

# ZnO/Fly ash catalyst for producing biodiesel from kapok seed (*Ceiba pentrandra*) oil

Decky Achmad N<sup>1</sup>, Yahya Dwi A. I.<sup>1</sup>, Yohaness Somawiharja<sup>2</sup>, Jiang-Min Chern<sup>3</sup>,  
Nyoman Puspa Asri.<sup>2,\*</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Adhi Tama Surabaya, Surabaya 601117, Indonesia

<sup>2</sup>Department of Food Technology, School of Tourism, Universitas Ciputra Surabaya, Surabaya 60219, Indonesia

<sup>3</sup>Department of Chemical Engineering and Biotechnology, Tatung University, Taipei 104, Taiwan

ARTICLE INFO	ABSTRACT
<p><i>Article history:</i> Received: 19 January 2023 Received in revised form: 27 April 2024 Accepted: 28 April 2024</p>	<p>The quantity of fossil fuels has decreased yearly due to increasing energy consumption, thereby requiring alternative renewable energy sources such as biodiesel from kapok seeds oil. Making biodiesel needs a catalyst that is classified into two based upon their phase: homogeneous and heterogeneous. This research employed a ZnO heterogeneous catalyst with fly ash support. It aims to synthesize and characterize the ZnO/fly ash catalyst, and investigate the effects of the molar ratio of oil to methanol, and the effects of the catalyst dosed to yield biodiesel. The catalyst was synthesized using co-precipitation, precipitation, and impregnation methods. The research variables included the catalyst dose (wt% oil) of 3, 4, 5, 6, and 7) and the mole ratios of oil to methanol of 1:9, 1:12, 1:15, 1:18, and 1:21. The results of this study showed that the best catalyst dose was 5% with a biodiesel yield of 58%. Meanwhile, the variable molar ratio of oil to methanol obtained the highest yield of 65% at 1:8. Hence, a zinc oxide catalyst with fly ash as support is great potential to produce biodiesel from kapok seed oil.</p>
<p><i>Keywords:</i> Biodiesel, kapok seed oil, ZnO, fly ash, yield</p>	

## 1. Introduction

Industrial development and increasing population have brought an impact on the high demand for energy supplies in the form of oil. Fuel oil (locally abbreviated as BBM) refers to a fossil fuel, which is included in limited amounts of energy (commonly called as non-renewable energy). Most of countries, including Indonesia, are still reliant on it [1]. Currently, fossil fuel is experiencing a crisis with an average decline of 12% per year with an increase in the annual energy consumption of approximately 4%. This is related to the absence of development of the renewable energy to reduce the dependence on fossil fuels [2].

The renewable alternative energy development, such as biodiesel, is an attempt to reduce the dependence on fossil fuels [3]. Biodiesel itself is environmentally friendly for being non-toxic, able to decompose naturally (biodegradable) and able to reduce emissions in the form of SO<sub>x</sub>, NO<sub>x</sub> and CO<sub>2</sub> [4]. In recent years, biodiesel has used raw materials in the form of edible oil, such as palm oil; this has then resulted in a shortage of palm oil for consumption in society. To avoid this, non-edible oils such as jatropha seed oil, *Calophyllum inophyllum* seeds and kapok (*Ceiba pentandra*) seeds (MBK) have been used. The use of MBK as a raw material for making biodiesel starts to be developed in Indonesia. For containing quite high triglycerides, around 80-85%, kapok seeds are able to replace palm oil as raw material for making biodiesel [5].

Hanifa [6] explained that making biodiesel uses a transesterification reaction that occurs between long chain

fatty acids (triglycerides) and alcohol, which can produce methyl esters and glycerol as side products. In general, this reaction uses homogeneous base (NaOH, KOH) or acid (H<sub>2</sub>SO<sub>4</sub>) catalysts [7]. Homogeneous catalysts have begun to be left for their corrosive nature to equipment and the difficulty in separating the catalyst from the product; thus requiring quite high cost. For this reason, heterogeneous catalyst has been developed then. In common, heterogeneous catalyst is in solid form, making it easier to separate from the product and it can be reused, such as ZnO [4]. As stated by Arifah et al., [8] ZnO from synthesis has a metal oxide absorption peak determined by stretching of the M=O bond (M refers to metal). This indicates that there are similarities between ZnO resulted from synthesis and commercial ZnO (Merck). Also, ZnO catalyst does not react with free fatty acids, which can form soap that can make it difficult to separate glycerol and can reduce biodiesel yield. The biodiesel produced from the transesterification process with a ZnO catalyst is quite high, i.e. 93.56%.

