Different scenarios of glycerin conversion to combustible products and their effects on compression ignition engine as fuel additive: a review

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ABSTRACT
In biodiesel production by trans-esterification, one of the essential compound is glycerin. Global glycerin production is increasing significantly, projecting a global value reduction for glycerol. Consequently the scientific community had been encouraged to investigate converting glycerol into more valuable products. In this research, the primary sources and processes of biodiesel production are surveyed. Where the processes that involve glycerin are reviewed and the diesel engine performance and emissions under variant states are discussed. According to the results of this study, it is reported that the choice of an optimal diesel/biodiesel significantly depends on the materials, additives and the engine condition. Glycerol etherification, carboxylation, and glycerol carbonate, however, had been identified as the widely manufactured and used additives. It is further observed that the use of these such additives has reduced several emissions, which is an important factor. In addition, it is suggested that using glycerin additives improves the properties of biodiesel. Acetone, on the other hand is introduced as one of the most important additives in the combination of diesel and biodiesel fuel due to the reduction of maximum emission. The presence of hydroxyl groups can reduce NOx. Finally, the diethyl ether additive can be mentioned which increases the thermal efficiency and increases the brake-specific fuel consumption (BSFC).

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1. Introduction
Today, the need for new energy sources is one of the major problems for all countries in the world. This is a problem not only for oil-importing countries but also for the major oil producers. The unavailability of fossil fuels, termination and environmental problems and price fluctuations of these resources are the most important contemporary human challenge. Greenhouse gas emissions from fossil fuels, including coal, gasoline, and oil, are alarming, while many governments are developing fossil energy use (Karmaker et al., 2019). Given the current environmental challenges and concerns, it makes more sense to find renewable energy sources (Akbarian & Najafi, 2019; Karimi et al., 2020; Karimmaslak et al., 2021; Najafi et al., 2021; Shoar et al., 2021). Renewable energy sources should be able to reduce the negative environmental impacts of fossil fuels. They are economically competitive with fossil fuels and do not reduce the process of food production (Hill et al., 2006; Shoar et al., 2019). EU’s policy on renewable energy use by 2030 is based on a soft governance approach (Akkari et al., 2020; Veum & Bauknecht, 2019). Due to the current market situation and increasing demand for green energy, the production of bioethanol and biodiesel will increase by 2030 (Bórawski et al., 2019). Predictions for the biofuel market for a ten-year period (2018–2027) show that global biodiesel production will be increasing from 36 billion liters in 2017–39 billion liters in 2027. Besides, global ethanol production will be increased from 120 billion liters in 2017 to 131 billion liters in 2027. Economic forecasts also show that prices for these biofuels will fall by 8 and 14 percent, respectively, over the next decade (Judge, 1988; Organisation for Economic Co-operation and Development (OECD), & Food and Agriculture Organization of the United Nations (FAO), 2018).

Biodiesel is mainly used to generate heat and power in diesel engines (Klein et al., 2018). The biodiesel building
is similar to that of diesel fuel (Xu et al., 2016). The cetane number and similar thermal value provide the capability to replacing diesel with biodiesel (Noor et al., 2018). Biodiesel can easily be blended with both diesel and alcohol blends (Yilmaz & Atmanli, 2017). Research showed that biodiesel cetane number was higher than that of diesel, but its thermal value was lower than that of diesel (Najafi et al., 2018). The biodiesel cetane number from oilseeds is lower than the biodiesel cetane number from animal oils (Ambata et al., 2018). Besides, the attendance of oxygen in the chemical structure of biodiesel results in cleaner combustion than that of diesel fuel. By biodiesel fuel combustion, emissions of PM, poly aromatic hydrocarbons and SO2 decrease. Biodiesel has a high flash point. Biodiesel does not have sulfur (Akbarian & Najafi, 2019; Hosseinzadeh-Bandbafha et al., 2018; Noor et al., 2018). Biodiesel can be mixed with diesel fuel in any proportion. It is currently common to use 5% biodiesel (B5) and diesel fuel mixes, and most countries are planning to use B20 fuel (Lewis et al., 2009). Researches showed that biodiesel–diesel fuel mixture up to 20% can be used in the conventional diesel engine. This 20% compounding rate was recommended in order to keep engine performance at a high level and also to reduce environmental pollution (Attia et al., 2018).

