

PRODUCTION OF ECO-FRIENDLY SOAP FROM GLYCERINE PITCH AND BLEND OIL

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ABSTRACT

Glycerine or glycerol is an alcohol with three hydroxyl (-OH) groups. It is a colourless, odourless, viscous and water-soluble liquid. Being a by-product from the production of biodiesel, glycerine is presently abundantly available. This situation is alarming since the surplus of glycerine could not be coped and part of the effort to reduce it is by incineration, which leads to environmental concern. On the other hand, glycerine pitch is an unwanted residue from oleo-chemical plant. Hence, there is an urgent need to utilize the abundantly available and cheap glycerine and the unwanted glycerine pitch. On the bright side, from previous research and application, glycerine can be transformed to other higher value-added products. Due to its moisturising properties, one of the main uses of glycerine is in the blending of eco-friendly soap. This study was aimed to investigate the blending process and properties of liquid soap. The starting materials used were lab grade glycerine and glycerine pitch waste. Both glycerines were mixed with sulphuric acid; underwent activated carbon treatment and evaporation for purification. Combination of glycerine and glycerine pitch obtained demonstrated very little absence of soap. Final observation showed good indicator of the utilization of glycerine pitch. This was proven from soap B with pH 8.3 that took 5.9 hours before the disappearance of soap.

Keywords: *Glycerine, Glycerine pitch, Activated carbon, Liquid soap, Eco-friendly.*

1. INTRODUCTION

The production of quality soaps at cheaper price has been a hitch to many soap producers. This has led to the production of soaps with poor qualities and high cost of production. Otherwise, nowadays most big brand companies are making alcohol based disinfectant as alternative to using soap. Our skin has good resident (good bacteria) and non-resident (bad bacteria) bacteria living on it [1]. Those products are like dropping atomic bombs on our skin which could potentially kill but at the same time destroy the delicate balance of our skin.

Besides, many of the chemicals that are added to soaps are capable of seriously damaging the human body (and some of these toxins may even cause death). One of the harmful ingredients in soap is triclosan which is known as pesticide that has antibacterial properties

[2]. It is often found in soaps because it helps to get rid of potentially dangerous bacteria that have built up on our skin during the day. Unfortunately, this antibacterial action that makes triclosan is one of the worst contributors to the growing problem of antibiotic resistance (which encourages the evolution of resilient bacteria that are extremely difficult to kill). Another important reason to avoid toxic soap ingredient such as triclosan is due to the endocrine disruptor. Endocrine disruptors cause potentially dangerous fluctuations in hormone levels, and triclosan has been proven to have a particularly strong influence on the female sex hormone, estrogen. The hormonal changes caused by triclosan can dramatically increase the likelihood of developing breast cancer. Due to this reason, toxic free soap or known as natural soap is desirable. Soap that comes from natural ingredient may not have any hazardous chemical and it is also environmentally friendly to the users [3].

Historically, glycerine is a clear nearly colourless liquid, having a sweet taste but no odour. K.W. Scheele had introduced glycerine in 1779 by heating a mixture of olive oil and litharge on washing with water, a sweet solution was obtained, giving on evaporation of water a viscous heavy liquid, which the discoverer called "the sweet principle of facts [4]. Since then, it has gained attention and became useful for various consumer products, such as soap [5-7]. Soap can be defined as a chemical compound or mixture of chemical compounds resulting from the interaction of fatty acids or fatty glycerides with a metal radical (or organic base) [8].

Glycerine pitch (also known as crude glycerine or waste glycerine) is one of the scheduled wastes generated from fatty acid plants in Malaysia through the refinement process of sweet water to pure glycerine [9]. Glycerine pitch has limited usage but there is effort to utilize it as fuel [10]. In actual fact, more research should be geared towards converting this waste into something useful such as soap. Conversion of glycerine to a usable state such as soap requires purification, which will meet the purity requirements for existing or emerging uses [11]. To purify glycerine and glycerine pitch, different methods have been applied such as filtration, chemical treatment, ion-exchange and also adsorption (using activated carbon). The glycerine undergoes physical and chemical treatment in order to increase its purity [12]. For chemical treatment, glycerine fraction can react with acid to convert the alkoxide salts to the corresponding alcohol and the fatty acid carboxylate salts to the corresponding free fatty acid. Extraction or decantation can be used to remove the resulting free fatty acid (FFA) [13]. For these reason, glycerine (lab grade) and glycerine pitch have been formulated to produce eco-friendly soap. The characteristic and properties of the glycerine as well as the liquid soap have been evaluated and analyzed.

