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Investigation of Ferri-alginate (Fe-Alg) as Environmentally Friendly Catalyst on the Formation of Solketal from Glycerol and Acetone

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Abstract. Alginate is a naturally occurring anionic carbohydrate polymer which could be coupled with metallic cationic molecules to form heterogeneous catalyst. However, the potency of the heterogeneous catalyst on the production of solketal was not explored. This research was proposed to investigate the potency of Ferri-Alginate (Fe-Alg) as a cheap and environmentally friendly catalyst in the solketal reaction. Fe-Alg was synthesized by reacting FeCl₃ to sodium alginate with different concentrations (0.1 -0.5 M). Fe-Alg catalyst was characterized both on the physical and chemical activity. By using BET analysis, it was indicated that the addition of FeCl₃ concentration increased the surface area of the catalyst. By using TGA/DSC analysis, it was found that Fe-Alg catalyst was stable up to 153°C. From GC/MS analysis, it was found that solketal was formed after the reaction of glycerol and acetone by using Fe-Alg as the catalyst.

1. Introduction

Alginate is a naturally occurring anionic carbohydrate polymer which is generally obtained from the cell walls of brown seaweed. Alginate is widely used in food, cosmetic, and pharmaceutical applications [1]. Alginate has a unique characteristic of an anionic molecule and can be combined with metallic ion molecules such as calcium alginate and sodium alginate to form a new molecule [2].

Currently, the development of low cost and environmentally friendly catalyst has increased [3]. Alginate from brown seaweed can be obtained easily, relatively cheap, and the material source is renewable. Furthermore, alginate is considered as non-toxic material for the environment. Alginate as the organic anionic molecule could be coupled with cationic metallic ion to form solid catalyst which is easily separated from the reaction mixtures. Furthermore, the catalyst can be reused, thus, lowering the cost and minimize the waste. For example, Zhang et al. [4] reported that copper (ii) alginate complexes could enhance the conversion value in the esterification of oleic acid. Cheryl-Low et al. [5] showed that aluminum alginate could be used in the esterification of palm fatty acid. However, to the best of our knowledge, the application of alginate as the anionic catalyst on the ketalization of solketal has not been explored so far.

Previous research mentioned that solketal can be synthesized by using glycerol and acetone on the ketalization process [6]. However, most of the previous researchers were done by using zeolite heterogeneous solid catalyst which is more expensive and could not be renewed [7]. The objective of this research was to investigate a novel ferri-alginate (Fe-Alg) as the cheap and environmentally



friendly catalyst on the production of solketal from glycerol and acetone. The catalyst was characterized both in the physical and chemical activity.

2. Methods

2.1. Catalyst preparation

Brown algae were collected from Ngadean beach, Yogyakarta. Fe-Alg was prepared by washing the algae to remove salt and other impurities by using tap water. The cleaned algae (with known weight) was then soaked in pure water with ratio 1:6 (w/w) for 2 h then pulped homogeneously by using a blending machine. Sodium carbonate was used to extract the pulped algae to obtain the alginate.

Extraction was performed in an extraction tube with volume 50 L equipped with a heater, temperature controller, timer, and mixer. The pulp brown algae were mixed with sodium carbonate (2% w/v) with a ratio of 1:20 (v/v) for 2 h at 80°C. The mixture of algae was then removed by filtering it to obtain alginate filtrate. The filtrate was then cooled to room temperature.

FeCl₃ was varied from 0.1 to 0.5 M to precipitate the alginate extract. The precipitation was done by using titration until the brown color was shown in the precipitated phase. Fe-Alg in the precipitated phase was obtained by using filtration, followed by drying at 80°C until constant weight.

2.2. Surface area determination

Brunauer–Emmett–Teller (BET) is widely used to determine catalyst activity by measuring the specific surface area of the catalyst. In this experiment, the surface area of Fe-Alg (904.5 mg) with different concentration was measured by using BET for 201.8 min, by using nitrogen as the gas carrier at output 300°C.

2.3. Thermogravimetric / Differential thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed by using TGA-2050 coupled with TGA-2100. Sample (20 mg) was used to determine the values by using aluminum as the holder. The heating rate was set to 10°C min⁻¹ under atmospheric pressure by employing nitrogen gas over the temperature range of 30 to 600°C.