Coal fly ash (CFA) waste, which is abundant in Indonesia, has the potential to be used as an affordable and environmentally friendly catalyst support now that its chemical composition is dominated by SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> (70%) [9]. Some of these oxides contain high porosity, which functions to avoid the formation of hydrogen bonds; hence, fly ash (FA) is highly suitable used as a catalyst support [10].

The researchers therefore conducted the synthesis of a ZnO/FA catalyst for the transesterification of kapok seed oil. The focus of this study is on the characterization of the synthesized catalyst. Also, we also studied the effects of catalyst dose and the molar ratio of kapok seed oil to methanol on the biodiesel yield produced.

\* Corresponding author. Tel.: 031 5948232; fax: 031 5994620

Email: [nyoman.asri@ciputra.ac.id](mailto:nyoman.asri@ciputra.ac.id)

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## 2. Materials and Methods

### 2.1. Materials

The material used included off-grade kapok seed oil obtained from local traders (Pasuruan) and FA (100 mesh), which was purchased online. Meanwhile, ZnCl<sub>2</sub>, NaOH, ethanol and methanol of pro analysis (PA) quality were obtained from the supplier (Merck).

### 2.2. Procedure

#### 2.2.1. Making zinc methoxide

It began by making sodium methoxide by reacting stoichiometrically with 9.83 grams of NaOH in 100 ml of methanol. ZnCl<sub>2</sub> was weighed as 16.75 gr (60% loading ZnO (wt.% to FA)) and dissolved in 80 mL of distilled water. The sodium methoxide solution was subsequently slowly dropped into the ZnCl<sub>2</sub> solution by stirring at 100 rpm until being constant to obtain a white precipitate. It was continued to stirring for 1 hour to make it completely mixed. Once the formed zinc methoxide precipitate was filtered, it was washed with distilled water for three times. Precipitate zinc methoxide was placed in the oven for a day at 120°C to remove water content and then the zinc methoxide was placed in a desiccator for cooling.

#### 2.2.2. Making catalyst ZnO/Fly Ash

FA (100 mesh pass size) was weighed for 10 gr and dissolved in 50 mL of distilled water. It was then stirred with a magnetic stirrer for 2 hours until being homogeneous. Similarly, zinc methoxide was dissolved in 50 mL of ethanol with a stirrer until being homogeneous. The solution of zinc methoxide was added to the FA dispersion, which had been stirred in drops until finished with stirring at a temperature of 70°C. Afterwards, the stirring was added for an hour to make it homogeneous. The mixture was evaporated at a temperature of 70°C to be slurry and placed in an oven at a temperature of 120°C to remove any water content. The catalyst was ground and calcined for 5 hours at 500°C. The catalyst was cooled in a desiccator. Then, it was ready to be characterized including the test of X-RF, SEM, X-RD and BET.

#### 2.2.3. Degumming process

100 mL oil was heated at a temperature of 70°C. H<sub>3</sub>PO<sub>4</sub> 85% was added as much as 0.1% of the oil volume, and then stirred within 1 hour. The oil was sprayed with half the volume of distilled water while stirring with a stirrer until the gum deposited. It was then left for 48 hours until 3 layers (oil, gum, and water) were formed. Subsequently, the top layer in the form of oil was taken and placed in the oven at 110°C within 24 hours to remove the water coming along with it.

#### 2.2.4. Making biodiesel

The transesterification process was conducted in the reactor of glass type batch (Figure 1). It consisted of a 3-neck flask (1), magnetic stirrer and heater (2), reflux condenser (3), waterbath (4), thermometer (5) and stative clam holder (6).