2.0 EXPERIMENTAL

Four samples labelled as A, B, C and D were prepared. The compositions of the samples are as shown in Table 1. The general flow of this investigation is as illustrated in Figure 1(a) whereas the production flow of soap is shown in Figure 1(b).

Table 1. Composition of samples A, B, C and D (in wt%)

Sample	Glycerine (Lab grade)	Glycerine Pitch
A	100 %	0 %
B	75 %	25 %
C	50 %	50 %
D	0 %	100 %

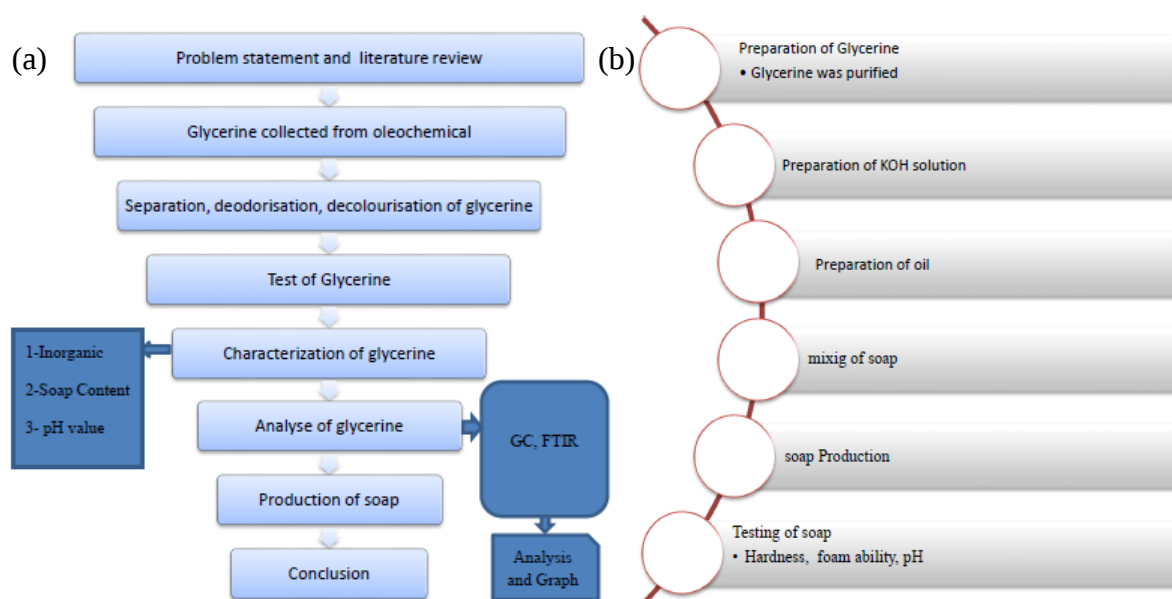


Figure 1. (a) Research flow Diagram and (b) Flow production of soap

2.1 Glycerine Production

Diluted sulphuric acid (6% solution) of 15 mL was added into the glycerine layer in a closed sample bottle and shaken vigorously. Separator funnel was used to separate the layers. Glycerine was then transferred into a beaker and 2g of fine activated carbon was added. For efficient mixing, glycerine carbon mixture was simultaneously heated and stirred. Then the mixture was left to cool for 5 minutes. Finally, the mixture was filtered by vacuum filtration to remove the activated carbon.

2.2 Test of Glycerine

2g of potassium bisulphate (KHSO_4) was placed in a test tube. About 5 to 6 drops of the prepared glycerine were added into the test tube and then gently mixed. The mixture was then heated and the odour emitted from the mixture was then noted.

