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Triacetin Production from Acetylation of Glycerol: A Review

Panida Sriratchatchawan, Srisin Eaimsumang and Apanee Luengnaruemitchai

Abstract— Due to its numerous applications, triacetin is regarded as the most valuable acetin when compared to other acetin. Glycerol from biodiesel production and acetic acid are considered as potential reactants for triacetin production due to the worthiness of the reactant price and safety. Acetylation reaction of glycerol and acetic acid generates monoacetin, diacetin and triacetin. Triacetin is a minority product from this reaction, therefore; many techniques are applied to the production process in order to complete high glycerol conversion and high triacetin selectivity. This article review highlighted the influence of operating parameters (molar feed ratio, reaction temperature, catalyst loading and reaction time) to glycerol conversion and acetin selectivity. Additionally, this review also included the gathering of data regarding to the catalyst selection for the acetylation of glycerol and acetic acid to achieve excellent catalytic performance.

Keywords—Acetylation reaction, Glycerol, Triacetin, Reaction condition, Acid catalyst

I. INTRODUCTION

Biodiesel is regarded as one of the most promising fuels developed to address the issue of energy scarcity. As demonstrated in Fig. 1, global biodiesel production has increased significantly from 2013 to 2019, owing to the influence of reduced greenhouse emissions policy [1]. Biodiesel can be produced via transesterification of triglyceride and alcohol with the assistance of acid or alkaline catalysts.

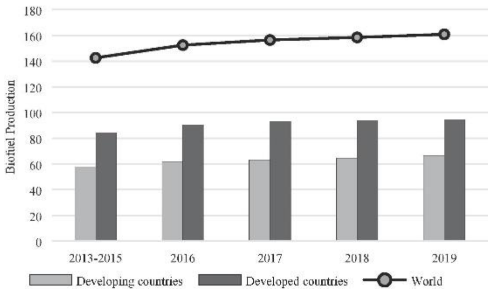

Fig. 1 Developing, developed and world biodiesel production (in thousand metric tons per capita) [1].

During the biodiesel production, glycerol was generated as a by-product from the reaction accounted for 10% of biodiesel produced [2]. Nevertheless, the glycerol, byproduct, from the reaction above is contaminated with other substances (crude glycerol); therefore, purification of crude glycerol is necessary [3]. Filtration, chemical additive and distillation are the common techniques used in the crude glycerol purification process. Glycerol can be used in various applications as demonstrated in Fig. 2 [3], for example, solvent and sweetener in food industry, moistener in drug and cosmetic industries and plasticizer in plastic industry [4].

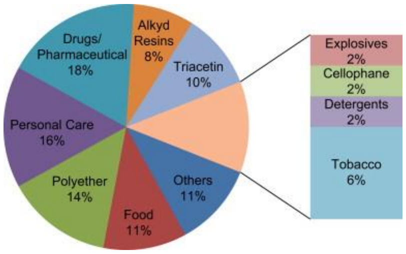

Fig. 2 Global glycerol consumption divided by applications [3].

Unfortunately, the market price of crude glycerol and purified glycerol are not high due to excess amount of glycerol in the global market, represented in Fig. 3. From this reason, utilizing crude glycerol to other high value chemicals is considered as an efficient solution.

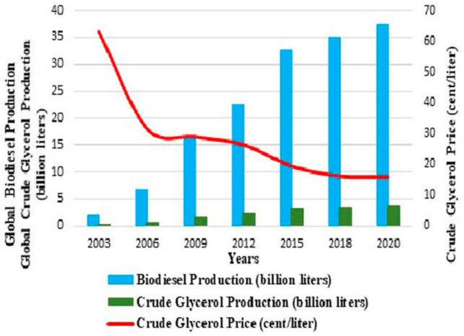

Fig. 3 The relation between global biodiesel, crude glycerol production and crude glycerol prices [4].

