

Utilization of Glycerol Derived from *Jatropha*'s Biodiesel Production as a Cement Grinding Aid

O. Farobie, S S. Achmadi, and L K. Darusman

Abstract—Biodiesel production results in glycerol production as the main by-product in biodiesel industry. One of the utilizations of glycerol obtained from biodiesel production is as a cement grinding aid (CGA). Results showed that crude glycerol content was 40.19% whereas pure glycerol content was 82.15%. BSS value of the cement with CGA supplementation was higher than that of non-supplemented cement (blank) indicating that CGA-supplemented cement had higher fineness than the non-supplemented one. It was also found that pure glycerol 95% and TEA 5% at 80°C was the optimum CGA used to result in finest cement with BSS value of 4.836 cm²/g. Residue test showed that the smallest percent residue value (0.11%) was obtained in cement with supplementation of pure glycerol 95% and TEA 5%. Results of residue test confirmed those of BSS test showing that cement with supplementation of pure glycerol 95% and TEA 5% had the finest particle size.

Keywords—biodiesel, cement grinding aid, glycerol, *Jatropha curcas*

I. INTRODUCTION

FOR the last few years, biodiesel industry in Indonesia has been growing rapidly to overcome the increasing energy needs in the future. Indonesia's high dependency on fuel amidst the reducing fossil fuel reserve has been anticipated by the government through the issuance of Presidential Regulation No. 5 Year 2006 on National Energy Policy and Presidential Instruction No. 1 Year 2006 on the Supply and Utilization of Plant Oils as Other Fuel. Increasing biodiesel production has resulted in an increased glycerol production as glycerol is the main by-product of biodiesel industry. In biodiesel production, 10% (w/w) crude glycerol is yielded [1]. It was estimated that an increase in biodiesel production may lead to an increase in glycerol production by 114% [2]. In 2010, the price of glycerol may go down from \$0.5 to \$0.35 per pound. Price reduction and production increase may result in glycerol having no selling value. The utilization of glycerol resulted from biodiesel production is facing great challenges. Effective conversion from glycerol into specific and useful products is potential to avoid environmental problems caused by glycerol waste and improve the efficiency of biodiesel production.

O. Farobie is with the Surfactant and Bioenergy Research Center, Bogor Agricultural University, Jln. Padjajaran No.1, Kampus IPB Baranangsiang, Bogor, West Java, Indonesia 16144 (e-mail: obiefarobie@gmail.com).

S S. Achmadi and L K. Darusman are with Department of Chemistry, Faculty of Mathematics and Science, Bogor Agricultural University, Kampus IPB Darmaga, Bogor, West Java, Indonesia.

One of the utilizations of glycerol obtained from biodiesel production is as a cement grinding aid (CGA). CGAs are supplementary organic substances (gas, liquid, or solid) added into the mill at low dosage (0.01-0.05%) during cement particle grinding process. CGA improves the efficiency of this grinding process, reduces particle size, and reduces energy use without impairing cement performance [3]. The use of CGA in cement production process brings some benefits including the improvement of separator efficiency to improve cement production per time unit, reduction in agglomeration process, cost saving as cement production process takes shorter time, and energy saving [4]. The effect of grinding aids has been explained mainly by two mechanisms. One is the alteration of the surface and mechanical properties of individual particles, such as a reduction of surface energy, and the other is the change in arrangement of particles and their flow in suspension [5-7].

Some common materials used as CGA include triethanolamine (TEA), mono- and diethyleneglycol (DEG), oleic acid, sodium oleic, dodecylbenzene sulfonic acid, and sodium lignosulfonic acid (from paper industry) [3], sugar cane baggase ash [8], beet molasses [9], triethanolamine with potassium hydroxide [10], dihydroxy compound class (ethylene glycol, propylene glycol, and polypropylene glycerol) [11], phenol, glycol, and alkanolamine [12], alcohols and glycols [13], fatty acids [14]. Katsioti *et al.* [15] also investigated the impact of some various cement grinding aids such as triethanolamine hydrochloride, triethanolamine, 2,4-pyrimidinedione, 1,1',1''-Nitrolotri-2-propanol (TIPA), 1,1'-Iminobisi-2-propanol (DIPA), 4-hydroxy-1,8-naphthyridine, benzene, and benzenamine on grindability and cement performance.

