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Research Article

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Extraction of $CaCO_3$ as Indonesia Natural Asphalt (Asbuton)'s impurities in acidic brine water solution using semi batch system with CO_2 gas cycle method to produce Asphalt

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ABSTRACT

Indonesia has the largest natural asphalt reserves located in Buton Island (Asbuton). Ironically, Indonesia imports significant amount of asphalt due to no useful technology to produce asphalt from the Asbuton. Objective of this research is to produce asphalt by extraction of $CaCO_3$ as Asbuton's impuritiesusing H_2CO_3 in brine waterassolvent in a semi batch extraction system.CO_2 is dissolved in brine water to produce H_2CO_3 as solvent. Reaction between$CaCO_3$ and H_2CO_3 produces calcium bicarbonate($Ca(HCO_3)_2$). This bicarbonate is then decomposed to$CO_2$and reinjected into the extract or to construct aCO_2cycle in semi batch system. The optimum results obtained at extraction conditions of 2 bars, 85^oC, ratio 0.02 g/mL, 0,5M NaCl and 100 minutes of extraction time.Product asphalt contains 55% asphaltand 45% impurities. The asphalt specification is suitable for hot-mix asphalt type5/55and can be applied to the asphalt mixture type ofACPen60.

Keywords: acidic brine water, natural asphalt, CO_2 cycle system, semi batch extraction

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INTRODUCTION

Road infrastructure is an important aspect in order to support national development. However, the high demand for asphalt is not able to be fulfilled by National production. On the other hand, Indonesia has the largest reserves of natural bitumen in the world, known as Asbuton. This natural asphalt is located in Buton Island, Southeast Sulawesi. Asbuton reserves about 700 million tons or equivalent to more than 100 years of Indonesian asphalt consumption. Stability of asphalt extracted from Asbuton is higher than asphalt oil, while strength and fatigue properties of Asbuton is qualified to replace the asphalt oil [1, 2].

The use of Asbuton as hot mix asphalt has been investigated [1,3]. Low penetration asphalt is more suitable to be applied for cases of a road with high traffic and hot climate such as Indonesia. However, the use directly of Asbuton with content of asphalt as low as 25%, causes high penetration value and therefore it is not appropriate to be applied in Indonesia [1]. Then, it is required a method to increase bitumen (asphalt) content in Asbuton. Table 1 shows that low penetration asphalt can be obtained from higher asphalt content and it is suitable for producing type 5/55 asphalt that is the best type to be applied in Indonesia.

Table 1. Hot mix asphalt from Asbuton [1]

Asbuton Properties	Unit	Hot-mix type	
		20/25	5/55
Asphalt Content	%	23-27	50-60
Grain Size	mm	1.18	1.18
Water Content	%	2	2
Penetration	dm	17-25	2-8

Extraction of asphalt itself or Asbuton's impurities is the proper method to increase asphalt content. Development of the asphalt extraction had been carried out through a variety of organic and inorganic solvents, such as kerosene, hexane, TCE and n-propyl bromide [3]. However, these extraction methods are only able to obtain small quantity of asphalt and required large energy in the separation process.

Impurities of Asbuton are dominated by $CaCO_3$ [1]. High content of $CaCO_3$ will decrease viscosity and deformation resistance of Asbuton [2], therefore extraction of $CaCO_3$ can be an alternative to obtain higher quality of Asbuton. $CaCO_3$ covers the asphalt and causes difficulty on the mobilization of asphalt out of the rock [3]. $CaCO_3$ solids can be dissolved in HCl, acetic acid and formic acid [3]. However, the high cost of the solvent, the difficulty of controlling waste, and the difficulty of regenerating of the solvent causes this process less economical.

Carbonic acid has relatively low solubility coefficient, but this acid is easily to be made as absorption-desorption cycle in water. H_2O-CO_2 solution dissolve $CaCO_3$ and the presence of NaCl in this solution accelerate the dissolution of carbonate solids. However, the salt ions in solution would decrease the solubility of CO_2 so it must be considered [4,5,6].

Asphalt production from Asbuton through extraction $CaCO_3$ using H_2CO_3 in acidic brine water solution has been carried out in sonicated batch system [7]. However, the system require a continuously flow injection of CO_2 and need higher energy to generate ultrasonic wave during the process.