2.3 Characterization of Glycerine

pH meter was used to measure the pH value of the solution. 20 g of the prepared evaporated glycerine was placed in a beaker then 100 mL of distilled water was added. The pH of the solution was measured.

For soap content, 50 mL of distilled water was dissolved together with 1g of evaporated glycerine. Then, a few drops of bromophenol blue indicator were added into the dissolved glycerine. Subsequently the solution was then titrated with 0.1 M hydrochloric acid (HCl, 37%, Merck) until a permanent light-yellow colour was formed. Finally, to check for inorganic matter, 5 mL of glycerine was boiled and gently ignited in an open Petri. The remaining residue after the ignition was checked.

2.4 Analysis for Glycerine

Infrared spectra of liquids were recorded using Perkin Elmer Spectrum One Fourier Transformation Infrared Spectrometer. The glycerine sample was compacted between two NaCl windows. The sample pellet was put in a sample holder and the spectrum was recorded at room temperature with 4cm^{-1} resolution in the range of $4000\text{-}400\text{cm}^{-1}$ in the transmittance mode.

Gas chromatography flame ionization detector (GC-FID), data analyzer 5880A series GC terminal with column Ultra-1: non-polar, 100% dimethyl polysiloxane ($20\text{m} \times 0.22\text{mm} \times 0.33\mu\text{m}$ film thickness) were utilized for quantification purposes.

2.5 Production of Soap

200 mL of glycerine was poured into beaker A and heated to 60°C . The glycerine was then stirred continuously and temperature was constantly monitored. 50 mL of water was measured and poured into the 250 mL beaker A as the glycerine was heated. After that 15g of KOH was measured (precaution: since KOH is hygroscopic, it will absorb moisture from the air causing it to weigh more and be less effective, so KOH must be kept covered) to be mixed in beaker B. Then, KOH was added to water to swirl and dissolve. 5g of citric acid was added to the solution and was stirred until everything dissolved in beaker B. 25 g of coconut oil was placed in 250 mL beaker C. Then, the coconut oil was heated as to melt the oil. The melted blending oil (beaker C) and KOH/Water (beaker B) solution was gently poured into the hot glycerine (beaker A). The soap was then heated and temperature maintained at 70°C . The soap was stirred constantly (using a stir bar) and continuously heated for 20 minutes. At this point, few drops of essential oil could be added to scent the soap. After 20 minutes, the soap was taken off the heat and allowed to cool at room temperature.

2.6 Characterization of Soap

2g of the soap was dissolved in 50 mL of distilled water in a 100 mL measuring cylinder and shaken vigorously for 2 min. It was allowed to stand for 10 min after which the height of the foam was determined. This was repeated thrice for each soap sample and the mean computed. The pH values of the soaps produced were analysed using a pH meter. 2g of the produced

soaps has been dissolved in 50 mL of deionised water and the pH determined using the meter. This was done thrice for each soap sample and the mean computed.

3.0 RESULTS AND DISCUSSION

3.1 Separation of Glycerine

The first step was the treatment of glycerine layer with diluted sulphuric acid (6% solution) (Figure 2). Instantly after the acid was added to the glycerine, the mixture became warm. This indicated an exothermic reaction. After allowed to settle for a minute, a translucent glycerine layer was formed under a dark free fatty acid (FFA) layer, followed by the precipitation of the catalyst salt at the bottom.

The glycerine was then treated with activated carbon to be decolourised and deodorised. This was achieved by treatment with activated carbon. After the treatment with activated carbon, the bright yellow colour of the glycerine faded to a lighter and pale yellowish colour (Figure 3 (a)). The odour of the glycerine sample was also minimized.

Activated carbon has an extremely large surface areas and superior adsorbent capability. One gram of activated carbon has surface area of 500 m², hence only a small amount of carbon was required to decolourise and deodorize the glycerine. The activated carbon was used in the form of fine powder. It managed to enhance a large number of sub-microscopic pores where the adsorption took place within the surface area of the activated carbon.

