IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

Aluminum-Alginate (Al-Alg) as Green Catalyst in Solketal Synthesis from Acetone and Glycerol

To cite this article: Mahreni 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **742** 012011

IOP Conf. Series: Materials Science and Engineering **742** (2020) 012011 doi:10.1088/1757-899X/742/1/012011

Aluminum-Alginate (Al-Alg) as Green Catalyst in Solketal Synthesis from Acetone and Glycerol

Mahreni[1]

[1]Chemical Engineering, Faculty of Engineering, Universitas Pembangunan Nasional Veteran Yogyakarta

E-mail : mahreni@upnyk.ac.id

Abstract. A catalyst is a chemical that can accelerate a reaction. So far, the catalyst uses precious metals (Pt, Au, Ag) which are heavy and expensive metals. In this research, a biodegradable Aluminum-Alginate (Al-Alg) green catalyst was synthesized using the precipitation method at room temperature. Aluminum is derived from Al $(NO_3)_3$ solution, and the Alginate used is brown algae extract in the form of Sodium-Alginate (Na-Alg). Previous research has reported that Aluminum-Alginate (Al-Alg) has been shown to accelerate the esterification reaction. In this research, Al-Alg was tried as a catalyst in the reaction of Solketal formation from Acetone and Glycerol. The purpose of this research is to prove the Al-Alg catalyst that has been synthesized using the precipitation method which can be used as a catalyst in the reaction of Solketal formation from Acetone and Glycerol. The research was carried out in two stages, namely the extraction of Alginate from brown algae using 2% by weight natrium-alginate solvent, then the second stage was the deposition of Na-Alginate using Al $(NO_3)_3$ solution. The precipitation was carried out at room temperature. The precipitate was dried, then its physical characteristicwas tested using FTIR and TGA/DTA; the chemical characteristic of the catalyst was tested through catalyzed reaction. The FTIR test results showed that the alginate molecule had been bound to Al molecule which was marked by a peak at the wave number of 1383.4 cm^{-1} which indicated the carboxylic group of COOH owned by Alginate, namely the *symmetric stretching vibration of the carboxylate group*. In addition, the peak at the wave number of 827 cm^{-1} showed that the C1 – H deformation vibration of b-mannuronic acid residues from Alginate. The peak at the wave number of 550 cm^{-1} proved that Aluminum (Al) had been bound to Alginate, and forming Al-Alg. The catalyst activity test was carried out by applying the Al-Alg catalyst in the catalyzing reaction of the formation of Solketal from Acetone and Glycerol. The reaction results were analyzed using GC-MS and it showed that the solketal was formed, and the selectivity was quite high at 96 %, proving that Al-Alg had the potential as a catalyst in catalyzing reaction.

1. Introduction

Solketal is an additive material to increase the gasoline octane number or increase the diesel cetane number [1]. The advantages of solketal are: biodegradable; do not contain metals; can be made from renewable raw materials; easy to make, so it can be classified as green chemical. So far Solketal has been synthesized using various types of catalysts, either homogeneous catalysts or heterogeneous catalysts. Homogeneous catalysts use hydrochloric acid, sulfuric acid, Para toluene sulfonic acid (PTSA), $FeCl_3$ and PWA (phosphotungstic acid) [2]. Solid (heterogeneous) catalysts that have been used are Amberlist and Zeolite [3]. The application of Al-Alg heterogeneous biodegradable catalysts has not been much studied.

The Al-Alg catalyst is synthesized using ionic reactions, between anions (carboxylic groups or COO^-) contained in alginate molecules, and Al^{+3}cations contained in Al $(NO_3)_3$ solution, then form molecular structures that resemble an egg box as illustrated in Figure 1. The negative charge of alginate molecules represented by carboxylic groups (COO^-) and OH^- on each Alginate monomer, can bind to the metal cation M^{n+} to form the egg box structure [4]. The valence metals two and three can bind to the Alginate molecule to form an Egg-box structure. Since alginate is a polymer composed of manuronic acid (M) and guluronic acid (G) monomers with the degree of polymerization reaching above 200, it is very effective as catalyst support with the main function of distributing the active component of the catalyst, in this case, metal cations. The catalyst activity increases if the active component of the catalyst can be well dispersed/distributed.