Glycerol resulted from *jatropha* biodiesel industry has similar physical and chemical properties as mono- and diethilene glycols (DEG) making it possible to act as a CGA. Paten [16] claimed that the CGA they used composed of 10-30% water, 10-80% triethanolamine, and 10-80% glycerol. However, the water contained in CGA made cement particles easy to coagulate. Therefore, an attempt was made to utilize glycerol resulted from *jatropha* biodiesel production in a composition of 85-100% glycerol without additional water.

In general, the study was aimed at utilizing glycerol resulted from *jatropha* (*Jatropha curcas*) biodiesel production as a CGA. In specific, the study was aimed at purifying glycerol resulted from *jatropha* biodiesel production, obtaining the most appropriate condition for CGA production, and obtaining the best formulation for the production of CGA from glycerol resulted from *jatropha* biodiesel production.

II. MATERIALS AND METHODS

A. Materials and equipment

Materials used in this study included jatropha seeds obtained from Indramayu (West Java, Indonesia), clinker Plan 4 from PT Indocement Tungal Prakarsa Cibinong, Indonesia, and synthetic gypsum. Equipment used included QP2010 Shimadzu gas chromatography–mass spectrophotometer (GC-MS), manometer, 45 µm cylindrical sieves, and a set of grinding machine.

B. Scope of Study

The study was conducted in four stages. The first stage was the preparation and purification of glycerol from biodiesel to produce pure glycerol. In the next stage, characterization and concentration determination of crude glycerol and purified glycerol were done by using a GC-MS. In the third stage, CGA preparation in various temperatures and triethanolamine (TEA) concentration was conducted. The temperatures were 80 and 90°C and TEA compositions were 0, 5, 10, and 15%. The last stage was product characterization by a blaine specific surface area (BSS) test and a residual test.

C. Purification of Crude Glycerol

Phosphoric acid 5% (v/v) was added into crude glycerol. The solution was stirred with a magnetic stirrer for 30 minutes. The resulted solution was left for 60 minute until three layers were formed. The bottom layer was a solid potassium phosphate salt, the middle layer a glycerol, and the top layer fatty acid remains [17]. The top and middle layers were separated from the solid bottom one by filtering the solution through a Buchner funnel. The resulted filtrate was separated by using a separation funnel and the bottom layer was taken as pure glycerol.

D. Glycerol Characterization

Purified glycerol was characterized by using a GC-MS and glycerol concentration analysis according to SNI 06-1564-1995. A Shimadzu P2010 GC-MS instrument with a capacity of 50 scanning frequency/second was used. An Rtx®-1MS (melted silica) filled with 100% dimethyl polycyloxan was used. GC-MS analysis was conducted by using distilled water and helium carrier.

E. CGA Preparation

CGA preparation was conducted in varieties of temperatures (80 and 90°C) and triethanolamine compositions (without TEA, and with TEA of 5, 10, and 15%). A completely randomized design was used. Data of BSS values and % residue were subjected to a Duncan Multiple Range Test. CGA preparation conditions are presented in Table 1.

F. Product Characterization

The resulted cement was characterized by BSS and residual tests. The tests were conducted by putting clinker (96.5%) and gypsum (3.5%) into a grinding machine of 3.5 kg capacity. In this machine, grinding and homogenization were done for 60 minutes. Cement was produced by using CGA and glycerol p.a. of about 0.05% (w/w) and without any CGA (blank).

The resulted product was then characterized by BSS and residual tests.

