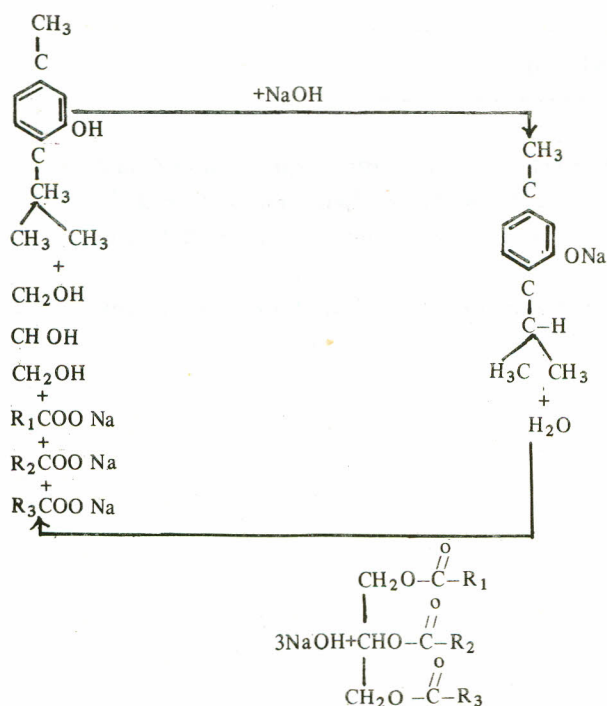
Table 2(B). Increase of temperature °C during the catalytic saponification of coconut oil.

Temperature of coconut oil before adding catalyst = 30°C.

| + 1% <i>p</i> -Chlorophenol | | + 1% Carvacrol | |
|-----------------------------|---------|----------------|----------|
| Time (min.) | Temp °C | Time (min.) | Temp. °C |
| After 0 | 48 | After 0 | 49 |
| 10 | 42 | 10 | 43 |
| 20 | 36 | 20 | 40 |
| 30 | 34.5 | 30 | 38 |
| 40 | 34.5 | 40 | 36 |
| 50 | 34.0 | 50 | 35 |
| 60 | 34.0 | 60 | 34 |

catalyst. Coconut oil is saponified in lesser time than cottonseed oil and the order of catalytic reactivity is *p*-chlorophenol > carvacrol. It is possible that the catalysts act as stabilisers in the water in oil system and shorten or completely eliminate the first slow step of saponification. Additionally the formation of phenolates, which dissolve in the soap layer, might accelerate the saponification process [3]. Therefore, a plausible representation of the idea is given below:





Many other substances such as menthol, trichlorobenzene, salicylaldehyde, dihydrocarvacrol, anethol, carbazol, benzil and sorbitol, when studied did not show any catalytic activity. Since these compounds did not thicken the emulsion within 10 minutes of admixture, therefore, no phenolate like formation was perhaps possible with these compounds. This argument is based on the fact that the compounds which raise the temperature and thicken the caustic solution and oil emulsion within a short time (10 minutes), show greater catalysis. The saponification — an exothermic reaction, generally takes place on the oil water interface. Therefore, those substances which are capable of becoming part of the interface will thus behave as better catalysts. Being better soluble in caustic solutions, the catalysts must also bring the caustic molecules in close contact with the oil molecules and consequently reduce the saponification time.

In conventional methods of soap making like the cold process the saponification is never complete although it is carried out for 70 hours. The hot process, which is the classical method, requires at least 8 hours' time and a large

amount of heat energy, affecting the wearing life of soap pans and the other processing equipments.

Generally, saponification is a slow process and is accomplished when fats react with alkalies under continuous agitation at raised temperatures and specific concentration of lye.

A number of organic compounds particularly those with hydroxyl groups such as α -naphthol, β -naphthol, thymol and cresol have already been studied as saponification catalysts [2]. In the present study, catalytic activity performance of similar substances was carried out and it has been found that *p*-chlorophenol and carvacrol act as excellent saponification catalysts (Table 1).

The catalysts used here are easily available organic compounds. As the saponification is carried out in the cold state, wearing and tearing of the pans and equipment is minimized. The multipurpose uses of catalytic saponification encompass savings in time, wearing strength, labour and fuel economy. All these factors contribute substantially in the production cost of the soap. Catalytic saponification is thus a simple, cheaper and economical method of soap making and when applied on a large and commercial scale will provide socio-economic dividends.

Pilot scale studies of the catalytic saponification are in progress and the results will be published separately. Economic gains, stipulated to be accruing from these studies, will thus be better worked out as a result of the large scale production experiments. Since the present procedure suggests complete elimination of the energy inputs it is expected that catalytic saponification will not only prove an attractive and novel technique but will also provide economic incentives both to the industry and the consumers alike.

REFERENCES

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