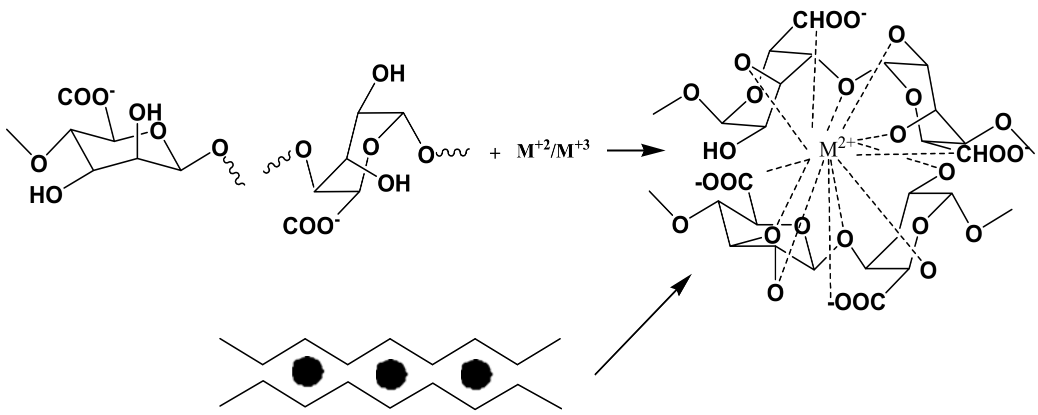


Figure 1. The interaction of Alginate molecules with the M^{2+} cation, forming the egg-box structure.

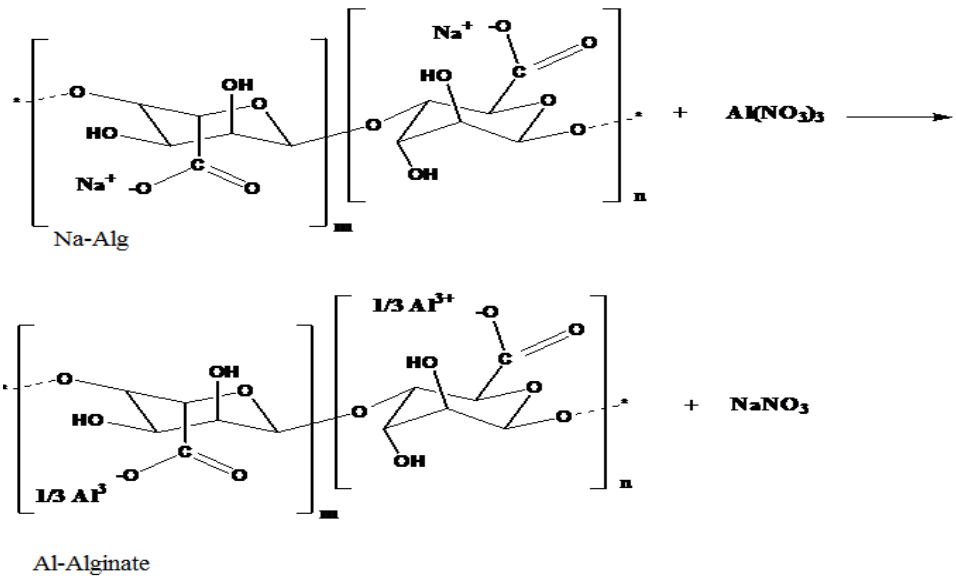


Figure 2. The ionic reaction of Na-Alginate and Al $(NO_3)_3$ to Al-Alg formation.

