



Catalysis of glycerol acetylation on solid acid catalyst: a review

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<https://doi.org/10.14710/jksa.23.12.414-423>



Article Info

Article history:

Received: 28th August 2020

Revised: 13th January 2021

Accepted: 14th January 2021

Online: 31st January 2021

Keywords:

acetylation; solid acid catalysts; glycerol; esterification; biodiesel

Abstract

Biodiesel is a substitute fuel that is environmentally friendly, biodegradable, and sustainable. The need for biodiesel continues to increase. Biodiesel is made through the process of transesterification of triglycerides and alcohol. Glycerol is a side-effect of biodiesel products with a capacity of 10% of the total weight of its production. Glycerol is the simplest glyceride compound and has several functions as a primary ingredient in chemical production. Through acetylation, glycerol is converted to a material that has a higher sale value. Both homogeneous and heterogeneous catalysts are the acetylation approach to achieve the desired product, namely acetyl glycerol esters (mono-, di- and triacetin). However, in the process, the catalyst's type and characteristics significantly affect the yield and conversion of the product and the deactivation or reusability of the catalyst, which can inhibit the catalyst's utilization and effectiveness; therefore, it must be studied further. Besides, the parameters that affect the reaction will also be assessed.

1. Introduction

Recently fossil fuels, including crude oil and coal, dominate the world's consumption energy stock [1]. On the other hand, due to the limitations of fossil fuels, which are increasingly depleting, research on alternative energy sources is an increasingly intensified option for solving these issues [2]. Biodiesel has emerged as the most favorable environmentally friendly biofuel, which has similar properties to fossil diesel with some advantages. It is a renewable and biodegradable fuel, a higher cetane index, low oxides of carbon and sulfur emissions [3, 4]. Biodiesel can be mixed with conventional diesel fuel no more than 20% without modifying the engine. However, the engine required a few modifications for more than 20% biodiesel blending [5].

Biodiesel is a biofuel that consists of a blend of mono-alkyl esters from fatty acids [6]. Biodiesel is a derivative fuel from biomass, vegetable oils, or animal fats [7]. This raw material includes material containing fatty acids (triglycerides or fatty acid methyl esters (FAME) in the state of free acids or associated with other molecules). It is reported that worldwide biodiesel

production for 2015 is about 3.1-1010 L and is estimated to rise by 11-1010 L in 2020 [8]. In Indonesia, biodiesel's domestic distribution reaches 75.43% of the total production, whereas biodiesel production reached 6.17 million kiloliters in 2018. This figure is expected to continue to increase, bearing in mind that production until mid-2019 has already reached 4.19 million kiloliters.

Biodiesel is generally synthesized through triglyceride transesterification with alcohol, typically methanol or ethanol, in the presence of a catalyst [9]. This process usually involves at least three methanol molecules, an alkali- or acid-based catalyst, and one or two phases of the reaction system under ambient or high-temperature and pressure conditions. This transesterification converts natural triglycerides into methyl/ethyl ester fatty acids (FAMES/FAEEs) and glycerol as a byproduct with an estimated portion equivalent to 10% by weight of the total biodiesel produced [9]. The sharp increase in biodiesel production in Europe, the US, and other parts of the world led to abundant glycerol stock [10]. Nevertheless, this glycerol cannot be directly discharged into the environment due to its high organic matter content. The major impurities in

crude glycerol are methanol, potassium and sodium salts, heavy metals, fatty acids, and other organic impurities. Some impurities may have a significant effect on microbial metabolism and are considered to be poisonous or recalcitrant compounds.

Glycerol is the simplest trihydric alcohol consisting of three hydroxyl functional groups, making this compound hydrophilic and hygroscopic (physiochemical) [11]. The use of glycerol is presently restricted caused by contamination with toxic material, i.e., methanol; therefore, it is currently being investigated to look for safer chemical additives [12, 13].

