ASPHALT PRODUCTION FROM ASBUTON BY SONICATED EXTRACTION OF CARBONATE SOLIDS USING ACIDIC BRINE WATER SOLUTION

Mohammad Nasikin*, Ivan Mery Devianto & Bambang Heru Susanto
Chemical Engineering Department, Faculty of Engineering, Universitas Indonesia,Depok 16424
*Corresponding Author E-mail: mnasikin@che.ui.ac.id

ABSTRACT

Natural asphalt from Buton Island (asbuton) has not been fully utilized up to now. One way of its utilization was extraction process to dissolve carbonate solids in asbuton using weak acid solution. The solution was acidic brine water solution that made by CO_2 injection in NaCl solution. Sonicated extraction was performed at various operating conditions, namely temperature (25 to 110°C), pressure (1 to 3 bar), NaCl concentration (0.1 to 2 M), and flow rate of CO_2 (0.2 to 1 L/min). All variables affect the amount of dissolved carbonate solids. Maximum of dissolved solids reached at temperature of 90°C, pressure of 3 bar, NaCl concentration of 0.5 M, CO_2 flow rate of 0.6 L/min, and ratio of 0.02 g/mL. Asphalt product contained 50.47% asphalt, 24.47% carbonate solids, and 25.06% other minerals.

Keywords : *asbuton, carbonate solid, sonicated extraction, acidic brine water.*

1. INTRODUCTION

Indonesia is one of countries that have the largest reserves of natural asphalt in the world, except the United States and France. Natural asphalt reserves in Indonesia is Buton Island, Sulawesi Tenggara. Indonesian natural asphalt is known as asbuton. Asbuton reserves in Indonesia can reach 677 million tons, then it is able to support road infrastructure in this country up to 200 years to come [1]. Moreover, the construction of road infrastructure is expected to continue in the future. In addition, stability of asbuton higher than petroleum asphalt so that asbuton is more durable than petroleum asphalt [1,2]. This shows that asbuton has great potential for this country. However, it has not been able to fully utilized up to now [3]. Therefore, asbuton has a bright future to be developed and utilized in Indonesia.

One way to get asphalt from asbuton was extraction process. Development of asphalt extraction has been done a long time, both the organic and inorganic solvents. Various kinds of organic solvents has been tested on natural asphalt extraction, for example, kerosene [4], hexane [5], TCE and n-propyl bromide [6]. These solvent dissolved asphalt component in asbuton. However, the use of these solvents will require substantial energy for distillation process so that process becomes uneconomical.

Carbonate solids is the most mineral in asbuton[7]. Acid solutions for the extraction of carbonate solids became the next choice to get asphaltfrom asbuton, one of which is HCl solution [8]. Carbonate solids of asbuton can also dissolve in weak acid so weak acid solution can be used to replace HCl solution, such as formic acid [9] and acetic acid [10]. These acids are less corrosive than HCl. However, formic acid and acetic acid were still difficult to be recovered.

Another weak acid solution to extract asbuton is H_2CO_3 (carbonic acid). Carbonic acid can be prepared by CO_2 injection in water or H_2O-CO_2 system. This system is able to dissolve various mineral solids, including carbonate solids [11,12,13,14,15,16,17,18]. The addition of NaCl in H_2O-CO_2 solution will be able to accelerate the dissolution of carbonate solids [19,20,21]. Dissolution of carbonate solids in sea water that containsCO$_2$ naturally also can be observed in the formation of caves around the coast.

The amount of dissolved solids can be enhanced by sonicated extraction which is compared with normal agitation. This is shown in various studies of ultrasound effects on the dissolution of mineral solids, such as dissolution ofmagnesia in aqueous CO_2solution [22], dissolution ofphosphate in HCl solution [23], and dissolution of colemanite in H_2SO_4 solution [24]. Thus, the use of sonicated extractionwill be applied in asbuton extraction.

In this study, acidic brine water solutionwas made from H_2O-CO_2-NaCl solution. It was used as solvent for asbuton extraction with sonication method. The main objective of this study were to obtain asphalt by dissolving carbonate solids through new process and solvent. This extraction was designed to dissolve carbonate solids partially. The process parameters used in this study were temperature, pressure, concentration of NaCl, flow rate of CO_2, and time.Asphalt purity was tested by ASTM C25-06 and SNI 03-3640-1994 thenit was supported by Fourier-Transform Infrared (FTIR) analysis, specific gravity test, and the Field Emission-Scanning Electron Microscope (FE-SEM) analysis.

2. METHOD AND MATERIALS

2.1 Materials

Main raw materials used in this experiment were asbuton, NaCl, CO_2, and distilled water. Asbuton was provided from Lawele, Buton Island, Sulawesi Tenggara. Asbuton was crushed to have a diameter of about 2 mm and then heated at 180°C. Asbuton used in this experiment was analyzed by SNI SNI 03-3640-1994and ASTM C25-06 to determine the composition of asbuton.NaCl pure from Merck Chemical Indonesia (99%) and distilled water were used for NaCl solution. CO_2supplied from Trigas has purity of 87%. Other solutions needed in this study were NaOH solution, HCl solution, and TCE solution.