Biodiesel is mono-alkyl fatty acid esters (FAAE), produced from triglycerides found in vegetable oils or animal fats. Various methods have been developed for biodiesel production, which was reviewed in Ambata et al. (2018), Mittelbach (2009), and Tabatabaei et al. (2019). Currently, biodiesel production by alkaline trans-esterification is very common because it costs less and has a higher conversion efficiency. Figure 1 shows the trans-esterification reaction from triglycerides in the presence of oil (Go et al., 2016; Haghighat Shoar & Najafi, 2021). However, acid catalysts for the trans-esterification process are not widely used in the industry (Boon-Anuwat et al., 2015). According to the theory, 1 mol of triglyceride and 3 moles of alcohol (such as methanol or ethanol) react together with a catalyst (such as NaOH) to produce 3-mole of ester (biodiesel) and 1 mol of glycerol.

In research by Ghazanfari et al. (2017), biodiesel was obtained by the trans-esterification method from oil (palm) and ethanol in the presence of NaOH catalysts. According to this method, the oil was warmed to 70°C and mixed at 600 rpm. In other reactor, ethanol, with 1/3 of the primary weight of the oil (with molar ratio of alcohol to oil of 6:1), was warmed to 70°C in the presence of a 0.1 wt% NaOH catalyst. Then alcohol and catalyst were added to oil and the solution was stirred at 600 rpm for 30 min and 70°C. After 8 h, the solution temperature was reduced to ambient temperature (25°C). Then the acidity of the solution was measured and by adding 46% hydrochloric acid, it was regulated to about 7. The operation of rinsing by using water at 50°C was performed by gravitation for 12 h (Ghazanfari et al., 2017). Figure 2 shows the steps of biodiesel production by trans-esterification.

The conversion efficiency obtained in the trans-esterification reaction depends on the type and percentage of catalyst purity, alcohol to oil ratio, reaction temperature and time, water mass, and amount of free fatty acids (Pitt et al., 2019). In a study by Ahmad et al. (2019), optimization of effective factors in the biodiesel production process from flaxseed oil was performed by a trans-esterification method using response surface methodology. They studied factors such as ratio of methanol to oil volume, catalyst weight percentage (KOH), reaction temperature and time. According to the results, the highest amount of biodiesel production was about 99.5% at optimum conditions with reaction temperature of 59°C, catalyst content of 0.51% primary oil, 33 min reaction time and molar ratio of 5.9:1 from methanol to cotton oil (Ahmad et al., 2019). Successful commercialization and marketability of biodiesel require stringent quality assurance standards. Evaluation of the quality of biodiesel is

\[ \text{Triglyceride} + 3 \text{CH}_3\text{OH} \xrightarrow{\text{NaOH}} 3 \text{Mixture of fatty Esters} + \text{Glycerin} \]
achieved by determining its chemical composition and physical properties. Properties and limits specified in the biodiesel standard should protect the efficiency and durability of automobile engines or combustion equipment (Carrero & Pérez, 2012). Biodiesel can only be used when it meets the required standards. These standards (Table 1) include a density at 15°C (according to NPEN 14214 standard: 2009), which is adapted from (Knothe, 2006), the amount of iodine (according to EN14111 standard) and some others (Caetano et al., 2012).

Biodiesel is produced from renewable energy sources, including vegetable oils or animal fats. Production of biodiesel from food sources can imperil food security, therefore, global efforts to produce biodiesel from non-food sources have increased. And biomass, which contains raw materials, is considered as an energy source. Plant oils and animal adiposes are green energy sources. Table 2, which is adapted from (Atabani et al., 2013), shows oils available from raw materials as well as their percentages of oil.

Sources of biodiesel production can be divided into three generations (Figure 3). In the first generation, biodiesel was produced from oil sources such as sunflower, soybean, date, coconut, castor, rapeseed, and sesame. By increasing the production of biodiesel from edible oils, there have been concerns about the utilization of arable land for the agricultural generation to produce biodiesel, which could lead to a shortage of food sources. In the second generation of biodiesel production sources, the tendency to use non-food sources has increased. As such, it was not competitive with food production (Yang et al., 2014).

Biodiesel sources in the third generation (Mofijur et al., 2019) do not directly compete with food and also do not lead to land-use change and environmental damage. These sources can make cheap biodiesel fuel available. For example, through the third generation, *Isochrysis aff. galbana* microalgae can be considered as more viable source for biodiesel production, partly due to the relative ease in producing a high oil yield (Atmanli, 2020). Therefore, third generation resources are a good alternative for the first and second generations (Singh et al., 2011). In the biodiesel production process by trans-esterification,
First generation: Biodiesel was produced from edible oils such as soybean, sunflower, coconut, rapeseed and sesame [26].

Second generation: mainly from non-edible sources such as waste oil from restaurants, slaughterhouse waste and oilseeds with industrial and sanitary applications [29].

Third Generation: Biodiesel is produced from unconventional oil sources such as algae [28].

