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Triacetin Synthesis as Bio-Additive from Glycerol Using Homogeneous and Heterogeneous Catalysts

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Abstract. The government tries to anticipate the needs of fuel in Indonesia. Efforts to develop new fuels have also been done. New fuels and renewable energy that has been developed are water, wind, bioenergy, solar, ocean, and geothermal. Bioenergy which now widely developed is biodiesel. The development of biodiesel industry which has increased rapidly, was accompanied by government policies that are written in the blueprint of the national energy management, make the biodiesel production grow rapidly. Glycerol as a by-product of the biodiesel industry is available abundantly, so it is necessary to study alternative uses. One alternative is to process glycerol into triacetin which can be used as bio-additive. The reaction between glycerol and acetic acid using a batch reactor was done on the mole ratio of catalyst/glycerol of 3.0%, the mole ratio of acetic acid/glycerol of 3/1, reaction temperature of 80-110°C and reaction time of 60 minutes. The optimum condition is achieved when the batch reaction was run with catalyst Amberlyst-15 at temperature of 110°C with conversion of 97.52% and selectivity triacetin of 89.74%.

Introduction

Indonesia is one of the prosperous countries in terms of energy because of its availability in abundance. The population growth rate is constantly rise so that energy demands also increases. This fact changes Indonesia which used to be the oil-exporting country become a net importer of oil. The government through the ministry of energy and mineral resources have the vision to seek and to replace the use of fuel by increasing the role of alternative energy from new renewable energy as a solution to reduce the dependence of fossil energy. The renewable energy consists of the energy of water, wind, biomass or biofuels, solar energy, ocean energy, and geothermal energy. Renewable energy that still needs to be processed before used is biofuels.

The government has adopted a policy to increase the percentage use of biofuels as an anticipatory step because of the reduced supply of oil from fossil fuels and the increasing market demand. This policy is included in the roadmap of biodiesel in the blueprint of the national energy management from 2006 to 2025. That blueprint is the mandate of the Presidential Decree No. 5 of 2006, which is become the national energy development reference. In the period of 2011-2015, the government has a target the supply of biodiesel as many as 3 million kL/year or 15% of existing solar supply. Later in the period of 2016-2025, this target increased to 6.4 kL/year which will be used as the transportation needs of 20% and consumption of 5%. Biodiesel is a diesel fuel from vegetable oil by trans-esterification. Biodiesel is one of the best alternatives fuels which have several advantages such as renewable, high cetane number, high viscosity, better lubrication properties of the fuel, has low sulfur content, and low emission.

The biodiesel production will produce glycerol as by product. As prediction, in 2020 Indonesia will produce glycerol 0.42 million kL/year. Glycerol would be a problem if it is not used and just dumped into the environment. Therefore, it is necessary to study alternative uses. There are several alternative utilization of glycerol into value-added materials. Glycerol into triacetin which can be used as bio-additive.

The abundance of glycerol will result in decreased sales value of glycerol as a byproduct of the biodiesel plant. It should be anticipated to improve the usefulness of glycerol both in terms of quantity and its variants. With the increasing usefulness of glycerol will result in the higher price of glycerol that will increase the profitability of biodiesel plants. Among the usefulness of glycerol has been investigated are polyglycidyl nitrate [1-4], bioaditive triacetin [5-8], as an ingredient in pharmaceutical products, polyether, emulsifiers, fabric softener, stabilizers, preservatives in bread, ice cream, cosmetic ingredients, and others [9, 10].