The purpose of this study is to test the physical properties of the Al-Alg catalyst and investigate the potential of Al-Alginate as a catalyst in the reaction of Solketal formation ftom Acetone and Glycerol

IOP Conf. Series: Materials Science and Engineering **742** (2020) 012011 doi:10.1088/1757-899X/742/1/012011

2. Material and Method

2.1. Materials and equipment

The main materials of Al-Alginate are: (1) Brown algae (*Sargassum sp.*), obtained from the southern coast of Yogyakarta (Ngedenan Beach); (2) Al $(NO_3)_6$ H_2O (pa), technical Na_2CO_3, which is directly used without pretreatment; (3) Aquadest; (4) 96 wt. % Ethanol; (5) 96 wt. % Acetone and (6) 96 wt % Glycerol. The equipment used are: (1) 50-liter volume extractor, equipped with temperature control, stirring speed and time; (2) Batch reactors, equipped with temperature control, stirring speed, condenser and time; (3) filtration equipment; (4) Drying ovens; and (5) a set of glassware.

Figure 3. The equipment of Al-Alg catalyst formation (a) Extractor and (b) Reactor

2.2. Flow diagram of the experiment

2.2.1. Production of Al-Alg Catalyst

The ingredients which directly used were $Al(NO_3)_3$ and $NaCO_3$, without any pretreatment. The making of the Al-Alg catalyst, firstly was weighing the brown Algae, then washed it with tap water to remove salt and dirt. The cleaned algae were drained for several hours until there was no more water dripping from the algae. The cleaned algae were soaked in aquadest in a ratio of 1:6 until all the algae were soaked for two hours, then blended it to form a homogeneous mixture (brown algae pulp). The next step was to make a 2%-weight Natrium carbonate solution. The natrium carbonate solution is used to extract Alginate from the brown Algae to form Alginate in the form of Natrium-Alginate salt. Natrium-Alginate is a form of soluble Alginate. The brown Algae extraction was carried out in an extractor with the volume of 50 liters and was equipped with a temperature regulator, stirrer speed regulator, and a timer. The ratio between the volume of Alga pulp and the volume of Natrium carbonate solution was 1:20 (volume/volume). The extraction was for two hours and at 80^oC. The extraction product was filtered, and the filtrate was cooled for the precipitation process using a solution of Al $(NO_3)_3$. The filtrate containing Natrium-Alginate would be converted to Al-Alginate in the precipitation process [5]. As the precipitate was the solution of Al $(NO_3)_3$ with concentration that varied from 0.1 to 0.5 M. The precipitation was carried out by titrating the solution of Natrium-Alginate extract with the solution of Al $(NO_3)_3$, drop by drop, and a brown precipitate would be formed. The titration was stopped after no more precipitate had formed. The precipitate was separated by filtration. Furthermore, the precipitate was dried in an oven at 80^oC to a constant weight, called the Al-Alg catalyst. The process of making catalyst and the Al-Alg catalys test can be seen in the flowchart in Figure 4.

