Effect of addition of dodecyl trimethyl ammonium bromide surfactant toward recovery of bitumen from asbuton with modified hot water process method

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Abstract. Asbuton is a natural asphalt that contained in rock deposits in Buton Island, South East Sulawesi. Asbuton used as an alternative of oil asphalt by separating bitumen from its minerals. The study was conducted to measure bitumen to improve bitumen with the addition of surfactant. In this study, the surfactant used is Dodecyl Trimethyl Ammonium Bromide (DTAB), which acts as a wetting agent to decrease the surface tension between bitumen and minerals. Bitumen was separated from asbuton using a modified hot water process that involved mixing and digesting process. Both of these processes performed on a stirred disc turbine tank and four baffles. The process of mixing preheating by stirring asbuton with diesel oil at 250 rpm for 30 minutes. Then the diesel-asbuton mixture was digested with surfactant Dodecyl Trimethyl Ammonium Bromide (DTAB) and Sodium Hydroxide and mixed at 1500 rpm for 30 minutes. The surfactant concentration used are 0.125%, 0.25%, and 0.375% and the temperature of 70⁰C, 80⁰C. The highest result obtained when the surfactant concentration is 0.25% and temperature of 80⁰C with 56.46% recovery.

Keyword : Bitumen, Hot Water Process, Dodecyl Trimethyl Ammonium Bromide (DTAB).

1. Introduction
Bitumen, better known as asphalt, is a mixture of hydrocarbon compounds consisting of compounds Apaltnenes, Resin, Aromatic, and Saturates. Asphalt based on the source can be divided into two, oil asphalt obtained from the petroleum refining process, and natural asphalt obtained from rock deposits such as Buton Asphalt (Asbuton) and tar sand. Asphalt is generally used in the process of road hardening which is a mixture of aggregates, fillers and bitumen as aggregate adhesives. Bitumen as an aggregate adhesive has a high viscosity at room temperature so that it can produce a mixture that has excellent resistance to road loads. [1]

Based on Pertamina's data, from 2016-2018, the annual import value of oil asphalt reached 1,107,000 tons, while Pertamina produced 350,000 asphalt per year using ex Middle Eastern crude oil. Local asphalt production is only able to supply 25% of the national asphalt requirement and 75% is supplied by imports from other countries. [2]

Indonesia possesses the potential for natural asphalt reserves, it better known as Buton Asphalt (Asbuton), which located on Buton Island, Southeast Sulawesi. According [3] the total asbuton reserves reached 677,247,000 tons, equivalent to 170,000,000 tons of asphalt, which is projected to be able to meet national asphalt requirements for around 100 years. The location of asbuton deposits spread over 70,000 ha from Sampolawa Bay to Lawele Bay along 75 km with a width of 12 km and Enreke region which belongs to Muna Regency, Southeast Sulawesi Province, with asphalt content contained in asbuton varying between 20-30%. This is a bitumen level that is quite large compared to the natural asphalt levels of other countries such as America (12-15%) and France (6-10%).

Various methods can do the process of separating bitumen from asbuton. Some methods that have been done are extraction methods using organic solvents and separation methods using hot water process. Extraction using organic solvents requires cost that is quite expensive and difficult to apply on an industrial scale. For this reason, various studies have been developed to obtain bitumen from asbuton with a cheaper method by using the hot water method. However, bitumen recovery using the hot water...
method is still not an optimal because of the use of surfactants are not appropriate. For this reason, the hot water process was chosen because of its feasibility to apply in industrial-scale with the addition of appropriate surfactants.

The study of bitumen separation from asbuton using hot water process plus DEX-diesel and NaOH solvents with variations of anionic surfactant was carried out by using Sodium Dodecyl Sulfate (SDS) [4], and Sodium Dodecyl Benzene Sulfonate (SDBS) [5]. The problem that occurs in the study is that the separation process has not involved with appropriate surfactants, thus the obtained bitumen is still not optimal. The results of the separation of bitumen there are still minerals that are followed so that the obtained bitumen is not pure. Surfactants and sealing agents can influence the separation of bitumen from asbuton. The purpose of adding surfactants and sealing agents is to reduce the surface tension of the solution so that it will help the release of bitumen from solids. The type of surfactant used in previous studies was an anionic surfactant. In addition to anionic surfactants, cationic surfactants are an alternative for the separation of bitumen from asbuton. [6] explain that cationic surfactants can reduce surface tension and change wettability for carbonate rocks. [7] succeeded in extracting calcite rock (one type of carbonate rock) with 72% recovery using cationic Dodecyl Trimethyl Ammonium Bromide (DTAB) surfactant via the inhibition method. In this case, asbuton has a very dominant carbonate content (around 86.66%) [3]. So, from these data, we hypothesize that DTAB surfactants can improve the extraction performance of asbuton rocks. In this study, solar is also used as a diluent to reduce bitumen viscosity and the addition of NaOH as a sealing agent between the solar-asphalt layer and the mineral layer so that the two layers do not mix in separation phase.