The catalyst was weighed respectively at a dose of 3, 4, 5, 6% and 7% (wt.% to oil), and put into a 3-neck flask. Methanol was then added based upon to the molar ratio of methanol and oil, i.e. 1:9, 1:12, 1:15, 1:18 and 1:21, heated to 65°C and allowed to stabilize for 30 minutes. 80 mL of oil was added to the mixture of methanol and catalyst, and the temperature was then increased up to 80°C. After the temperature was stabilized, the transesterification operation time was calculated for 5 hours. The filtrate and sediment were separated using a centrifuge for 15 minutes at a speed of 4000 rpm. The filtrate was separated was placed in an oven at 110°C for 24 hours to remove methanol. The biodiesel obtained was measured using the formula as in equation (1).

$$\text{Yield} = \frac{\text{Biodiesel Mass}}{\text{Oil Mass}} \times 100\% \quad (1)$$

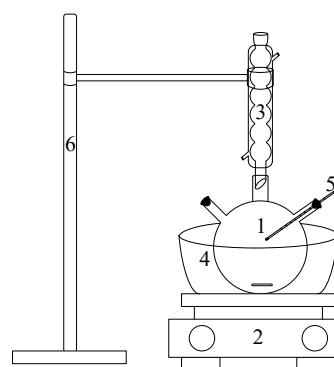


Fig. 1. A series of transesterification equipment

Remark:

- |                              |                  |
|------------------------------|------------------|
| 1. 3 Neck Flask              | 4. Waterbath     |
| 2. Magnetic Stirrer + Heater | 5. Thermometer   |
| 3. Reflux Condenser          | 6. Stative Clamp |

## 3. Results and Discussion

### 3.1. Research results (biodiesel characteristics)

Table 1. Data of research results

Parameter	Mole Ratio of Oil : Methanol				
	1:9	1:12	1:15	1:18	1:21
%FFA (%w/w)	7,14	6,50	6,32	5,53	5,27
Density (gr/mL)	0,904	0,895	0,892	0,888	0,887
Saponificati on number	198,89	196,84	193,73	192,71	188,47
Water Level (%w/w)	0,08	0,09	0,08	0,07	0,05
Viscosity (cSt)	2,28	2,06	2,01	2,23	2,33
Yield (%)	52	53	58	65	56

### 3.2. Discussion

#### 3.2.1. Characteristics of fly ash

Table 2. Analysis of XRF fly ash

Component	% Mass
SiO <sub>2</sub>	30,7
Fe <sub>2</sub> O <sub>3</sub>	27
CaO	23,5
Al <sub>2</sub> O <sub>3</sub> and pengotor	11 and 7,8

Table 2 shows that the composition FA oxide was dominated by Si, Fe, Ca and Al oxides (92.2%) with SiO<sub>2</sub> as the highest component (30.7%). Therefore, FA is very suitable for use as a support catalyst as its mechanical properties are very good [11]. After doping with 60% ZnO loading, a shift in component composition occurred (Table 3). *Characteristics of catalyst ZnO/FA*

3.2.1.2. Analysis in XRF of catalyst ZnO/FA

Table 3. Analysis of XRF ZnO/FA ash catalyst

Component	% Mass
ZnO	66,41
SiO <sub>2</sub>	11
Fe <sub>2</sub> O <sub>3</sub>	7,93
CaO; Al <sub>2</sub> O <sub>3</sub>	7,85; 3,2

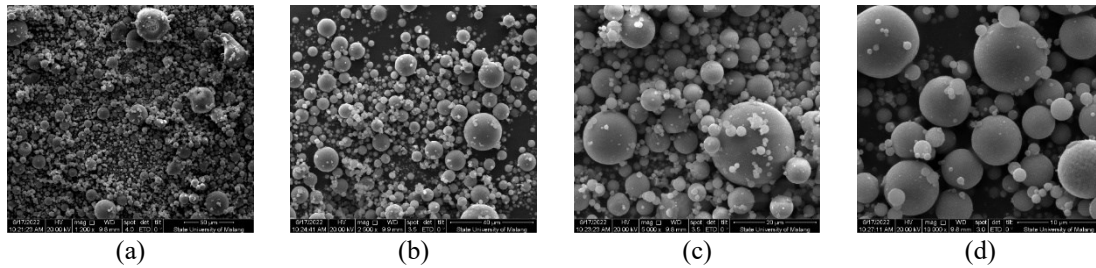


Fig. 2. The results of the analysis of Fly ash SEM with (a) 1200x magnification; (b) 2500x magnification; (c) 5000x magnification and (d) 10000x magnification