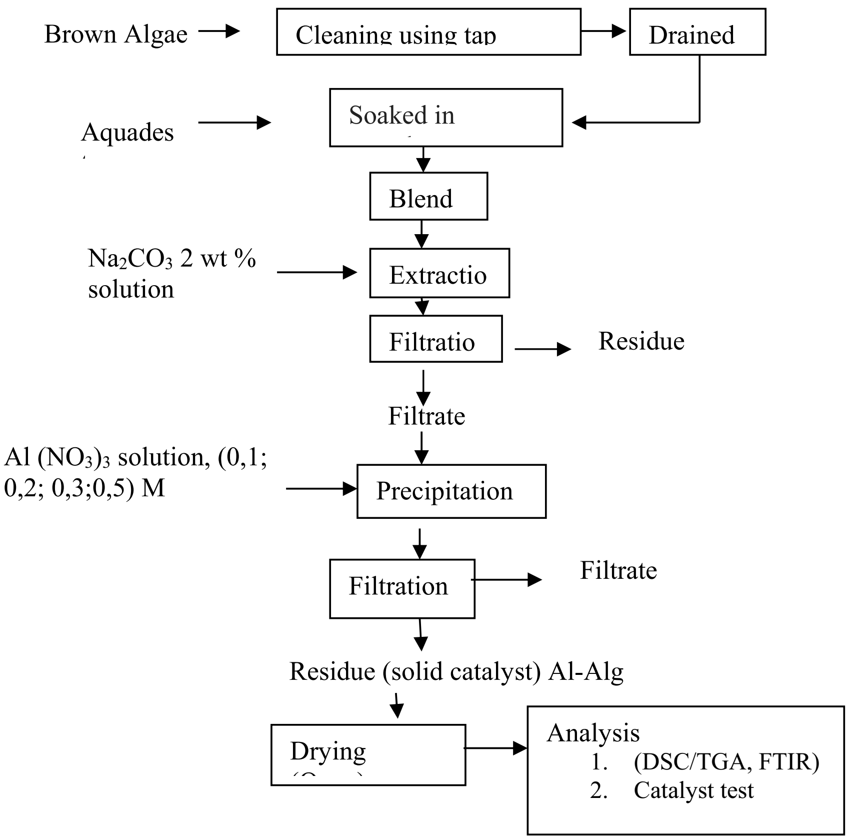


Figure 4. Flowchart of making of Al-Algcatalyst from brown Alga (*Sargassum sp)* and $Al(NO_3)_3$

2.2.2. Activity characterization of Al-Alg catalyst

To test the catalyst activity, the catalyst is used directly in the Solketal formation reaction. The catalyst test was carried out by mixing acetone and glycerol, ethanol and catalyst Al-Alg. After that, heated the mixture in the reactor equipped with a temperature controller, stirrer and condenser. After the temperature reached 63°C, the temperature was kept constant, and the heating was carried out for four hours. After that, the heater was turned off, and the reaction mixture was cooled to reach room temperature. Then the catalyst was separated, and the filtrate distilled to product purification. Purification of the Solketal (the main product) was performed where the distillation was carried out at boiling temperatures of acetone, ethanol, water, solketal, and glycerol. Soketal were analyzed using GCMS to determine the components presented in the distillate phases. The catalyst test process can be seen in 5.

IOP Conf. Series: Materials Science and Engineering **742** (2020) 012011 doi:10.1088/1757-899X/742/1/012011

