Study on the Influence of Surfactant Addition for Bitumen Separation from Asbuton Rocks using Hot Water Process

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Abstract. Indonesia has a bitumen reservoir in a form of rocks located in Buton Island, Southeast Sulawesi. These rocks contain both bitumen and mineral. Bitumen was mostly used for road preparation, hence bitumen had to be separated from its mineral. It was concluded from previous researches that bitumen extraction using the hot water process had a low bitumen recovery. One way to improve its recovery was by adding surfactant. This research aimed to study the effects of anionic and cationic surfactant addition to the percent recovery of bitumen. There were three main processes of bitumen extraction using hot water namely; preparation, mixing-preheating, and digesting. First, asbuton rocks were ground into fine material, then it was sieved using sieve number 30. Then it was continued by mixing asbuton and diesel oil with a ratio of 60:40 at 250 rpm at 60°C for 30 minutes. Then the second process was done by mixing diesel oil-asbuton and wetting agent solution that contains Sodium Dodecyl Benzene Sulfonate (SDBS) as anionic surfactant and NaOH at 1500 rpm for 30 minutes. The other mixture is Dodecyl Trimethyl Ammonium Bromide (DTAB) as a cationic surfactant and NaOH. In this research, the concentrations of surfactant used were 0.125; 0.25; 0.375; 0.5%, the used NaOH concentrations were constant at 0.5% (% mass), while the variation of temperature used were 60, 70, 80, to 90°C. The product of the digestion process was taken into beaker glass for 24 hours to separate into 3 layers by gravitational force. The top layer is a bitumen-diesel oil solution. The result showed that the performance of SDBS is better than DTAB, this could be because DTAB is positively charged, yet the minerals are negatively charged, so they tend to bind. It can be concluded from this study that the highest percent recovery of bitumen was 72.30 % at a temperature of 90°C with SDBS surfactant concentration of 0.125%, which means anionic surfactant had a better result than cationic surfactant.

1. Introduction

Buton Island, Southeast Sulawesi has a bitumen reservoir in a form of rocks called asbuton. Asbuton as a natural asphalt contains minerals that had to be separated to get its bitumen. Bitumen is the preferred geologic term for the sticky, highly viscous semi-solid hydrocarbon presents in most natural petroleum. It mostly contains pitch, resin, and asphalt. Bitumen is a natural hydrocarbon and has mostly replaced tar as the binding agent in asphalt-based roads. In the chemical term, bitumen is defined as a thick viscoelastic fluid, at room temperature, consists of hydrocarbons and their derivatives [12]. It mostly contains saturate, which is a complex mixture of polyalkyl structures, aromatics, resin, and asphaltenes.
Based on the asphalt market projection, Indonesia's demand is estimated to reach 1.5 million tons per year. On the other hand, Indonesian asphalt producers only reach a little bit above 300,000 tons per year, and the rest must be imported from other asphalt producing countries [1]. In general, the most used asphalt is petroleum asphalt because of its high content of bitumen. However, petroleum asphalt is highly dependent on the availability of petroleum. The other alternative is natural asphalt. Asbuton is one example of natural asphalt. Asbuton reserves approximately reach 677 million tons and able to provide for infrastructure needs in this country for up to 200 years. The asphalt content in Asbuton varies around 20 - 30% based on its source [2]. One of the common methods of bitumen separation is extraction using the solvent method. By using hydrocarbon solvent and non-polar derivatives such as TCE (trichloroethylene) and n-propyl bromide, carbon tetrachloride (CCl₄), Pertasol, Kerosene, and Diesel fuel obtains the result that it requires large amounts of organic solvents making it less efficient. Thus, it is estimated to have a high operating cost, making it inefficient to be applied on an industrial scale [3-4].

The other developing method is extraction using hot water which is initiated by Clark in 1920 to separate bitumen from Athabasca oil sand. This bitumen extracting method uses high-temperature water and non-polar solvent's addition to oil sand. This method is relatively more efficient. The difference between Athabasca oil and asbuton is in its mineral content, Athabasca oil sand’s mineral is silica (SiO₂) [5], while on asbuton contains a lot of calcium carbonate (CaCO₃). High temperature can reduce the surface tension on the asbuton, while the non-polar solvent attracts the bitumen to separate from its other contaminant because of the same polarity on solvent and bitumen.

This hot water method needs some modifications to be applied to asbuton separation, this is because CaCO₃ has a higher solubility than SiO₂ in the water. Some modifications to the hot water process are done by adding surfactants and NaOH. Surfactant and NaOH have a role as a surface tension reduction of bitumen and mineral. In NaOH addition serves as a sealing agent that becomes a seal between layers of diesel fuel-bitumen with a layer of rock so the layers will not be mixed. NaOH addition also worked as alkaline conditioning because asbuton’s natural surfactant is optimum in alkali conditions [6].