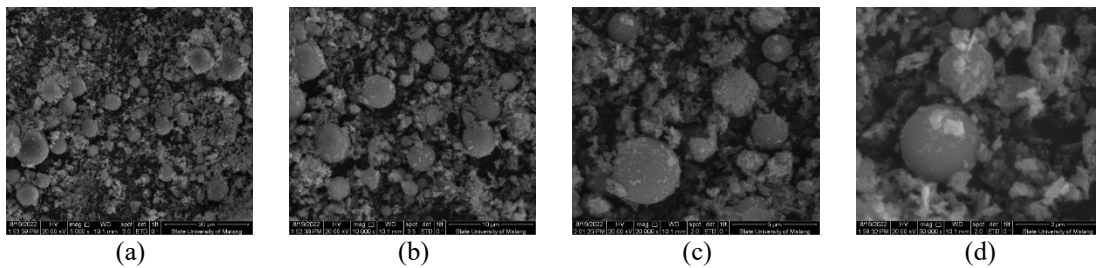


Fig. 3. The results of the analysis of SEM ZnO/FA with (a) 1200x magnification; (b) 2500x magnification; (c) 5000x magnification and (d) 10000x magnification

3.2.1.1. XRD Analysis

Figure 4 shows the diffractogram of ZnO/FA based upon JCPDS besides FA peak (SiO<sub>2</sub> peak appeared at an angle of 2θ (26.65°; 39.4°; 50.0°; 59.9° and 67.8°), CaSiO<sub>2</sub> at an angle of 33.1° and Ca<sub>2</sub>AlSiO<sub>2</sub> at angle 42.3°) [12], ZnO peak also appeared at angle of 2θ (31.4; 33.8; 35.8; 46.8; 55.9; 61.7; 65.5; 66.9; and 68.2). Figure 5 shows the diffractogram of the ZnO/FA catalyst and FA. The FA diffractogram was still visible at an angle of 2θ, indicating that the appearance of ZnO crystals did not affect the presence of the FA component (only its intensity changed). It was proven at the angles of 26.65°, 50.1° and 67.8° that still had SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and CaO. The appearance of the ZnO peak indicated that ZnO has been successfully doped on the FA surface as an active site, which functioned to increase catalyst activity.

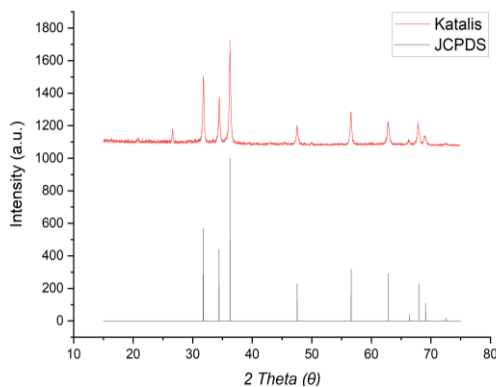


Fig. 4. Graph of comparison in XRD Analysis between ZnO/FA Catalyst and JCPDS

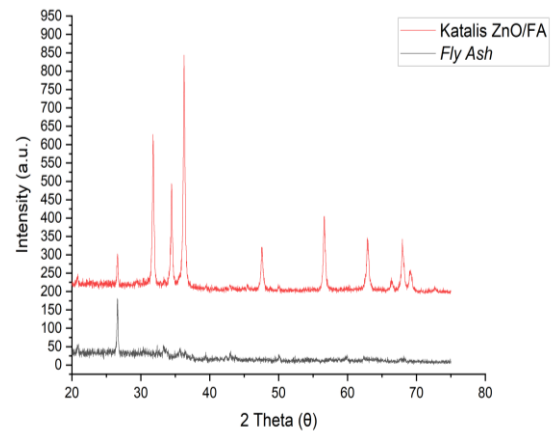


Fig. 5. The Graph of the comparison in the XRD analysis between ZnO/FA catalyst and fly ash