2.2 Experimental Procedure

Extraction experimentswere carried out in a tubular batch reactor (150 mL) heated by constant temperature and equipped with a ultrasonic probe, a pressure gauge,a thermostat bath, and a thermocoupel as shown in Fig.1. After adding 100mL of NaCl solution to the reactor, injection rate of CO_2 to reactor was regulated to desired value for 15 minutes and then temperaturewas adjusted to desired value. 2 gram of asbuton added to the reactor before system pressure was regulated to desired value,.Ultrasonic probe was usedat amplitude of 60% with ultrasonic processor power of 800 W. CO2 was continuously fed to the reactor during extraction to maintain saturation conditions.

At a certain time interval, asphalt was collected immediately from the solution. Furthermore, the asphalt was heated and weighed to determine the amount of dissolved solids. Asphalt will be tested by standard ASTM C25-06 to estimate carbonate solids content and its density testing. FTIRanalysis will be used to review the presence of carbonate solids qualitatively.FE-SEM analysis was used to observe morphologies of samples and presence of carbonate solid.Extraction process for asbuton was tested under reaction conditions which were as follows: temperature from 25 to 110°C, pressure from 1 to 3 bar, flow rate of CO_2 from 0.2 to 1 L/min, and concentration of NaCl from 0 to 3 M. The overall chemical reactions involved in the multiphase extraction system are as follows :
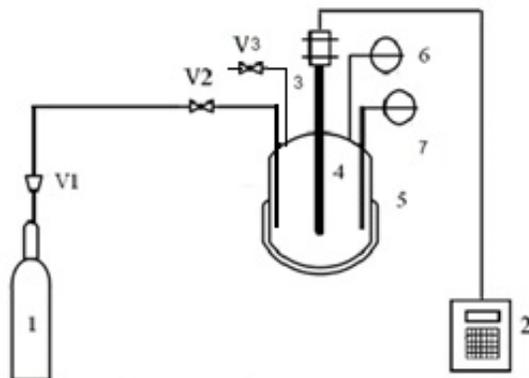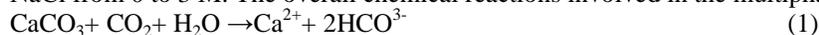
$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^{3-} \qquad\qquad (1)$$
$$MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2HCO_3^{3-} \qquad\qquad (2)$$

Figure1. Schematic diagram of experimental apparatus : 1. CO_2 tank ; 2. Ultrasonic homogenizer; 3.Ultrasonic probe; 4.
Reactor; 5. Thermostatic bath; 6. Pressure gauge ; 7. Thermocoupel

3. RESULTS AND DISCUSSION

3.1 Characteristic of Asbuton

Asbuton from Lawele were previously found to contain mineral and asphalt [7]. Asphalt from asbuton has high viscocity because the asphaltene content is high [7]. On the average, asbuton contain30.08% asphalt and 69.92% mineral [7]. The minerals in asbuton are $CaCO_3$, $MgCO_3$, $CaSO_4$, CaS, H_2O, SiO_2, Al_2O_3, and Fe_2O_3 [7]. Asbuton samples were characterized by soxhlet extraction or SNI 03-3640-1994method and ASTM C25-06 method, so their asphalt contents can be determined. The results of that is showed in Table 1.

Table 1 shows that the asbuton contains more mineral solids than asphalt. Asphalt in the asbuton reached 37.90%. The average content of carbonate solids in asbutonwas 43.28% of the total mass of asbuton. So, the sample of asbuton contained 37.90% asphalt, 43.28% carbonate, and18.82% other minerals.Othermineralsolids could have been SiO_2, $CaSO_4$, CaS, and others. These solids have very low solubility in water and acid when compared to carbonate solids and then itwas still remain and stick to the asphalt.

Table1.Composition of asbuton

Component	Percentage (%)
Asphalt	37.90
Carbonate solid	43.28
Other minerals	18.82

