Selective esterification of glycerol diacetin and triacetin over rice husk biosilica catalyst with microwave heating

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Abstract. Selectivity towards diacetin and triacetin was investigated in esterification of glycerol using rice husk biosilica catalyst. The reaction was carried out in a microwave-irradiated batch reactor using acetic acid to glycerol molar ratio of 1:3, catalyst amount of 3% and 5% of the glycerol volume, and reaction time of 20 and 30 minutes. The biosilica catalyst was prepared by treating rice husk with hydrochloric acid and followed by calcination at 600°C. SEM analysis of the resulted catalyst reveals significant change of rice husk morphology and its XRD analysis shows the characteristics of amorphous silica. Furthermore, FTIR analysis of the reaction sample reveals the presence of an ester group of triacetin at 1709.5 cm⁻¹. Product distribution of the glycerol esterification identified by GC-MS shows the highest total selectivity for diacetin and triacetin of 79.3% at the reaction condition of 30 minutes and 3% catalyst loading. However, individual selectivity for triacetin as the final product of this consecutive esterification steps was low, less than 5%.

1. Introduction
The rapid increase of biodiesel production has led to the wider availability of crude glycerol as a by-product in the chemical industry. Thus, the efficient utilization of excessive and cheap glycerol is becoming a new research topic at present, in which the etherification and esterification processes to fuel additive are considered as the promising route to the conversion of glycerol [1]. Esterification of glycerol with acetic acid using a catalyst to get mono, di and tri esters of glycerol acetates is one of the proposed solutions for the conversion of relatively low-priced glycerol to valuable products. Glycerol acetates, also known as acetoins consisting of monoacetin, diacetin and triacetin have great industrial applications [2]. Monoacetin and diacetin exist in two different isomers. Monoacetin and diacetin have applications in the food industry, cryogenics and biodegradable polymers, while diacetin and triacetin may act as an additive in various fuels and triacetin is mainly used as a humectant [3]. Particularly, the diacetin and triacetin products have been established as oxygenated fuel additives that can enhance the cold flow properties of conventional diesel fuel, increase cetane number, and reduce noxious gas emission [4]. They could lead to possible attainment of 100% atom efficiency in diesel engines by blending triacetin with fatty acid methyl ester (FAME) since the physicochemical properties of triacetin blended FAME are similar to biodiesel fuel [5].

The glycerol esterification can be carried out with the help of an acid catalyst and the reaction is reversible, as illustrated by Figure 1. Without the presence of strong acids, the esterification reaction...
will proceed very slowly, but will reach equilibrium in a short time when strong acids and alcohols are employed [6]. The use of heterogeneous catalysts is an alternative in the glycerol esterification reaction. The advantages of solid catalysts consist of ease of product separation and catalyst recycling [7]. Silica catalysts can be used because they have acidic sites instead of acid groups in homogeneous catalysts. In addition, real silica is easily obtained in nature both in the earth's crust and from organisms. Rice husk is one of the potential sources of silica because rice husk has an abundant amount of silica which is 18.0-22.3% [8]. Combustion of rice husk ash which is controlled at high temperatures (500-600°C) will produce silica ash which can be used for various chemical processes [9].

![Diagram of glycerol esterification reaction with acetic acid]  
*Figure 1. Three consecutive reversible steps of glycerol esterification with acetic acid [2].*

The microwave heating method has different characteristics from conventional heating because heat is generated internally due to the vibrations of the molecules of the material that the microwaves want to heat [10]. As the result, microwave radiation can increase the speed of reactions in both batch and continuous processes. Since, thermal energy from microwaves is delivered directly to molecules that react through chemical reactions, heat transfer is more effective than conventional heating where heat is transferred from the environment [11].

2. Research methodology  
2.1. Materials and instruments  
The materials used in this study were rice husks from the Tungkopsudistrict (Aceh Besar), filter paper (Whatman), technical grade glycerol (Merek), distilled water, acetic acid, and hydrochloric acid. All materials were purchased from commercial sources. Analytical instruments for catalyst and reaction characterizations consisted of X-Ray Diffraction (XRD) Shimadzu 6100, Fourier Transform Infra-Red Spectroscopy (FTIR) Shimadzu 8400, and Gas Chromatography-Mass Spectrometry (GC-MS) Shimadzu QP 2010 Plus.
2.2. Research procedure

2.2.1. Preparation of catalyst. Rice husk was washed with water and dried in the sun. 100 grams of dried rice husk was immersed in 600 mL of 3 N HCl solution at 100°C for 2.5 hours. Subsequently the wet material was dried and calcined at temperature of 600°C for 4 hours in the furnace. 25 grams of rice husk ash are washed with distilled water while filtering with Whatman filter paper to remove impurities. Finally, it was dried at 100 °C for 2 hours in an oven.

2.2.2. Esterification of glycerol. The reaction solution was prepared for glycerol to acetic acid molar ratio of 1: 3;20 mL glycerol was charged into the reaction flask and followed by adding 43.2 mL acetic acid. This mixture of glycerol and acetic acid was preheated to 100 °C over a hot plate. A gradually increasing temperature was applied during preheating to avoid evaporation of reacting solution (acetic acid boiling point 117.9 °C). After the temperature reached 100°C, the biosilica catalyst amounting 3% or 5% of the glycerol volume was charged into the reaction flask. The reactor was arranged as shown in Figure 2. Microwave unit used was a household type (Model NN-ST 342M, Panasonic) operating at frequency 2.45 GHz. The reaction was initiated by turning the microwave on for irradiation time of 20 and 30 mins at stirring speed of 400 rpm. The microwave power output was set medium (520 watts). Solution reaction during reaction course observed using an infrared thermogun was in a range of 95-100 °C. After the irradiation period was completed, the reaction mixture was cooled down to room temperature and then filtered out to separate the catalyst from the glycerol acetate containing solution.