S. Panida, The Petroleum and Petrochemical College, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand (corresponding author e-mail: panida.sriratch@gmail.com)

E. Srisin, The Petroleum and Petrochemical College, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand

L. Apanee, The Petroleum and Petrochemical College, Chulalongkorn University, Pathumwan, Bangkok 10330, Thailand, Center of Excellence in Catalysis for Bioenergy and Renewable Chemicals, Chulalongkorn University, Bangkok 10330, Thailand (e-mail: apnee.l@gmail.com)

Triacetin can be accounted as a significant glycerol derivative because it occupied for 10% of global glycerol consumption (see Fig. 2). In addition, the market trend of triacetin is growing up 5 - 10% yearly [5]. The well-known applications of triacetin are plasticizer in cigarette filters [6], food additive (E1518) [7] humectant in cosmetics [8] and fuel additive [9]. For fuel additive application, adding 10% of triacetin to mixture of rape-seed methyl ester (biodiesel) can significantly improve cold flow properties of biodiesel (see Table 1). Interestingly, triacetin can be added into both of commercial diesel and biodiesel to reduce carbon monoxide and opacity emission [10]. Besides, triacetin can improve the anti-knocking of gasoline by adding 10% of triacetin into gasoline resulting in raising the motor octane number (MON) and research octane number (RON) of gasoline [11].

TABLE 1
COLD FLOW PROPERTIES OF MIXTURES OF RAPE-SEED METHYL ESTERS AND TRIACETIN

Mixture of rape-seed methyl ester and triacetin				
Parameter	RME	RME + 1% Tri	RME + 5% Tri	RME + 10% Tri
Density (gcm^{-3})	0.8592	0.8615	0.8689	0.8806
Freezing point (ºC)	-7	-16	-16	-17
Viscosity (Cst at -10 ºC)	n/a	n/a	n/a	n/a

Acetylation reaction is a practical way to convert glycerol to high-value chemicals. Theoretically, monoacetin, diacetin and triacetin can be generated from this reaction. As illustrated in Fig. 4, the reaction can be divided to two pathways, depending on reactants which are carboxylic acid and acetic anhydride. The article from [12] reported that the Gibbs free energy values of triacetin production using acetic acid and acetic anhydride are in positive (endergonic) and negative (exergonic), respectively. Thus, triacetin formation by using acetic anhydride as a co-reactant is preferable. Unfortunately, the operation acetylation of glycerol and acetic anhydride could be considered as a harmful operation due to the heat release from the reaction. Although, triacetin formation from acetic acid process is very small due to the highest Gibbs free energy in triacetin formation step, acetic acid process is more prevalent than acetic anhydride owing to its compatible price and safety.

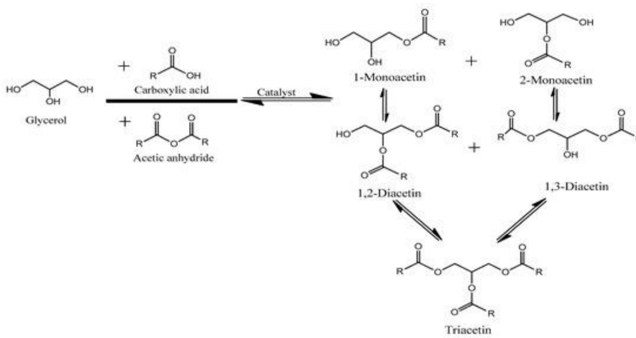

Fig. 4 Acetylation reaction of glycerol with carboxylic acid or acetic anhydride [13].

In this work, the reviewer collected the essential data which can improve the productivity of triacetin, i.e., influence of operating parameters and catalyst selection criteria. Table 2 represents the abbreviation and denotation of the following contents.

TABLE 2
ABBREVIATIONS AND THEIR DENOTATION

Abbreviation	Denotation
Gly	Glycerol
AA	Acetic acid
AD	Acetic anhydride
RME	Rape seed methyl esters
Mono	Monoacetin
Di	Diacetin
Tri	Triacetin
X_{Gly}	Glycerol conversion
S_{Mono}	Monoacetin selectivity
S_{Di}	Diacetin selectivity
S_{Tri}	Triacetin selectivity
n/a	Not measurable

II. INFLUENCE OPERATING PARAMETERS

A. Reactant and molar feed ratio

Carboxylic acid is recognized as a desirable reactant for this reaction because acetic anhydride is expensive and harmful for the acetin production. In order to investigate the significance of alkyl length of carboxylic acid to glycerol conversion, various carboxylic acids were arranged in the experiment [14, 15]. The results (see Table 3) reveals that the shorter chain of alkyl group can promote acetin productivity and in a case of MoO_3/SiO_2, there are no triacetin formation for long chain alcohol because longer chain of alkyl group can be a cause of steric hindrance. Moreover, the bulky molecule of alcohol can create electronic repulsion which directly affects to the un-bonded atom of acetic acid and glycerol.