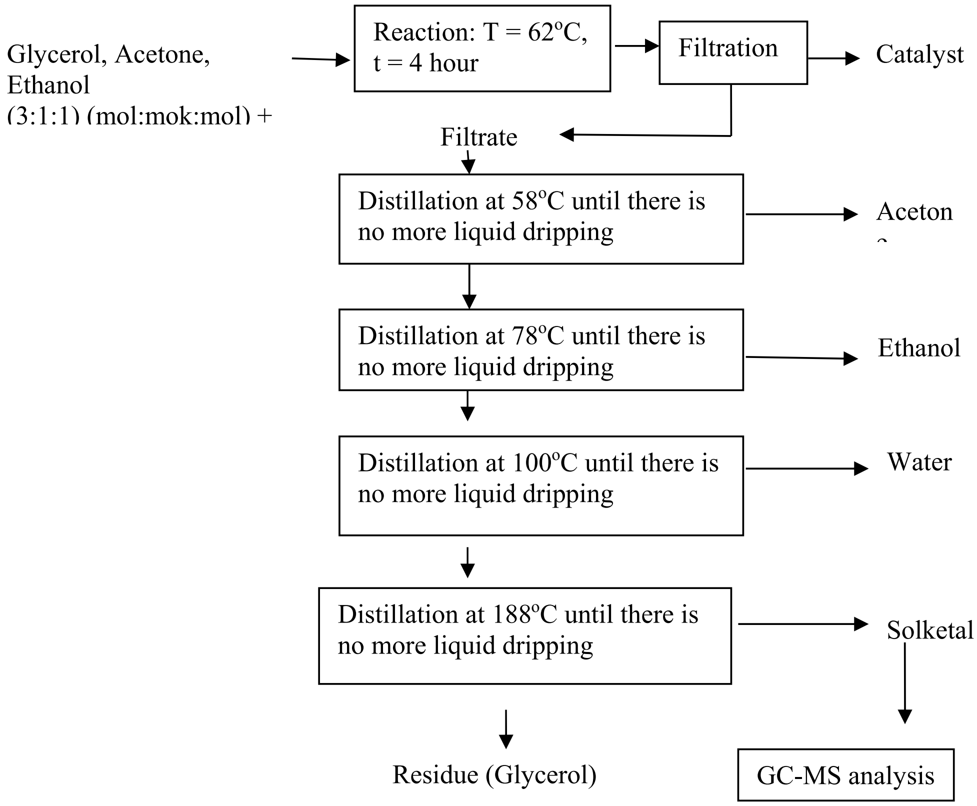


Figure 5. Flowchart of the Al-Alg catalyst test process as a catalyst in the reaction of Solketal formation from Acetone and Glycerol

2.3. Test of Al-Alginate using TGA/DTA

The thermogravimetric (TG) measurement is carried out to determine the thermal properties of the Al-Alginate catalyst. The analysis was performed using TGA-2050 thermogravimetry which was combined into a TGA-2100 thermal analyzer (both from TA Instruments) using a 20-mg sample mass and an alumina sample holder. The heating speed was 10°C min^{-1} below Nitrogen atmospheric. The measurement (DSC) carried out in DSC-910 modulus was combined into the TGA-2100 thermal analyzer (both from TA Instruments) using the sample mass of 20.0 mg in a closed aluminum sample container with a central pin hole with the heating rate of 10°C min^{-1} below Nitrogen atmospheric.

3. Results and Discussion

3.1. FTIR analysis

The results of FTIR analysis of Al-Alginate catalyst can be seen in Table 1 and Supplementary 1 (see supplementary). Based on the FTIR pattern, wavelength around 3453 cm^{-1} contributed to O-H bending from Alginate (Manuronic and Guluronic Acid), and the peak visible in the fingerprint area on 1633 cm^{-1} as scissoring band of O-H. The other peak on 577 cm^{-1} may be contributed to metal oxide (Al-O) vibration.

Table 1. The results of FTIR analysis of Al-Alginate catalyst produced by researcher (Mohamed, *et al.*, 2017) and the results of the author's research

Information	Wave number (cm^{-1})	Research results of [5] [6]	Wave number (cm^{-1})	Author's research results of Al-Alginate
Weak	1316.79	C–C–H		
Weak	1125.53	O–C–H		
Weak	1094.66	C–O stretching		
Strong	1035.6	C-O stretching vibration	1036	C–O stretching vibrations
Weak	948.2	C–O stretching vibration of uronic acid residues		
Weak	902.83	C1–H deformation vibration of b-mannuronic acid residues		
Strong			827	C1–H deformation vibration of b-mannuronic acid residues
Weak	818.76	C1–H deformation vibration of b-mannuronic acid residues		
Strong			577	Metal oxide (Al-O) vibration
Strong	1416	Symmetric stretching vibration of the carboxylate group	1383.4	Symmetric stretching vibration of the carboxylate group
Strong	1611.57		1633	O-H bending from $Al(OH)_3$
Strong			2329	
Strong	2942.16	C-H stretching vibration		
Strong	3421.05	Hydrogen bonded O-H stretching vibration	3453	O-H bending from Alginate

3.2. TGA/DTA analysis

The Al-Alg catalyst test results using TGA/DTA are shown in Supplementary 2**.** Supplementary 2 shows the Al-Alg TGA/DTG pattern. The thermogravimetric (TG) measurement is carried out using TGA-2050 thermogravimetry, combined into a TGA-2100 thermal analyzer (both from TA Instruments) using a sample mass of 18.961 mg and the alumina sample holder. The heating speed is 10°C min^{-1} below the atmosphere of Nitrogen at a speed of 30 ml/min. The detector DTG-60 serial number is C30565100652TK. The results of the TGA analysis are shown by the thermogravimetric analysis curve (TGA) and the differential thermogravimetric Analysis (DTG) of Al-Alg at a heating rate of 10^{o}C/min below the Nitrogen atmosphere, as presented in Supplementary 2. The Al-alginate weight reduction stage is located at the wide temperature. In the zone (from 30 to 600^{o}C), the decomposition temperature of the onset crystal water content (Tonset, defined as the temperature at which a 5% weight loss occurs) from Al-Alg is at 67 to 179^{o}C, and the peak is at 121.4^{o}C. At the time of the release of crystal water requires a certain amount of heat, and this is seen in the DTG curve, a decrease in temperature indicates the release of water is an endothermic process, and the temperature drops to 25oC from the initial temperature.