TABLE I
 CGA PREPARATION CONDITIONS

	Glycerol composition (%)	Temperature (°C)	TEA composition (%)
Sample 1	100	80	0
Sample 2	95	80	5
Sample 3	90	80	10
Sample 4	85	80	15
Sample 5	100	90	0
Sample 6	95	90	5
Sample 7	90	90	10
Sample 8	85	90	15

III. RESULTS AND DISCUSSIONS

A. Glycerol Yielded from Purification

Elimination of impurities from glycerol can be done by the addition of phosphoric acid. This acid reacts with potassium hydroxide catalyst remains to form potassium phosphate salt (Figure 1A). Methanol remains that do not react can be eliminated by heating glycerol at 65°C, a temperature at which methanol evaporates. In addition, phosphoric acid converts soap back into free fatty acids (Figure 1B).

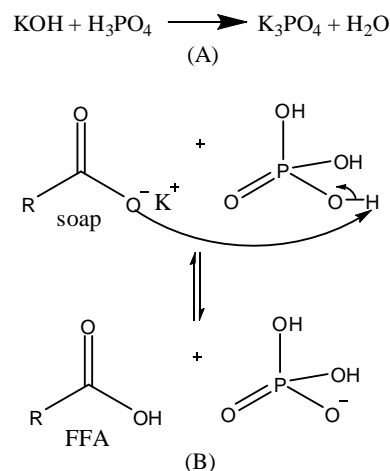


Fig. 1 Reaction of potassium phosphate salt (A) and free fatty acid formation (B)

It was found that the addition of phosphoric acid into crude glycerol resulted from this study formed 3 layers of mass distribution percentages as follows.

- Top layer (FFA) (38.98%), solid in room temperature.
- Middle layer (glycerol) (40.34%), liquid.
- Bottom layer (K₃PO₄ salt) (20.68%), solid.

The mass distribution percentages obtained in this study was presented in Figure 2. The figures were different from the previous study that obtained mass distribution percentages of palm-based biodiesel of 33.9% glycerol, 10.5% fatty acids,

and 65.2% salt [18]. These differences might be caused by different fatty acid compositions of jatropha and palm oil. In addition, the amount of catalyst added in the production of biodiesel from palm oil was higher than that in the production of biodiesel from jatropha oil resulting in more salt in palm-based biodiesel production. However, the mean percentages of palm-based and jatropha-based glycerol were not significantly different.

TABLE II
COMPARISON OF GLYCEROL RATE

Source	Glycerol rate (%)
SNI 06-1564-1195 [19]	minimum 80
Ooi <i>et al.</i> [18]	51.4
Kocsisová and Cvengroš [17]	70
British Standard	80
Results of this study	82.15

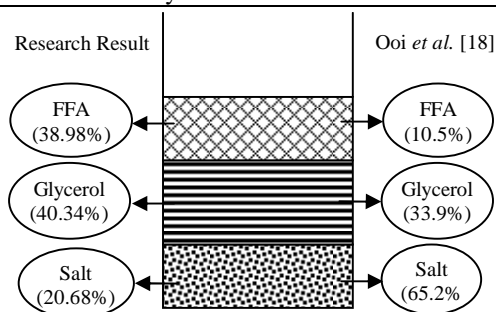


Fig. 2 The mass distribution percentage of layers

The layers formed by the addition of phosphoric acid are presented in Figure 3. Figure 3 (A) was taken after the mixture was left for 5 minutes, while Figure 3 (B) was taken after the temperature of the mixture was under room temperature. The difference of the two figures was found in the top layer (FFA). This layer was found as liquid at temperatures above 25°C and solid at temperatures below 25°C.