Dissolution of $CaCO_3$ in H_2CO_3 solution formed calcium bicarbonate solution ($Ca(HCO_3)_2$). This bicarbonate is easily decomposed by heating to produce CO_2, $CaCO_3$, and water. CO_2 formed can be recycled to the extractor to reduce required CO_2 in the extraction.

In this research, acidic brine water is made by recycled dissolving CO_2 in NaCl solution to be used to extract $CaCO_3$ on Asbuton in a semi batch extractor. Asphalt obtained will be floating on solution, while the $CaCO_3$ is produced in evaporator as decomposition product of calcium bicarbonate ($Ca(HCO_3)_2$). Make-up of CO_2 is needed to keep the pressure constant. Variables conducted are pressure, extraction temperature, ratio of Asbuton-solvent, and extraction time. Purity of Asbuton is tested by FTIR and asphalt density.

EXPERIMENTAL SECTION

Materials

Materials used in this experiment were Asbuton, NaCl, CO_2, and distilled water. Sample Asbuton was provided from Lawele, Buton Island, Southeast Sulawesi, Indonesia. Sample was crushed and screened to 2 mm of diameter. Composition of Asbuton and asphalt as extraction product were analyzed by SNI 03-3640-1994 and ASTM C25-06. NaCl used is as technical grade. CO_2 is supplied from Trigas with 87% purity.

Experimental Procedure

Schematic diagram of equipment used is shown in Fig. 1. Solution of 0.5 M NaCl 600 mL is inserted into the evaporator, then CO_2 is also injected to assist bubbling process. Temperature of evaporator is set at 110^{o}C. The injection of CO_2 is role as CO_2 make-up.

12 grams Asbuton and 100 mL 0.5 M NaCl is inserted into the extractor and stirring at 300 rpm. Pressure of the extractor is set to 2 bar. After temperature of solution in extractor was approaching the extraction temperature, CO_2 gas and NaCl solution from evaporator is flowed into the extractor to conduct a semi batch extraction system. Extraction was conducted for a defined extraction time

After the extraction process, asphalt was separated from the solution and rinsed with the distilled water. Furthermore, the asphalt was heated at 200^{o}C for 20 minutes and weighed to determine the amount of dissolved $CaCO_3$. Purity of the asphalt product was tested by its density. FTIR analysis will be used to identify the presence of the remaining $CaCO_3$, in the Asbuton.

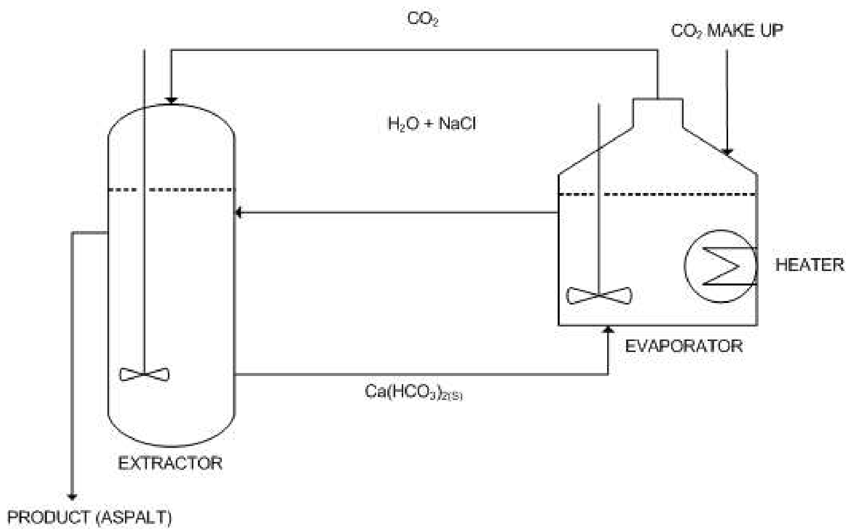

Fig 1. Schematic diagram of experimental apparatus

RESULTS AND DISCUSSION

Application of CO_2 cycled on semi-batch system extraction.

Semi-batch extraction was carried out at temperature of 80°C and 85°C. As comparison, the previous result in batch system at 3 atm is also displayed.