2. Experimental
2.1 Material
The Asbuton derived from Kabungka, Southeast Sulawesi, Indonesia; Dex-Diesel Fuel from Pertamina; Sodium Hydroxide (NaOH); and Commercial Dodecyl Trimethyl Ammonium Bromide from Shanghai Worldyang Chemical Co., Ltd., China with 99% purity.

2.2 Experimental Outline
The study method is described on Fig. 1

![Figure 1. Experimental Flow Diagram.](image)

2.3 Equipment
The equipment used in this study were digester tanks (Figure. 2), consist of 30 mesh sieves, 40 mesh and equipment, 500 ml erlenmeyer, 1000 ml and 2000 ml beaker glass, separating funnel, analytic balance, 10 ml pycnometer, thermometer, and vacuum pump.
2.4 Raw Material Preparation
Asbuton is reduced in size using a crusher/hammer until reach size of 30-40 mesh.

2.5 Bitumen Extraction from Asbuton
Asbuton weighed 280 grams then added dextol-diesel 420 grams and then put into the digester tank. Then the pre-mixing process of asbuton and dextol-diesel mixture was carried out under conditions according to the experimental variable for 30 minutes. The next step is added DTAB surfactant as a wetting agent and Sodium Hydroxide as a sealing agent. The mixture stirred during the digestion process for 30 minutes. After the digesting process is complete, the asbuton mix transferred into the container and then 1.5 liters of water is added and waits for three days until a three-layer separation occurs. The results of the separation are then put into a separating funnel to separate the bitumen-diesel mixture with the water that still carried into the solution. The filtered solution was analyzed for its weight and density to determine the percent recovery of bitumen.

2.6 Bitumen Recovery Analysis
The initial bitumen content of Asbuton was determined by extraction method using soxhlet according to SNI 03-3640-1994 procedure regarding asphalt extraction. Determination of the initial content of bitumen in Asbuton is done using the following equation:

\[
\text{Initial Bitumen Content} = \frac{\text{Asbuton Mass} - \text{Mineral Mass}}{\text{Asbuton Mass}} \times 100\% \tag{1}
\]

The solution from the digestion process, which separated from the remaining minerals is measured in term of mass and density. Based on the density of the solution obtained, the concentration of bitumen can be determined using a calibration curve. The extracted bitumen mass is determined based on the mass data and the concentration of the bitumen as measured by the equation:

\[
\text{Bitumen extraction mass} = \text{top layer mass} \times \% \text{bitumen concentration} \tag{2}
\]

2.7 Recovery Analysis
Percent recovery is defined as a comparison between total bitumen extracted from extraction and initial bitumen content in Asbuton. The following equation to calculate percent recovery:

\[
\text{Percent Recovery} = \frac{\text{Mass of Extracted Program}}{\text{Initial Bitumen Content Mass}} \times 100\% \tag{3}
\]

3. Result and Discussion
The process of separating bitumen from asbuton in this study using hot water process consisting of four stages of the process: pre-treatment, mixing (mixing and pre-heating), cooking (digesting) and bitumen separation process.
The first stage of bitumen separation from asbuton is pre-treatment. Asbuton used in this study is asbuton from sieve with a size of 30-40 mesh. Particle sizes greater than 30 mesh is classified as coarse particles which make bitumen separation less effective because the absorption surface area is smaller than filtered asbuton. While the size of the asbuton that exceeds 40 mesh, the separation process will be difficult to separate. The process of separating bitumen from minerals is influenced by shear forces so that if the particle size is very small, there will be no shear force between the bitumen and the mineral hence the bitumen is retained in the mineral. The size of the particles that are too small can make the particles dissolved into the bitumen so that it will mix in the top layer. The presence of these dissolved particles will be detrimental to the bitumen separation process economically.

