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Asphalt Production by Extracting $CaCO_3$ as Buton Natural Asphalt Impurities in Hot Acidic Brine Water

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Abstract: The research aims to obtain asphalt from Buton's natural asphalt (Asbuton) by extraction. The extraction is to remove the Asbuton's impurities, $CaCO_3$, in hot acidic brine water in H_2CO_3 solution. The solution is made by dissolving NaCl in various concentrations in H_2CO_3 solution made by injecting CO_2 with various rates. The extraction is conducted in various temperatures, extraction times and ratio of sample and solution. The extraction is conducted in batch extractor with high speed rotation of impeller to distroy Asbuton. The asphalt product is obtained after $CaCO_3$ has been extracted from Asbuton. The purity of asphalt in this research is analyzed using ASTMC 25-06, ICP-AES, FTIR and its density. The presence of H_2CO_3 in hot NaCl solution can extract $CaCO_3$ in Asbuton to obtain high purity of Asphalt. The optimum result is obtained at condition 70°C, ratio 1g Asbuton/L solvent, flow rate of CO_2 4L/min and NaCl concentration 1 M for 15 minutes extraction. With those conditions, $CaCO_3$ can be dissolved up to >90%. The asphalt produced contains 97% asphalt and 3% impurities, especially $CaCO_3$. This asphalt has met the specification for hot mix asphalt type 5/55 and can be implemented in asphalt mixture AC Pen 60.

Key words: Asbuton · Acidic brine water · Batch extractor · Asphalt

INTRODUCTION

The demand of asphalt to build the road in Indonesia is high and this high demand cannot be fulfilled by domestic production [1]. Indonesia have the world's best and biggest natural asphalt deposit in Buton Island, known as Asbuton. The Asbuton deposit can reach up to 700 million tons or 300 years of Indonesia's demand of asphalt. The specifications and quality, including the stability of Asbuton is better than oil asphalt, so it has better durability if it is used as road asphalt [2-5].

The manual for Asbuton as Hot mix has been created [6]. Asbuton as hot mix can be seen on Table 1. Table 1 shows that Asbuton can be used in hot mix for asphalt type 20/25 or 5/55.

Asphalt with low penetration characteristic is suitable to apply in Indonesia because it meets the needs of Indonesia's road whose volume is high and hot climate. However, if Asbuton whose degree of asphalt is about 25% is used as hot mix, the hot mix will have high penetration. In order to be applying in Indonesia, the degree of asphalt must be increased to yield a hot mix with low penetration.

Table 1: Asbutonas Hot mixed Asphalt

Asbuton Characterictics		Type of 20/25	Hotmixed 5/55
Asphalt content	%	23-27	50-60
Particle Size	mm	1,18	1,18
Water Content	%	2	2
Penetration 25°C, 100 g, 5s	mm	17-25	2-8

The development of asphalt extraction from Asbuton has be investigated in various solvents, both organic and inorganic, e.g. kerosene [7], hexane [8], TCE and n-propyl bromide [9]. However, various methods have not yet satisfyingly yielded asphalt to meet hot mix criteria and can only yiled low asphalt and it requires a high energy and produce untreated waste.

Asbuton; s mineral contents are dominated of limestone, $CaCO_3$ [10, 11]. This mineral covers the asphalt to prevent it to mobilize outside. The high $CaCO_3$ content enables the Sutton to deform [12]. The limestone, $CaCO_3$, meanwhile, can dissolve in acidic solution to enable the extraction of $CaCO_3$ from Asbuton in various acidic solution as alternatives to obtain asphalt. The use of strong acid requires a high operating cost and it is hard to treat the waste and also it is hard to regenerate the solvent making it less economical way to do.

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Various acidic solvent, including H_2CO_3, have been investigated for the solvent to extract $CaCO_3$ from Asbuton [13, 14]. The use of weak acid has been successfully extracted $CaCO_3$ to yield asphalt but it still needs some improvements to increase the asphalt content of the product.

Extraction has also used hot water mixed with diesel fuel to modify the Clark Hot Water Process [15]. However, this process aims to extract asphalt from Asbuton, not to extract $CaCO_3$. The is process is less effective when it is applied in Asbuton because Asbuton has different properties with Utah Tar Sand which was used to develop this technique.