3.2 Enhancement of Extraction by Sonication

Sonication methodwere used in this study to enhance the amount of dissolved solids in 0,5 M NaCl solution at 70°C with CO_2 flow rate of 0.4 L/min. Figure 2 shows that the effect of ultrasoundwith amplitude of 60% was increase the amount of dissolved carbonate solids when compared toagitation rate of 500 rpm.Ultrasound effect is able to produce cavitation bubbles in the solution. The collapse of cavitation bubbles around the solid surface form irregular fluid flow at high speed. This effect will reduce the diffusion layer between solids and acid solution so that the mass and heat transfer become easier. In addition, the collapse of cavitation bubbles near the surface can erode, puncture, or crack solid in asbuton. This will expand the contact area between solids and solution to react so that more dissolved solids [25,26].It was supported by several studies that use ultrasound effect to increase solubility of minerals [22,23,24].
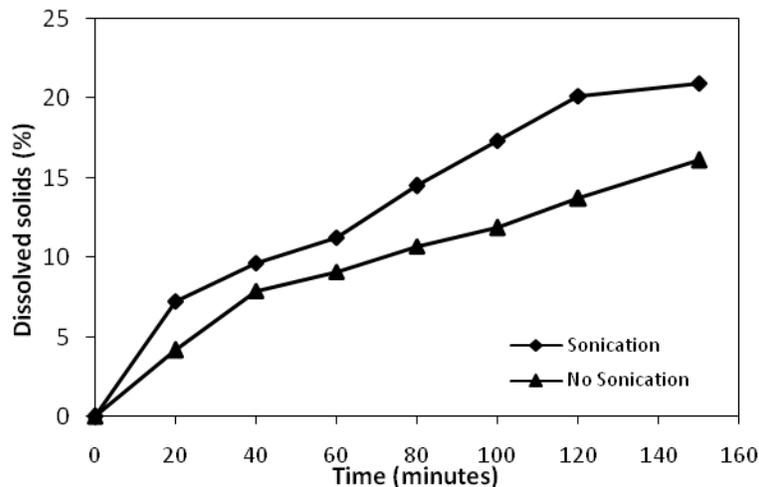

Figure2. The effect of sonication in asbuton extraction

3.3 Effect of Temperature

Effect of temperature on the extraction process at 2 bar can be seen in Figure 3 and 4. Figure 3 and 4 shows that the temperature rise will increase the amount of dissolved solids in the range of 25-90°C and decrease the amount of dissolved solids at temperatures of higher than 90°C.This effect is closely associated with the activation energy.
Constant of the reaction will increase when the temperature is raised so that the reaction rate will increase as well [12,13,14,16,17,18].Temperature increase affect the reaction to be controlled by the difussion of H$^+$ ions towards the boundary layer to the solidsurface. H$^+$ ions at solid surfacewould facilitate the dissolution reaction [12,14].Not only affect the chemical reactions, temperature also affects the physical properties of asbuton. Asbuton has softening point at 79.5°C [27]. Heating process up to 90°C resulted in asbuton will be softened. Asbuton which is softened reduce inter-particle density of asbuton. In addition, the adhesive forces between the mineral solids and asphalt can be reduced and even disappear at certain temperatures [28]. Both of these cause the solids can be separated from the asphalt then the contact surface area between solution and mineralcan be increased.
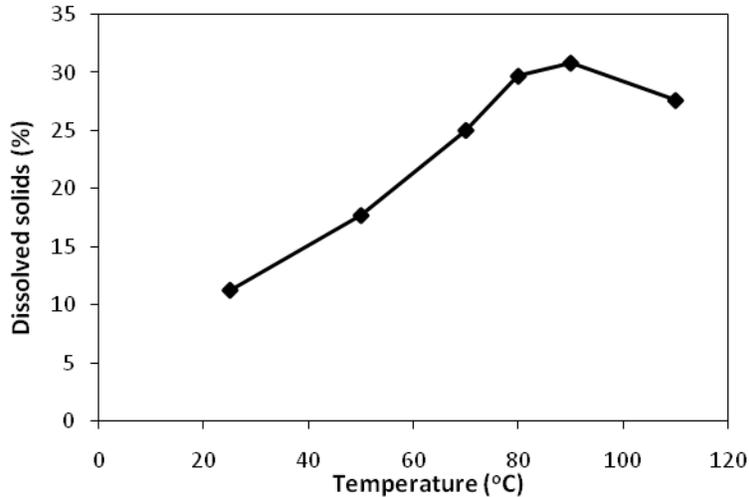
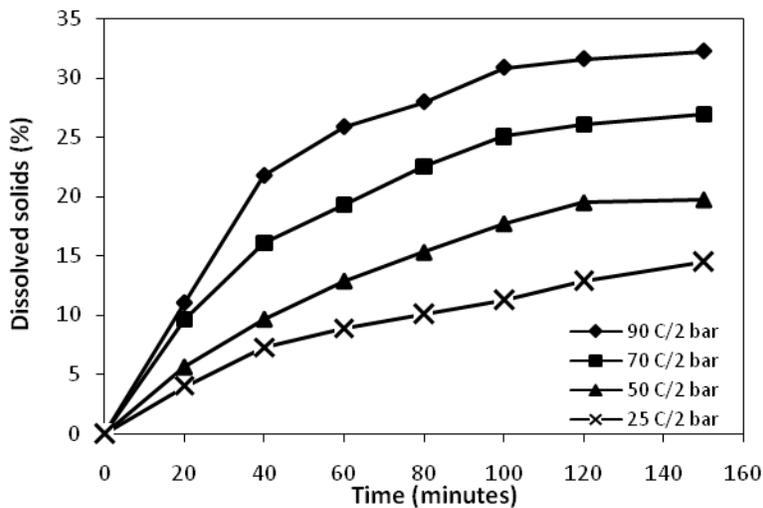*Figure3. The effect of temperature in asbuton extraction*