TABLE 3
ACETYLATION OF GLYCEROL WITH DIFFERENT CARBOXYLIC ACID

Catalyst	Co-reactant	Catalytic activity				Ref
		X_{Gly} (%)	S_{Mono} (%)	S_{Di} (%)	S_{Tri} (%)	
Ag_1PW	Acetic acid	96.8	-	-	-	[14]
	Propanoic acid	70.9	-	-	-	
	1-Butanoic acid	64.3	-	-	-	
20 mol% MoO_3/SiO_2	Acetic acid	68	81.3	16.5	2.2	[15]
	Propanoic acid	41	100	0	0	
	Pentanoic acid	39	100	0	0	
	Hexanoic acid	35	100	0	0	
	Heptanoic acid	30	100	0	0	

In a case of acetic acid, to obtain triacetin, acetylation reaction requires at least three moles of acetic acid over one mole of glycerol, whereas triacetin was composed of three acetate group attached on the glycerol backbone, as shown in Fig 4. According to Le Chatelier's principle, an excess of acetic acid results in a greater amount of triacetin. From the results in Table 4, at specific catalyst, reaction temperature, catalyst weight and reaction time, it can be concluded that increasing of molar feed ratio can increase glycerol conversion, diacetin selectivity and triacetin selectivity. In contrast, monoacetin selectivity trends to decrease after adding more molar feed ratio. In the experiment of [16], they concluded that with using acidic cesium phosphotungstate (CsPWA) as a catalyst for acetylation reaction of glycerol and acetic acid, low amount of molar feed ratio (1:4) is not adequate to produce triacetin. This finding agrees with other experiments [11, 17-21] that at low ratio of glycerol over acetic acid (1:3 and 1:4) was obtained low glycerol conversion and trace triacetin selectivity. On the other hand, large amount of monoacetin were generated instead because monoacetin requires only one mole of acetic acid to form tetrahedral intermediate and turns to monoacetin. Thus, adding excess amount of acetic acid can improve the productivity of triacetin since the chemical equilibrium of the reaction move directly towards to the product side [13]. With the test of an experimental design (DoE) using three factors: molar feed ratio, reaction temperature and reaction time, the statistical analysis can be summarized that the most influence operating parameter to glycerol conversion and triacetin selectivity is molar feed ratio of glycerol over acetic acid owing to the smallest value of *p-value* of the factor and highest coefficient in predicted equation of glycerol conversion and triacetin selectivity [17]. However, the drawback of adding overmuch acetic acid into the reaction was reported by [22]. The excess of acetic acid can produce an effect of retrace of the reaction resulting in lower triacetin selectivity.

B. Reaction temperature

The limitation of reaction temperature depends on feedstock boiling point. Boiling point of glycerol and acetic acid are 290 ^{o}C [23] and 117.9 ^{o}C [24], respectively. To prevent acetic acid evaporation which is a reason to decrease reaction activity, the limited operating temperature is specified as less than acetic acid boiling point. Notwithstanding, the over limit temperature operation can be carried out with the assistance of purging gas, so in some experiment nitrogen gas and Teflon-lined stainless-steel autoclave were applied to the reaction [11, 18, 22]. As shown in Table 5, glycerol conversion, diacetin and triacetin selectivity tend to increase and monoacetin decrease when the temperature increased [11, 16-20, 22, 25-27] because this reaction is naturally endothermic reaction. Moreover, the results also corresponded to Arrhenius equation. For this equation, rate constant is a function of temperature, so increasing temperature will improve rate constant [28]. For kinetic energy, when the reaction temperature increases, the average kinetic energy of the reactant also increases and it directly affects to the frequency of collisions. In addition, [27] reported that at the reaction temperature above 100 ^{o}C, acetic acid can produce more acylium ion due to its dehydration. In acetylation reaction acylium ion is required to attack on the hydroxyl group of glycerol to produce acetin product as shown in Fig 5.