In this research, it is undergone by modifying Clark Process to use hot water to extract $CaCO_3$. The hot water used is a NaCl solution (hot brine water) to increase the solubility of $CaCO_3$. Furthermore, to increase its solubility, a CO_2 gas is added to brine water to form hot acidic brine water. The presence of a CO_2 gas will form H_2CO_3 to increase the solubility of $CaCO_3$ [16- 23]. Simultaneously, the presence of NaCl in H_2O-CO_2 solution to boost the solublity of $CaCO_3$ [24-28] by shifting the equilibrium to form $Ca(HCO_3)_2$ to increase the solubility of $CaCO_3$ significantly and to yield a high asphalt content.

MATERIAL AND METHOD

Materials: This research uses Asbuton, NaCl, CO_2 gas and aquades. Asbuton is obtained from Lawele, Buton Island and South-east Celebes. Asbuton is shattered and sieved to obtain a 2 mm diameter. The content of Asbuton is analyzed using ASTM C25-06, ICP-AES and density. Qualitatively, Asbuton is analyzed with FTIR. The NaCl is used to make a brine water solution. The CO_2 gas is used with with 87% purity.

Equipments: Extraction is conducted with batch reactor as shown in Figure 1. The extractor is equipped with a high speed impeller (3000 rpm) as the cutter of Asbuton. The extractor is also equipped with heater and pipe for CO_2 gas flow.

The NaCl solution (1-3%) is added into extractor to make brine water and it is heated to 50-90°C. Asbuton is, furthermore, added to extractor when the desired temperature is reached with Asbuton/Solvent ratio between 1-5 g Asbuton/L Solvent together with CO_2gas whose flow rate is between 1-6 L/minutes. The time taken is from 5-15 minutes. Asphalt produced is discharged through the bottom of the extractor. The $CaCO_3$, hence, is disposed together with hot acidic brine water.

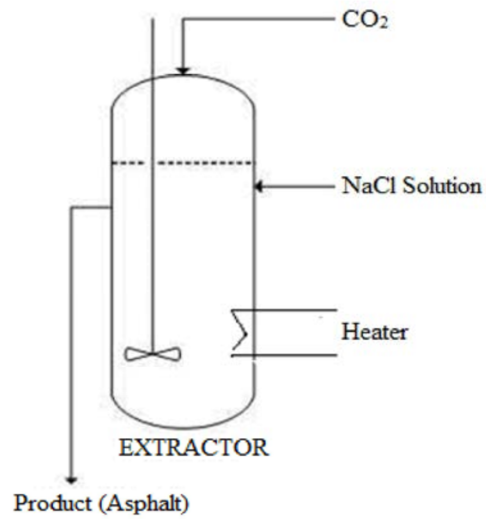

Fig. 1: Schematic of Apparatus

Table 2: Composition of Asbuton

	Analysis Methods	
	ASTM C 25-06	ACP-AES
Compounds	Composition wt%	
Asphalt	31.9	30.3
$CaCO_3$	43.3	44.9
$CaSO_4$, CaS, SiO_2, Al_2O_3, Fe_2O_3	24.8	
Na_2O		0.7
MgO		1.6
SiO_2		4.5
SrO		0.1
Al_2O_3		11.0
TiO_2		0.7
MnO_2		0.1
Fe_2O_3		6.1

RESULT AND DISCUSSION

Asphalt content and Mineral in Asbuton

Before and after the extraction, the asphalt content and Asbuton are analyzed using ASTM C25-06 and ICP-AES. Table 2 shows the result of Asbuton's composition analysis.

Table 1 shows that both ASTM and ICP-AES method gives the similar result, the asphalt content is 30% with most of impurities is $CaCO_3$with 43% composition as impurities. This composition has met the previous publications which have said that the asphalt content is Asbuton [2, 3, 5, 6]. To increase the asphalt content, the $CaCO_3$ content accounting more than 43% is lowered with extraction in hot acidic brine water.

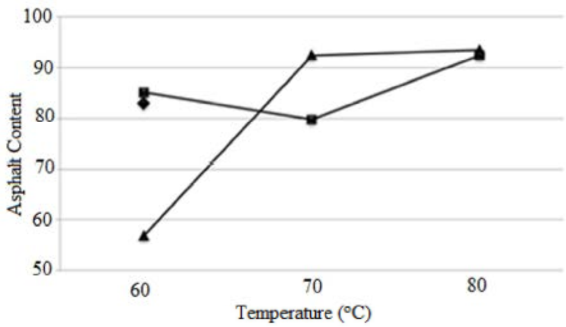

Fig 2: Asphalt Content as Extraction Product at Various Extraction Temperatures (Concentration of NaCl: 0% ♦, 1% ■, 2%▲)