Glycerol can be transformed into a high-value oxygen-based fuel additive by esterification [14, 15] or acetylation with the aid of catalysts [16]. However, some researchers also do it with the reaction of inhalation and hydrogenolysis [17]. The esterification process is chosen because it is more economical and easier to use a derivative product. Besides, the product of glycerol conversion is environmentally friendly and renewable because it is not derived from petroleum product derivatives [18]. Glycerol triheptanoate, glycerol-mono-stearate, lecithin, tri-tetra-butyl glycerol, mono-oleate-glyceride, tri-acetyl-glycerol, glycerol-tri-benzoate, and glycerol maleate esters are products that can be produced from processing glycerol through the esterification process [18]. The main products of acetylation of glycerol with acetic acid and/or acetic anhydride are mono-, di-, and tri-acetyl glycerides (MAG, DAG, and TAG) [9, 19]. These acetate esters (known as mono-, di-, and tri-acetin) have shown multipurpose industrial applications, including: cryogenic, cosmetic, and fuel additives [9]. The various products of processed glycerol depend on the catalyst used.

Commercial processes, including the acetylation (esterification) homogeneous catalysts, generate environmental problems caused by large quantities of hazardous effluent production. However, homogeneous catalysts can obtain higher triacetin conversion, yield, and selectivity [20]. Moreover, the homogeneous catalyst is less desirable because it is dangerous, corrosive, difficult to remove when separating catalysts, less environmentally friendly, and expensive [21]. The development of environmentally friendly processes by using heterogeneous catalysts is also considered. Heterogeneous catalysts can assist effortlessly in product separation with catalysts when leaving the reaction system.

This study presents the development in using a byproduct of biodiesel processed by catalytic acetylation to improve glycerol's value using acetic anhydride as an acylating agent to produce glycerol acetyl ester (mono-, di-, and tri-acetyl glycerol/acetin) [22]. In this case, the content or trend to be discussed is the application of the catalyst, type, and performance of catalysts, catalyst reuse and deactivation, and parameters that affect the acetylation reaction.

2. Acetylation of Glycerol

2.1. The Use of Glycerol Acetylation Products

Acetylation of glycerol with acetic acid is one way to obtain beneficial chemicals such as MAG, DAG, and TAG. MAG and DAG are utilized in cryogenic liquid and starting polyester materials [23, 24]. MAG is particularly used to manufacture explosives (dynamite), leather tanning, and solvents for dyes, while DAG can act as a softener agent, plasticizer, printing ink, and solvent [25]. TAG is widely applied in the food industry as a moisture protector, emulsifier, and binder, in medicine as an anti-fungal agent, in cosmetics to maintain moisture in creams/lotions, in the production of photographic films as well as various perfumes, and also act as fuel additives and a viscosity reducer for biodiesel [23]. These additives can reduce engine exhaust fumes due to reducing carbon molecules in the fuel mixture. The combination of biodiesel with 10% triacetin is known to improve engine performance in all aspects [26].

2.2. Reaction Mechanism

Figure 1 shows the acetylation of glycerol with acetic acid as an acetylating agent. It consists of three-step reactions catalyzed by acid successively, where every stage is controlled by chemical equilibrium due to water formation as a byproduct. Traditionally, glycerol acetylation proceeds with homogeneous acids such as sulfuric acid, hydrofluoric acid, and p-toluene sulfonate acid. Unfortunately, this acid catalyst has several major disadvantages because it is toxic, corrosive, and challenging to remove from the reaction mixture. Therefore, to overcome this difficulty, solid acid catalysts are expected to replace hazardous mineral acid catalysts. The glycerol acetylation reaction has mostly been studied in batch reactors with excess acetic acid using solid acid catalysts such as ion exchange resins, silica-based, zeolite-based, zirconia-based, metal oxide-based, heteropolyacids-based, and carbon-based [27, 28, 29, 30].