Figure4. The effect of temperature in asbuton extraction at various times

At temperatures higher than 90°C, the amount of dissolved solids become fewer. This can occur due to the effects of dissolved CO_2 reduction becomes more dominant.Increasing temperature up to 110°C reduced the pH value to 4.1.Decreasing dissolved CO_2 reduced the content of H^+ ions in the NaCl solution and then the solubility of carbonate solids is decreased.In addition, decreased dissolved solids could be caused by hydrate formation in solution at 110°C. Previous study investigated that higher temperature (150°C) supported formation of hydrate in solution then dissolution rate of carbonate solids was decreased [17]. Previous studies show that the maximum temperature of asbuton extraction is 80°C for formic acid and acetic acid solution [9,10].

From the Arrhenius equation, the activation energy can be obtained by plotting ln k versus 1/T as shown in Figure 5. Gradient line shows the value of activation energy. Activation energy was obtained at 24.84 kJ/mol for dissolution of carbonate in asbuton extraction. This activation energy value is still in the range of carbonate dissolution process, 8-60 kJ/mol [14].
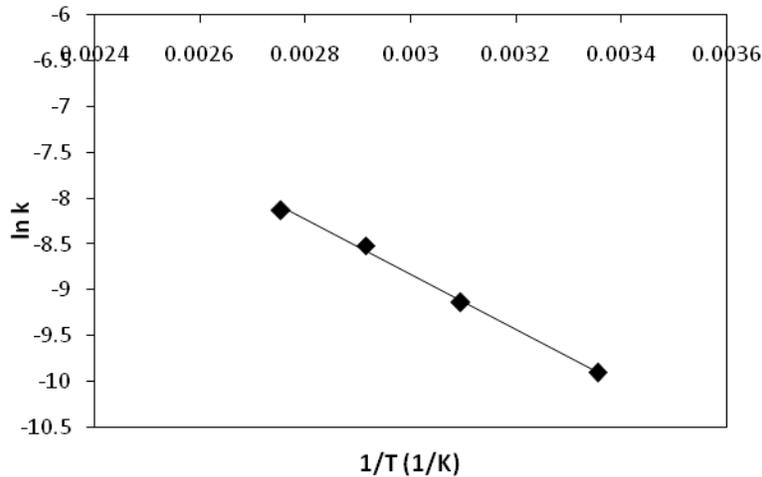
Figure5. ln k vs 1/T to determine activation energy

3.4 Effect of Pressure

Asbuton extraction was performed in 0.5 M NaCl solution at 70°C with various pressure in the range of atmospheric pressure up to 3 bar. Pressure affected asbuton extraction process as shown in Figure 6. Increasing pressures up to 3 bar increased the amount of dissolved solids.High pressure causedthe dissolved CO_2 into more and more then many H^+ ions are formed [29]. This was supported by decreased pH value from 4.33 to 3.8. If many H^+ ions are formed in solution, the amount of dissolved solids will increase. Therefore, increasing pressure increased the amount of dissolved carbonate solids of asbuton as shown by previous studies [15,16,17,18].
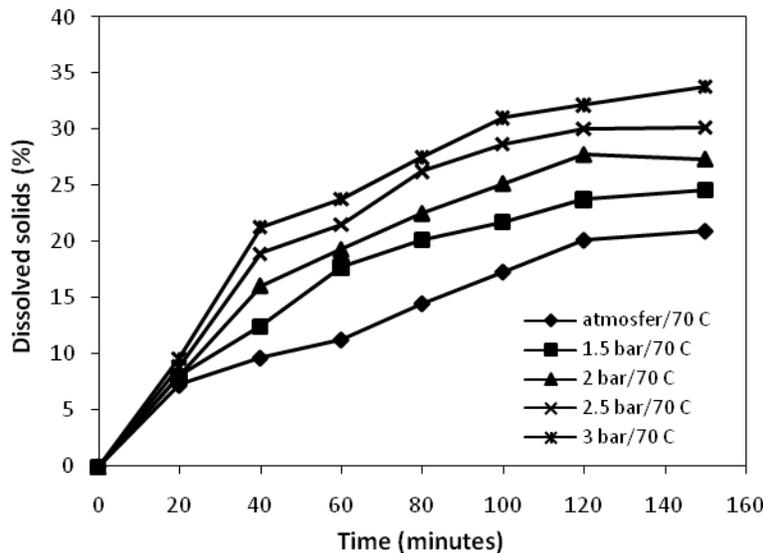

