

HASIL CEK_Operation Conditions In Syntesize of Bioaditive From Glycerol as By- product Biodiesel-A Review

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Operation Conditions In Syntesize of Bioaditive From Glycerol as By-product Biodiesel : A Review

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Abstract

Triacetin is a good bioaditive as anti knocking agent and give increasing performance biodiesel machine. The variables studied process for syntesize of bioaditive are reaction time length, the mole ratio between glycerol and acetic acid, and the reaction temperature. Besides, in the process also much studied the effect of various catalysts to the conversion and the results obtained. . The effect of triacetin can increase motor octane number (MON) and research Octane number (RON), decrease cetane number (CN) and give better biodiesel performance.

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Keywords: Triacetin, glycerol, batch, continuous, reactive distillation

1. Interoduction

Glycerol is a by product of biodiesel Industries. There are many value added products synthesized from glycerol i.e. polyglycidyl nitrate [1-4], propylene glycol [5,6], 1,3 propanediol [7], medicinal ingredients, poly ether, resin, explosives and others [8] and triacetin [9,10]. Synthesis of triacetin has been conducted since 1963. Triacetin was converted from glycerol and acetic anhydride [11-13]. In other studies, the synthesize have tried using glycerol and acetone [14] and use three compounds as well as glycerol, acetic acid and anhydrous acetate [15]. However, many studies were conducted using glycerol and acetic acid.

Production of triacetin is generally carried out by batch process with glycerol and acetic acid using both homogeneous and heterogeneous catalysts. Heterogeneous catalysts were selected to facilitate the separation of the product with the catalyst upon exiting the reactor, while the homogeneous catalyst was used to obtain higher conversion, yields and triacetin selectivities. Triacetin has several usefulness: in pharmaceutical products, poly eters, emulsifiers, softening agents, stabilizers, preservatives in bread and ice cream, cosmetic ingredients [8,16,17].

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Triacetin may also be used as perfumes, synthetic resins, medicines, toothpastes and the food industry [18] In addition, triacetin as fuel additive can give effect to waste cooking biodiesel on engine performance and exhaust emissions [19,20]. The effect of triacetin increase motor octane number (MON) and research Octane number (RON) and lower cetane number (CN) (Table 1 and 2)[9,21].

Table 1. Cold properties Improvement when mixing triacetin with glycerol

Parameters	Biodiesel	Biodiesel +	Biodiesel +	Biodiesel +
		1% of Triacetin	5% of Triacetin	10% of Triacetin
Density (g/cm)	0.859	0.862	0.869	0.881
Melting point (°C)	-7	-16	-16	-17
Viscosity at -10°C (cSt)			931.2	453.9

Table 2. Triacetin properties as fuel additive

Density g/cm	Boiling point. °C	Engine test					
		Motor octane number		Research octane number		Cetane number	
1.10	259	gasoline	10% mix	gasoline	10% mix	gasoline	10% mix
				85.3	88.0	97.0	98.3

2. Raw material.

In the beginning, triacetin was made from anhydrous glycerol and acetic material. The reaction was carried out at a temperature of 393-408 K in a batch reactor without the use of a catalyst [11] and using Amberlist-35 catalyst. The reaction reaches equilibrium at 30 minutes [12]. The use of anhydrous glycerol and acetate can yield 100% of triacetin selectivity when using H-Beta or K-10 catalyst at 333 K with molar ratios of acetic anhydrous / glycerol of 4:1 and reaction time of 20 minutes. The other catalysts that can be used are amberlyst-15 at 333 K with molar ratios of acetic anhydrous / glycerol of 4:1 and reaction time of 80 minutes or using a Niobium phosphate catalyst at 393 K with acetic anhydrous/glycerol of 4:1 and reaction time of 80 minutes [22].