C. Catalyst loading

In acetylation reaction of glycerol with acetic acid, the acid catalyst acts as proton donor to carbonyl group of acetic acid to form acylium ion. A bigger amount of acid sites will be presented in a process when the catalyst loading is increased. According to the results from Table 6, it can be concluded that high loading of catalyst can promote catalytic activity [18-20, 22]. Glycerol conversion, diacetin and triacetin selectivity were elevated by adding amount of catalyst. However, at high amount of catalyst, the results indicate slightly change of catalytic activity.

D. Reaction time

Refer to Fig. 5, longer reaction time straightforwardly affects to the selectivity of monoacetin, diacetin and triacetin. To produce large amount of triacetin, longer reaction time is preferred than short reaction time because triacetin is a hindmost product. As illustrated in Table 7, the results shows that glycerol conversion and triacetin selectivity increase and monoacetin decrease when reaction time increase [16, 17, 19, 20, 22, 29]. Furthermore, the observation of diacetin selectivity from [22] described that decreasing in diacetin selectivity is a signal of triacetin formation. However, the optimization result from [17] demonstrated that at the same reaction condition of 1:9 (glycerol/acetic acid), reaction time of 115 ^{o}C and 5 wt% of catalyst to glycerol, the highest glycerol conversion and triacetin selectivity did not occur on the longest reaction time (9 hours), but took a place on reaction time of 8 hours. Thus, the overmuch reaction time is not necessary because acetylation reaction is a reversible reaction, so triacetin can be considered as a reactant for the reversible reaction of acetylation resulting in a decrease in triacetin selectivity [30].

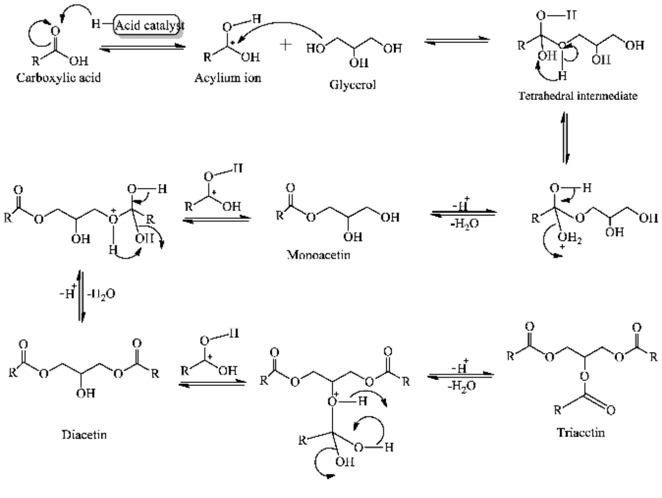

Fig. 5 Acetylation reaction mechanism [13].

III. CATALYST SELECTION

A. Phase of catalyst

Nowadays, catalyst was classified into two categories which are homogeneous catalyst and heterogeneous catalyst. Homogeneous catalyst means that the catalyst and reactants are in the same phase. In contrast, the heterogeneous catalyst has a different phase compared to the reactants. In acetylation of glycerol and acetic acid, many homogeneous were tested in acetylation reaction such as *p*-toluenesulfonic acid [31], phosphoric acid, hydrochloric acid, nitric acid and sulfuric acid [32]. These kind of catalysts exhibited excellent catalytic performances due to its great protonation ability, diffusivity, heat transfer, contact area and well-defined active site.