Figure6. The effect of pressure in asbuton extraction

3.5 Effect of Flow Rate of CO_2

Asbuton extraction was performed in 0.5 M NaCl solution at 90°C and 2 bar with variousflow rate of CO_2in the range of 0.2 L/min up to1 L/min.Flow rate of CO_2 affected asbuton extraction process as shown in Figure 7 and 8. Figure 7and 8 show that increasing flow rate of CO_2 from 0.2 to 0.6 L/min increased the amount of dissolved solids and increasing flow rate of $CO_2$from 0.6 to 1 L/min decreased the amount of dissolved solids. It can be concluded that the maximum flow rate at 0.6 L/min. The cause of the increased the amount of dissolved solids was increasing the number of H^+ ions due to an increasing dissolved CO_2 by CO_2 injection. pH value was decreased from 4.36 to 3.83 after increasing flow rate until 0.6 L/min. This result is similar to the dissolution of magnesia in H_2O-CO_2solution that influenced by injection rate of CO_2 [30].

Increasing flow rate of CO_2 did not always increase the amount of dissolved solids, such as in the range of 0.6 to 1 L/min. pH value was increased from 3.83 to 4.8 after increasing flow rate from 0.6 to 1 L/minThis can be happen because the reduction of dissolved CO_2 caused by residence time of bubbles and size of bubles. Increasing flow rate shortened the residence time of bubbles from the bottom to the surface of reactor. Short residence time of bubbles reduced contact time between CO_2 and water. In addition, the larger bubbles were formed at high flow rates and it could reduce contact surface area between CO_2 and water.
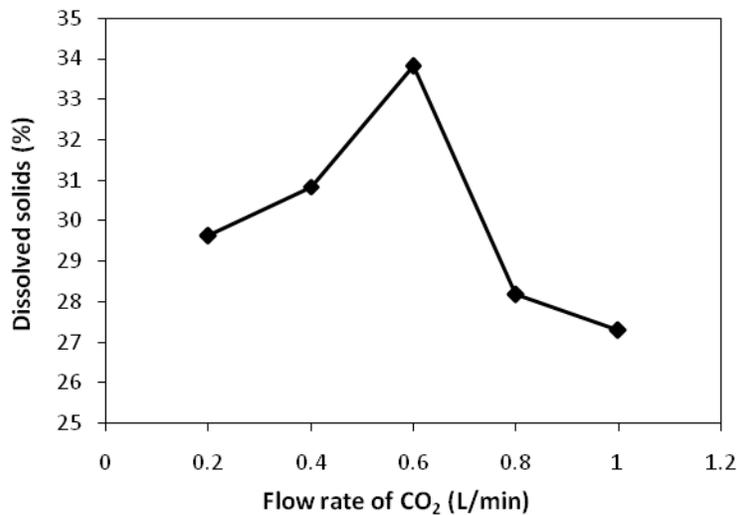

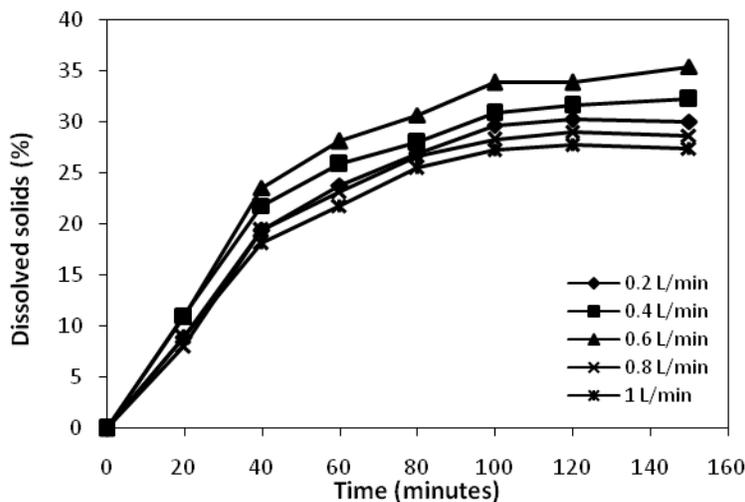*Figure7. The effect of flow rate of CO_2 in asbuton extraction*

Figure8. The effect of flow rate of CO_2 in asbuton extraction at various times

3.6 Effect of NaCl Concentration

Asbuton extraction was performed at 90°C, 2 bar, 0.4 L/min with variousNaClconcentration in the range of 0 up to2 M.Figure 9and 10 show increasingNaCl concentration increased the amount of dissolved solids and then it reached maximum value at 0.5 M. Increased the amount of dissolved carbonate solids at concentration of 5 M can be happen because the influence of ionic strength in this solution. Although increasing NaCl concentration will reduce the solubility of CO_2 [30], this effect is not dominant in the concentration until 0.5 M.The ionic strength will increase and then decrease ion activity coefficient. The reduced ion activity coefficient increased solubility of carbonate solids. This effect has been demonstrated in the dissolution of $CaCO_3$at low concentration of NaCl by various authors [21,32].