As shown in Fig.2, higher dissolved $CaCO_3$ for batch system as compared to semi batch system was due to higher operating pressure and continue supply of CO_2. While lower of $CaCO_3$ dissolved at 80°C as compared to at 85°C in semibatch system was caused by limitation of dissolve rate of $CaCO_3$.

From Fig 2, the optimum extraction time is 100 minutes at 85°C. Above 100 minutes, the dissolve of $CaCO_3$ reduced. This was caused by reduction of surface contact between $CaCO_3$ and acid solution. The similar phenomenon was also reported by Nierode et.al.[8] and Morse et.al.[9] that surface contact in asphalt extraction is reduced due to agglomeration happen due to asphalt surface properties.

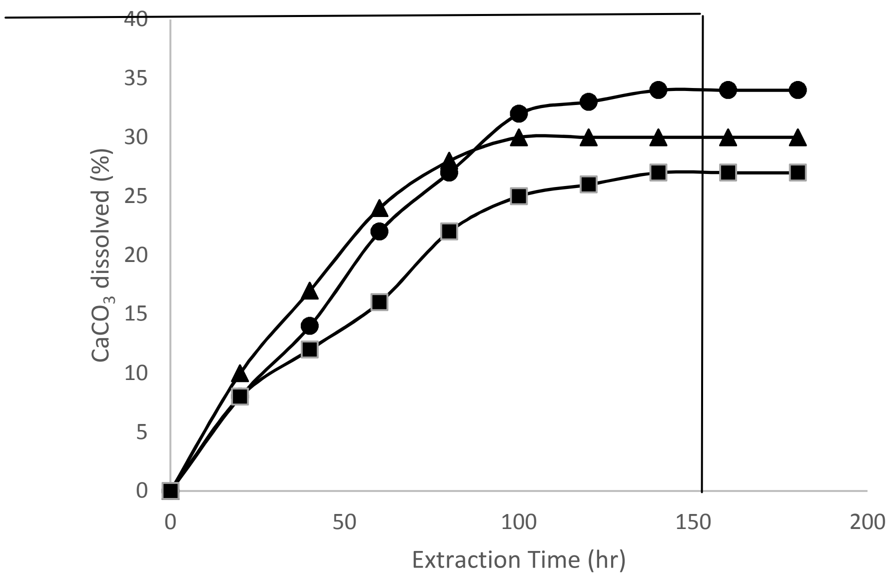

Fig 2.Percentage of $CaCO_3$ dissolved on CO_2 cycled semi batch extraction system
(▲batch 3 atm,85°C; ● semibatch 2 atm,85°C ■; semibatch 2 atm,80°C)

Make-up of CO_2 on the semi batch system can be seen in Fig 3. For comparison, data from previous work in batch system is also displayed [7]. Fig 3 shows that make-up of CO_2 increases with the time. At 100 minutes, make-up of CO_2 on the batch system 54 times larger than the semi-batch system. It is proved that the semi-batch system can reduce the high of CO_2 requirements due to CO2 supply from decomposition of calcium bicarbonate in the evaporator.

In addition, make-up of CO_2 on the semi-batch system is close to stoichiometric required. This indicate that semi-batch system promotes the reaction in the extraction close to the ideal condition and the recycled CO_2 give significantly contribution to provide CO_2. However, the ideal reaction condition is reached at extraction time lower than 100 minutes, otherwise the make-up of CO_2 increase significantly.