The faster degradation rate is characterized by the rising temperature or exothermic process. The exothermic process started at 220^{o}C and ended at 380^{o}C. Then the weight of Al-Alginate decreased more rapidly, and the Alginate degradation produced H_2O, CO_2, and occurred at temperatures of 410 to 600^{o}C where the reaction to release water and carbon dioxide occurred exothermically so that the temperature increased. The exothermic peak occurred again at temperatures of 550 to 600°C. Weight loss in the first stage of thermal degradation was in linewith the intensive evolution of small molecules and the degradation of alginate by the glycosidic bonding fracture to form compoundsbetween releasing small molecules, such as H_2O and CO_2 [7]. In general, the chemical reactions occurred during the process of thermal degradation in the alginates, involving dehydroxylation, decarboxylation, decarbonylation, and breaking down the macromolecular chains into smaller fragments. The reaction produced residues and gas. The estimated residues were Al and carbon. The final sample weight was 2.5 mg, from the initial sample which was 18.961 mg, proved that Aluminum and Alginate had been formed. Alginate is an organic material that will be degraded to produce CO_2 and small molecules, and the residues are Aluminum oxide and Charcoal. Charcoal is an inorganic component, such as SiO_2, and the metal oxides contained in brown algae that dissolved in the solvent when extracted.

3.3. Chemical characteristic test of Al-Alg catalyst using GC-MS
The purpose of testing the catalyst's chemical properties is to determine the potential of the Al-Alg catalyst as the catalyst in the reaction of Solketal formation from Acetone and Glycerol. The results of the analysis showed that the reaction using Al-Alg as catalyst produced a Solketal with a selectivity of 96.83%. Prove that Al-Alg has great potential for the formation of solketal from Acetone and glycerol

4. Conclusion

Research in the synthesis of Al-Alg catalysts has been carried out. Al-Alg is an environmentally friendly catalyst that can be made from renewable sources (*Sargassum sp*.). From the results of the analysis found that Al-Alg proved to be able to act as a catalyst in the reaction of the formation of Solketal from Acetone and Glycerol. The main product selectivity is high at 96% Solketal. Therefore Al-Alg is very important to be a catalyst in the future

References

[1] Maraísa Gonçalves, Raphael Rodrigues, Thalita S. Galhardo, Wagner A. Carvalho. Highly selective acetalization of glycerol with acetone to solketal over acidic carbon-based catalysts from biodiesel waste Fuel 181 (2016) 46–54. http://dx.doi.org/10.1016/j.fuel.2016.04.083.

[2] Roberto Espositoa, Maria Elena Cucciolito, Angela D'Amoraa, Rossella Di Guida, Fabio Montagnaro, Francesco Ruffo. Highly efficient iron (III) molecular catalysts for solketal production. Fuel Processing Technology 167 (2017) 670–673. http://dx.doi.org/10.1016/j.fuproc.2017.08.018

[3] Nuryoto1, Hary Sulistyo, Wahyudi Budi Sediawan, Indra Perdana. Sintesis Bioaditif Gasoline Melalui Ketalisasi Gliserol Menggunakan Katalisator Padat. Jurnal Bahan Alam terbarukan 5(2) (2016) 74-83. DOI 10.15294/jbat.v4i2.7431.