At concentration higher than 0.5 M, the reduction of CO_2solubility becomes dominant and supported by the negative effects of ionic strength. The presence of many salt ions cause free water molecules into fewer in solution [18]. Reduced free water molecules causes $CO_2$is difficult to dissolve and then H^+ ions are difficult to form.Furthermore,

the negative effect of high ionic strength triggered complex reaction mechanisms in solid surface to form hydrates [16,18]. In fact, the high ionic strength can lead to the precipitation of carbonate solid [33].
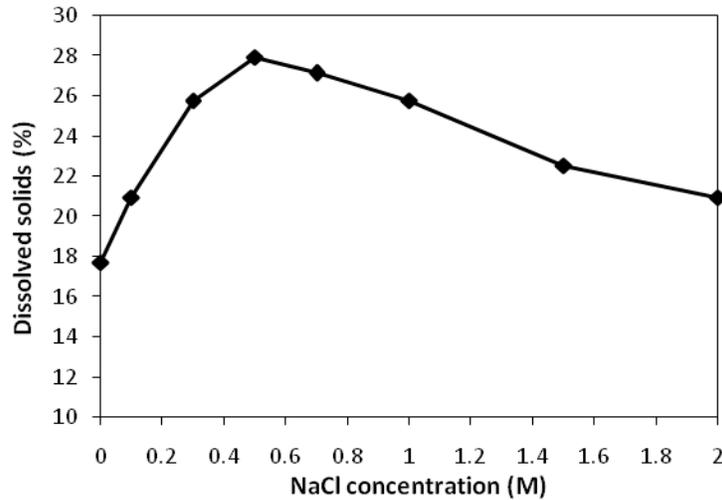

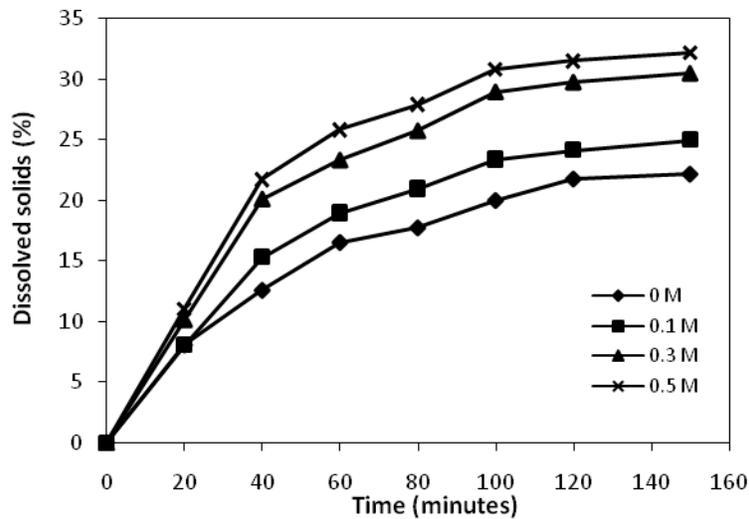*Figure9. The effect of NaCl concentration in asbuton extraction*

Figure10. The effect of NaCl concentration in asbuton extraction at various times

3.7 Specific Gravity Testing

Minerals contained in asbuton cause its specific gravity value reached 1.56, as shown in Table 2. Table 2 shows that there wasreduction of specific gravity between asbutonand asphalt products. Asphalt product was obtained at the optimum condition of the variations, i.e. 90°C, 3 bar, 0.5 M, and 0.6 L/min.A reduction in specific gravity values indicated that carbonate solids were dissolved in acidic brine water. However, specific gravity of asphalt products was still higher than petroleum asphalt.This shows that the existence of solids contained in asphalt. In previous study with formic acid solution, specific gravity was also reduced and its value was able to achieve 1:14 [10]. Asphalt product was tested by SNI 03-3640-1994and ASTM C25-06 then its contained 50.47% asphalt, 24.47% carbonate solids, and 25.06% other mineral solids

Table2. Specific gravity of some components

Components	Specific Gravity
Asbuton	1.56
Petroleum asphalt	1.034
Asphalt product	1.34

3.8 FTIR Analysis

FTIR analysis must be performed on asbuton and asphalt products to identify components of asphalt, carbonate solids and other minerals. FTIR spectra of asbuton can be seen in Figure 11 with wavenumber range of 500-4000 cm^{-1}. In Figure 11, there are strong absorbances at wavenumber of 2924 cm^{-1}, 2855 cm^{-1}, 1458 cm^{-1}, 1033 cm^{-1}, 874 cm^{-1}, 711 cm^{-1}, and 515 cm^{-1}.