![Figure 2](image)

**Figure 2.** Experimental setup for the glycerol esterification (1. Microwave; 2. Reflux condenser; 3. Reaction flask; 4. Thermocouple; 5. Magnetic Stirrer; 6. Magnetic bar).

2.3. Characterization

Biosilica samples were accordingly characterized by SEM for surface morphology and XRD for silica content and crystallinity. XRD was equipped with software Match! 3 (Version 3.5.3.109). FTIR analysis was performed to determine functional groups in acetic products. The presence of certain functional groups was identified by comparing with standard spectra of diacetin and triacetin that already exist in the reference [12]. Later, the selectivity for diacetin and triacetin was calculated from the product distribution resulting from GC-MS analysis.

3. Result and discussion

3.1. SEM analysis

Figure 3 shows the morphological differences between rice husk and rice husk ash. The morphology of rice husk looks more evenly and structured which shows the basic components of rice husk, while the morphology of rice husk ash is uneven, and pores of rice husk ash appear larger. Acid treatment of
lignocellulosic biomass such as rice husk leads to hydrolysis of hemicellulose and cellulose. As leaching of the cellulosics took place, loss of rice husk structural form occurred [13].

![SEM micrographs](image)

(a) Rice husk and (b) rice husk ash at 1000x magnification.

### 3.2. XRD Analysis

XRD analysis was carried out on rice husk samples prior to and upon acid treatment and calcination. Figure 4 shows difference spectra profile between these two samples; raw rice husk shows presence of sharp peaks due to its crystalline property, while rice husk ash spectra resembles amorphous phase. The acid treatment followed by calcination caused removal of crystalline components such as cellulose, hemicellulose and alkali metals, leaving amorphous silica as the main component in the treated rice husk [13]. It is revealed by the presence of the broad diffused peak at $2\theta = 22.07^\circ$ which corresponds to typical amorphous nature of silica.

![XRD spectra](image)

Figure 4. XRD spectra of rice husk and rice husk ash.

### 3.3. Product Identification

Figure 1 shows that esterification of glycerol by acetic acid results in monoacetin, diacetin, triacetin and water. First, FTIR was used to identify the presence of functional groups related to products of the reaction. Figure 5 presents FTIR spectra of two different reaction time samples indicating the occurrence of O-H stretch of monoacetin, diacetin and remaining glycerol at 3100-3400 cm$^{-1}$ and the ester group at 1690-1760 cm$^{-1}$. Later functional group corresponds to acetin and signal at 1709.5 cm$^{-1}$ is related to a C=O stretch of the ester of triacetin confirming that the triacetin was obtained [12,14].
3.4. Selectivity for diacetin and triacetin

Further chemical identification by GC-MS analysis was carried out to determine constituents in the reaction samples. Table 1 presents product composition for the reactions at different catalyst loading and irradiation time. It is found that the reaction products consisting of 1-monoacetin, 2-monoacetin, 1,3-diacetin, 1,2-diacetin, and triacetin. It suggests the glycerol esterification by acetic acid taking place via consecutive route as given in Figure 1. Formation of monoacetin and diacetin isomers was also reported in our previous work [15,16].

**Table 1.** Product composition for the reaction with glycerol to acetic acid molar ratio of 1:3.

| Catalyst | Time (minute) | Sample No. | 1-monoacetin (%) | 2-monoacetin (%) | 1,3-diacetin (%) | 1,2-diacetin (%) | triacetin (%) |
|----------|---------------|------------|------------------|------------------|------------------|------------------|---------------|
| 3%       | 20            | 1          | 30.1             | 9.2              | 11.3             | 48.3             | 1.0           |
|          | 30            | 2          | 11.2             | 9.5              | 9.4              | 68.0             | 1.9           |
| 5%       | 20            | 3          | 22.1             | 0.0              | 26.5             | 47.6             | 3.7           |
|          | 30            | 4          | 24.5             | 15.4             | 9.6              | 47.3             | 3.1           |

![Figure 5. FTIR spectra of reacting samples after reactions for 20 min (sample 1) and 30 min (sample 2) with glycerol to acetic acid molar ratio 1:3 and catalyst content 5%.

![Figure 6. Total selectivity for diacetin and triacetin](image-url)
Di and triacetins are commercially important chemicals used as fuel bioadditives. Therefore, its total selectivity for both acetins becomes interest of this work. Figure 6 shows the maximum total selectivity reached 79.3% from the reaction using catalyst loading of 3% and irradiation time of 30 min. Further increase in the catalyst loading did not improve the total selectivity. Whereas with conventional heating methods the total selectivity reaches more than 34.8% after 4 hours of reacting [15]. It reveals that microwave heating contributes significantly to reduction in reaction time and increase in the total selectivity for diacetin and triacetin.

4. Conclusions
Microwave as alternative heating was effective to enhance selectivity of glycerol esterification towards diacetin and triacetin; eco-friendly bioadditives for diesel fuel. Rice husk biosilica prepared by acid treatment was used to catalyze the reaction. FTIR and GC-MS analyses confirm that the reaction synthesized monoacetin, diacetin and triacetin. The total selectivity of diacetin and triacetin reached a maximum of 79.3% at reaction time of 30 min, a much shorter than time required by the reaction with conventional heating method. This microwave-assisted reaction system with solid catalyst is potential to replacetraditional homogenous esterification of glycerol.

5. References
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