Based on the type of catalyst used, the reaction mechanism can be distinguished into two categories, i.e., acetylation catalyzed with Brønsted or Lewis acid [30]. In general, the reaction mechanism of acetylation glycerol using Brønsted acid involves three steps, as follows:

1. A proton attaches the oxygen-free electron pair of acetic acid to the catalyst. It is then continued by attaching the –OH group of glycerol as a nucleophile on by the oxygen atom as electrophiles leading to the loss of a proton from the –OH group to form water molecules Eg. (1) [31]. Different MAG isomers can be generated during this esterification step [29]. The presence of catalyst does not affect the conversion of MAG. However, the high selectivity and yield of di- and tri-acetyl ester highly are determined by the type of catalyst and reaction conditions.
2. The presence of a second nucleophile from glycerol attacks on the –OH group of MAG formed in Eq. (1) produces DAG. Therefore the amount of water formed as a product of the reaction will be more significant [8, 32].

3. Last step, the third pair of free electrons on the oxygen of the $-OH$ group on DAG is attacked by a third nucleophilic to produce TAG and water (Eq. 3). Overall, three moles of water molecules will be formed in succession at each esterification step to form a TAG [8].

In the Lewis acid-based acetylation [30], metal cation (M^+) of the catalyst assists the Lewis acidic site (L^+) in interacting with the carbonyl oxygen from acetic acid. The tetrahedral intermediates are generated by attacking the nucleophile of glycerol to generate carbon cations. Then the tetrahedral intermediate produces ester by releasing water molecules.

3. The Glycerol Acetylation Reaction Catalysts

In the glycerol acetylation reaction, classes of strong acids such as H_3PO_4 , HCl , HNO_3 , and H_2SO_4 are the best types of homogeneous catalysts and are the most often used. Several researchers have also tested sulfuric acid as a homogeneous catalyst, and it is said that this catalyst is the best among several types of liquid catalysts [26]. It is also supported by research [9], which tests homogeneous catalytic activity using four different types of conventional acids: phosphoric acid, chloride acid, nitric acid, and sulfuric acid. The last acid has the highest glycerol conversion value.