The absorbance for the -CH$_3$ group at about 2924 cm^{-1} is common in asphalt component. This may be due to -CH$_3$ substituents on aromatics rings in asphalt. Asphalt component show the absorbances at about 2855 cm^{-1}, 1601 cm^{-1}, 1458 cm^{-1} , and 1376 cm^{-1} can be attributed to C-H stretching in -CH$_3$, C=C stretching, C-H deformation in -CH$_2$ and -CH$_3$, respectively. This spectra similiar to FTIR spectra of asphaltene as asphalt component [34,35].

Strong absorbance at 1458 cm^{-1} also shows the characteristics of calcium carbonate and magnesium carbonate. Similarly, the absorbances in the region around 874 cm^{-1} and 712 cm^{-1} which indicates the presence of that compound [36]. These absorbances shows the C-O bond in the CO_3^{-2} as a characteristic of carbonate solid compound.

Absorbances in the region around 1088 cm^{-1} and 515 cm^{-1} indicate the presence of Si-O bonds in SiO_2 as a characteristic of silica [36]. In the region 3600-4000 cm^{-1}, indicating the presence of C-H bonds in aromatic compounds and the presence of hydroxyl group (O-H) and N-H groups. Thus, it can be concluded that the asbuton contained mostly asphalt, carbonate solids, and silica solids.

The second of FTIR testing was performed on asphalt products using acidic brine water in the range of 500-4000 cm^{-1} as shown in Figure 12. Figure 12 shows that the strong absorbances could be seen at wavenumber of 2924 cm^{-1}, 2855 cm^{-1}, 1600 cm^{-1}, 1453 cm^{-1}, 1376 cm^{-1}, 1034 cm^{-1}, 874 cm^{-1}, 711 cm$^-$1, and 515 cm^{-1}. In Figure 12, absorbance at the region of 3600-4000 cm^{-1} indicated the presence of hydroxyl group (O-H) and N-H groups. Absorbance at about 2924 cm^{-1} shows the aliphatic groups of C-H bond in -CH$_3$ groups are common to asphalt components. It is possible for the -CH$_3$ on aromatic rings contained in component of asphalt. While the absorbances around 2855 cm^{-1}, 1600 cm^{-1}, 1458 cm^{-1}, and 1376 cm^{-1} can be attributed to C-H stretching in -CH$_3$, C=C stretching, C-H deformation in -CH$_2$ and -CH$_3$.
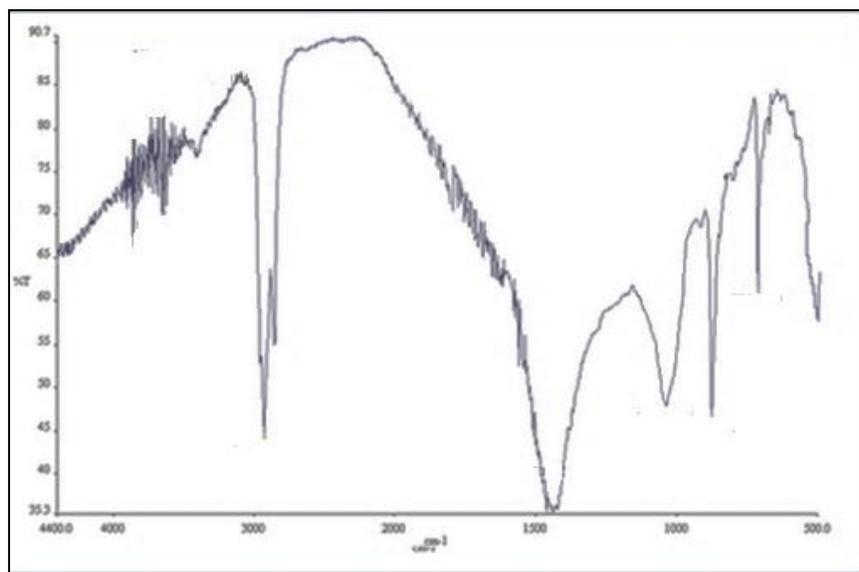