[4]. Guillermo Simóa, Encarnación Fernández-Fernándeza, Josefina Vila-Crespo, Violeta Ruipérez, José Manuel Rodríguez-Nogales. Research progress in coating techniques of alginate gel polymer forcell encapsulation.. Carbohydrate Polymers 170 (2017) 1–14. http://dx.doi.org/10.1016/j.carbpol.2017.04.013

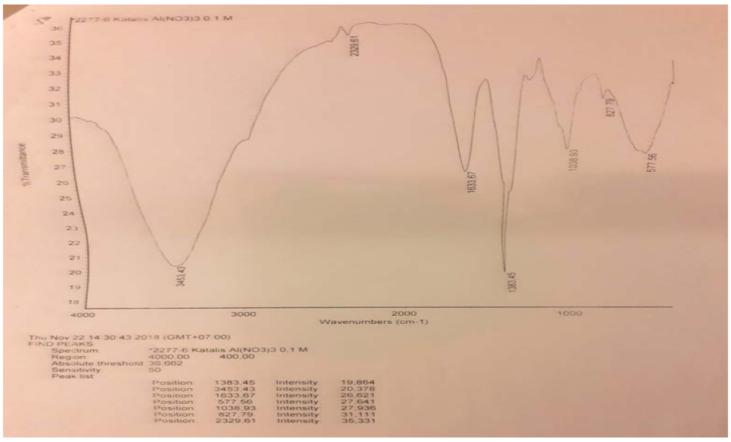
[5] Etik Mardliyati, Damai Ria Setyawati, Sabar Pambudi, Suryandaru, Retno Kusumaningrum, M. Ikhlasul Amal Preparation of Aluminum Hydroxide by Precipitation Method for Vaccine Adjuvant Application, Int. Journal of Engineering Research and Application www.ijera.com ISSN : 2248-9622, Vol. 7, Issue 11, (Part -5) November 2017, pp.21-25

[6] Mohamed Fertah, Ahmed Belfkira, El montassir Dahmane, Moha Taourirte, Franc¸ois Brouillette. Extraction and characterization of sodium alginate from Moroccan Laminaria digitata brown seaweed. Arabian Journal of Chemistry (2017) 10, S3707–S3714.

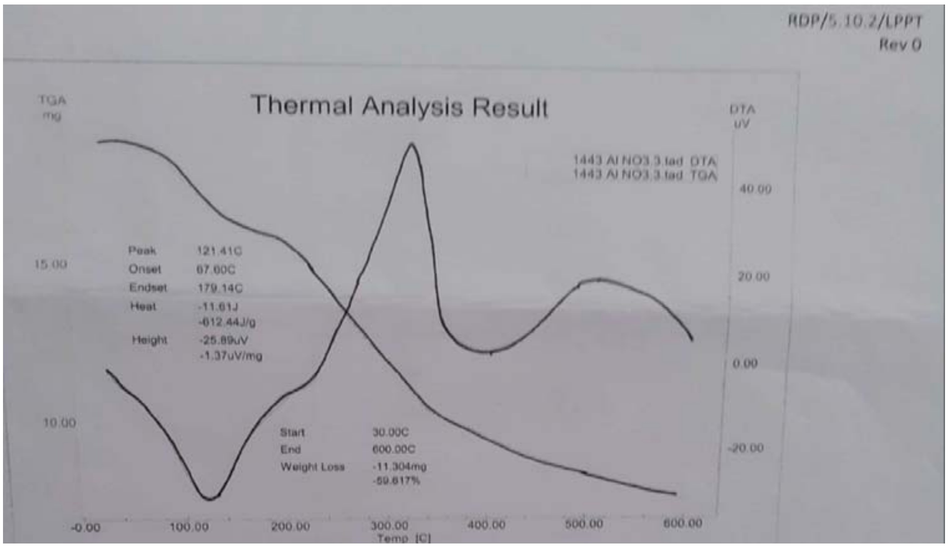
[7] Liu Y, Li Z, Wang J, Zhu P, Zhao J, Zhang C, Guo Y, Jin X, Thermal degradation and pyrolysis behavior of aluminum alginate invesitagted by TG-FTIR-MS and Py-GC-MS,*Polymer Degradation and Stability* (2015), doi: 10.1016/j.polymdegradstab.2015.04.010.