TABLE 4
EFFECT OF MOLAR FEED RATIO OF GLYCEROL OVER ACETIC ACID TO CATALYTIC ACTIVITY

Catalyst	Reactor	Reaction condition				Catalytic activity				Ref
		Molar feed ratio (Gly/AA)	Reaction temperature (ºC)	Catalyst weight	Reaction time (h)	X_{Gly} (%)	S_{Mono} (%)	S_{Di} (%)	S_{Tri} (%)	
PrSO$_3$H-SBA-15	Round bottom flask	1:3	100	5 wt.%	6	87	48	44	8	[17]
		1:6				98	27	55	18	
		1:9				100	20	57	23	
PrSO$_3$H-SBA-15	Teflon-lined stainless-steel autoclave	1:3	125	4 wt.%	4	57	58	33	9	[11]
		1:6				76	28	47	25	
		1:9				78	17	44	39	
CsPWA	Round bottom flask	1:4	85	7 wt.%	2	69	65	35	0	[16]
		1:6				92	59	35	6	
		1:8				98	25	59	16	
		1:10				98	26	58	16	
Amberlyst-15	Teflon-lined stainless-steel autoclave	1:4	100	5 wt.%	4	95	41	52	7	[18]
		1:6				96	27	59	14	
		1:8				98	21	60	19	
WO$_3$-polypyrrole	Round bottom flask	1:3	110	0.4 g	10	90	42	47	11	[19]
		1:4				92	34	45	21	
		1:5				95	15	35	50	
		1:6				100	6	26	68	
		1:7				100	10	27	63	
MoO$_x$/TiO$_2$–ZrO$_2$	Round bottom flask	1:3	120	5 wt.%	3 h	91	60	35	5	[20]
		1:4				93	56	37	6	
		1:5				95	55	39	7	
		1:6				100	52	40	8	
3% Y/SBA-3	Teflon-lined stainless-steel autoclave	1:4	110	4 wt.%	3 h	100	11	34	55	[22]
		1:6				100	10	35	55	
		1:8				97	19	25	56	

TABLE 5
EFFECT OF REACTION TEMPERATURE TO CATALYTIC ACTIVITY

Catalyst	Reactor	Reaction condition				Catalytic activity				Ref
		Molar feed ratio (Gly/AA)	Reaction temperature (ºC)	Catalyst weight	Reaction time (h)	X_{Gly} (%)	S_{Mono} (%)	S_{Di} (%)	S_{Tri} (%)	
PrSO$_3$H-SBA-15	Round bottom flask	1:6	85	5 wt.%	6	97	32	58	10	[17]
			100			98	27	55	18	
			115			98	24	58	18	
PrSO$_3$H-SBA-15	Teflon-lined stainless-steel autoclave	1:9	100	4 wt.%	4	78	20	52	28	[11]
			125			78	17	44	39	
			150			69	7	50	43	
CsPWA	Round bottom flask	1:8	65	7 wt.%	2	65	68	32	0	[16]
			75			88	30	64	6	
			85			98	25	59	16	
			95			98	25	59	16	
Amberlyst-15	Teflon-lined stainless-steel autoclave	1:6	60	5 wt.%	4	70	82	18	0	[18]
			80			87	59	39	2	
			100			96	27	59	14	
WO$_3$-polypyrrole	Round bottom flask	1:6	50	0.4 g	10	60	75	21	4	[19]
			70			69	40	40	20	
			90			83	20	55	25	
			110			99	4	65	31	
MoO$_x$/TiO$_2$–ZrO$_2$	Round bottom flask	1:6	40	5% wt.%	3	19	100	0	0	[20]
			80			51	89	11	0	
			120			100	52	40	8	
3% Y/SBA-3	Teflon-lined stainless-steel autoclave	1:4	90	4% wt.%	2.5	54	62	30	8	[22]
			100			78	35	42	23	
			110			100	11	43	46	

			120			100	9	45	46	
10% Sulphated silica	Round bottom flask	1:3	50	0.2 g	2	92	79	18	3	[26]
			110			100	28	60	12	