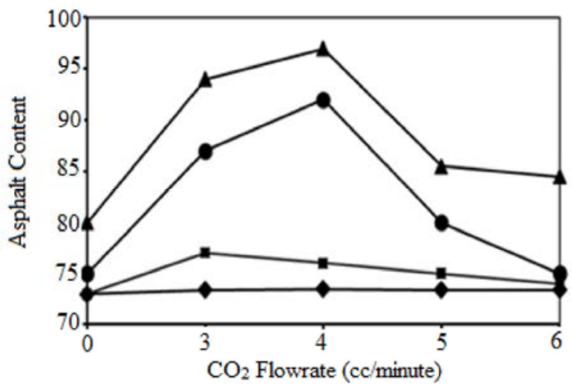

Fig. 3: Effect of CO_2 on Asphalt Concentration (♦: 50°C ■: 60°C ▲: 70°C •: 80°C)

$CaCO_3$ Extraction in Hot Acidic Brine Water: Batch extraction is conducted at 1 bar. With temperature 60-80°C, the CO_2 flow rate from 0-6 L/Minute, time take from 5-15 minutes with NaCl concentration 1-3% and impeller speed at 3000 rpm. The asphalt content produced is shown at Figure 2.

A Figure 2 show that the presence of CaCO3 dissolved increases the asphalt content. During the extraction with brine water without NaCl, the asphalt has 82% content. This shows that the sue of impeller with high rpm can shutter the Asbuton to increase the efficiency of $CaCO_3$ extraction to produce higher asphalt content rather than only using low rpm impeller as has been reported in previous research [13].

Figure 2, moreover, shows that the effect of increasing NaCl in solvent will increase the solubility of $CaCO_3$to increase the asphalt content. For NaCl 2%, the maximum asphalt content is 97% at 70°C. The presence of Cl^- ions causes the ion strength to increase, hence the solubility of $CaCO_3$ increases too [23, 2, 25, 27]. The extraction condition with NaCl 2% and 70°C are the optimum conditions to produce maximum asphalt content.

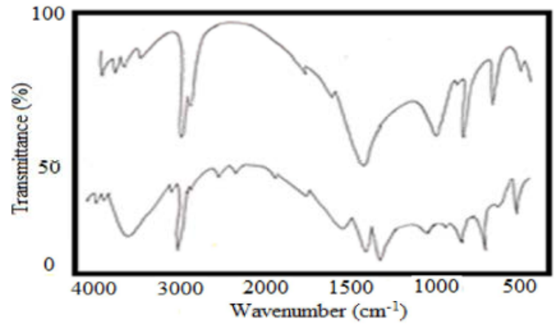

Fig. 4: FTIR Spectra of Asbuton (A) Extracted Asphalt (B)

Figure 3 shows that the effect of flow rate of CO_2gas to the extraction efficiency by being showed of asphalt content. The presence of CO_2enables the solubility of $CaCO_3$to increase because of the forming of $Ca(HCO_3)_2$.For the rate 4 L/minute at 70°C, $CaCO_3$dissolved reaches maximum causing the asphalt content up to 97%. Figure 3 also shows that increasing the rate more than 4 L/minute can cause the H_2CO_3 concentration to reach the saturation, it, hence, undergoes a decreasing number of $CaCO_3$ extracted. $CaCO_3$ dissolves decreases at 50°C and 80°C affected by the flow rate of CO_2 and the decreasing of H_2CO_3 concentration at high temperature [24].

FTIR Analysis: FTIR spectrum for Asbuton and the product of extraction can be shown at Figure 4. Figure 4 shows that the peak rage from wavelength 500-4000 $cm^{-1}$for Asbuton and also the asphalt produced. The peak with strong absorbance appears at wavelength 2924 cm^{-1}, 1458 cm^{-1}, 1033 cm^{-1}, 874 cm^{-1} and 711 cm^{-1}.

The absorbance for $-CH_3$group at 2924 $cm^{-1}$is the general characteristic for asphalt components caused by aromatic ring in asphalt. The asphalt component also shows the absorbance at 2855 cm^{-1}, 1601 cm^{-1} and 1376 cm^{-1}linked with the stretching of C-H in $-CH_3$, the stretch of C=C and C-H deformation in $-CH_2-CH_3$. This spectra is similar to FTIR spectra of pure asphalt [28].