Physical adsorption was the primary way by which the activated carbon works to remove contaminants from glycerine solution. Adsorption of contaminants from solution occurs due to the differences of adsorbate concentration in the solution and in the carbon pores. The adsorbates shift from the solution through the pore channels to reach the area where the attractive forces are stronger. Prior to its usage, the carbon was first heated to 100°C to activate it. The reason for the need of activation is to free the adsorption sites (especially water) of the activated carbon, thus increasing the adsorbance efficacy and efficiency. It can be deduced that activated carbon has successfully decolourised and deodorised the glycerine sample, due to its absorption capability and large surface area.

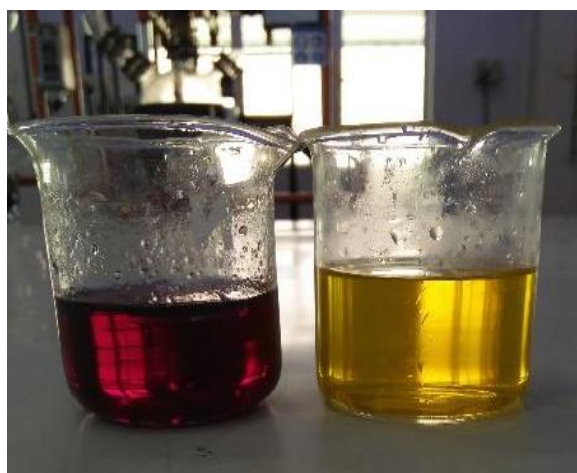


Figure 2. Glycerine solution before and after treated

3.2 Test of Glycerine

When the purified glycerine was initially tested with potassium bisulphate, pungent odour was released from the mixture after heating (Figure 3(b)). As the mixture was heated, dehydration occurred and aldehyde acrolein was formed as shown in Equation 1. The pungent odour was the result of acrolein formation.

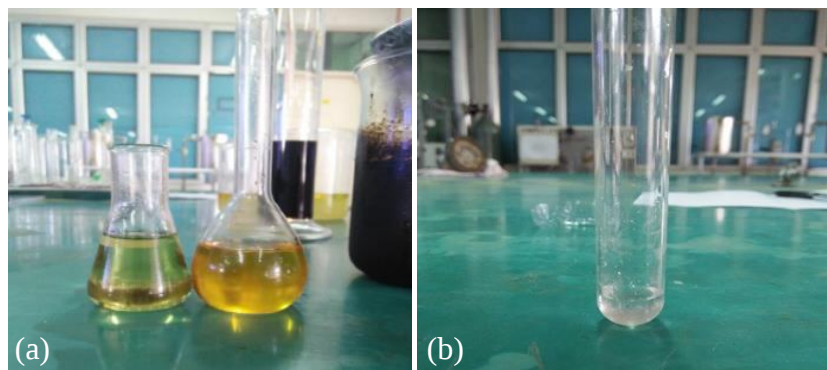
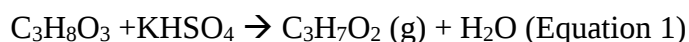


Figure 3. (a) Decolourised glycerol by activated carbon and (b) Glycerine reacted with potassium bisulphate

3.3 Characterization of Glycerine

Tests for reducing substances (inorganic matter) were performed to determine the content of impurities in glycerine. These common substances are more commonly found in crude glycerine. The presence of these impurities can be the benchmark for the degree of purity of glycerine. For this test, inorganic substances were not detected as all of the glycerine was totally volatilized. As no inorganic matter was present, no residues or stain were observed.

3.4 Analysis of Glycerine

The glycerine was analyzed using FTIR and GC-FID. For FTIR, Infrared spectroscopy detects the vibration characteristics of chemical functional groups in a sample. When an infrared light interacts with the matter, chemical bonds will stretch, contract and bend. As a result, a chemical functional group tends to adsorb infrared radiation in a specific wavenumber range regardless of the structure of the rest of the molecule. Figure 4 shows the FTIR spectrum of produced glycerine.