TABLE 6
EFFECT OF CATALYST LOADING TO CATALYTIC ACTIVITY

Catalyst	Reactor	Reaction condition				Catalytic activity				Ref
		Molar feed ratio (Gly/AA)	Reaction temperature (ºC)	Catalyst weight	Reaction time (h)	X_{Gly} (%)	S_{Mono} (%)	S_{Di} (%)	S_{Tri} (%)	
CsPWA	Round bottom flask	1:8	85	3 wt.%	2	56	69	31	0	[16]
				5 wt.%		70	61	34	5	
				7 wt.%		98	25	59	16	
				9 wt.%		98	26	58	16	
WO$_3$-polypyrrole	Round bottom flask	1:6	110	0.1g	10	90	42	47	11	[19]
				0.2g		92	34	45	21	
				0.3g		95	15	35	50	
				0.4g		100	6	26	68	
				0.5g		100	10	27	63	
MoO$_x$/TiO$_2$–ZrO$_2$	Round bottom flask	1:6	120	2.5 wt.%	3	56	55	38	7	[20]
				5 wt.%		60	52	40	8	
				7.5 wt.%		60	53	39	8	
3% Y/SBA-3	Teflon-lined stainless-steel autoclave	1:4	110	1 wt.%	3	20	62	34	4	[22]
				2 wt.%		42	55	35	10	
				3 wt.%		71	27	36	37	
				4 wt.%		100	12	33	55	
				5 wt.%		100	12	34	54	

TABLE 7
EFFECT OF REACTION TIME TO CATALYTIC ACTIVITY

Catalyst	Reactor	Reaction condition				Catalytic activity				Ref
		Molar feed ratio (Gly/AA)	Reaction temperature (ºC)	Catalyst weight	Reaction time (h)	X_{Gly} (%)	S_{Mono} (%)	S_{Di} (%)	S_{Tri} (%)	
PrSO$_3$H-SBA-15	Round bottom flask	1:6	100	5 wt.%	3	97	34	56	11	[17]
					6	98	27	55	18	
					9	98	26	54	20	
CsPWA	Round bottom flask	1:8	85	7 wt.%	0.5	85	36	54	10	[16]
					1	91	31	57	12	
					1.5	97	28	58	14	
					2	98	26	58	16	
WO$_3$-polypyrrole	Round bottom flask	1:6	110	0.4 g	2	59	76	23	1	[19]
					4	70	27	45	28	
					6	83	20	50	30	
					8	97	14	40	46	
					10	100	3	25	72	
MoO$_x$/TiO$_2$–ZrO$_2$	Round bottom flask	1:6	120	5 wt.%	1	53	84	16	0	[20]
					3	90	66	31	3	
					5	100	46	41	13	
3% Y/SBA-3	Teflon-lined stainless-steel autoclave	1:4	110	4 wt.%	1	100	64	25	11	[22]
					2	100	27	32	41	
					3	100	12	33	55	
AC500S	Round bottom flask	1:5	120	5 wt.%	1	92	58	42	0	[29]
					2	95	35	58	7	
					3	96	34	57	9	

On the other hand, the drawbacks of using homogeneous catalyst are toxicity, separation process and contamination. Eventually, heterogeneous acid catalyst are considered as a better option.

B. Surface properties

Pore size of catalyst and size of reactant chemicals which involved in acetylization reaction must be considered. The surface properties directly involve to the mass diffusion, reactant selective and product selective. If the pore size of the catalyst is smaller than the target product size, the production of the desired product will be forced to halt due to a lack of capacity. Table 9 demonstrated the dimension of reactant and product molecules. The comparison between appropriate and non-appropriate pore size was conducted by [29]. The results (see Table 8) illustrates that the non-appropriate pore size catalyst (H-Y) zeolite hardly convert glycerol into triacetin equated to appropriate pore size catalyst (AC500S) because the pore size of the zeolite (0.8 nm) is smaller than triacetin critical diameter (1.021 nm). Since we assumed that the active sites of the catalyst were located inside the catalyst, triacetin barely form inside due to the steric hindrance. In contrast, the interesting discussion from [18] reported that smaller pore size of catalyst could assist triacetin formation. In the experiment, Amberlyst 15 and Amberlyst 36, which have pore size diameter of 30 nm and 24 nm, respectively, were employed in acetylation reaction of glycerol and acetic acid. Amberlyst 36 provided better triacetin selectivity than Amberlyst 15 at a 50% glycerol conversion because the reactant could easily enter into the catalyst active site through its smaller pore size diameter, allowing the reaction to occur continuously.