**Figure 3.** Classification of fuel generations.

Glycerin is produced as a by-product (Anger et al., 2011). By increasing the biodiesel utilization in the world, the glycerol production amount is increasing. Excess glycerol has created a new challenge. Although there are a wide range of potential applications for crude glycerol, glycerol produced in the trans-esterification process has a low purity, which limits its conversion to other materials (Monteiro et al., 2018). Studies showed that biodiesel production was drastically increasing (Nomanbhay et al., 2018), and consequently, glycerin production was also growing. It was expected that this trend would continue until 2030. Figure 4 is adapted and reproduced from (Nomanbhay et al., 2018). This figure shows the global glycerol production trend by 2030. This amount of glycerin is anticipated to be about 48500 million cubic meters.

Due to the increasing production of glycerin and its environmental problems, it needs to be managed and transformed into more valuable and environmentally friendly products. Therefore, in this research, the conversion of glycerin to other materials is investigated. The production of glycerin occurs in both edible and non-edible oils and its amount is approximately the same as 10% by volume of the transesterification process material produced. Glycerin is produced during the trans-esterification reaction, which is one of the most efficient and common methods for biodiesel production,
and therefore glycerin is produced during different steps of this process. Therefore, various edible and non-edible oils do not play a significant role in the production or non-production of glycerin. However, the use of edible waste oils (second-generation) and non-edible oils (third-generation), which have no competition with human food is recommended. These sources are much more economical and feasible. In this research, the study is conducted with emphasis on non-edible oils, although as mentioned above, glycerin production is due to various stages of the transesterification method and its amount for all various sources is about 10% by volume. Different ways of producing glycerol products are investigated at first. Then the materials from these methods and their applications are analyzed. Finally, the possibility of using glycerin-derived products as an additive for diesel fuel and their impacts on performance and emission of the engine are investigated on a diesel engine.

2. Glycerin

Glycerol, being a chemical product commercially known as glycerin, is colorless, odorless, and viscous at room temperature (Christoph et al., 2000). It is classified as three-component alcohols with formula C\textsubscript{3}H\textsubscript{8}O\textsubscript{3} according to IUPAC and is known as 1, 2, 3-propanetriol. Glycerol is completely soluble in water, alcohol and in many common solvents such as ether and dioxane, due to its three hydrophilic hydroxyl groups, but it is insoluble in hydrocarbons. This is true for glycerin with 95% purity. Table 3 shows some of the glycerol physical properties at 293 K (Pitt et al., 2019) that make it difficult to use for new products. Usually, glycerol obtained from the trans-esterification process has a purity of 90-92%, adapted from (Christoph et al., 2000).

| Property            | Amount              | Property           | Amount   |
|---------------------|---------------------|--------------------|----------|
| Molecular weight    | 92.09 g/mol         | Viscosity          | 1.412 cSt|
| Density             | 1.261 g/cm\textsuperscript{3} | Melting Point      | 17.8°C   |
| Boiling Point       | 20°C                | Fire Point         | 160°C    |
| Heat Value          | 4.32 kcal/g         | Surface Tension    | 64 MN/m  |

2.1. Glycerol reforming processes (GRP)

Glycerol is a fundamental chemical for biological refineries. Glycerol produced during the biodiesel production process is the primary feedstock for bio-factory (Yazdani & Gonzalez, 2007). Glycerol is a crude substance for the production of intermediates or chemical materials at various industrialization and application sectors (Monteiro et al., 2018). In general, glycerol can be used for the following usages:

(a) Production of chemical products;
(b) Manufacture of polymer compounds;
(c) Generation of biofuels;
(d) Refinement and direct utilization from glycerol.

Therefore, the extension of novel technologies for the utilization of glycerol is essential (Monteiro et al., 2018). Production of chemical materials, foods, polymers, fuel additives, hydrogen, and energy industries such as fuel cells, gasification industries, and anaerobic digestion are important destinations for glycerol conversion from biodiesel production.

Glycerol as an attractive substance (Karam et al., 2008) is used for the synthesis of many products such as surfactants (Pirog et al., 2013) and solvents (Favier et al., 2018). Besides, glycerol as a promising crude substance for microbial surfactants, can create modern antimicrobial materials for use in food, pharmaceutical, health, agricultural and practical applications (Pirog et al., 2013). Due to the high demand for renewable energy sources, glycerol has a tremendous potential to become a valuable material, which can be used as a fuel additive to petroleum derivatives, have a good perspective in the oil industry. Converting glycerol to oxygenated fuels by a variety of methods such as etherification and esterification have attracted attention (Rahmat et al., 2010). For example, glycerol triacetate (GT) compound was used as a fuel additive by glycerol esterification on the CI engine (Akbarian & Najafi, 2019). General methods for converting glycerol to other substances are shown in Figure 5. In the following, methods for converting glycerol to more valuable materials are discussed.