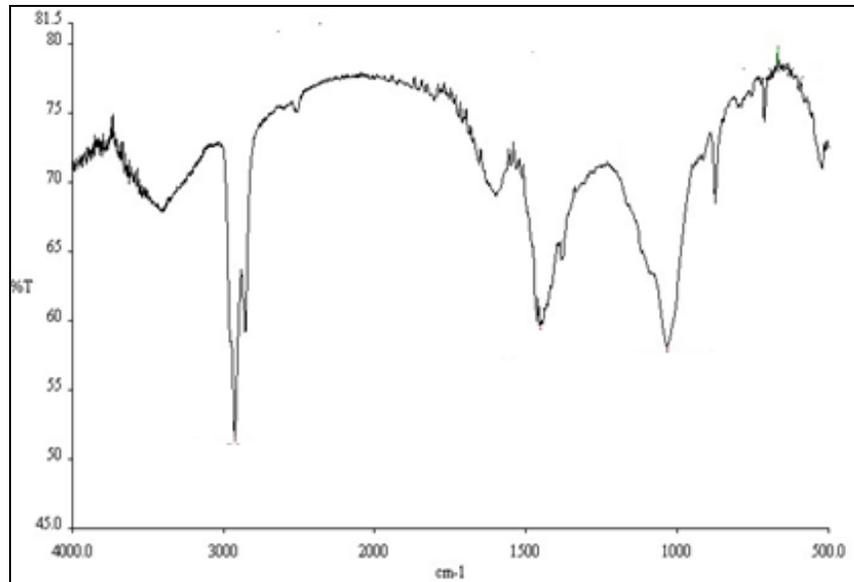
Figure 11. FTIR spectra of asbuton

Figure12. FTIR spectra of asphalt product using acidic brine water

The absence of large peak at 1458 cm^{-1} region, as in asbuton rock spectra, indicated that carbonate solids content in asphalt product was reduced after extraction using acidic brine water. Moreover, absorbances in the wavenumber of 711 cm^{-1} and 874 cm^{-1}as shown also supports the reduction ofcarbonate solidscontent in asphalt product. Strong absorbances at 1033 cm^{-1} and 515 cm^{-1} indicated the presence of SiO_2 compounds as same as asbuton spectra.Thus, it can be concluded that extraction process has dissolved carbonate solids partially. However, silica solids are still remaining in the asphalt product.

3.9 FE-SEM Analysis
Figure 13 shows the FE-SEM result for asbuton and asphalt products. In Figure 13(a), the morphology of asbuton surface is very uneven or irregular because many mineral solids sticked to the asphalt. The presence of asphalt can be shown in dark-colored crevice between the solids. Solids that sticked to asphalt have size at the micro scale.This image is similar to the morphology of mixture of heavy oil, sand, and other aggregates in Canada [37].Asbuton extraction with acidic brine water reduced the amount of carbonate solids. This is supported by the comparison between Figure 13(a) and 13(b). Figure 13(b) shows the morphology of asphalt surface is flatter than asbuton surface. This image is also like liquid surface as the physical characteristics of asphalt. Asphalt surface On the surface of asphalt products, asphalt can be seen clearly and little solids stick to the asphalt, unlike asbuton surface.
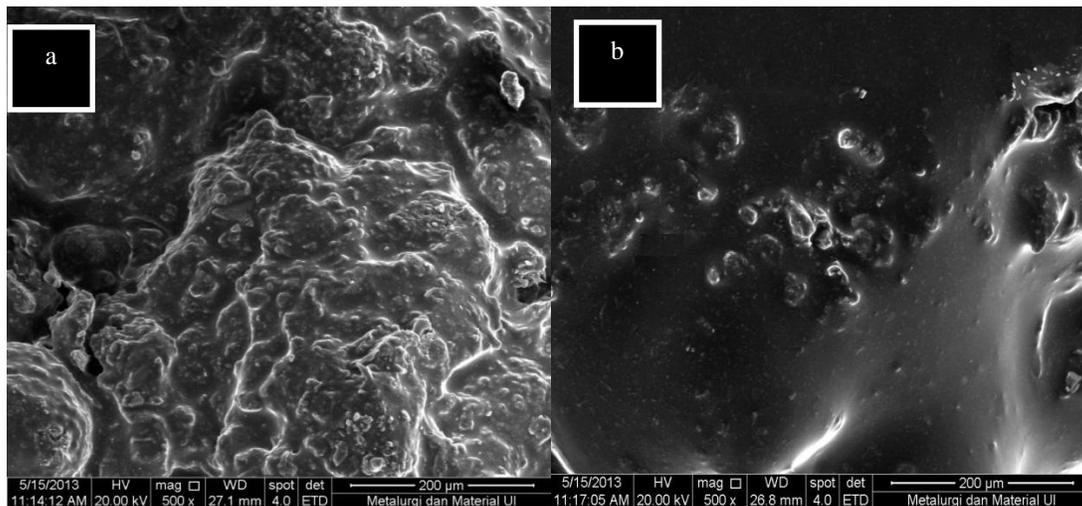
Figure 13. FE-SEM results for asbuton (a) and asphalt product (b)

4.   CONCLUSION

Sonicated extraction of asbuton in acidic brine water solution increased the amount of dissolved carbonate solids compared to normal agitation. Parameters that affect sonicated extraction were temperature, pressure, flow rate of CO_2, and concentration of NaCl. The optimum condition in this case is, temperature of 90^oC, pressure of 3 bar, CO_2 flow rate of 0.6 L/min, and NaCl concentration of 0.5 M. At the optimum conditions, the asphalt product contained 50.47% asphalt, 24.47% carbonate solids, and 25.06% other mineral solids. Asphalt product has specific gravity value greater than petroleum asphalt, namely 1.34. FE-SEM images and FTIR spectra of asphalt product showed the presence of asphalt and residual carbonate solids because the extraction process just partially dissolved carbonate solids.Activation energy required for the extraction process was 24.84 kJ/mol.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

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