The next stage is mixing and pre-heating. At this stage 280 grams of asbuton are added with 420 grams of diesel fuel. The most efficient ratio of solar asbuton is 60:40 [8]. Asbuton is a natural asphalt with a viscosity of 15.4 Pa. [9]. From Table 1, the bitumen viscosity between 0.5-102 Pa.s can be classified in class II tar sand, which requires diluents to improve bitumen recovery. The addition of this diluent proposes to reduce the bitumen viscosity. Solar is chosen as a diluent because it has a light density so that it can cause soluble bitumens in diesel fuel to separate and be in the top layer in a three-phase separation process [10]. Besides that, diesel fuel is easier to use because the boiling point is higher than kerosene. The diesel fuel is relatively safer and the possibility of danger of burning is slighter than kerosene. Stirring speed in the mixing and preheating process is 250 rpm for 30 minutes at the temperature according to the variable. This process called penetration time. Penetration time is the time required for diluent to interact with bitumen at a specific temperature with simple stirring. [11]

| Kelas | Karakter Bitumen | Viskositas Bitumen pada 50°C (Pa.s) | Proses |
|-------|------------------|----------------------------------|--------|
| I     | Light            | <1.5                             | Tidak membutuhkan diluent |
| II    | Moderate         | 0.5-102                          | Penambahan diluent secara optional |
| III   | Heavy            | 102-108                          | Perlu penambahan diluent |
| IV    | Very heavy       | >108                             | Bitumen tidak dapat menggunakan Hot Water Process untuk pemisahan |

After the mixing and preheating process, the next step is digesting. Asbuton mixed with diesel fuel is added with NaOH solution and DTAB surfactant as much as 30% of the total mass mixture. Then the mixture is stirring for 30 minutes at a speed of 1500 rpm at the temperature according to the variable. Bitumen separation that occurs in asbuton containing solid bitumen tends to be dominated by mechanical forces [10]. The stirring speed of 1500 rpm was obtained from previous studies for the separation of bitumen from asbuton. After the digestion process, the mixture is put into a container filled with water then left to stand for three days until three layers formed. The top layer is a bitumen-solar mixture, while the middle layer consists of water, surfactants, and minerals dissolved in water. The lowest layer is consist of asbuton solids that are not extracted, deposited minerals and a little water. The addition of water helps to add a second layer so that the bitumen-diesel does not return to binding to its mineral. Then the top layer is taken and filtered using filter paper with the help of a vacuum jet pump to separate the fine minerals that included in the top layer. After that, it is put into a separating funnel to separate the bitumen-diesel with water. Furthermore, the solar-bitumen is weighed and analyzed for its density.

The conditions set for this study are particle size, asbuton and diesel ratio, wetting agent ratio, stirring speed, turbine disc impeller type, penetration time, digesting time and sodium hydroxide concentration. The variables in this study were the concentration of Dodecyl Trimethyl Ammonium Bromide (DTAB) surfactant and temperature. The bitumen content obtained by the soxhlet extraction method, according to SNI 03-3640-1994 was obtained at 18.86%.

In this study, the NaOH concentration used is 0.125%. The role of NaOH in the separation of bitumen from asbuton is to activate the natural surfactants in the form of carboxylic groups contained in bitumen. When NaOH which is alkaline has contact with bitumen which is acidic nature, will cause a
saponification reaction to be occurred. During the saponification reaction, the natural surfactant will be produced in the form of carboxylic groups, which affect the contact angle, surface tension, and others.

3.1 Effect of DTAB Concentration on Bitumen Recovery

From Figure 3, the best bitumen recovery when the surfactant concentration is 0.25%. Based on the study of [12], the higher the concentration of surfactant given, the smaller the contact angle produced. However, the concentration of DTAB must remain below the critical Michelle point (CMC) value. Because the results of the study give a declining trend, hence it is necessary to optimize the DTAB concentration around the CMC point for optimal percent of bitumen recovery.

![Figure 3. Effect of DTAB concentration on bitumen recovery at temperatures of 70°C and 80°C](image)

Based on [10], the addition of caustic in large quantities which also functions as a wetting agent tends to cause the sand molecules to be dispersed and eventually emulsify with the bitumen layer making it difficult to separate them from flotation.

3.2 Effect of Temperature on Bitumen Recovery

From Figure 4, the bitumen recovery increases with increasing temperature. This case happened because an increase in temperature will help to reduce the bitumen viscosity. The lower the bitumen viscosity, the easier the bitumen to escape from its minerals [11]. The increase in temperature also affects the wettablity so that the surfactant solution is more easily penetrated to the mineral bitumen layer. [12].

![Figure 4. Effect of Temperature on bitumen recovery at various DTAB concentration](image)

4. Conclusion

The highest bitumen obtained at 0.25% DTAB concentration and temperature 80°C produces bitumen recovery of 56.46%. From this study, it can be concluded that the need for further studies on the separation of bitumen from asbuton because the highest potential of asbuton and the surfactant used is still not appropriate.
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