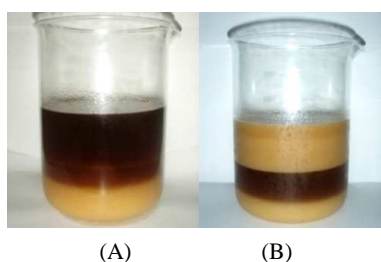


Fig. 3 The layers formed by the addition of phosphoric acid at temperature above 25°C (A) and at temperature below 25°C (B)

From solution separation, a filtrate with two layers was obtained. The top layer was free fatty acid (FFA) remains with a pH of 5.0, while the bottom one was glycerol with a pH of 6.87 (Figure 4A). Glycerol solution resulted from this filtration is presented in Figure 4B. It can be seen that glycerol resulted from the filtration was clearer than crude glycerol. Besides, purified glycerol did not solidify even though it was placed at under room temperature. This made purified glycerol easier to handle further.

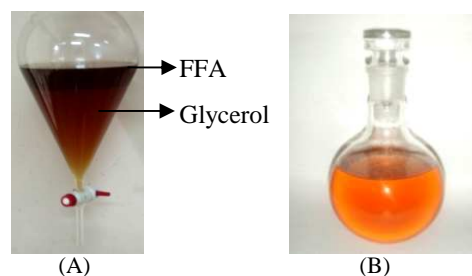


Fig. 4 The layer of FFA and glycerol (A) and purified glycerol (B)

B. Glycerol Characteristics

Results of GC-MS analysis showed that crude glycerol revealed more peaks than pure glycerol (Fig. 5). This indicated that crude glycerol still contained other compounds. Qualitative analysis done by GC-MS showed that purification of crude glycerol resulted in purer compounds that were indicated from the reduction in the number of impurities from 17 in crude glycerol to 11 after purification.

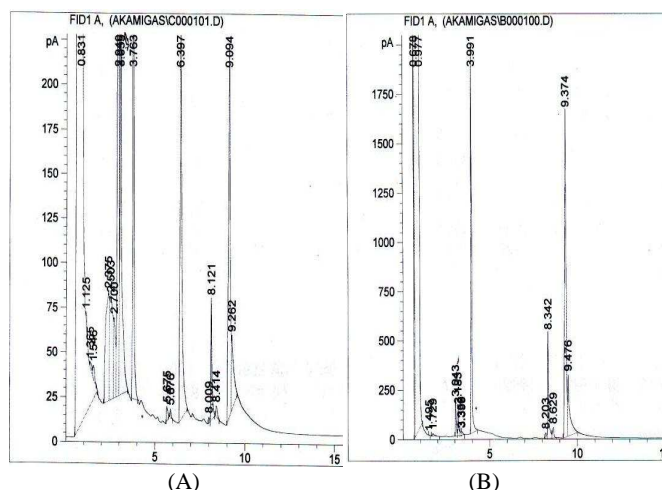


Fig. 5 GC-MS spectrum of crude (A) and purified glycerol (B)

Qualitative analysis on glycerol before and after purification was conducted by using glycerol concentration determination referring to SNI 06-1564-1995 [19]. Glycerol concentration had to be determined to assess its purity level. Results showed that crude glycerol obtained from jatropha was 40.19% and glycerol concentration after purification was 82.15%. This indicated that jatropha glycerol could be used as a CGA as according to Tran *et al.* [20], 50-90% is the best glycerol concentration for CGA. Required glycerol concentration for commercial use at the minimum is 80%, according to SNI 06-1564-1195 or 70% according to Kocsisová and Cvengroš [17]. Comparison of glycerol concentrations from several literatures are presented in Table 2.

C. Texture of Products

Physically, the resulted cement with CGA supplementation was finer than one without CGA (blank) (Figure 6). The finery rate of CGA-supplemented cement was higher than glycerol p.a.-supplemented cement and blank cement.



Fig. 6 Resulted cement with and without CGA supplementation

TABLE III
 COMPARISON OF CEMENT BSS VALUES

Source	BSS value (cm ² /g)
SNI 15-2049-2004	Min. 2,800
ASTM C150-049	Min. 2,800
PT Indocement Tunggal Prakarsa, Tbk	3,100-3,500
Results of this study	4,274-4,836

Another advantage of CGA-based glycerol is that this type of glycerol is capable of eliminating ball coating and dispersing ground materials. Results showed that cement particles obtained without CGA was easier to adhere to the ball mill than those obtained from cement with CGA (Figure 7).