From the four samples that have been analysed, the absorption peak at around 3300 cm^{-1} was attributed to the group in the sample. The broader adsorption was due to the hydroxyls groups from water and the glycerol molecules, as glycerine is hygroscopic by nature [14, 15]. The C-H stretching band was seen at around 2939 cm^{-1} , while the bands for C-H scissoring and bending appeared at the region of $1410 - 1450 \text{ cm}^{-1}$. The bands at around 1000 cm^{-1} -

1300 cm^{-1} were contributed by the C-O group stretching in the sample. The presence of some impurities was shown by the absorption peak at 1652 cm^{-1} (C=O group), corresponding to the oxidation products of glycerol, such as glyceraldehyde, dihydroxyacetone and free fatty acids.

The GC chromatogram of the purified glycerine is illustrated in Figure 5. Apart from the peak corresponding to the solvent; another small peak appeared at the retention time 18.4th minute, which indicated the presence of glycerine. The intensity of the peak was very low because the purified glycerine was very viscous, which required the addition of ethanol as dilution solvent.

For sample A and B, the glycerine was clearly manifested and purified as one peak of glycerine was shown. The peak appeared at the retention time of 18.4th minute. The presence of ethanol in this chromatogram was due to the dilution with glycerine. Peak of glycerine also appeared for sample C and D, but other peaks apart from glycerine were also detected indicating that the samples were not completely purified.