TABLE 8
PHYSICO-CHRMICAL PROPERTIES OF THE HETEROGENEOUS CATALYST AND THEIR CATALYTIC ACTIVITY

Catalyst	Surface property		Acidity				Catalytic activity				Ref
	S (m^2/g)	D_p (nm)	Brønsted acid site (mmol/g)	Lewis acid site (mmol/g)	Total acid site (mmol/g)	Acid density (mmol/m^2)	X_{Gly} (%)	S_{Mono} (%)	S_{Di} (%)	S_{Tri} (%)	
H-Y zeolite[a]	884	0.8	0.59	0.24	0.83	9.33E-04	88	60	39	1	[29]
AC500S[a]	483	3.8	6.07	n/a	6.07	1.26E-02	96	34	57	9	
Amberlyst 15[b]	45	30.0	n/a	n/a	4.70*	1.04E-01	97	21	59	20	[18]
Al-MCM-41[b]	935	3.0	2	52.00*	0.21*	2.25E-04	53	80	19	1	
Al_2O_3[b]	230	4.2 [33]	0	69.00*	0.17*	7.39E-04	33	89	11	0	
SO_3H-SBA-15[c]	463	5.0	n/a	n/a	0.60	1.30E-03	100	21	57	22	[34]
SO_3H-SBA-16[c]	921	6.5	n/a	n/a	0.40	4.34E-04	52	36	46	18	
SiO_2[d]	606 [35]	n/a	n/a	n/a	0.03 [35]	5.23E-05	44	86	11	3	[15]
1 mol% MoO_3/SiO_2[d]	583 [35]	n/a	n/a	n/a	0.18 [35]	3.14E-04	100	56	28	17	
10 mol% MoO_3/SiO_2[d]	284 [35]	n/a	n/a	n/a	0.71 [35]	2.48E-03	100	36	31	33	
20 mol% MoO_3/SiO_2[d]	106 [35]	n/a	n/a	n/a	0.94 [35]	8.84E-03	100	17	33	50	
Amberlyst-15[e]	41	20.2	n/a	n/a	5.10	1.24E-01	100	31	57	12	[31]
Nb_2O_5.nH2O[e]	23	13.0	n/a	n/a	0.50	2.17E-02	82	70	29	1	
SZ-470[e]	74	10.0	n/a	n/a	n/a	n/a	91	55	40	5	
Dry-Sz[e]	120	6.0	n/a	n/a	1.00	8.33E-03	93	66	31	3	
SAS[e]	640	4.6	n/a	n/a	1.70	2.66E-03	100	0	51	49	
SSBA[e]	489	9.4	n/a	n/a	1.20	2.45E-03	100	5	62	33	

a: Reaction condition of molar feed ratio of 1:5 (Gly/AA), reaction temperature of 120 °C, catalyst amount of 5 wt% and reaction time of 3 hours
b: Reaction condition of molar feed ratio of 1:6 (Gly/AA), reaction temperature of 100 °C, catalyst amount of 5 wt% and reaction time of 4 hours
c: Reaction condition of molar feed ratio of 1:5 (Gly/AA), reaction temperature of 130 °C, catalyst amount of 2.5 wt% and reaction time of 1 hours
d: Reaction condition of molar feed ratio of 1:10 (Gly/AA), reaction temperature of 100 °C, catalyst amount of 10 wt% and reaction time of 8 hours
e: Reaction condition of molar feed ratio of 1:3 (Gly/AA), reaction temperature of 105 °C, catalyst amount of 5 wt% and reaction time of 3 hours
*Brønsted acid site and Lewis acid site was calculated in a unit of area/g

TABLE 9
DIMENTIONS OF GLYCEROL AND ACETIN MOLECULES [29]

Molecule	Critical diameter, d_c (nm)	Length, l (nm)	Volume, V (nm^3 x10^{-3})	Surface area, S (nm^2 x10^{-2})
Glycerol	0.646	0.385	90.80	111.12
2-Monoacetin	0.592	0.514	125.56	146.36
1-Monoacetin	0.859	0.309	133.30	153.23
1,2-Diacetin	0.780	0.385	190.56	203.90
1,3-Diacetin	0.943	0.312	165.87	189.98
Triacetin	1.021	0.385	208.36	228.39