One of the problems encountered in the hot water process with modifications to separate bitumen from asbuton is the low recovery. The surfactant types may affect low recovery bitumen from asbuton. Surfactant has an important role in bitumen separation using hot water process because it can decrease the surface tension between bitumen and minerals contained in asbuton which caused bitumen-diesel fuel layer trapped in mineral able to lift to the surface.

One of the best surfactants for the Bitumen Separation process is Sodium Dodecylbenzene Sulfonate (SDBS) as anionic surfactant based on its Hydrophilic Lipophilic Balance (HLB), and Dodecyl Trimethyl Ammonium Bromide (DTAB) as cationic surfactant based on the usual usage of this surfactant for cationic surfactant in a carbonate reservoir. The usage of SDBS had already been used, in several pieces of research by Irfin (2019, 2020), though in the research SDBS was added with other sealing agents such as Sodium Carbonate and Sodium Tripolyphosphate. It motivated us to conduct research studying the effect and comparing the performances of Sodium Dodecyl Benzene Sulfonate and Dodecyl Trimethyl Ammonium Bromide as surfactants and NaOH for bitumen separation process with hot water as a medium to get higher recovery.

2. Methodology
Asbuton, originated from Kabungka, Buton, Southeast Sulawesi, was used as the main material for this research. Asbuton was crushed into smaller parts then was screened with the size of 40 mesh, and the used parts were retained in a 30 mesh sieve. For the initial content of bitumen, extraction by Trichloroethylene (TCE) solvent using SNI 03-3640-1994 method was used. Dodecyl Trimethyl Ammonium Bromide (DTAB) and Sodium Dodecyl Benzene Sulfonate (SDBS) was obtained from Sigma Aldrich Chemical Company, Inc, meanwhile, Natrium Hydroxide was obtained from SAP Chem.
The bitumen extraction process is carried out in a digester tank with a diameter of 10.8 cm and a height of 20 cm with a baffle to reduce the occurrence of vortex and thermocouple as a temperature reader. The digester tank was equipped with an impeller turbine disk type for the mixing process whereby the impeller rotation is adjusted using a rotary controller. The digester tank was placed in a water bath. The water bath is equipped with a temperature control functioning as a heating medium.

The visualization of the process is shown in Fig 1.

![Fig 1. Scheme of digester tank in bitumen extraction using the hot water method.](image)

Bitumen separation process from natural asphalt like asbuton using hot water method consists of three process stages, namely premixing-preheating process, digesting, and bitumen purification process. A diluent is added to decrease the viscosity of asbuton to help the effectiveness of this hot water digesting process [7]. In this research, there are 4 kinds of additive, namely diesel fuel as a penetrating agent, Sodium Dodecylbenzene Sulfonate (SDBS), and Dodecyl Trimethyl Ammonium Bromide (DTAB) surfactant as a wetting agent, and Sodium Hydroxide as sealing agent.

In the premixing-preheating stage, asbuton rocks were ground into fine material, then it was sieved using sieve number 30. Then the second process was done by mixing diesel oil and asbuton with a ratio of 60:40 at 250 rpm at 60°C for 30 minutes. Then the second process was done by mixing diesel oil-asbuton and wetting agent solution that contains Sodium Dodecyl Benzene Sulfonate (SDBS) as anionic surfactant and NaOH at 1500 rpm for 30 minutes. The other mixture is Dodecyl Trimethyl Ammonium Bromide (DTAB) as a cationic surfactant and NaOH. The value of NaOH is 0.5% of the total mass because optimum pH for this process is not allowed to be more than 11, so both asbuton’s natural surfactant and surfactant addition will work effectively. In the last process, the product of the digestion process was taken into beaker glass for 24 hours to separate into 3 layers by gravitational force. The top layer is a bitumen-diesel oil solution.

By the presence of hot water, it is expected that the bitumen contained in asbuton rocks will be easily dissolved. The surfactant is added to lower surface tension, thus the wetting effect can occur and make the bitumen soluble in the diesel fuel. Besides, NaOH serves as a sealing agent, which functions as a seal so that the mud layer does not bind back with the bitumen-diesel fuel layer. In this research the variables used are concentration of surfactant SDBS and DTAB added by 0.125%, 0.25%, 0.375%, and 0.5%, constant concentration of NaOH added by 0.5%, temperature variable of 60º, 70º, 80º, and 90º C.

The bitumen concentration in the top layer can be obtained by measuring the density of the layer using a pycnometer and calibration curve. Mass of bitumen obtained in the experiment can be delivered as follows

\[ m_b = m_o \times B \]
While bitumen’s recovery can be calculated by using the equation below:

\[ Y = \frac{m_d}{B_0} \times 100\% \] (2)

Where \( m_d \) is mass of bitumen extracted, \( m_o \) is mass of oil layer on the surface, \( B \) is bitumen’s concentration from the calibration curve, \( Y \) is bitumen recovery, and \( B_0 \) is mass of initial bitumen content in asbuton.