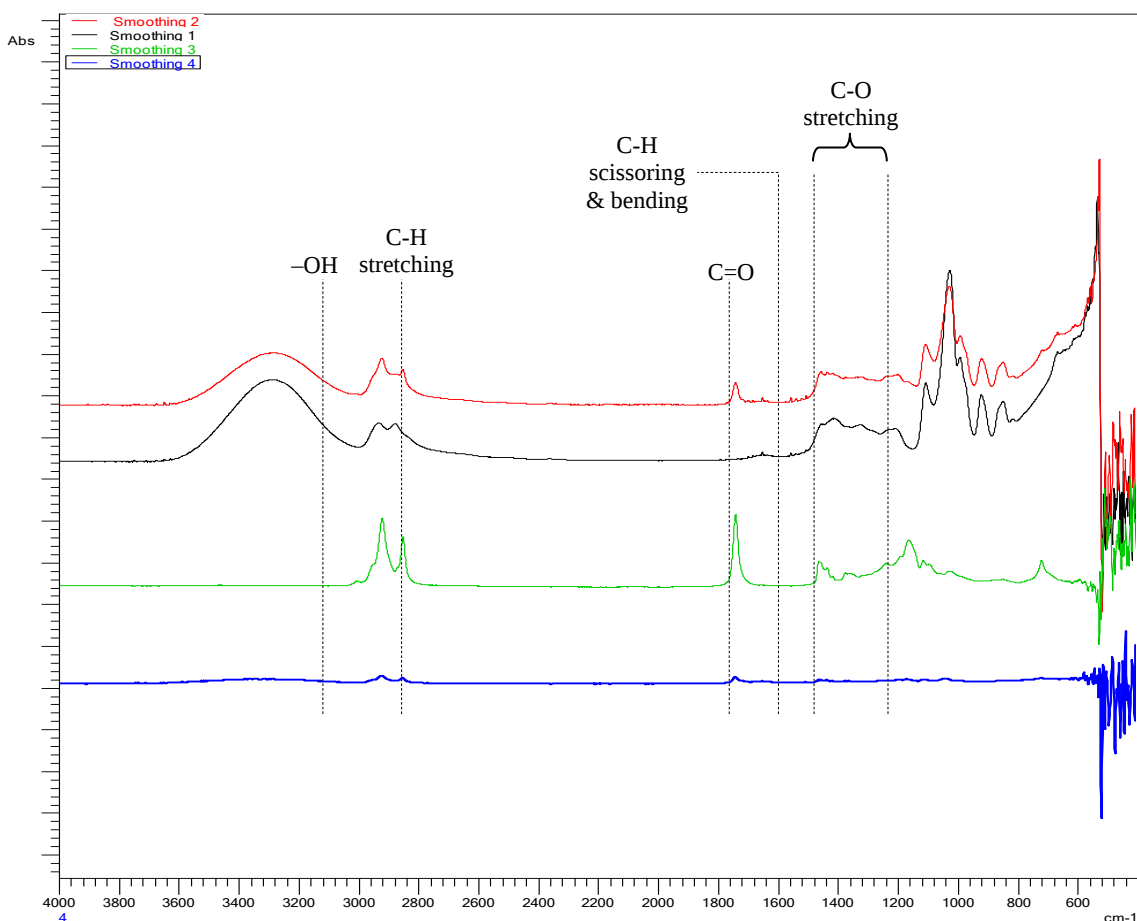


Figure 4. FTIR spectrum of produced glycerine

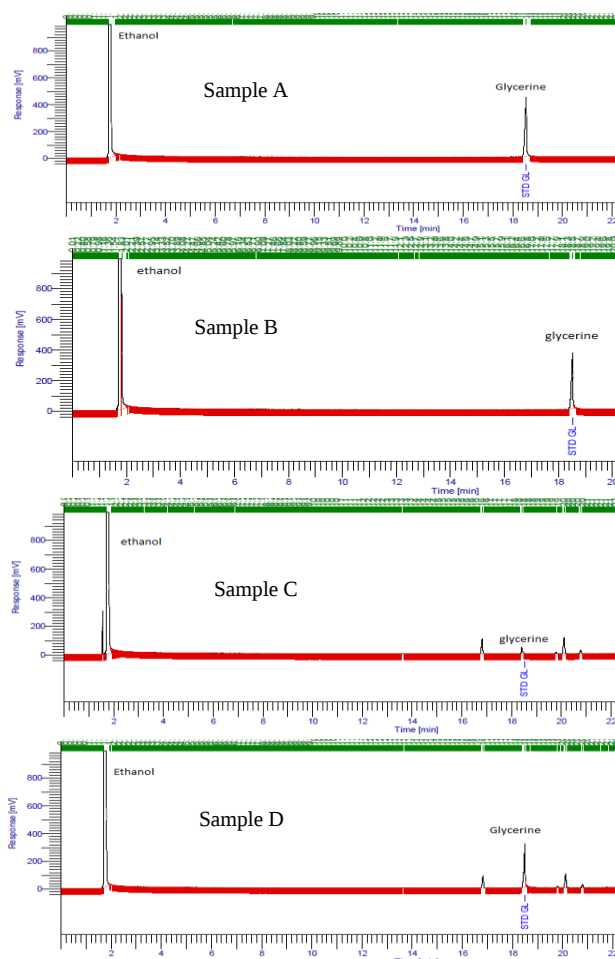


Figure 5. The chromatogram of glycerine for Sample A, B, C and D

3.5 Production of Soap

In this process, when the water was added into the beaker containing KOH pellets, it has become warm. It was due to the reaction of both potassium hydroxide with water is strongly exothermic, in other words, they generate heat and give off hydrogen.

For the preparation of oil, the oil has been heated for it to decompose. Different oils have different smoke points. When coconut oil has been heated past its smoke point, the structure of the fats started to break down, a process known as denaturing. This can cause the formation of harmful free radicals and is the point at which the oil will lose its nutritional benefit. Free radicals cause oxidative damage to cells, which can prevent the cells from functioning normally, increase nerve cell injury and possibly contribute to disease and illness.

Fats and oils are the ester functional group of an organic acid and glycerol. They are known as triglycerides and have three fatty acid molecules attached to each of the carbons in the glycerol skeleton. Soaps are the sodium or potassium salts of long chain fatty acids. When triglycerides in fat/oil react with aqueous NaOH or KOH, they are converted into soap and

glycerol (Figure 6(a)). This reaction is the alkaline hydrolysis of esters. Since this reaction leads to the formation of soap, it is known as the saponification process. The soap molecule has two parts: a polar group ($-\text{COO}-\text{K}^+$) and a non-polar group (R -hydrocarbon). The polar group is called the head and the non-polar group is called the tail. Thus, the soap molecule has a polar head and a non-polar hydrocarbon tail. The polar head is hydrophilic in nature (water loving) and the non-polar tail is hydrophobic (water repelling). Figure 7 represents the reaction taking place in this process.