The results of the XRD analysis could then determine the crystal size based on the Full Width Half Maximum (FWHM) obtained from the graphic XRD spectrum data. As stated by Sumadiyasa & Manuaba, [13], to determine the crystal diameter, the Scherrer equation (equation 2) is used:

$$D = \frac{K \times \lambda}{\beta \times \cos\theta} \quad (2)$$

Remarks:

- D = Diameter of crystal (nm)
- K = Crystal form factor (0.9-1.0)
- λ = X-ray wavelength (0.15406 nm)
- β = Value of Full Width Half Maximum (rad)
- θ = Diffraction angle (degrees)

Table 4. The diameter of ZnO/FA catalyst

2 Theta ( $\theta$ )	FWHM	D (nm)
20,81	0,1599	53,1502
26,60	0,1599	55,5641
29,42	0,1599	57,0384
30,34	0,0400	230,1243
31,78	0,2399	38,9553
33,46	0,1599	59,5524
34,46	0,2799	34,4231
36,28	0,2799	35,2082
45,45	0,1199	94,4471
47,57	0,2799	42,0677
56,61	0,3198	45,1387
62,89	0,3998	43,6047
66,36	0,1999	99,1083
67,94	0,2799	75,5706
69,08	0,3998	55,6501

Table 4 shows that the largest diameter at  $30.34^\circ$  was 230.124 nm and the smallest one at an angle of  $34.46^\circ$  was 34.42 nm. Table 3 also shows varying results due to the agglomeration or accumulation of substances at one point when making the catalyst, so that calculations using the Scherrer formula became less accurate [14].

### 3.2.1.3. SEM analysis in ZnO/fly ash catalyst

Figure 2 shows the morphology of fly ash, which appeared in the form of solid and dense balls. Meanwhile, Figure 3 shows the morphology of the ZnO/FA catalyst. There was a change in morphology where apart from the solid balls of fly ash which remained unchanged, there was a white flower shaped morphology of ZnO attached to the surface of the fly ash. This showed that the ZnO doping successfully adhered to the fly ash surface. This was supported by the results of XRF analysis of ZnO/fly ash (Table 3). In addition to the 4 main components of fly ash ( $\text{SiO}_2$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ) there was also a ZnO content of 66.41% in accordance with the experimental procedure where the ZnO loading was 60% (wt % of fly ash).

### 3.2.1.4. BET analysis in ZnO/Fly ash catalyst

Yusuff, et al., [12] stated that FA has the characteristics of surface area, total pore volume to very small pore diameter. As shown in Table 5, the FA sample had a surface area of only 0.075  $\text{m}^2/\text{gr}$ ; this is in accordance with previous research which had small surface area. However, after ZnO doping treatment with 60%, the loading of the surface area increased to 14,849  $\text{m}^2/\text{gr}$ . This is supported by the results of XRD and SEM analysis where there was a change in the crystallization phase and when calcined at a temperature of  $500^\circ\text{C}$ , the surface area increased. Thus, it can be concluded that the ZnO/FA catalyst can be used as a catalyst for catalytic reaction processes [13].

Table 5. The results of BET analysis in fly ash and ZnO/FA catalyst

Sample	BET Surface Area ( $\text{m}^2/\text{gr}$ )
Fly ash	0,075
ZnO/FA	14,849

### 3.2.2. The effects of catalyst dose on the yield crude biodiesel

Figure 6 presents the results of biodiesel analysis with variable catalyst dose. A 5% catalyst dose had a fairly high yield (57.5%), and it then decreased in the addition of 6 and 7% catalyst dose. Arifah, et al. [8] stated that catalysts play an important role in reducing the activation energy so as to accelerate the reaction rate, which results in an increase in the biodiesel yield obtained. However, in an excess of catalyst, the viscosity of the mixture will increase, thereby inhibiting the mixing process, which in turn will affect the collision factor between particles; as a consequence, it reduces the rate of the transesterification reaction and ultimately reduces the biodiesel yield.