Synthesis of triacetin with solid catalysts have been carried out using phosphotungstic [11], Amberlyst-15 or SAC-13 (Nafion-SiO_2) [12], Amberlyst-15, K-10, the acid Niobic, HZMS-5 and HUSY [13], Zirconia-based solid acid [14] tungstophosphoric acid (TPA) [15], and PW2_AC [16]. The use of solid catalysts has ease of product purification process. Many studies have also been conducted to study the reaction kinetics with cation-exchange resin as a solid catalyst [5, 17]. While the reaction kinetics without catalyst was studied by Galan *et al* [10]. Then the study of continuous process and reaction kinetics using a packed bed reactor and cation exchange resin as catalyst were proposed by Fukumura *et al.* [18] and Mufrodi *et al.* [6, 8]. The reaction mechanism is simplified into three consecutive main reactions:

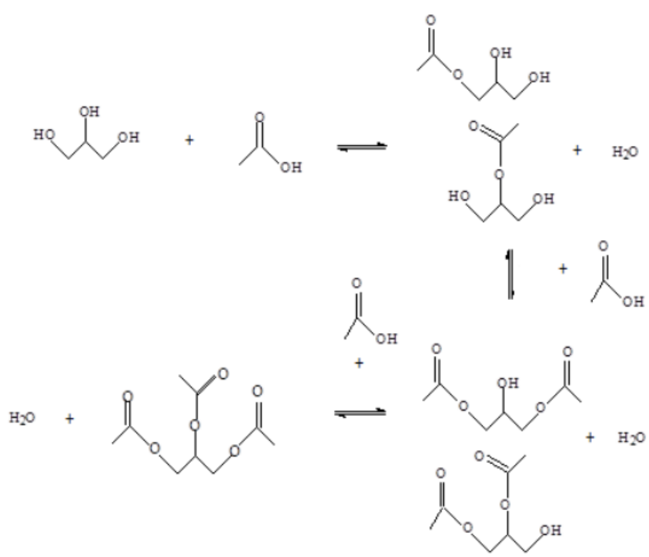

Fig. 1. Reaction mechanism

Methods

The chemicals used in the experiments were acetic acid, 98% purity (Petrochemical Chang Cun), glycerol, 93% purity (P & G Chemicals), amberlyst-15, silica-alumina, modified zeolite and sulfuric acid (Merck Index No. 016-020-00-8) as catalysts.

The reaction was done in a three-neck flask equipped with a heating mantle, cooling system, mercury stirrer, thermometer and sampling equipment (Fig. 2). The reaction between glycerol and acetic acid was done with the mole ratio of catalyst/glycerol of 3% using several types of catalyst: acetic acid, amberlyst-15, silica-alumina and modified zeolite. The reaction temperatures were 80ºC, 90 ºC, 100 ºC, and 110ºC.

Fig. 2. Batch reactor

Samples were analyzed using gas chromatography (GC) agilent 6890N MSD 5975B, Model Number: Agilent 19091S-433, HP-5ms column of 5%. Phenyl methyl siloxane, the temperature of the detector: MS Quad 150°C, the injector volume of 1 microliter, the injector temperature 275°C, and the injector pressure of 3.27 psi.

Results and Discussion

Experiments of triacetin from glycerol and acetic acid to the reaction temperature variation run at 80ºC and 90ºC, the mole ratio of catalyst/glycerol of 3% and the mole ratio of acetic acid/glycerol of 3/1. The temperature was before boiling water (100ºC). The effect of various acid catalysts on Glycerol conversion and product selectivity at temperature 80ºC and 90ºC can be seen in Table 1.

Table 1. The effect of various acid catalysts on Glycerol conversion and product selectivity at 80ºC and 90ºC

	Catalyst	Conversion, %		Selectivity, %					
		80ºC	90ºC	Monoacetin		diacetin		Triacetin	
				80ºC	90ºC	80ºC	90ºC	80ºC	90ºC
1.	Sulfuric acid	87.69	89.52	16.41	13.74	23.85	24.61	59.74	61.65
2.	Amberlyst-15	98.23	98.85	02.94	2.63	14.64	12.74	82.42	84.63
3.	Silica alumina	84.56	86.22	20.38	20.05	32.74	30.99	46.88	48.96
4.	Modified zeolite	86.03	87.94	19.35	18.12	27.43	25.43	53.22	56.45

Table 1 shows that glycerol conversion and triacetin selectivity are higher when the reaction temperature is increased from temperature 80°C to 90°C for all catalysts various. The best performance of catalysts is amberlyst-15, with maximum conversion is 98.85% and triacetin selectivity is 84.63%. In general, the temperature rose of 80°C to 90°C will result in decreased selectivity of monoacetin and diacetin. The increase in the average glycerol conversion of temperature from 80°C to 90°C with catalyst acetic acid, amberlyst-15, silica alumina and modified zeolite are 2.09%, 0.06%, 1.96% and 2.22%.