The preparation of triacetin may also be carried out by react glycerol and acetone with p-toluensulfonic acid monohydrate as a catalyst which was reacted for 16 hours. Then it was reacted with acetic anhydrous at room temperature for 4 hours [14]. There was also research on the preparation of triacetin which reacted glycerol with acetic acid and then added anhydrous acetate. Research was done by continuous process [15]. On the next progress, triacetin was made using glycerol and acetic acid with or without catalyst. This process is mostly done by researchers.

3. Operating conditions.

Table 3 explains that the use of different catalysts has an effect on monoacetin, diacetin, or triacetin results. Reaction time (3 hours) resulted in a higher percentage of triacetin product distribution compared to a shorter reaction (1 hour)[23].

Table 3. Influence of catalyst and reaction time to conversion of Glycerol and product distribution

Catalyst	Conversion, %		Product distribution, %					
	2		Monoacetin		Diacetin		Triacetin	
	1 h	3 h	1 h	3 h	1 h	3 h	1 h	3 h
Blanko	36	85	89	73	11	25	0	2
p-TSA	100	100	10	8	57	55	33	37
Amberlist-15	97	100	35	31	54	57	11	12
Nb ₂ O ₅ nH ₂ O	51	82	91	70	9	29	0	1
SSBA	100	100	15	5	74	62	11	33

The experiment to investigate the effects of temperature changes and reagent comparisons on the conversion of glycerol and the selectivities of monoacetin, diacetin and triacetin by using zirconia based solid acid catalysts WO_x/TiO_2-ZrO_2 or WTZ, dan MoO_x/TiO_2-ZrO_2 or MTZ. The results obtained can be seen in Table 4. and 5. [19].

Table 4. Effect of temperature in acetylation of glycerol on various catalysts, with molar ratio of acetic acid/glycerol 1/6; catalyst 5% w/w of glycerol; reaction time of 3 hours.

Catalyst	temperature (K)	Conversion of Glycerol (%)	Selectivity		
			Monoacetin	Diacetin	Triacetin
WTZ	313	12.61	100	-	-
	353	42.68	91.99	8.01	-
	393	99.02	53.21	40.01	6.78
MTZ	313	18.57	100	-	-
	353	50.72	88.87	11.13	-
	393	~100	52.03	40.45	7.52

From Table 4 it can be said that glycerol conversion and selectivity are higher when the reaction temperature is increased from 313 K to 393 K.

Table 5. Effect of the the mole ratio of acetic acid/ glycerol in various Catalysts (catalyst 5% w/w of glycerol; temperature of 393 K; reaction time of 3 hours)

Catalyst	Acetic acid/ glycerol	Glycerol Conversion, %	Selectivity		
			Monoacetin	Diacetin	Triacetin
WTZ	3:1	85.05	65.89	30.04	4.07
	4:1	87.24	63.87	31.16	4.97
	5:1	93.89	58.83	35.29	5.88
	6:1	99.02	53.21	40.01	6.78
MTZ	3:1	90.66	59.56	34.98	5.43
	4:1	92.68	55.81	37.07	6.23
	5:1	94.61	54.64	39.08	6.78
	6:1	~100	52.03	40.45	7.52

1 Table 5 shows that the increase in mole ratio of reactants between acetic acid and glycerol leads to increased glycerol conversion and diacetin and triacetin selectivity. The best triacetin yield was achieved under 10 mmol glycerol, 30 mmol acetic acid, 0.2g catalyst, reacted in 300w microwave, temperature of 403 K and reaction time of 30 minutes with starbon-400-SO₃H as catalyst. Conversion of glycerol is more than 99% with triacetin selectivity of 77% [16].

1 The method to produce triacetin has been done in two steps to obtain high selectivity and conversion. The esterification of glycerol with acetic acid was carried out with various catalysts. In the experiment Amberlyst-35 was obtained as the best catalyst. The experiments were carried out under operating conditions temperature of 378 K, the molar ratio of acetic acid: glycerol of 9: 1, with a catalyst of 0.5g. After reacting for 4 hours under optimum conditions, 0.1 mol of acetalhydrate was added and after a reaction of 15 minutes, 100% triacetin selectivity was obtained [22]. The effect of reaction temperature, comparison of reactants and the use of the amount of PW-in-S2 catalysts to the synthesise of triacetin has been studied. The effect of variation on temperature 313, 363, and 393 K resulted in the increase of glycerol conversion of 29%, 62%, and 87%. The effect of glycerol / acetic acid reagent ratio of 1/6, 1/11 and 1/16 for reaction time for 4 hours resulted in glycerol conversion of 48%, 49%, and 74%[24].