The peak with strong absorbance at 1458 cm^{-1}shows the calcium carbonate characteristic and magnesium carbonate. Comparing the absorbance at wavelength in Figire 4 A and B can be shown that absorbance decreases significantly after the extraction indicating the decrease of $CaCO_3$. Absorbance at 874 $cm^{-1}$and 712 cm^{-1}which are also showing the presence of carbonate compound undergoes an absorbance decrease also after the extraction. The absorbance decrease for carbonate compound shows the success of $CaCO_3$extraction in this research.

Table 3: Density of Asphalts

Type of Asphalt	Density (g/mL)
Asbuton	1,56
Asphakt from crude oil	0,99
Asphalt in this research	0,98

Table 4: Asbuton Content in Hotmixed in Asphalt Concrete (AC) Pen 60

Asbuton Type	Asbuton Content (%)
- Asbuton (20/25)	3,0
- Asbuton(5/55)	1,0

The absorbance at 1033 cm^{-1} dan 515 cm^{-1}shows the presence of Si-O bond in SiO_2as the characteristic of a compound. This absorbance also decreases after extraction. This shows that the extraction does not only decrease the $CaCO_3$ content in Asbuton, but also decreases other minerals content to gain higher purity of Asphalt produced.

Absorbance at area 3600-4000 cm^{-1}shows the presence of C-H bond in aromatic compound and the presence of hydroxyl group (O-H) and N-H group showing the presence of asphalt in Asbuton. The peak shows that the presence of asphalt increases significantly after the extraction. The result of ASTM ad ICP-AES show that the asphalt content at optimum operation is 97% and $CaCO_3$ and other minerals are 3%.

Asphalt Density: The bulk content of mineral in Asbuton makes the density reach to 1.56 g/mL, as shown in Table 3. The extraction can dissolve $CaCO_3$ to decrease the density of Asbuton because of the decrease of minerals and more asphalt content.

This research produces asphalt with density at 0.98 g/cc. this result accounts for the asphalt content up to 97% w/w, so that this asphalt has almost met the pure asphalt criteria to blend with ready mixed asphalt. Asphalt produced for the extraction from Asbuton has lower density than oil asphalt because Asbuton is consisted by short-chain hydrocarnon [10].

Asphalt Usage: Asphalt that commonly used in Indonesia is asphalt AC penetration 60 [5]. The proportion of Asbuton for various asphalt types AC Pen 60 can be shown in Table 4.

Table 4 shows that the usage of Asbuton 5/55 can be more effective because it only needs Asbuton as low as 1%. In other hand, the low asphalt content in hot mix will increase the stability, tension and deformation strength [12].

CONCLUSION

The extraction of Asbuton in hot acidic brine water can yield asphalt with composition of 97% asphalt and 3% impurities, mostly is $CaCO_3$. This asphalt accounts for similar character with pure asphalt. The optimum condition for extraction is pressure at 1 bar, temperature at 70°C, NaCl concentration at 1% w/w, ration 1g Asbuton/L solvent and flow rate for CO_2 4 L'minute. These operation conditions can alsmot dissolve all the $CaCO_3$ in Asbuton. The ashplat produced from this extraction has density as low as 0.98 g/ml. the FTIR Spectra shows the presence of asphalt ad also the small presence of carbonate compounds, although the extraction in this research can almost dissolve most of the carbonates.

REFERENCES

1. Suryana, N., 2007. Analysis of Failure Factor in Using Asbuton, Road and Bridge Research and Development Center. Department of Public Work Indonesia Publication.**,** 3-10.
2. Affandi, F., 2006. Asbuton Purification for Hot Mixing, 2006.. Journal of Road and Bridge, 3(3): 6-28.
3. Harry, F., B.S. Subagio and B.I. Siswosoebrotho, 2006. Evaluation of Strength Modulus for Asbuton Mixing. Proceeding of KRTJ Seminar IX, pp: 1-15.
4. Subagio, B.S., R.H. Karsaman and I. Fahmi, 2003. Fatigue Characteristic of HRA Mix using Indonesia Rock Asphalt (Asbuton) as a filler. Proceedings of EASEC Seminar., pp: 1-10.
5. Suryana., 2007. Procedure of Asbuton Mixing. Department of Public Work of Indonesia's Publication, pp: 11-15.
6. Sayono., 2000. Extraction Process for Purification of Asbuton, Indonesia Paten, ID 0004877.
7. Purwono, S., B. Muhrachman, D.T. Yulianti and Suwati, 2005. Mass Transfer Coefficient of Asbuton Extraction. Forum Teknik, 29: 40-49.
8. Gardiner, M. and J.W. Nelson, 2000. Use of Normal Propyl Bromide Solvents for Extraction and Recovery of Asphalt of Cements. NCATReport, 00-06: 2-7.
9. Kurniadji, 2007. Modul Trainer of Trainee : Asbuton for Road Hardening. Research & Development Center for Road and Brigde, Department of Public Work of Indonesia's Publication, pp: 22-25.