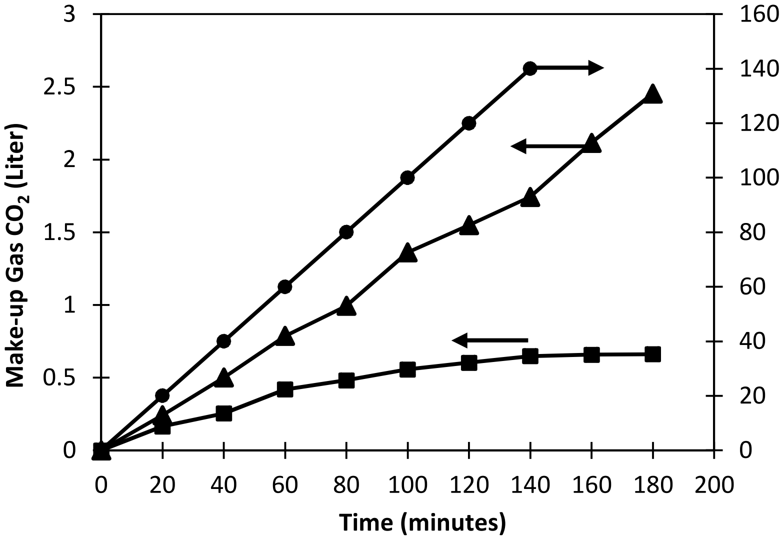

Fig 3.Make-up of CO_2on Asbuton extraction
(● batch 3 bar,85^{o}C; ▲ semibatch 2 bar, 85^{o}C; ■ stoichiometric)

Effect of Solid/Liquid Ratio

Extraction was performed in various solid-liquid ratio in the range of 0.015 to 0.04 g/mL. Fig 4 shows that increasing solid-liquid reduces the amount of dissolved solids. The high ratio of solid/liquid means more asphalt and inert solid in acidic brine water including carbonate solids. If the amount of solvent only capable to dissolve a certain amount of solids, then increasing solid-liquid ratio in constant volume will decrease the percentage of dissolved solids.

Fig 4 shows that the optimum ratio is obtained at 0.02 g/mL. The dissolved $CaCO_3$ reduced at ratio below 0.02 g/mL. This is caused by the reduction of stirring performance that affect to the homogeneous property of the solution. Prokovsky et.al reported that dissolution of $CaCO_3$ in brine water is very affected by degree of homogeneity of the solution [10]. Liu et.al [11] was also reported that concentration and degree of homogeneity of CO_2 in the solution is very affected by diffusion that depend on the stirring performance.

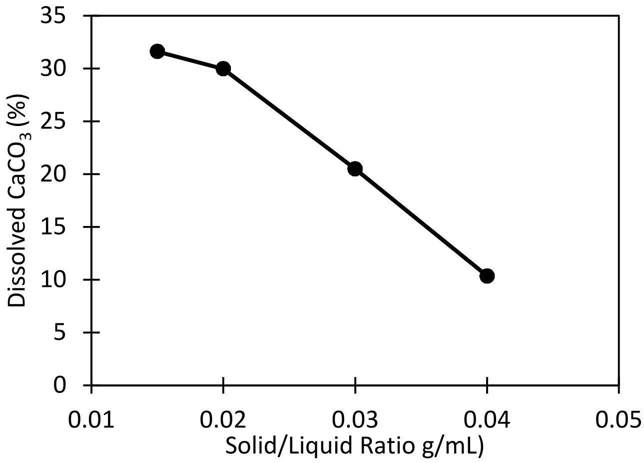

Fig.4.The effect of solid-solvent ratio in Asbuton extraction

Density Testing

Asphalt is a hydrocarbon compounds. Minerals in Asbuton cause its density reached 1.56 g/mL. Table 2 shows that density of asphalt from extraction product is lower than density of the origin Asbuton. The reduction of density indicated that carbonate solidswere partially dissolved in acidic brine water. Calculation by comparing density of the origin Asbuton and produced asphalt results that the product asphalt contains 55% asphalt and 45% impurities with mainly $CaCO_3$.

Table 2. Density of Asphalts

No	Type of Asphalt	Density (g/mL)
1	Asbuton	1,56
2	Asphalt from crude oil	1,03
3	Asphalt (produced in this research)	1,30

FTIR Analysis

FTIR analysis is performed forasphalt from extraction product to identify components of asphalt.For comparison, FTIR spectra of original Asbuton shows spectrum with wavenumber range of 500-4000 cm^{-1} with strong absorbance 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 is due to $-CH_3$ substituents on aromatics rings in asphalt. Asphalt also shows the absorbances at around 2855 cm^{-1}, 1601 cm^{-1}, and 1376 cm^{-1}that can be attributed to C-H stretching in $-CH_3$, C=C stretching, C-H deformation in $-CH_2$ and $-CH_3$, respectively.

Strong absorbance at around 1458 cm^{-1} shows the characteristics of calcium carbonate and magnesium carbonate. These absorbances shows the C-O bond in the CO_3^{-2} as a characteristic of carbonate solid compound.Similarly, the absorbances in the region around 874 cm^{-1} and 712 cm^{-1} indicate the presence of that compound [12].