C. Acidic properties

For acetylation of glycerol with acetic acid, Brønsted acid catalyst is foremost. As illustrated in Fig. 5, Brønsted catalyst is a crucial key to complete the reaction because protonation of carbonyl group of acetic acid is desired to from acylium ion. Then, oxygen atom from glycerol will attach to the acylium ion. After that, the intermediate appears, monoacetin will present with water (by-product). Monoacetin will be used as a reactant in further reaction to produce diacetin and triacetin, consecutively. From the catalytic performance results (see Table 8), it clearly confirms that Brønsted acid site is predominant. In detail, the experimental of various heterogeneous acid consisting of Amberlyst-15 and Al_2O_3 was conducted. Basically, Amberlyst-15 was known sulfonic acid resin resulting in high Brønsted acid site. For Al_2O_3, it was considered as Lewis acid catalyst. Under the same reaction condition, Amberlyst-15 exhibited superior glycerol conversion and triacetin selectivity as compared with Al_2O_3 [25]. The effect of Brønsted acid catalyst was investigated using propyl sulfonic acid grafting on SBA-15 (PrSO_3H-SBA-15) and SBA-16 (PrSO_3H-SBA-16). The characterization result explained that Brønsted acid site was generated on PrSO_3H-SBA-15, but for PrSO_3H-SBA-16 the Brønsted acid cannot formed owning to pore blocking. For this reason, $PrSO_3H$-SBA-15 displayed higher glycerol conversion and triacetin selectivity compared to $PrSO_3H$-SBA-16. Meanwhile, acid density (total acid site/surface area) also plays an important role. As shown in Table 8, high total acid density could favor triacetin formation. However, the researchers from [31] proposed that too high acid density can be a cause of steric hindrance due to the dense of acid site.

D. Reusability

The heterogeneous catalyst must has great reusability because it directly involves to the production cost, product impurity and environmental deterioration. Thermal degradation, leaching of functional group or metal and structure collapse are the main reasons of deactivation of heterogeneous catalyst. To reuse the catalyst, most of the catalyst can be regenerated with using different techniques such as thermal-regeneration or chemical-regeneration. The study of reusability of Amberlyst-36 was performed under reaction conditions of 1:6 (glycerol/acetic acid), reaction temperature of 100 ^oC and 2 hours operation time with four consecutive runs. The regeneration of catalyst was completed using warm water and hydrothermal treatment at 80 ^oC overnight. With the characterization result of sulfur contents of the catalyst, it reveals that the functional group of the catalyst was leaching out from the resin due to resin degradation resulting in decreasing glycerol conversion and triacetin selectivity [25]. Besides, the reusability of sulfonic acid functionalized on different material supports was proposed by [31]. Propyl sulfonic acid functionalized on SBA-15 (SSBA) and amorphous silica (SAS) were tested in six consecutive recycle runs. The XPS spectra of S 2p indicated that the sulfonic acid functional group from SAS was leaching out after six cycles passed resulting in a drastic decrease in glycerol conversion. On the contrary, SSBA still preserved the active functional group for acetylation reaction, so glycerol conversion of the catalyst was slightly decreased from 100% (first run) to 95% (sixth run) [31].

IV. CONCLUSION

To add the value of biodiesel by-product (glycerol), acetylation of glycerol with acetic acid was considered. With the concerning of triacetin production improvement, many parameters were emphasized. Molar feed ratio of glycerol over acetic acid was claimed as the most influence operating parameters compared to reaction temperature and reaction time. The abundant amount of acetic acid can impel glycerol conversion and triacetin formation. Similarly, increasing reaction temperature, catalyst loading and reaction time can promote triacetin production. With the environmental and processing issue, solid catalyst is more preferable in a process. The presence of Brønsted acid site on the heterogeneous acid catalyst promotes the process of triacetin formation. The sufficient physical properties of the heterogeneous catalyst, especially pore size diameter, and reusability are considerably required.

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