2.1.1. Glycerol aqueous phase modification process (GAPR)

The glycerol aqueous phase modification process (GAPR) is a potential pathway for the manufacture of fluid and H\textsubscript{2} fuels. GAPR is usually accomplished in continuous current with a moderate temperature (200–260°C) and high pressure (20–50 bar). The conversion to aqueous phase occurs without any pre-evaporation steps. The GAPR reaction is according to Eq. (1) (Roslan et al., 2019):

\[
\begin{align*}
C_3H_8O_3 + 3H_2O & \rightarrow 3CO_2 + 7H_2 \\
C_3H_8O_3 & \rightarrow 3CO + 4H_2 \\
CO + H_2O & \rightarrow CO_2 + H_2 
\end{align*}
\] (1)

Fluid alkanes can be directly manufactured from glycerol during a continuous process (Figure 6). The process implicates the catalytic transformation from glycerol into
H₂ and CO synthesis gas mixtures, which are combined by FT synthesis process (Fischer-Tropsch). Syngas (synthesis gas) can be manufactured from concentrated glycerol at 548 K, pressures of 1–17 bar and 10% weight of Pt-Re catalyst (1:1). The major intermediates when converting glycerol to syngas include acetone and ethanol (Simonetti et al., 2007). As an application of synthesis gas from H₂ and CO produced by the APR method, the production of saturated and unsaturated liquid fuels can be mentioned (Domínguez-Barroso et al., 2019). Using Pt-Ni/Al₂O₃ catalyst at 200°C, 80.3% of glycerol can be converted to H₂.

The best way to increase the economic values of biodiesel is to convert raw glycerol into valuable products such as H₂ and syngas. H₂ production from glycerol is accomplished by various processes such as aqueous phase modification, pyrolysis, steam modification, partial oxidation, and dry modification reactions. In large-scale industrial applications, Ni-based catalysts are used as the most common catalyst, because this type of catalyst
is easily accessible, cheap and has high catalytic activity (Roslan et al., 2019).

The GAPR process is an endothermic process. As such, this method requires high energy consumption; but the advantages of this process are its high speed and selectivity. Due to the harsh conditions and high cost of this method, there has been little research performed on this method, yet this method can convert glycerol into liquid fuels (alkanes).

2.1.2. Glycerol reduction process (GRP)

Glycerol reduction process (GRP) with hydrogen produces ethylene and propylene glycol (Figure 7). Glycerol is hydrogenated by metal catalysts and hydrogen and it is converted to products such as propylene glycol ethylene glycol and 1, 3 – propylene glycol. The major product of the glycerol reduction process is propylene glycol (propanediol).

Hydrogenolysis of glycerol to propane-diol is accomplished by using Ni, Pd, and Cu chromate catalysts. Propanediol conversion is reduced due to excessive hydrogenolysis of propylene glycol at 473 K and 13.79 bar. Besides, with decreasing water content, the efficiency of propanediol increases. Cu chromate catalyst (CuO.Cr2O3) at 473 K is used to generate propanediol from glycerol. The reaction is executed by forming an intermediate, which is acetal (hydroxy-acetone). Figure 8 is adapted and reproduced from (Dasari et al., 2005). Studies of different catalysts at 473 K and 13.79 bar pressure indicated that the highest conversion rate of glycerol to propylene glycol was obtained by chromite copper catalyst.

Besides, the highest glycerol conversion is achievable by using CuNi/Al2O3 and CuNi/ZSM-5 catalysts at 80 and 85%, respectively. With these catalysts, about 25% of the production is propylene glycol. By hydrogen addition, the glycerol conversion achieves above 90% in all catalysts. Single mono-metal catalysts, compared with bimetallic samples from copper, produces higher propylene glycol. CuAl2O3 showed the highest performance to convert to propylene glycol (with 70% efficiency) (Freitas et al., 2018). In this method, selectively the intermediate hydroxyl category converts glycerol to the tosylxy group, afterward separates the changed group by using catalyst hydrogenolysis. By this novel approach, the transformation of glycerol to 1, 3-propanediol was performed in 3 stages: (1) acetylation, (2) tosylxylation and (3) de-tosylxylation. Steps for the establishment of 1, 3-Proplene glycol are shown in Figure 9, which is adapted and reproduced from (Wang et al., 2003).