10. Siswosoebrotho, B.I., W. Tumewu and N. Kusnianti, 2005. Evaluation of Lawele Buton Natural Asphalt in Asphalt Concrete Mixture. Proceedings of the Eastern Asia Society for Transportation Studies, 5: 857-867.
11. Singh, M, P. Kumar and M.R.Maurya, 2013. Strength Characteristics of SBS Modified Asphalt Mixes with Various Aggregates, Construction and Building Materials, 41:815-823.
12. Lisminto., 1996. Pure Asphalt Production. Indonesia Paten. ID 010445.
13. Nasikin, M., A.Y. Saputra and B.H. Susanto, 2015. Extraction of $CaCO_3$ from Asbuton for Asphalt Production, Journal of Chemical and Pharmaceutical Research., 7(5): 677-682.
14. Devianto, I.M., B.H. Susanto and M. Nasikin, 2013. Asphalt Production from Asbuton Rock using Formic Acid. International Conference on Quality in Research. Yogyakarta, Indonesia.
15. Kumar, R., 1995. Pilot Plant Studies of A New Hot Water Process for Extraction of Bitumen. The University of Utah Publication..
16. Nierode, D.E. and B. B. Williams, 1971. Characteristics of Acid Reaction in Limestone Formations. Society of Petroleum Engineers Journal., 251: 406-418.
17. Morse, W. and R.S. Arvidson, 2002. The Dissolution Kinetics of Major Sedimentary Carbonate Minerals. Earth-Science Reviews., 58: 51-84.
18. Pokrovsky, O.S., S.V. Golubev and J. Schott, 2005. Dissolution Kinetics of Calcite, Dolomite and Magnesite, Chemical Geology., 217: 239-255.
19. Gledhill, D.K. and J.W. Morse, 2006. Calcite Dissolution Kinetics in Na-Ca-Mg-Cl Brines, Geochimica et Cosmochimica Acta., 70: 5802-5813.
20. Pokrovsky, O.S., S.V. Golubev, J Schott and A. Castillo, 2009. Calcite, Dolomite and Magnesite Dissolution Kinetics in Aqueous Solutions at Acid to Circumneutral. Chemical Geology, 265: 20-32.
21. Finneran, D.W. and J.W. Morse, 2009. Calcite Dissolution Kinetics in Saline Waters. Chemical Geology, 268: 137-146.
22. Gornitz, V., 2009. Encyclopedia of Paleoclimatology and Ancient Environments. Springer: Nederland, pp: 361-374.
23. Ellis, A.J., 1963. The Solubility of Calcite in Sodium Chloride Solutions at High Temperatures, American Journal *of* Science,l 261: 259-267.
24. Coto, B., C. Martos, J.L. Pena, R. Rodriguez and G Pastor, 2012. Effects in the Solubility of $CaCO_3$: Experimental Study and Model Description. Fluid Phase Equilibria, 324: 1-7.
25. Duan, Z. and D. Li., 2008. Coupled Phase and Aqueous Species Equilibrium of the H_2O-CO_2-NaCl-$CaCO_3$ System with NaCl Concentrations up to Saturation of Halite. Geochim. Cosmochim. Acta, 72: 5128-5145.
26. Duan, Z. and R. Sun, 2003. An Improved Model Calculating CO_2 Solubility in Pure Water and Aqueous NaCl Solutions. Chemical Geology, 193: 257-271.
27. Liu, Y., M. Hau, G. Yang and B. Han, 2011. Solubility of CO_2 in Aqueous Solutions of NaCl, KCl, $CaCl_2$ and Their Mixed Salts at Different Temperatures and Pressures, Journal of Supercritical Fluids, 56: 125-129.
28. Leon-Bermudez and Salazar., 2008. Synthesis and Characterization of The Polystyrene-Asphaltene Graft Copolymer by FT-IR Spectroscopy, CT&F - Ciencia, Tecnología Futuro, 3: 157-167.