3. Result and Discussion

Asbuton is a natural asphalt with a viscosity of 154 poise[8], with bitumen viscosity between 5-1000 poise belonging to Tar Sand class III which requires diluent to increase bitumen recovery[9]. The addition of diesel fuel serves as a softening agent or penetrating agent to reduce the viscosity of the bitumen. Diesel fuel was chosen because of its light density and the polarity property of diesel fuel. Besides, diesel fuel is a non-polar solvent so that the non-polar bitumen will dissolve in the diesel fuel. Additionally, important parameters to improve the recovery of bitumen are surface properties. Modification of surface properties was performed by the addition of Sodium Dodecylbenzene Sulfonate (SDBS) surfactant, Dodecyl Trimethyl Ammonium Bromide (DTAB) surfactant, and NaOH. The surfactants serve as a wetting agent for reducing the bitumen interfacial tension, the SDBS surfactant is selected because it has a small Hidrophile Lipophile Balance (HLB) value wherein the smaller the HLB value, it tends to be more hydrophobic, so it binds the bitumen better [4]. The addition of NaOH serves as a base to activate the natural surfactant from asbuton, and as a separator between minerals and bitumens in order not to re-bind [6]. Bitumen will be detached from the minerals when it is in pH condition of base or pH 8.5-11.5.

![Fig. 2. The result of SDBS concentration and operating temperature to bitumen recovery.](image)

![Fig. 3. The result of DTAB concentration and operating temperature to bitumen recovery](image)
Figure 2 shows that the highest bitumen recovery is in the SDBS value at 0.125%, and after that, the recovery tends to decrease. A similar result is given by DTAB, in Figure 3, in which bitumen recovery is at a peak at the surfactant concentration of 0.125%, and for further addition, the result tends to decrease. This means that the optimum value of SDBS is 0.125% because at 0.1277% is Critical Micelle Concentration (CMC) of this surfactant specifically on 90°C temperature. As well as DTAB, the optimum value of concentration is 0.125% at 80°C because it has a CMC point at 0.13% [13] slightly higher than SDBS. CMC is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system go to micelles. CMC is important for surfactants. Surface tension and critical micelle concentration (CMC) are physical values that characterize the surface-active properties of compounds. If it exceeds the CMC value, the surface tension of the solution will not decrease again, so the addition of the surfactant will make a decrease in recovery. This means that the contact angle of solids in high concentration surfactant is low, which also means the wettability tend to be oil-wet [14]. The total solution (Rwa) that is too large can cause too many excessive amounts of particles from the surfactant addition and NaOH thus increasing the mineral hydrolysis causing the minerals to mix with the bitumen diesel fuel mixture. This can lead to three things: firstly the mineral falls together with the top layer (bitumen-diesel fuel) by forming a homogeneous bitumen-diesel fuel-mineral layer making it difficult to separate, the emulsion between bitumen and water due to too much surfactant being added or part of the top layer (diesel fuel-bitumen mixture) along with minerals in the lower layers are not completely separated from minerals [9].

Sodium Dodecylbenzene Sulfonate in nature of water base is selected as a wetting agent because it can minimize the emulsion that occurs between the water layer with the diesel fuel-bitumen layer and able to bind the mineral layer thus the bitumen-diesel fuel layer obtained can be completely separated from the mineral layer. The SDBS surfactant absorbed on the surface and the interface will change the surface properties thus affecting the bitumen release efficiency. After water and bitumen contacts, the SDBS surfactant is absorbed on the water-bitumen surface thus lowering the interfacial tension between the water-bitumen by breaking the hydrogen bonds on the bituminous surfaces, because SDBS surfactants have hydrophilic groups in the form of alkyl and hydrophobic chains of sulfonic groups (SO₃)[10].

Meanwhile the usage of Dodecyl Trimethyl Ammonium Bromide (DTAB) surfactant as cationic surfactant results in poor recovery, this could be because this surfactant is positively charged, yet the minerals are negatively charged, so they tend to bind, so both surfactant and asbuton’s mineral are harder to separate.
Bitumen is a non-polar compound thus it binds with the hydrophobic group of surfactant and the hydrophilic group binds to water when a concentration of surfactant is added then the surfactant will form a micelle with a hydrophobic group binding around the inner bitumen [11]. If the mixture’s condition is above CMC, it can cause the bitumen mixture to form a colloidal suspension state, and it makes the mixture harder to separate. In Figure 4, it can be seen that hydrophobic groups binding in molecular structure between the bitumen and the surfactant, so the bitumen will be lifted to the surface. While the addition of NaOH is acting as a sealing agent that plays the role of coating bitumen-diesel fuel thus it does not bind back with minerals after separation. The highest bitumen recovery is using SDBS as a surfactant which is resulted in 72.3% at the temperature of 90ºC.

4. Conclusion
The extraction with the addition of SDBS surfactant results in a better recovery than DTAB, with concentration of surfactant is 0,125%. The best value of Recovery is at 72.3%.

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