Nanoparticles synthesis (AuNPs), specifically with greenways, due to its bio-adaptability and various usages in different threads, has received a lot of attention. The establishment of permanent AuNPs with a controlled scale mostly needs the utilization of surfactants. These stabilizing factors may damage catalytic actuality and also have noxious effect on the bio-adaptability of AuNPs and surfactants. Therefore, in the study (Parveen et al., 2019), the effects of glycerol and water ratio, pH, temperature, ionic strength on stability and particle size distribution were investigated. Such AuNPs obtained in this way by the reduction method were environmentally friendly and have useful applications in catalytic and medical fields (Parveen et al., 2019).
Glycerol reduction is another effective way to produce different products from glycerol under mild conditions. In this method, glycerol is hydrogenated using metal catalysts. This method does not require high-temperature conditions in the glycerol aqueous phase modification process, so it is more economical. Synthesis parameters indicate that the ability to reduce and stabilize glycerol is associated with pH and percentage of glycerol in the reaction medium, respectively. The main products produced by this method include 1,2-propanediol (propylene glycol) and 1, 3-propane (diethyl and ethylene glycol). A major product of the glycerol reduction process is propylene glycol, which is not harmful to the environment.

2.1.3. Glycerol dehydration process (GDP)

From the Glycerol Dehydration reaction, two important acrolein chemicals and 3-hydroxy-propionaldehyde (3-HPA) can be prepared directly. In the primary stage, the glycerol dehydration process results in the establishment of enols that are in balance with hydroxy-acetone and 3-hydroxy-propionaldehyde. Then in the second step, it is formed by the dehydrogenation reaction of acrolein or by the reaction of retro-aldol in the presence of O2 and formaldehyde. Figure 10 is adapted and reproduced from (Katryniok et al., 2009). Acetaldehyde may be quickly converted to acetic acid.

Different studies on the method of dehydrating glycerol to acrolein were performed (Table 4) (Dasari et al., 2005; Domínguez-Barroso et al., 2019; Freitas et al., 2018; Katryniok et al., 2009; Parveen et al., 2019; Simonetti et al., 2007; Wang et al., 2003). Acrolein is a chemical material and is used as an industrial and pesticide chemical. So dealing with it requires safety tips (Auerbach et al., 2008). The conversion process of glycerol dehydration to acrolein is accompanied by adverse reactions and leading to the establishment of byproducts. This causes the formation of coke on the catalyst and changes its color from white to black. Besides, the catalyst increases weight and becomes inactive, and its efficiency and selectivity for acrolein production are reduced. 90% of glycerol conversion, with 80% selectivity of acrolein, is achievable in supercritical conditions at 34.5 MPa, 673 K and in the vicinity of H2SO4 catalyst. In order to improve the efficiency of this process, the authors propose to increase the concentration of glycerol and H2SO4 and work at higher pressures (Watanabe et al., 2007). After the acrolein product, the product of 3-hydroxy propion aldehyde (3-HPA) is another glycerine-derived substance during the dehydrogenation procedure. 3-HPA is an important industrial intermediate that can be converted into a number of large-scale conventional chemicals. Figure 11 is adapted and reproduced from (Zheng et al., 2008). These include acrolein, acrylic acid, 3-hydroxy propionic acid (3-HPA), malonic acid, acrylamide and 1, 3-propanediol.

3HPA is important for several chemicals and polymer materials and is also momentous for various chemical materials and polymer. Poly 3HP is a polyester that is tolerable to degradability. Figure 12 is adapted and reproduced from (Zaushitsyna et al., 2017). Different studies on dehydrating glycerol to 3-hydroxy propionaldehyde were performed (Auerbach et al., 2008; Sardari et al., 2013; Sardari et al., 2014; Zaushitsyna et al., 2017).
Numerous attempts have been made to develop glycerol conversion processes into precious chemical materials, which suggests that this is a major source for some future glycerol applications. These include the generation of 1,2-propylene glycol, 1,3-propylene glycol, and acrolein. According to these results, alkaline pretreatment is a suitable solution to increase acrolein production. The use of catalysts also improves the production of acrolein and in the meantime, the SiW20-Al / Zr10 catalyst performs well. Another important product from the glycerol dehydration method is 3-hydroxy propionaldehyde, which is an important industrial intermediate, and it turns into some of the most common chemicals on a large scale. However, given the usual use of glycerol, the actual market seems to be unable to consume all produced glycerol. Therefore, in the future, a purification step is needed to achieve the degree of purity on an industrial scale.