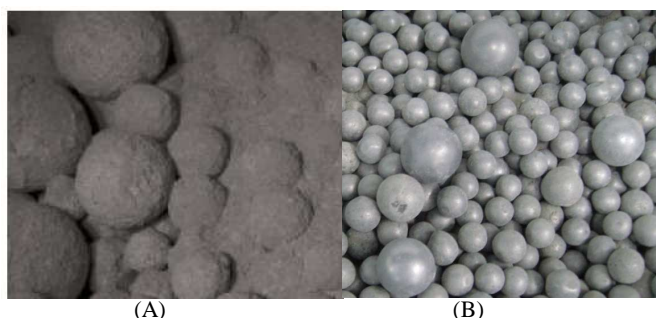


Fig. 7 Ball mill at CGA-none supplemented cement (blank) (A) and CGA-supplemented cement (B)

The factor with the most important role in the process of ball coating is electrostatic force. Cement raw materials, in this case, clinkers that are made of calcium silicate, calcium aluminate, and calcium aluminophosphate [21] possess positive and negative charges distribution when it is ground into smaller particles. This charge involves electrostatic forces leading to agglomeration. This agglomeration makes cement particles easy to adhere to the ball mill. Glycerol-based CGA as an organic compound functions as an electrostatic force reducer allowing agglomeration to take place. In addition, electrostatic force resulted from CGA-supplemented cement was much higher than that from non-supplemented cement although the resulted van der Waals force was similar [22]. As resulted electrostatic force got higher, the ball mill got clearer giving its higher capability to produce finer particles. Therefore, CGA-supplemented cement had higher fineness level than the one without CGA supplementation.

D. BSS

BSS analysis was done in order to quantitatively assess the fineness of resulted cement. Results showed that in general, CGA supplementation resulted in cement with higher BSS values. Theoretically, as BSS value gets higher, the cement gets finer so that its mechanical power gets higher [23]. This indicated that CGA-supplemented cement was finer than the one without CGA supplementation.

BSS values of some glycerol-based CGA as jatropha biodiesel by-products are given in Figure 8. It was seen that BSS values of cement with CGA supplementation was higher than that of cement with p.a. glycerol supplementation. In addition, cement with glycerol p.a. supplementation had higher BSS values than blank cement.

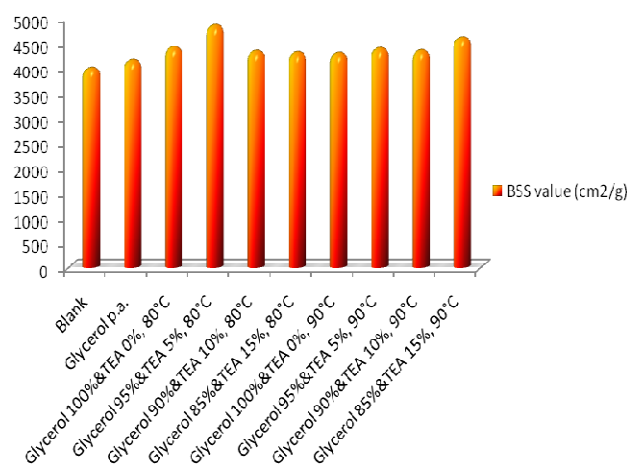


Fig. 8 BSS values of blank cement and CGA-supplemented cement after 1 hour grinding

The order of the fineness of cements produced in this study are as follows: cement supplemented with CGA from this study > cement supplemented with glycerol p.a. > blank cement. It was also found that the most optimum CGA for cement particle grinding was the one with the composition of 95% purified jatropha glycerol and 5% TEA which was mixed at 80°C. The BSS value from this cement was found to be 4,836 cm²/g. This figure met the requirement of minimum BSS level set in SNI 15-2049-2004 and ASTM C150-049 [24], namely 2,800 cm²/g (Table 3).