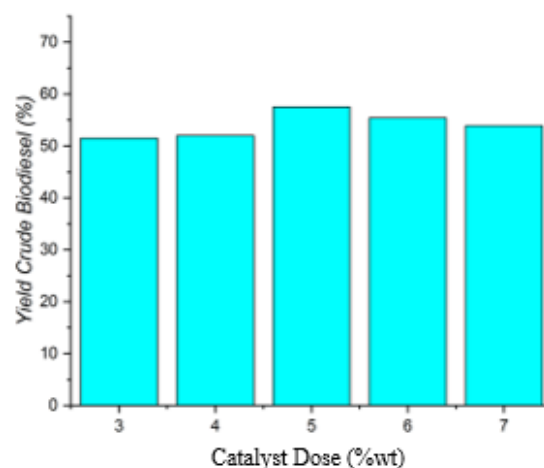


Fig. 6. Yield crude biodiesel in catalyst dose

### 3.2.3. The effects of the ration of oil and methanol on yield crude biodiesel

Figure 7 shows that the highest crude biodiesel yield was at a ratio of 1:18 with a percentage of 65% and the lowest one was at a ratio of 1:9 with a percentage of 52%. This was because the molar ratio could maximize a contact between oil and methanol. Arifah, et al., [8] stated that a high molar ratio can determine the high shift of the reversible reaction towards equilibrium; thus, it can increase the conversion of oil into biodiesel. Roy, et al., [15] explained that methoxide ions ( $\text{MeO}^-$ ) are produced from methanol through adsorption or abstraction of hydrogen ( $\text{H}^+$ ) from the catalyst. The methoxide ion will attack the glycerdia carbonyl carbon ( $-\text{CO}-\text{R}_1$ ) from triglycerides which are then converted into methyl esters or fatty acids. This also shows a decrease in the mole ratio of 1:21.

Moeksin, et al., [16] stated that the amount of methanol used during the transesterification process will produce a lot of excess methanol. During settling, a layer will form at the top in the form of excess methanol, so that the methanol does not fully react with the oil. Excess methanol will reduce the concentration of the catalyst, thereby increasing the formation of glycerol. The presence of high glycerol in biodiesel products will push the reaction back to the left, which will then produce monoglycerides and later on can reduce biodiesel yield [17].

The yield results obtained from this research were found lower compared to research by Yusuff et al., [12] and Babajide et al., [6]. This might be determined by several factors. First, the temperature used during transesterification in this study was



80°C, much lower than the transesterification temperature used by them of 150°C and 160°C respectively.

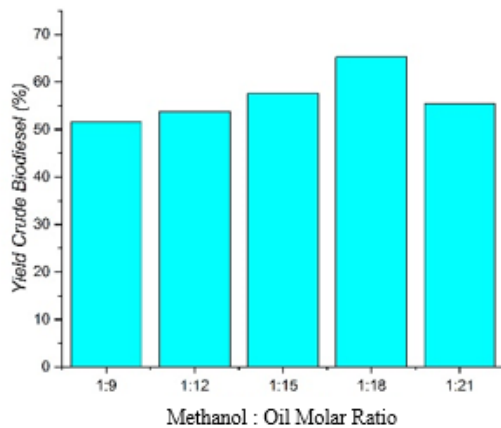


Fig. 7. Crude biodiesel yield at the ratio of molar methanol: oil

For the second factor, Yusuff et al., [12] in their research conducted the pre-treatment of fly ash and used the used cooking oil with low free fatty acids (FFA), whereas in this study, there were no pre-treatment carried out on fly ash and it used kapok seed oil as raw material. with a high FFA level of 10%. Babajide et al., [18] used soybean oil with lower FFA. However, we identified a potential pathway to increase catalyst activity, for instance by treating fly ash before using it as a buffer, or functionalizing it with sulfonate to be a super acid, which can increase insensitivity to FFA.

#### 4. Conclusion

Based on the results and discussion, the zinc oxide catalyst with fly ash (ZnO/fly ash) support using 60% ZnO loading was successfully synthesized. The synthesized catalyst had the characteristics of a specific surface area of 14,849 m<sup>2</sup>/gr, a ZnO content of 66.41%, and a crystal diameter in the range of 34.46-230.12 nm. The ZnO/fly ash catalyst was applied to make biodiesel from kapok seed oil through a transesterification process. At a temperature of 80°C and a reaction time of 5 hours, the highest biodiesel yield of 65.25% was obtained at a ratio of kapok seed oil and methanol of 1:18, and a catalyst dose of 5% (Wt.% to oil).

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