The effect of various acid catalysts on glycerol conversion and product selectivity at temperatures 100°C and 110°C can be seen Table 2.

Table 2. The effect of various acid catalysts on glycerol conversion and product selectivity at 100°C and 110°C

No	Catalyst	Conversion, %		Selectivity, %					
		100°C	110°C	Monoacetin		Diacetin		Triacetin	
				100°C	110°C	100°C	110°C	100°C	110°C
1.	Sulfuric acid	90.21	93.45	16.83	13.07	20.74	19.61	62.43	67.32
2.	Amberlyst-15	96.42	97.52	00.19	00.03	11.89	10.23	87.92	89.74
3.	Silica alumina	88.65	87.43	17.98	18.47	33.97	32.84	48.05	47.69
4.	Modified zeolite	89.22	89.02	15.13	15.95	24.65	24.63	60.22	59.42

The reaction between glycerol and acetic acid will produce triacetin as the main product, monoacetin and diacetin as intermediate products, and water as a side product. The reactions are series-parallel reactions and reversible reactions. The glycerol conversion and triacetin selectivity were calculated at a reaction temperature of 100°C and 110°C. These temperatures were chosen because the boiling point of water is 100°C. As seen in Table 2, the performance of two catalysts, acetic acid and amberlyst-15, increase in the higher temperature, but the performance of silica-alumina and modified zeolite decrease. Therefore, for sulfuric acid and amberlyst-15 catalysts, if the reaction temperature is increasing from 100°C to 110°C than glycerol conversion and triacetin selectivity are increasing too. For silica-alumina and modified zeolite catalysts, if the reaction temperature is increasing from 100°C to 110°C than glycerol conversion and triacetin selectivity are decreasing. The best results get on the mole ratio of catalyst and glycerol of 3%, the temperature of 110°C, the reaction time of 60 minutes, using catalyst amberlyst-15 with glycerol conversion of 97.52% and triacetin selectivity of 89.74%.

This paper also studies the effect of the addition of triacetin into biodiesel. Biodiesel can be made using waste cooking oil [19, 20] and chicken fat [21]. Biodiesel performance without triacetin, mix with 10% and 20% triacetin can be seen in Table 3.

Table 3. Properties of biodiesel without and with triacetin

No	Analysis	Product analysis				Analysis method (ASTM)
		Standard Biodiesel	Biodiesel+0% of triacetin	Biodiesel+10% of triacetin	Biodiesel+20% of triacetin	
1.	viscosity kinematic (40°C), mm^2/s	2.3-6.0	4.821	4.594	4.211	D 445
2.	Flash point, °C	>100	177	141	129	D 93
3.	pour point, °C	<18	9	12	6	D 97

High viscosity causes atomized fuel to become large granules so that fuel injection cannot be carried out properly if sprayed into the combustion chamber. The lower the viscosity of the fuel, causes the better the fuel combustion. The addition of triacetin on biodiesel has an impact on reducing viscosity so that biodiesel is more flammable. Flashpoint is the lowest temperature at which a solvent can form an ignitable mixture in air near the surface of the liquid. Decreased of the flash point makes biodiesel more combustible. Similarly, a decrease in pour point will make it easier for biodiesel to flow at lower temperatures. Adding triacetin to biodiesel causes flash point and pour point to decrease so that biodiesel performance is getting better.

Conclusion

At the synthesize of triacetin from glycerol and acetic acid, in general, the temperature rose of 80°C to 90°C will result in decreased selectivity in monoacetin and diacetin. The optimum conditions are mole ratio of catalyst and glycerol of 3.0%, the temperature of 110°C, the reaction time of 60 minutes, and using Amberlyst-15 as a catalyst. The best results are glycerol conversion of 97.52% and triacetin selectivity of 89.74%.

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