BSS level of cement supplemented with glycerol p.a. (0.05% w/w) was 4,139 cm²/g. This was not too different from the previous study [4]. They found that cement supplemented with glycol-based CGA had BSS value of 4,077 cm²/g and the one supplemented with their product (Sika Grind 0.03% w/w) had BSS value of 4,117 cm²/g. Meanwhile, Maeder *et al.* [25] found BSS values of 3,530 and 3,640 cm²/g for triethanolamine-based CGA with 1 hour grinding time and triisopropanolamine-based CGA, respectively. These differences were suspected to be caused by different materials and number of and ball mill used. This might be true as materials and number of ball mill was found to affect cement fineness rate although the grinding time was just the same.

It was also found that TEA composition, reaction temperature, and their interaction gave significant effect on BSS value ($\alpha = 5\%$). Results of a Duncan test ($\alpha = 5\%$) showed that at 0, 5, and 15% but not 10% TEA compositions, each temperature gave different BSS values.

E. Residue

In addition to BSS, a residue test can be used to assess cement fineness. This test is done by using a cylindrical sieve with a pore diameter of 45 μm . This test is based on the notion that as the percentage of resulted residue decreases; the more particles can be sieved through. Therefore, lesser percentage of residues indicates finer cement. Results of the residue test done in this study are presented in Table 4. It was seen that blank cement (without CGA supplementation) had a bigger residue percentage than that supplemented with CGA. The difference was significantly high indicating that CGA was able to significantly increase cement fineness.

Cement made from Portland clinker material had residue percentage of 0.5-0.8% while that made from clinker plan 4 had 0.11-0.59%. The residue percentage of cement is affected by chemical composition of clinker. If the metal oxide content of the clinker increases, it will be easier for the clinker to be separated into positive and negative charges. This makes the resulted cement easier to get agglomerated allowing a higher residue percentage level. The composition of metal oxides in Portland clinker and the clinker used in this study (clinker plan 4) is given in Table 5. It was shown that the composition of metal oxides in Portland clinker was higher than that in clinker plan 4. Therefore, the residue percentage of cement with Portland clinker was higher than that of cement with plan 4 clinker.

It was found that TEA composition, reaction temperature, and their interaction significantly ($\alpha = 5\%$) affected residue percentage. Results of a Duncan test also showed that at 0, 5, and 15% TEA compositions, each temperature gave significant differences in residue percentages ($\alpha = 5\%$).

IV. CONCLUSION

Results of glycerol measurement in biodiesel by-product showed that jatropha crude glycerol content was 40.19%. Meanwhile, after purification, glycerol content was found to be 82.15% indicating that pure glycerol could be used as a cement grinding aid (CGA). Results of a BSS test showed that CGA-supplemented cement had a higher BSS value than that with no CGA supplementation (blank) indicating that CGA-supplemented cement was finer. This was confirmed by the results of residue test that showed smaller residue percentage in supplemented cement than in blank cement. The most optimum CGA composition to refine cement particles was the one made at 80°C with 95% jatropha glycerol and 5% TEA. CGA-supplemented cement had a BSS value of 4,836 cm^2/g and a residue level of 0.11%. Cement's BSS value and residue percentage were affected ($\alpha = 5\%$) by TEA composition and CGA reaction temperature. It was recommended that further studies on the effect of the amount of CGA added to cement raw materials on BSS value and residue percentage be

TABLE v
 COMPARISON OF CHEMICAL COMPOSITIONS IN CLINKER

Chemical Composition (%)	Portland Clinker (Anna <i>et al.</i> [26])	Clinker Plan 4
SiO ₂	25.21	21,3
Al ₂ O ₃	5.13	4.85
Fe ₂ O ₃	3.97	2.76
CaO	59.99	65.36
MgO	1.29	3.22
SO ₃	1.32	0.37
Na ₂ O	0.25	0.20
K ₂ O	0.64	0.55

conducted.

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