2.1.4. Oxidative dehydration of glycerol to acrylic acid (ODG)

Acrylic acid is one of common products made of glycerin. The dehydration reaction is coupled with aerobic oxidation to transform acrolein to acrylic acid directly. In this process, the oxidative exothermic reaction is accompanied by the dehydrating endothermic reaction. Figure 13 is adapted and reproduced from (Li & Zhang, 2016). An investigation by dos Santos et al. (2019) performed the

| Target | Materials | Method | Results | products | Ref. |
|--------|-----------|--------|---------|----------|-----|
| 1 Production of 3- hydroxy propionic acid from glycerol by a novel recombinant Escherichia coli BL21 strain | Using Escherichia coli SH254 to produce 3-HP | Glycerol dehydration at first was performed by using the dhaB of Klebsiella pneumonia DSM 2026. And then with aldH of E. Coli K-12 MG1655, aldehyde di-hydrogenase was performed. | Using the E. coli SH254 compound, 3-HP maximum yields were 6.5 mmol L-1 (10.58 gL-1). It is expected that the highest selective conversion and amount of 3-HP production from glycerol will be 6.6 mmol g-1 cdw h-1 and 0.48 mmol-1, respectively. It is expected that the production of 3-HP can be improved by further control of SH254. | Improve 3-HP production | Raj et al. (2008) |
| 2 Biotransformation of glycerol to 3-hydroxypropionaldehyde: Improved production by in situ complexation with bisulfite in a fed-batch mode and separation on an anion exchanger | Combining 3HPA with bisulfite | The potential of combining 3HPA with bisulfite and then attaching it to the anionic resin to recover the production of 3-HPA solution with remarkable performance was investigated. | The use of resin-bonded functional groups allows for much easier separation of 3-HPA from Bioproducts by glycerol processing. | Production of 3-HPA | Sardari et al. (2013) |
| 3 Semicarbazide-functionalized resin as a new scavenger for in situ recovery of 3-hydroxypropionaldehyde during biotransformation of glycerol by Lactobacillus reuteri | Application of Semicarbazide-Functionalised Resin | The application of Semicarbazide resin for 3-HPA adsorption was investigated. And were evaluated as an alternative to the reported methods for topical removal of 3-HPA by its production from glycerol biotransformation with Lactobacillus reuteri. | Semicarbazide applied resin is a non-toxic material for 3-HPA. And has a high connection capacity for 3-HPA. Improves the production of 3HPA by using resin. By decreasing the capacity and adsorption time, 3-HPA from the resin is obtained better. | Production of 3-HPA improves. | Sardari et al. (2014) |
| 4 Crosslinked, cryostructured Lactobacillus reuteri monoliths for production of 3-hydroxypropionaldehyde, 3-hydroxypropionic acid and 1,3-propanediol from glycerol | Lactobacillus reuteri | Lactobacillus reuteri cells, as potential biocatalysts for the conversion of glycerol, into potential bio-based chemicals such as 3-hydroxy propionaldehyde, 3-hydroxy propionic acid and 1, 3-propanediol, was investigated | Under optimum conditions, 19.7 g/L 3HPA was produced from the carbohydrazide compound at a rate of 9.1 g/Lh with a 77% molar yield. | 3-hydroxy propionaldehyde, 3-hydroxy propionic acid, and 1,3-propanediol | Zaushitsyna et al. (2017) |
|   | Target Materials Method Results Products Ref. |
|---|-------------------------------------------------|
| 1 | Coke-tolerant SiW20–Al/Zr10 catalyst for glycerol dehydration to acrolein SiW20–Al/Zr10 catalyst Catalytic activities have been investigated under various conditions such as temperature 270–330°C, glycerol inlet concentration 0.5–20 wt%, and catalytic loading 0.1–0.9 wt%. The results of the activity show that the SiW20-Al/Zr10 catalyst has long-term stability and is a suitable choice for acrolein production. This enhances catalyst activity and stability. RSM optimization showed that the selective amount of 87.7% acrolein from 97.0% glycerol conversion could be obtained at 300°C, 0.5 and 10 wt% of SiW20-Al/Zr10 catalyst. Selective production of 87.7% acrolein from 97.0% conversion of glycerol Talebian-Kiakalaieh and Saidina Amin (2017) |
| 2 | Microwave-assisted catalytic dehydration of glycerol for sustainable production of acrolein over a microwave absorbing catalyst WO3 / ZrO2 @ SiC catalyst Glycerol dehydrogenation was investigated for the production of stable acrolein in a Microwave with WO3 / ZrO2 @ SiC catalyst. Microwave heating was provided higher temperature distribution in the catalyst bed than conventional (electric) heating, as a result, the yield of acrolein at a lower temperature is higher and has better catalytic stability. Therefore, it is a new method for the sustainable production of acrolein. Sustainable production of acrolein Xie et al. (2018) |
| 3 | High-Performance Phosphate Supported on HZSM-5 Catalyst for Dehydration of Glycerol to Acrolein HZSM-5 catalyst The high yield of phosphate on the HZSM-5 catalyst was investigated for the Dehydration of glycerol to acrolein. The HZSM-5 zeolites were modified under alkaline pretreatment with various metal hydrophosphates. Catalytic activity and stability are enhanced by strong acid and proper distribution. According to research results, Sn1/4H2PO4/ HZSM-5 performs well in catalytic activity. High acrolein production was 83% at baseline and 68% acrolein yield after 30 h. Zhang et al. (2018) |
| 4 | Effect of the treatment with H3PO4 on the catalytic activity of Nb2O5 supported on Zr doped mesoporous silica catalyst. Case study: Glycerol dehydration The catalyst with wt % 8 Nb2O5 A catalyst with wt % 8 Nb2O5 was applied to semi-porous silica zirconium with different amounts of phosphoric acid (Nb / P = 0.1–1). To alter their tissue properties and to modify their acidic properties. Therefore, the catalyst with Nb / P = 0.2 had the most favorable acidic distribution and was able to achieve a less damaged structure, which resulted in the conversion of glycerol and acrolein production to 74%, after 2 h, at 350°C. Glycerol conversion and acrolein production 74% Garcia-Sancho et al. (2017) |
| 5 | Mechanistic study of glycerol dehydration on Brønsted acidic amorphous aluminosilicate Brensted acidic amorphous aluminosilicate (ASA) Glycerol dehydration was performed on Brensted acidic amorphous aluminosilicate. DFT calculations were performed to investigate the mechanism of dehydration of glycerol. With ASA, acrolein and then acetol is produced with the lowest activation energy. Amorphous alumina silicate showed a prominent optimum value for acrolein (46.5%) and this is the optimal amount for acetone (10.8%). This selectivity depends on whether the OH group is at first eliminated by the Brønsted proton. Acrolein (46.5%) and acetone (10.8%) Yun et al. (2016) |
Table 5. Continued.