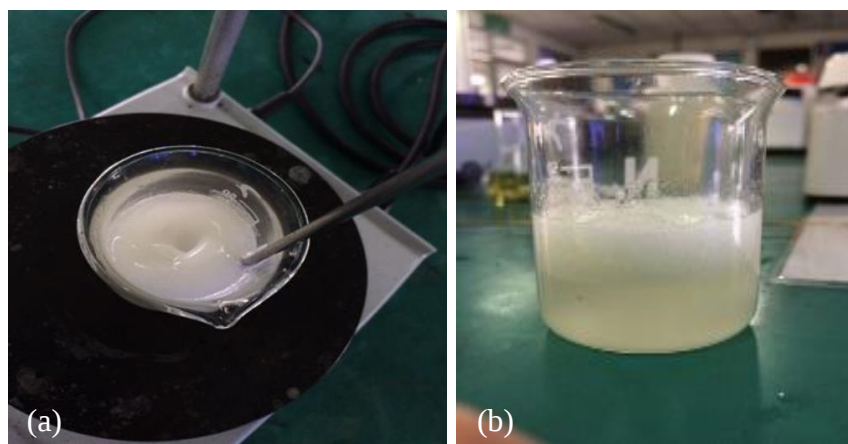


Figure 6. (a) The produced soap and (b) foam ability of soap

Reasonable foam ability has been shown from the soap that was produced, as illustrated in Figure 6(b). This was due to the addition of coconut oil after the saponification. Coconut oil has been cited to provide lather to handmade soap. In the soap produced, coconut oil has acted as an emollient. Coconut oil was added after the saponification at a level that the soap had begun to thicken so that they do not react with the soap. However, a slight amount of potassium hydroxide solution was added to maintain the liquid soap condition. Otherwise, glycerine should be added to increase the moisturizing trait of soap.

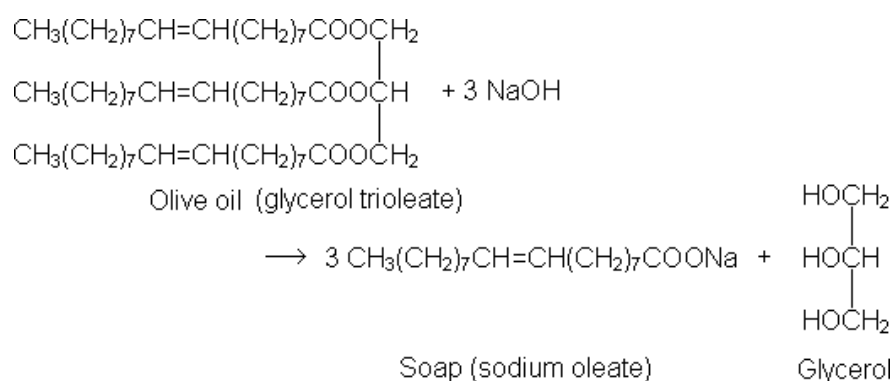


Figure 7. Reaction of oil with KOH

3.6 Characterization of Soap

Typical soaps are important for cleansing purposes and healthcare in preventing the spread of infectious diseases. These soaps are salts made from mixing of animal or vegetable oils (acid) with potassium hydroxide (KOH) with pH value around 7.5 - 9. In this investigation, soap samples A, B, C and D recorded pH range between 8 to 9, which is a good pH range for soap. If the pH value is higher (>9), human skin could be affected and cause possible injuries. From the pH value, it evident that the soap produced is safe for use. Figure 8 illustrates the pH values of all the samples.

Foaming effect was also present for soap samples A, B, C and D. Sample A showed the highest foam ability, followed by sample B, C and finally D. The foaming effect was comparable with typical soaps containing foaming agents such as ammonium lauryl sulphate and sodium dodecyl sulfate (sometimes referred to as sodium laureth sulfate). These ingredients also functioned as surfactants other than as foaming agents. A surfactant acts to reduce the surface tension of water, and allowing the dirt to be washed away. It also can break up oil or sebum on the skin.