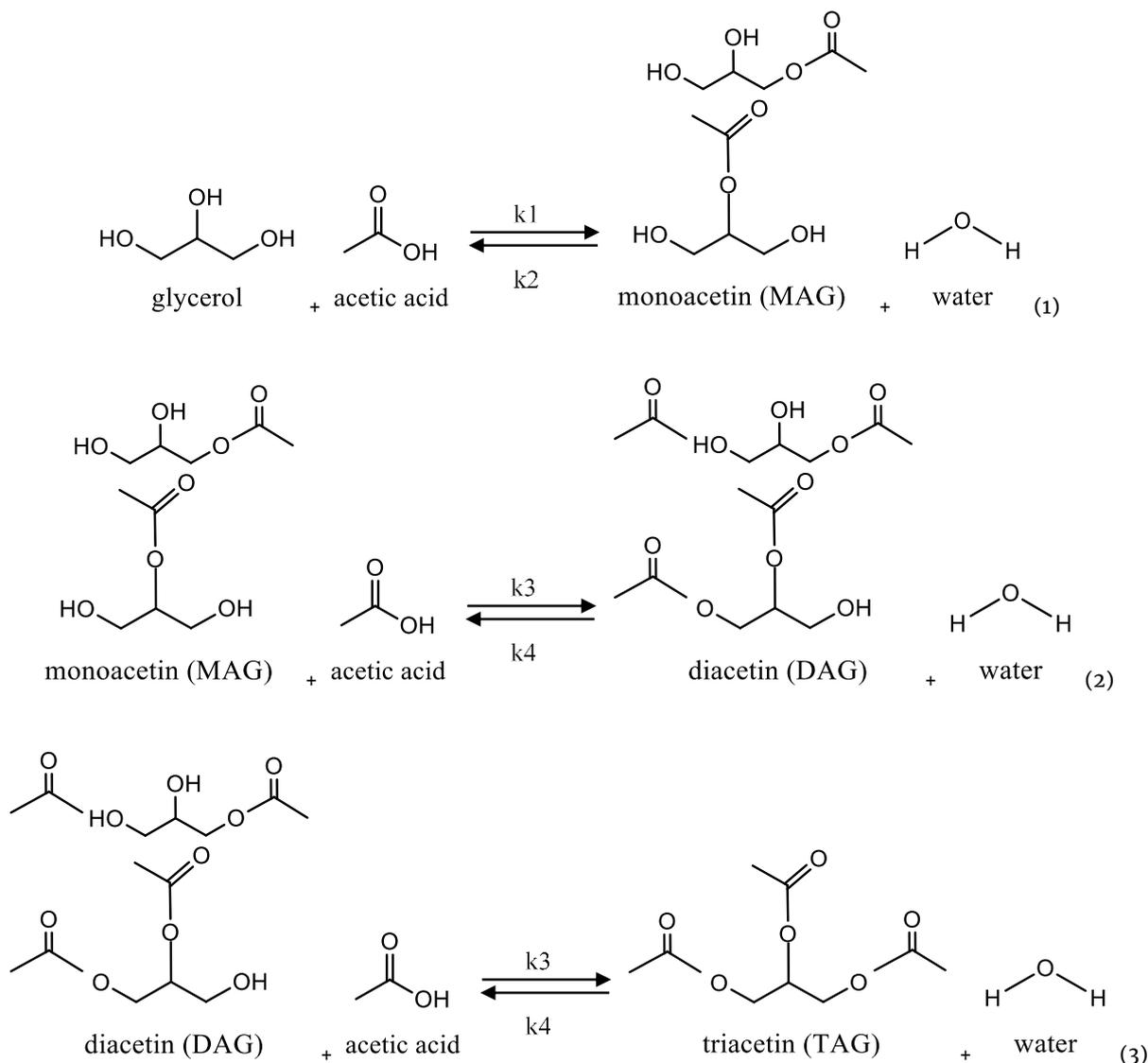


Figure 1. Mechanisms of Acid-Catalyzed Reaction of Glycerol and Acetic Acid [26]

Meanwhile, heterogeneous catalysts are catalysts in the solid phase, with the reactants being in the liquid or gas phase. Various types of solids are commonly used in heterogeneous catalyzes, such as metals, metal oxides, or metal sulfides, as shown in Table 1. These materials can be used in pure form or mixed form. Besides, the catalyst can be acidic and alkali. In general, glycerol acetylation uses a solid acid catalyst [21]. Some of the advantages of solid acid catalysts are the catalyst can be easily separated and reused several times without losing its activity; the

reaction is generally clean, and the product is obtained in high purity, and the reaction is selective [28].

Different types of heterogeneous solid acid catalysts can be classified based on their solid base as follows:

1. The silica-based solid acid catalyst

The oxide of silica materials has been paid attention to as catalyst support in heterogeneous catalysis. This material's main component is a glass substance, which is

naturally available [28]. Fortunately, mesoporous silica materials have a high specific surface area, well-ordered mesoporous structure, large pore sizes, and inexpensive resources [28, 33]. Generally, silica oxide is doped with other materials to increase its activity and selectivity, for instances: aluminum chloride [34], boron trifluoride [35], zinc salt [36], perchloric acid [37], sulfuric acid [38], sulfonic acid [39, 40, 41], and yttrium substance [42].

2. A zeolite-based solid acid catalyst

Zeolites are aluminosilicate minerals arranging in a three-dimensional network as molecular sieves, which generally owing formula as $xM_2/nO \cdot xAl_2O_3 \cdot SiO_2 \cdot zH_2O$ and can be obtained naturally and synthetically [28, 30]. It was reported that the ratio of Si-Al affects glycerol conversion, DAG, and TAG selectivity [43, 44]. Conversion of more than 90% was reached after 60 minutes for the H-Y catalyst and 90 minutes for H-beta and H-ZSM-5. Moreover, at the same reaction time conversion measured, DAG and TAG selectivity of H-Y and H-beta approached 90%, while H-ZSM-5 was only 30%. Gonçalves *et al.* [45] reported that H-ZSM-5 and HUSY showed lower conversion and TAG selectivity, 30 and 14%, respectively, after 30 minutes reaction. The lack of performance of zeolite H-ZSM-5 and HUSY may be caused by pore structure and surface acid site density [44].

Interestingly, a biosolid-based catalyst prepared by thermal hydrolysis was performed on glycerol acetylation [46]. This material contained silicon oxide, iron oxide, aluminum oxide, and some residue oxides forming a complex mixture. High conversion at around 90% was achieved after 4 hours of reaction at 120 °C using catalyst loading of 16 wt%.