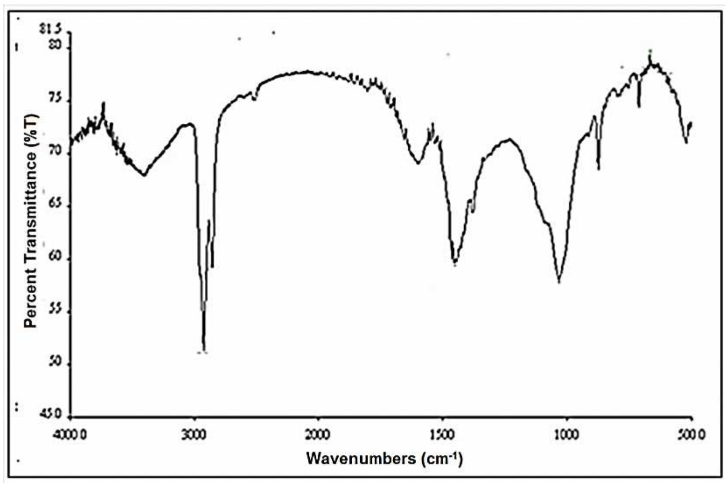

Fig. 5. FTIR of Product Asphalt

FTIR for asphalt product in the range of 500-4000 cm^{-1} is shown in Fig5. Fig 5 shows that the strong absorbances can be seen at wavenumber of 3400 cm^{-1}, 2988 cm^{-1}, 2833 cm^{-1}, 1600 cm^{-1}, 1487 cm^{-1}, 1200 cm^{-1}, 1035 cm^{-1}, 874 cm^{-1}, 711 cm-1, and 500 cm^{-1}. In Fig 6, absorbance at the region of 3600 cm^{-1} indicated the presence of hydroxyl group (O-H) and N-H groups. Absorbance at about 2988 cm^{-1} shows the aliphatic groups of C-H bond in-CH_3 groups that are commonly exhibited by asphalt components. While the absorbances around 2833 cm^{-1}, 1600 cm^{-1}, and 1200 cm^{-1} can be attributed to C-H stretching in $-CH_3$, C=C stretching, C-H deformation in $-CH_2$ and $-CH_3$, sulphur and nitrogen compounds in the asphalt.

The absence of large peak at 1487 cm^{-1}, indicated that carbonate solids content in asphalt product was reduced after extraction using acidic brine water. In additional, absorbances in the wavenumber of 711 cm^{-1} and 874 cm^{-1} as shown also supports the reduction of carbonate solids content in asphalt product. Thus, it can be concluded that extraction process in this research is dissolved carbonate solids partially.

Usage

Asphalt that commonly used in Indonesia isasphalt with type AC Pen 60. Proportion Asbuton for various types of asphalt and the estimated content for each type of fluxing can be seen in Table 2. Table 2 shows that by using Asbuton type 5/55 or 5% Asbuton which contains 55% asphalt in 100% mixture, the use of Asbuton increases the asphalt quality shown by the lower penetration value. In addition, low $CaCO_3$ content in asphalt product improve the performance of stability, tensile strength, viscosity and higher deformation resistance of the hot mix asphalt products [1].

Table 2 Level of Asbuton and estimate levels of fluxing in hot mix asphalt [1]

Type of fluxing	AC pen 60
Fluxing levels. % weight of the total mixture	6,0
Asbuton levels. % weight of the total mixture	
- Asbuton type (20/25)	3,0
- Asbuton type (5/55)	1,0

CONCLUSION

Extraction of Asbuton's impurities using H_2CO_3 in brine water solution produces asphalt which contains 55% asphalt and 45% other mineral solids. The optimum extraction conditions is performed at 2 bar, 85^{o}C, 0.5 M NaCl, ratio of 0.02 g/mL, with 100 minutes extraction time. This condition can dissolve about 45% $CaCO_3$, and requires CO_2 make-up of 0.15 L/g of Asbuton. FTIR spectra of the asphalt product indicates the presence of the asphalt and residual unextracted carbonate solids. Specification of the produced asphalt is suitable for hot mixed asphalt type 5/55 with AC Pen 60.
Pen 60.

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