| Target Materials Method | Results | Products | Ref. |
|-------------------------|---------|----------|------|
| Dehydration of glycerol to acrolein using H-ZSM5 zeolite modified by alkali treatment with NaOH | Increased acrolein production | Decolati et al. (2014) |
| Glycerol dehydration over micro- and mesoporous ZSM-5 synthesized from a one-step method | 70% acrolein | Neves et al. (2018) |

Figure 11. Use of enzymes in the production of 3-HPA and application of this intermediate in the preparation of other chemicals.

Oxidative dehydration of glycerol for the generation of stable acrylic acid using H, Fe-MCM-22 catalysts, in which H, Fe-MCM-22 catalysts were reported to be highly active in the dehydration oxidation of glycerol and its conversion to acrylic acid. Fe is a marvelous metal, mostly due to its Fe$^{3+}$ or Fe$^{2+}$ regeneration cycle, which has made it affordable and low costly response, also it is low toxic than V, W or Mo (dos Santos et al., 2019).

Balancing tissue properties and regeneration of H, Fe-MCM-22 catalysts leads to a better dehydration function of glycerol. This is especially true for low Fe amount catalysts. The performance of H-Fe-MCM-22 catalysts is related to other catalysts caused by regenerated molecules or blended oxides. Even in more difficult moods, it also acts as an enhancer of the molar ratio of oxygen to glycerol. Low iron catalysts increase the selectivity of acrylic acid. Vanadium-based catalysts also have good potential and are used for glycerol conversion and acrylic acid production without significant reduction. Vanadium is a non-toxic and widely available metal and it has the

Figure 12. Metabolic pathway for biological transfer of glycerol to 3HP and 1, 3-PDO with 3HPA as intermediates with Lactobacillus reuteri cells along with various enzymes, mediators and effectors factors.

Figure 13. Oxidative dehydration of glycerol to acrylic acid (ODG).
potential to achieve sustainable manufacture from acrylic acid. But results showed that He-MCM-22 was a promising catalyst for sustainable manufacture from acrylic acid instead of V\textsubscript{23} catalysts (dos Santos et al., 2019).

In general, the ODG to acrylic acid is a thermally equilibrated process because it has both exothermic and endothermic phases. Acrylic acid is a widely used substance derived from glycerin and the toxicity of this substance is low. In the production of this material, H, Fe-MCM-22 has been reported as the best catalyst because of its high activity. Compared to other glycerol conversion methods, less research has been performed on this method.

### 2.1.5. Glycerol etherification (GE)

Glycerol ethers are manufactured from esterification of glycerol via iso-butene in the presence of homogeneous acidic catalysts (Vlad et al., 2011). Figure 14 is adapted and reproduced from (Zheng et al., 2008). By reacting glycerol with isobutene in etherification, the production of mono-ether, di-ether and tri-ether can be attained. Different syntheses have been undertaken to convert di-ethers and tri-ethers from glycerin to higher ethers. ‘Superior ethers’ may be consumed as an octane booster for car fuel (Behr & Obendorf, 2002).