3. The ion exchange-based solid catalysts

The use of macroporous polymers that can exchange ions within the polymer itself is the challenge in glycerol acetylation due to its low thermal stability [28, 30]. Some papers reported the application of Amberlist-15, 36 and 70, Dowex 50Wx4, Dowex 50Wx8, Dowex Monophere 650C, Purolite CT-275 on glycerol acetylation [17, 29, 31, 45, 47, 48, 49, 50], sulfonated resin of styrene cross-linked with trimethylolpropane triacrylate (TMPTA) [51], and sulfonated resin of styrene cross-linked with ethylene glycol dimethacrylate (EGDMA) [52]. Copolymeric Amberlyst resins essentially contain styrene and di-vinylbenzene made by Rohm and Haas, while Dowex resins are Amberlist functionalized with the sulfonic group [29]. Purolite CT-275 is a commercial macroporous strong acid ion exchange catalyst made of macroporous polystyrene and divinylbenzene [50]. High conversion of glycerol acetylation on those materials was achieved at more than 90% within 2 hours. However, DAG and TAG selectivity varied depending on catalyst loading, temperature reaction, and molar ratio glycerol-acetic acid [29, 48]. Fortunately, the presence of water in the reaction system does not change the catalyst activity.

The sulfonated resin of TMPTA and EDGMA was compared to Amberlyst 36 resin. The first resin was reported that the turnover number of sulfonated TMPTA

was higher (62.3 h⁻¹) than that of Amberlyst 36 (51.1 h⁻¹) [51]. While, The ion exchange capacity of EDGMA was less than that of Amberlyst 36, but they showed a comparable result in catalytic activity [52].

4. The zirconia-based solid acid catalyst

Sulfated zirconia (SZ) is a unique acid catalyst owning firm Bronsted and Lewis acidity caused by the effect of electron revocation from the sulfate group attached with the zirconia surface [53]. It is usually the promising catalyst among various solid acid for esterification due to high stability without leaching out [53, 54, 55, 56]. However, the presence of water affects the activity [53]. The mesoporous structure can be prepared by calcinating at temperatures more than 550 °C, although the surface area and sulfate loading of the SZ material is reduced as the temperature increase [57].

Popova *et al.* [24] studied zirconia modified with mordenite performed on glycerol acetylation, resulting in that glycerol conversion and DAG and TAG selectivity reached 93% and 81% for 3 hours reaction, respectively. Catalytic performance on zirconia supported heteropolyacids (HSiW/ZrO₂, HPW/ZrO₂, and HPMo/ZrO₂) and zirconia-zeolite also was carried out [22, 58]. The conversion on heteropolyacids-zirconia catalysts showed better than that on conversion than zirconium oxide and glycerol conversion. DAG and TAG selectivity on HSiW/ZrO₂ was higher than other prepared catalysts: ~100% and 93%, respectively.

5. The carbon-based solid acid catalyst

Carbon materials are relatively cheap and widely available. Such catalysts are typically prepared with biomass such as sucrose, fructose, starch, cellulose, or maize straw as a carbon precursor and condensed or fuming sulfuric acid as a sulfonation reagent. These carbon materials functionalized with -SO₃H are used as solid acid catalysts because they have good catalytic stability and activity at high temperatures [28]. Textural properties such as porosity and pore size play an important role in connecting the sulfonic compound [59]. Also, the proportion of micropores and mesopores influences the surface area; thus, more active catalytic groups are attached during the sulfonation process. Graphene-based materials as two-dimensional carbonaceous materials are also promising materials for catalysts because their physical, chemical and mechanical properties improve any catalytic action [60]. The carbon-based catalysts are feasible for industrial application due to cheaper and environmentally benign. Fadhil *et al.* [61] investigated that activated carbon acid catalyst prepared from FET waste converted 74.44% free fatty acid up to the 5th cycle.