2.4. Ketalization of glycerol and acetone using Fe-Alg catalyst

Fe-Alg was used in the solketal formation by reacting it in the mixture of glycerol, acetone, and ethanol at 3:1:1 mole ratio. The catalyst (2.5 g) was used with a concentration of 0.2 M. The reaction was done at 62°C for 4 h. The result was filtered to obtain filtrate and separate the catalyst. The staged distillation was then employed to separate impurities in the filtrate then analyzed by using GC/MS. The catalyst was reused by washing it using 96% v/v ethanol then dried at 80°C for 2 h. The used catalyst was employed again in the solketal reaction and repeated for three times.

3. Results and discussion

3.1. Catalyst activity

Fe-Alg activity was measured by using BET. Table 1 demonstrated that the addition of FeCl₃ in the alginate increased the surface area of the catalyst. The highest surface area (4.38 m² g⁻¹) was found at F5. This result was in agreement with the previous researcher who mentioned that the structure of alginate changed when interacted with cation molecule and formed Egg Box [8]. The size of the molecule was expanded and hollow spaces was increased. It clearly indicated that the addition of Fe³⁺ increased the hollow spaces, thus, the surface area of Fe-Alg was increased. However, the surface area

is relatively low compared to other catalyst such as sulfonated hydrothermal carbons in the solketal reaction [9]. This surface area could be increased by employing calcination at above 600°C.

Table 1. Effect of FeCl₃ concentration on the surface area of Fe-Alg

Run	FeCl ₃ (Molar)	Surface area Fe-Alg (m ² g ⁻¹)
F1	0.1	1.45
F2	0.2	2.01
F3	0.3	2.48
F4	0.4	3.69
F5	0.5	4.38

3.2. GTA/DTA profile

Physical analysis of Fe-Alg was shown in Fig. 1. It demonstrated that the degradation rate in TGA was decreasing with the increasing of temperature. Degradation temperature of Fe-alg was recorded at 129 to 221 °C with the peak at 153.25°C. The degradation rate was noted with the increasing of temperature which indicated that the process is exothermic. The exothermic reaction was occurred from 260°C and ended at 400°C. Then, the weight of Fe-Alg significantly degraded from 450 to 600°C and released H₂O, and CO₂. It was recorded that the weight loss was decreasing up to 45.95% above 153.25°C. Generally, the chemical reaction on the thermal degradation employed dihydroxylation, decarboxylation, decarbonylation, and break the macromolecule chain to smaller fragments. The resulting residue could be analyzed using FTIR and MS which will be done in the next project.

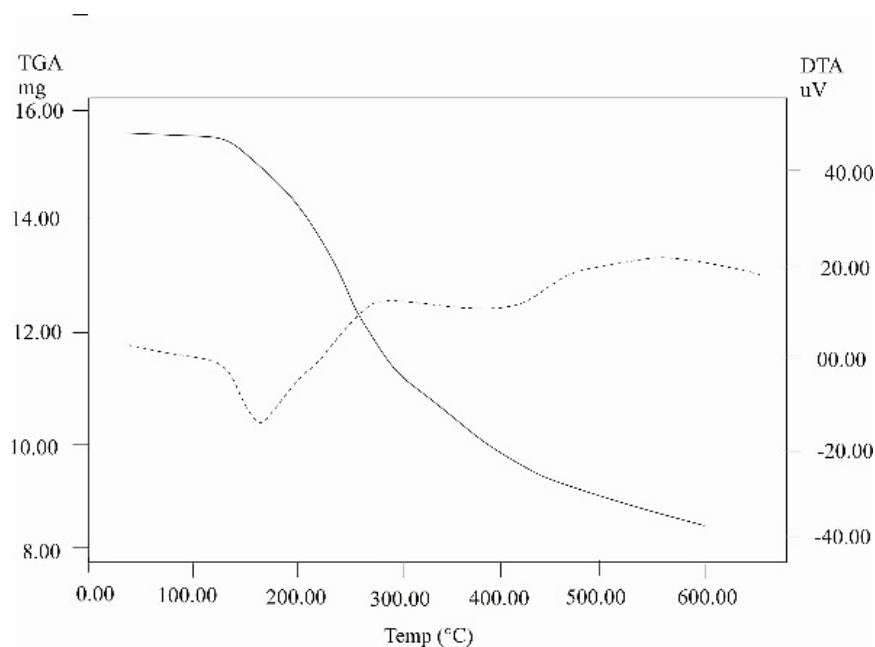


Figure 1. TGA and DTA profile from Fe-Alg under various range of temperatures. Dashed line is DTA. Full line is TGA

3.3. Chemical analysis

Chemical reaction was done by analyzing the distillate from the glycerol and acetone reaction by using Fe-Alg as the catalyst. From GC/MS analysis, it clearly indicated that the reaction resulted solketal with selectivity 0.568 (Fig 2 Supplementary 1).