IOP Conf. Series: Materials Science and Engineering **742** (2020) 012011 doi:10.1088/1757-899X/742/1/012011

Supplementary

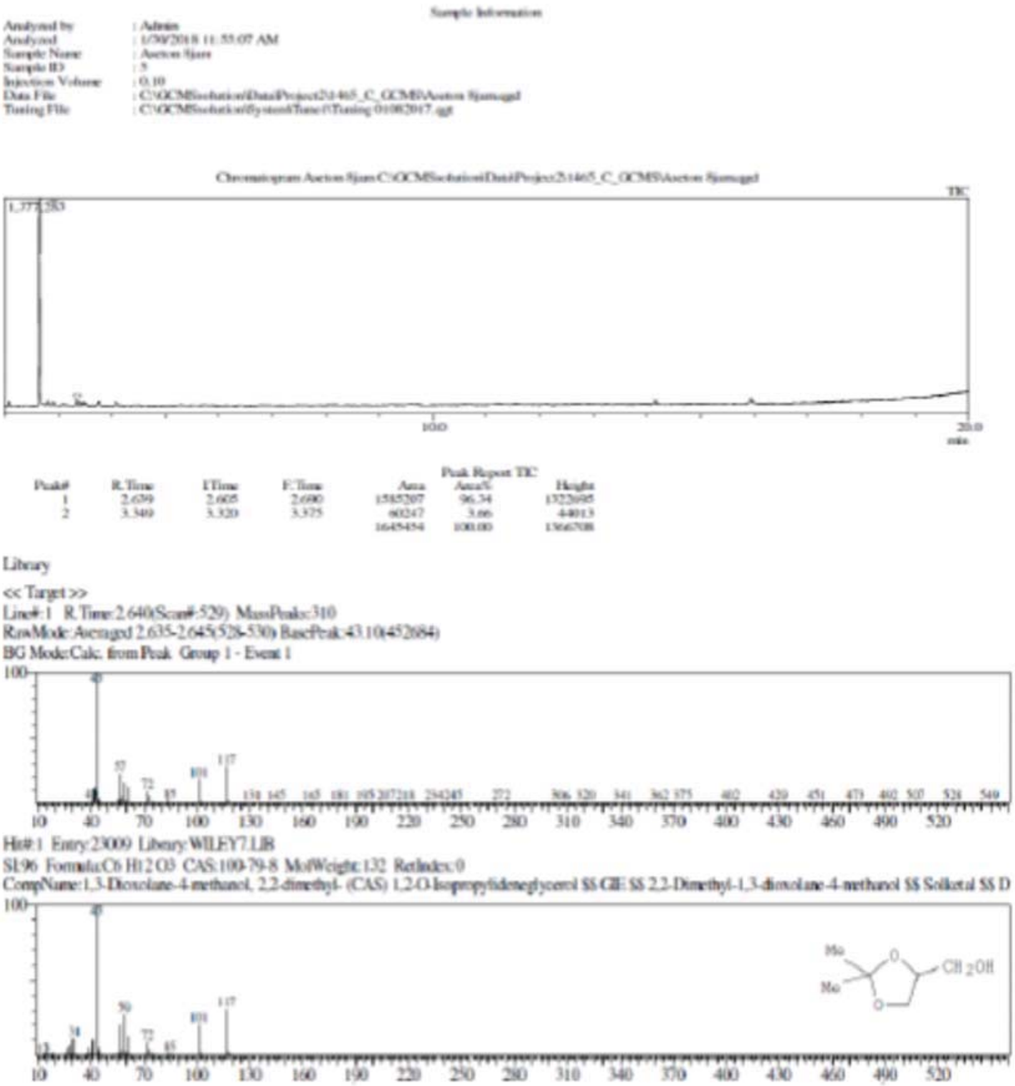


Supplementary 1. The result of the FTIR analysist of Al-Alginate catalyst



Supplementary 2. TGA/DTA analysis results of Al-Alg catalyst

IOP Conf. Series: Materials Science and Engineering **742** (2020) 012011 doi:10.1088/1757-899X/742/1/012011



Supplementary 3. The results of GC-MS analysis in the reaction of Acetone and Glycerol using Al-Alg as catalyst at the temperature of 63ºC during for four hours with the ration between the acetone mole and the Glycerol = 2:1 (mol/mol).