There is no quantitative method for the determination of foaming capacity of soap. The foaming capacity of soap depends upon concentration of soap in the sample. Solutions of different soap are prepared by dissolving their equal weights in equal volumes of distilled water. These solutions are shaken vigorously to produce foam and then they are allowed to stand. Time taken for the disappearance of foam is measured for different samples. The longer the time taken for the disappearance of foam in a given sample of soap, the greater is its foaming capacity. In the case of sample A, it can be correlated that the properties from glycerine contributed the most as both foaming and surfactant. Sample A contained the most good quality glycerine and no glycerine pitch at all (Figure 8).

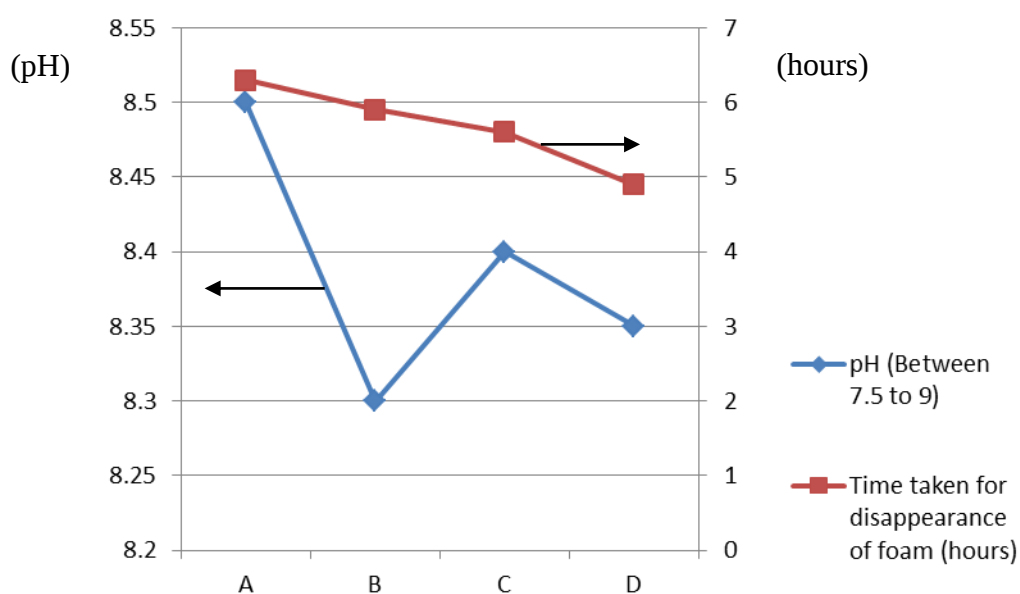


Figure 8. Reaction of oil with KOH

Nonetheless, samples B, C and D capability in the foaming capacity proved that it has potential to be further improved and developed using combination of glycerine-glycerine pitch as well as 100% glycerine pitch. This study has proven that glycerine pitch, which is deemed invaluable, can be converted to higher value-added product in the form of eco-friendly soap. In this case soap B (pH = 8.3) has been performing very well considering it originated from glycerine pitch content (25%) but yet it managed to have the longest time (5.9 hours) before the foam disappeared, indicating stronger soap physical properties. Even though soap A has the longest time, it originated 100% from the lab grade glycerine.

4.0 CONCLUSION

Glycerine and glycerine pitch were successfully converted and formulated as an eco-friendly soap. Glycerol content is a significant criterion for the glycerine as it determines the purity percentage of the glycerine. Final glycerine product showed reasonable purity after treatment with diluted sulphuric acid and subsequently activated carbon. It can be concluded that the addition of glycerine pitch affected the properties of the eco-friendly soap. However, this study proved that glycerine pitch has the potential to be used as raw material to produce eco-friendly soap. This has been proven from soap B with pH 8.3 that took 5.9 hours before the disappearance of soap.

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