4. Type of catalyst.

Research on triacetin production with batch process has been done, mainly by using solid catalyst. Asetilation triacetin from glycerol and acetic acid by $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ catalyst and obtained the best results at 450 K [25]. Then by using the same catalyst but different temperature conditions (403 K), get a better result that is 93.6% triacetin [26]. Meanwhile, using the aminosulfonic acid catalyst get a yield of 92% [27]. with a phosphotungstic acid, reactant ratio reactan of 3.8%, a temperature of 405–428 K and a reaction time of 7 hours obtaining a triacetin yield of 84.6% [28]. Another study using p-toluensulfonic acid, obtain triacetin yield of 92% [29].

The has been studied of tungstophosphoric acid catalyst (TPA) was conversion of glycerol and selectivity depend on the acidity of the catalyst, which corresponds to the amount of niobic acid from the lanthanum used [30]. The optimum conditions were achieved at reaction time for 4 hours, reaction temperature 393 K, ratio of acetic acid: glycerol = 1: 5 and weight of catalyst 25% TPA / Nb_2O_5 200 mg [31]. Asetilation using PW2_AC catalyst after 3 h reaction, the biggest glycerol conversion was 86% with 25% monoacetin selectivity, 63% diacetin, and triacetin 11% [24]

Acetylation from glycerol using catalysts Amberlyst-15, Amberlyst-36, Dowex 50Wx2, Dowex 50Wx4 and Dowex 50Wx8 conducted at 378 K and atmospheric pressure. The best catalyst used Amberlyst-15 with acetic acid conversion 95.6% and acetylation yield of the glycerol for monoacetin and diacetin mixture was 74.8%. [32]. Conversion of glycerol and selectivity of triacetin at the temperature 383 K for Zr-zeolite catalyst was 94.56% and 26% [33]. The various catalysts used and the conversion of glycerol and the selectivity of monoacetin, diacetin, and triacetin can be seen in Table 6

Table 6. Effect of various acid catalysts on Glycerol conversion and product selectivity

No	Catalyst	Glycerol conversion, %	Product selectivity, %			Ref.
			Monoacetin	Diacetin	Triacetin	
1.	Amberlyst-15	97	31	54	13	[30]
3.	HUSY	14	79	14	0	
4.	Amberlist-15	100	21.1	63.8	15.1	[34]
5.	HUSY	94	72.7	25.7	1.6	
6	Amberlist-15	99	0	1	99	[35]

Table 6 shows that in general, the use difference condition with th same catalyst has a difference glycerol conversion and product selectivity. The instrumentations used for analysis was gas chromatography (GC) and Chromatography mass spectrometry (GCMS) [36]

The production of triacetin using continuous reactive distillation with condensor and reboiler resulted in glycerol conversion of 98.51%. Reactive distillation can be used as a place of reaction and purification products in one place. The column is operated at atmospheric pressure, the temperature of acetic acid and glycerol feed streams is 391 K and 373 K [37].

Conclusion

Triacetin was made from glycerol and acetone, glycerol an anhydrous acetate, glycerol with acetic acid and then added anhydrous acetate and glycerol and acetic acid. The best reactan to syntesis triacetin is glycerol and anhydrous acetate. The operating conditions (reaction time, reaction temperature, reactant ratio, mechanism or method, type of catalyst used) in a reaction mostly affect the expected results. The vactor mostly affect to the syntesis triacetin are type of catalyst used and reaction temperature. The effect of triacetin increase motor octane number (MON) and research Octane number (RON), decrease cetane number (CN) and give better biodiesel performance.

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