Table 2. GC/MS result from the reaction of glycerol and acetone by using Fe-alg 0.5 g.

Number of peak	Retention time (minute)	Component	Selectivity
1	2.2	Vynil Methyl Esther	0.408
2	2.32	Methyl Ethyl Ketone	0.002
3	3.16	Diacetone Alcohol	0.0008
4	3.94	Solketal	0.568
5	4.2	Butanoic acid, 3 hydrxy, 3 Methyl	0.147
6	4.42	Propane 1,1 di propoxy	0.0017
7	4.48	1,2,3 Propanediol (glycerol)	0.0045

However, other byproduct was also appeared such as vinyl methyl ester which has 0.408 selectivity (Table 2, Supplementary 2). The selectivity of solketal could be increased by employing calcination of the catalyst at above 600°C to increase the internal pore size. Thus, the active surface area could be increased and higher selectivity could be obtained.

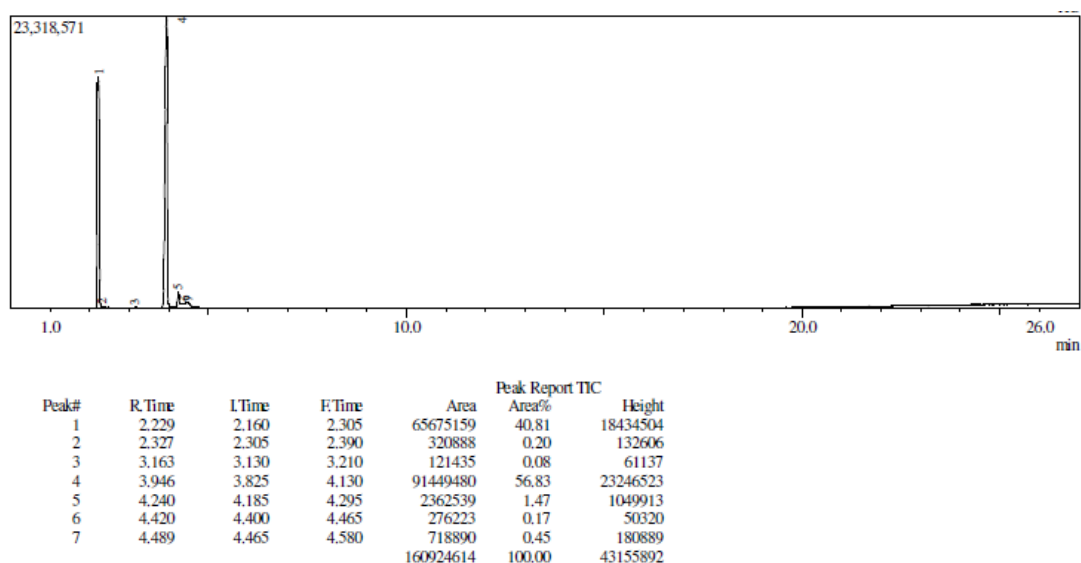


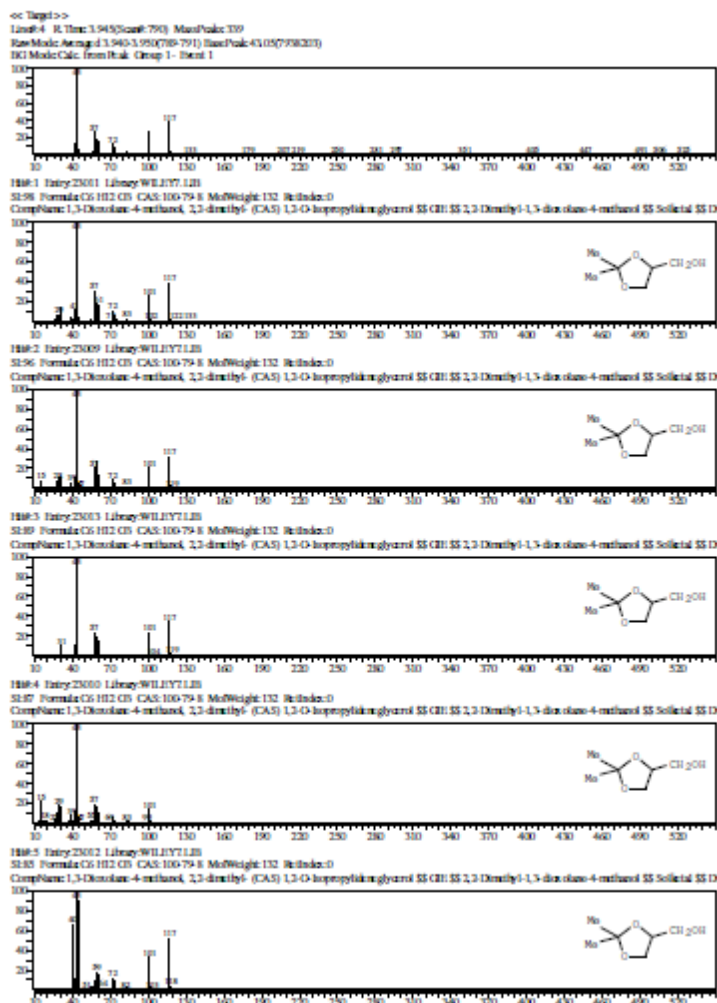