To accurately cover the various types of carbon-based (AC) catalysts mentioned in the literature, these catalysts have divided into two categories: (i) functionalized catalysts covering all types of AC catalysts in which the active part is covalently attached to the AC support material; (ii) supported catalysts covering all type of AC catalysts, in which the porous carbon material

or AC was used as support for active catalysts [62]. Okoye *et al.* [63] prepared a glycerol-based carbon catalyst to performed glycerol acetylation. This acetylation reaction converted 99% glycerol and produce 88% DAG and TAG. It was also studied carbon-based material for acetylation, i.e., activated carbon M, carbon gel X activated carbon N, and graphite oxide [33, 64, 65, 66].

The various types of heterogeneous acid catalysts have been experimented with in triacetin synthesis (Table 1). Not all of the above catalyst types can be utilized

in the glycerol acetylation reaction. Most of them are based on silica, zirconia, zeolite, carbon. Aminosulfonate [67], niob acid, which supports tungstophosphoric acid (TPA), and dodecatungstophosphoric acid (PW) are supported on the activated carbon, Amberlyst-15, and so on [8]. The differences in terms of selectivity, activity, whether or not the catalysts are utilized in the reaction are influenced by factors such as temperature, pressure, amount of catalyst, molar ratio, acidity level, and reaction time.

Table 1. The application of heterogeneous catalysts to the glycerol esterification (acetylation)

Catalyst	Acidity level (mmol/g)	Reaction Parameters				Selectivity (%)			Conversion	Ref.
		Catalyst loading	Molar Ratio (AA: GL)	T (°C)	Reaction Time (hours)	MAG	DAG	TAG		
Silica-based:										
Silica (SO ₃ H/SBA-15)	n.a.	0.05 g	5:1	130	3	21.3	57.2	21.5	100	[41]
Silica Alumina	3.2	0.64 g	6:1	80	8	88.5	11.2	0.3	71	[8]
PrSO ₃ H-SBA-15	1.2	0.64 g	6:1	80	8	15.8	64.6	19.6	100	[8]
Zeolite-based:										
HZSM-5	1.2	1.6 g	9:1	110	4.5	-	47.7	44.5	97.1	[68]
H-USY	n.a.	5 wt %	8:1	100	2.5	8	34	58	90	[17]
H-USY	0.286	n.a.	9:1	110	4.5	73.8	20.6	5.6	78.4	[68]
Ion exchange-based:										
PTA-H ₂ N-PDVC	6.78	4 wt %	6:1	100	3	3.3	41.3	55.4	99	[69]
Amberlyst-15	4.9	0.64 g	6:1	80	8	21.1	63.8	15.1	100	[8]
Amberlyst-70	n.a.	5wt%	6:1	105	4	2.5	51.7	45.8	100	[48]
Zirconia-based:										
Zirconia	0.7	5 wt %	6:1	120	3	52.03	40.45	7.52	~100	[70]
TPA ₃ /ZrO ₂	0.84	0.15 g	6:1	100	6	60	36	4	80	[25]
TiO ₂ -ZrO ₂	n.a.	5 wt%	6:1	120	3	54.7	39.4	5.88	91.5	[70]
WO _x /TiO ₂ -ZrO ₂	n.a.	5 wt%	6:1	120	3	53.2	40.0	6.8	99	[70]
MoO _x /TiO ₂ -ZrO ₂	n.a.	5 wt%	6:1	120	3	52	40.5	7.5	~100	[70]
Carbon-based:										
Carbon (AC-SA5)	±10 μ mmol/g	0.8 g	8:1	120	3	38	28	34	91	[9]
SO ₃ H-glycerol-carbon	3.68	5 wt %	8:1	100	2.5	-	-	100	100	[17]
PW ₂ -AC	n.a.	0.2 g	16:1	120	3	25	63	11	86	[71]
TAC-673	1.35	5 wt %	9:1	100	4	n.a	n.a	17	99.6	[33]

3.1. Effect of reaction parameters: reaction temperature, catalyst loading, the molar ratio of reactants, and reaction time

The reaction of glycerol with acetic acid is a complex of acid-catalyzed consecutive reactions. MAG, DAG, and TAG and their respective isomers are gradually formed. Every step is controlled by reversible chemical equilibrium (see Figure 1). Researchers have examined the performance of reactions under several conditions to determine kinetic and thermodynamic models through acetylation. These models are created by utilizing test to depict forms, showing the impacts of reaction parameters on the rates of reaction, and clarifying the standards

constructing rates law and selectivity [68]. The reaction rate is obtained by observing the chemical kinetics of a reaction and depends on different factors such as reaction temperature, glycerol molar ratio to acetic acid, catalyst loading, and reaction time. The acquired data gives knowledge into the fitting parameters adjusted to accomplish the maximum results [8].

3.1.1. The effect of reaction temperature

Zhou *et al.* [31] informed the kinetic study of glycerol acetylation catalyzed on Amberlyst-15 by varying temperatures from 80 to 110°C. The result showed that an increase in the temperature reaction increased the

conversion of glycerol and acetyl selectivity (DAG and TAG) while the selectivity of MAG decreased gradually. A similar study examined using heteropolyacid supported on zirconia oxide exposed that increasing the temperature from 60 to 120°C significantly increases the glycerol conversion from 54.4% to 100% by adjusting the increase of DAG and TAG selectivity and the decrease of MAG [22]. The rising temperature assists in converting MAG to form DAG and TAG. Because glycerol acetylation is a consecutive reaction that is highly endothermic, then the extent of esterification increased by an increase in reaction temperature, which may explain the formation of the dominant MAG product at lower temperatures [22]. However, an increase in reaction temperature from 100 to 120°C reduces glycerol conversion when the reaction is carried out in the liquid phase because some acetic acid begins to vaporize [26]. This study shows that since the number of collisions between atoms increases with higher reaction temperatures, constants, and reaction rates, glycerol's conversion also increases with a corresponding increase in DAG and TAG selectivity and the sacrifice of MAG.

3.1.2. The effect of the catalyst load

It was informed that increasing the catalyst loading between 0.2–0.8 g linearly increases DAG and TAG selectivity at the constant molar ratio of reactants due to an increase in the number of available active sites. However, the saturation is achieved at 0.8 g without significant changes in the tested selectivity, with the increasing loading of different catalysts on the equal catalyst support [9]. Ghoreishi and Yarmo [72] observed two desorption peaks (centered at 280 and 550°C), which was associated with the presence of moderate and robust acidic sites. If the higher the number of sulfate ions, the higher the amount of NH₃ dissolved and, consequently, the catalyst's catalytic activity. Thus, it can be noted that increasing the loading of the catalyst increases the

acetylation of MAG and DAG to TAG [72]. This finding might result from an increase in the number of active acid sites available and accessible in the reaction mixture [8].

3.1.3. The effect of molar ratio

It has been studied that the molar ratio of acetic acid to selected glycerol has no significant effect on changes in TAG selectivity. It indicates that the range of the molar ratio of acetic acid to glycerol is 8:1 to 24:1, which is an excess that shifts the balance to the TAG product [17]. In the meantime, Mufrodi *et al.* [20] suggest that the higher the concentration of acetic acid on the glycerol molar ratio, the greater the selectivity to di- and triacetin, and vice versa. That is similar to what was explained: glycerol conversion increases linearly with a molar ratio of glycerol/acetic acid to 1: 8 [9]. Excessive carboxylic acid used in acetylation reactions may shorten the time needed to achieve equilibrium [12] and provide more acetylation agents that form DAGs and TAGs through further acetylation reactions. Therefore, it can be inferred that the increased molar ratio between acetic acid and glycerol tends to increase glycerol conversion.

3.1.4. The effect of reaction time

A good catalyst is a catalyst that can convert raw materials into products in a short time. In this case, glycerol's conversion and selectivity to di- and triacetin increase with the remaining time, whereas monoacetin selectivity decreases because di- and triacetin products are formed respectively by the esterification reaction [70]. The increasing reaction time increases glycerol conversion and acetyl ester selectivity [42]. Moreover, it was observed that there is no TAG formation in the first 30 minutes [42] but also reported a little TAG formation (<7%) within 30 minutes of reaction [22]. This difference is likely due to differences in experimental conditions and catalyst types during esterification.