Figure 2. GC/MS profile of the reaction from glycerol and acetone with Fe-Alg 0.5 M

4. Conclusion

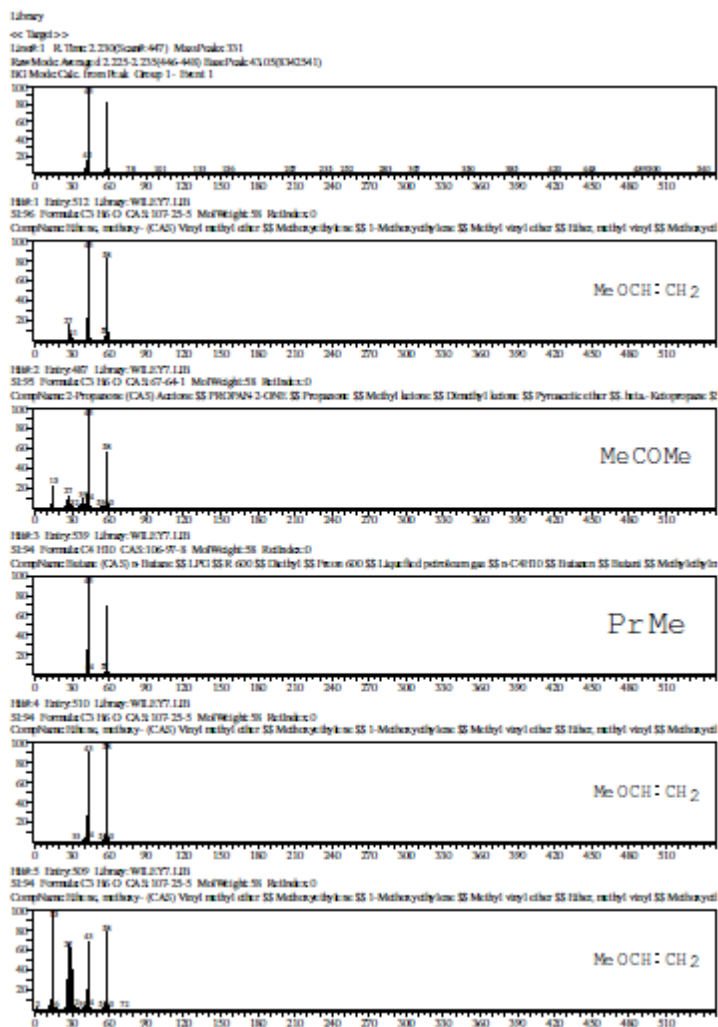
The environmental friendly catalyst, Fe-Alg, was successfully synthesized by using Sodium alginate and FeCl₃. From TGA/DTA result, it showed that organic molecule alginate was interacted with Fe³⁺ and formed Fe-Alg. From BET analysis, the highest surface area was obtained from 0.5 M FeCl₃ with surface area 4.38 m² g⁻¹. From GC/MS result, it showed that Fe-Alg could be used as the catalyst in the formation of solketal from glycerol and acetone reaction with selectivity of 0.568. Further experiment is needed to increase the selectivity.

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Supplementary 1 . Solketal result from GC/MS at retention time 3.946



Supplementary 2 . Vinyl Methyl Esther result from GC/MS at retention time 3.946