Table 2. Reusability of glycerol acetylation catalysts

Catalyst	1 st cycle conversion and selectivity (%)				n	n th cycle conversion and selectivity (%)				Ref.
	X _G	S _{MAG}	S _{DAG}	S _{TAG}		X _G	S _{MAG}	S _{DAG}	S _{TAG}	
Dowex 650C	100	13	54	34	5	100	13	54	34	[49]
Heteropolyacid supported on hallosite nanotubes	38	n.a.	n.a.	98	3	17	n.a.	n.a.	100	[73]
HSiW/ZrO ₂	100	n.a.	n.a.	n.a.	4	100	n.a.	n.a.	n.a.	[22]
Amberlyst 70	100	0	9.4	85.4	3	100	1.7	39.9	54.7	[48]
N-methyl-2-pyrrolidinium hydrogen sulfate	100	12	58	30	3	100	22	60	18	[32]
Microporous zeolite H-Y	100	0	100	100	3	100	10	20	80	[44]
Activated C 500S	70	0	0	100	3	70	0	35	65	
3%Yttrium grafted mesoporous silicate (SBA-3)	100	9	36	55	4	80	18	32	50	[42]
Amberlyst 36	82	40	45	5	4	50	72	25	3	[47]

X_G = Glycerol conversion; S_{MAG} = Monoacetin selectivity; S_{DAG} = Diacetin selectivity; S_{TAG} = Triacetin selectivity

3.1.5. The catalyst reusability

Acetylation is usually performed with cycles under the same optimum conditions to test the catalyst's reusability. The catalysts are removed from the liquid

material and then washed and dried, followed by the next run using catalysts. Table 2 shows the performance of some catalysts reusability. The report states that SO₃H - glycerol-carbon can be reused ten times based on glycerol conversion and TAG selectivity [17], and activated carbon

(AC-SA5) four times reuse [9]. Meanwhile, various commercial catalysts, especially for Amberlyst-35, are deactivated after the second reuse cycle. The phenomenon of deactivation of the catalyst is related to thermal degradation, fouling, poisoning, washing accompanied by the transportation of the surface of catalyst particles, steam-solid and/or solid-solid reaction, and the presence of destruction/friction [74], leaching of sulfonate groups on the catalyst and partial blocking of the pores and surface of the catalyst by an adsorbed reactant, which limits the entry of the glycerol molecule into the active site [48, 75].

Usually, the reliability test is performed by the same repeat-use catalyst with or without treatment to assess the catalytic converter's deactivation time. Besides, a heat screening method is used to determine the catalyst's stability [76]. Similar heterogeneous solid catalysts can be used up to four cycles for carboxylation and acetylation, and the loss of its active core in this route is a sign of deactivation [77]. In order to achieve stable results without significantly reducing catalytic activity, techniques such as solvent washing (ethanol, methanol, water, and acetone), drying (from 4 hours to night and even days), and calcination were used [8].

4. Conclusions

After reviewing some studies on glycerol esterification/acetylation, it is concluded that Homogeneous and heterogeneous catalysts can be used to modify glycerol acetylation with acetic acid to obtain the desired product, i.e., acetyl ester. Also, the use of homogeneous catalysts is favored because they can be used under mild reaction conditions on glycerol acetylation to obtain a reasonably high product result. However, constraints such as the separation of the catalyst from the difficult reaction media, disposal, recycling, and corrosion problems in the reactor and pipeline will increase production costs.

Heterogeneous catalysts can also adjust the acetylation reaction rate to the desired results and in consecutive cycles. The reaction factors, such as the type of catalyst, physicochemical properties, temperature, catalyst loading, and molar ratio, clearly influence the acetylation reaction rate. The optimal parameters can then be used to convert glycerol acetylation with acetic acid to acquire the desired product, i.e., glycerol acetyl ester (mono-, di-, triacetin) with the maximum conversion. However, constraints such as the separation of the catalyst from the difficult reaction media, disposal, recycling, and corrosion problems in the reactor and pipeline will increase production costs.

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