Oxygenated compounds can be considered as fuel additives with the function of octane resonator. For example, methyl tri-butyl ether has explosive properties and is added to the fuel as octane enhancers. Glycerol tri-butyl ethers (GTBEs), as additives for diesel fuel and biodiesel, increase the fuel octane number and they are soluble in nonpolar fuels. Alcohols and ethers offer different and specific benefits in providing clean fuel. Methyl tri-butyl ether (MTBE) has been the preferable product, but a positive future outlook is predictable for less volatile ethyl tri-butyl ether (ETBE) and methyl tri-ethyl ether (TAME) (Ancillotti & Fattore, 1998; Noureddini, 2001).

Different researches on etherification of glycerol are reviewed (Table 6) (Ancillotti & Fattore, 1998; Behr & Obendorf, 2002; Bookong et al., 2015; Bozkurt, Baglar, et al., 2019; Bozkurt, Yılmaz, et al. 2019; Cannilla et al., 2015; Decolatti et al., 2014; dos Santos et al., 2019; Estevez et al., 2016; Ishak et al., 2016; Kim et al., 2007; Klepacova et al., 2007; Li & Zhang, 2016; Neves et al., 2018; Noureddini, 2001; Okoye et al., 2017; Vlad et al., 2011; Yun et al., 2016). Glycerol acetylts and glycerol ethers are known as fuel additives (Bozkurt, Yılmaz, et al. 2019; Ishak et al., 2016; Kim et al., 2007). One promising way to transform glycerol into high-value chemicals is to yield acetone by acetylation of glycerol. The major outcomes of glycerol acetylation are mon-acetin, di-acetin, and tri-acetin. These actions have great commercial importance. They are mostly consumed as a fuel additive in transport (Okoye et al., 2017; Zheng et al., 2008). The production of glycerol ethers can be one of the promising approaches because its synthesis helps as a desirable solution in technical, economic, and strategic fields. Some wonderful alternative production from glycerol are mono, di, and tri-acetyl-glycerols, which are mostly consumed in food, cosmetic, pharmaceutical and plastic industries (Rahmat et al., 2010).

As a result, it is highly desirable to add low-cost glycerol to valuable chemicals or substances. Glycerol etherification with acetic acid is used to produce glycerol acetate as a bio-additive from biodiesel, which provides a promising approach to glycerol use. This pathway leads to the establishment of glyceryl-mono-acetate (MAG), glyceryl-di-acetate (DAG) and glyceryl-tri-acetate (TAG), which are widely used in degradable polyesters as well as cosmetics (Rahmat et al., 2010).

Many of the recent methods that use glycerol as a raw material are in the expanding phase yet, and some have been commercialized. Accordingly, the straight transformation of glycerol to important chemical materials have engrossed many considerations. Glycerol ethers are produced by using different catalysts during the etherification process; Based on the comparison of results in the above table, when BEA di-silicate zeolite catalysts react with glycerol, they produce high amounts of di and tri-butyl-glycerol. Therefore, these ethers may be utilized as oxygen fuels to improve diesel fuel.

#### 2.1.6. Polymerization to poly-glycerol

Poly-glycerol is a branched structure, it is liquid and has high viscosity. It is completely solvable in liquid and polar solvents, for example, ethanol. Besides, it is non-volatile at normal temperatures. Glycidol is a derivative of glycerol and is used in the controlled synthesis of poly-glycerol. For example, one type of rapidly emerging polymers is PGs. PEG is a promising alternative for medical applications (Ampatzidis et al., 2014; Gheybi et al., 2018). Poly-glycerols (sometimes called ‘poly-glycidols’) represent classes of extremely bio-matchable and multi-hydroxyl polymers that can be propounded as polyethylene glycol (PEG). Figure 15 is adapted and reproduced.

**Figure 14.** Provision of glycerol ethers from the reaction between glycerol and isobutene with different molar ratios.
A novel type of exothermic polymers based on modified monomers poly-glycidol (1, 2, 3-exoxypropanol) has been proposed. During heating, the water reactivity and solubility of the polymer (glycidol-ethyl glycidyl carbamate) are obtained by modifying the hydrophilicity of the hydroxyl groups from the poly-glycidol chain with ethyl isocyanate.

Linear poly-glycidols with high molar masses are provided using activated monomeric anionic resins. Table 6.

**Table 6. Different studies on the etherification of glycerol.**

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 1 Etherification of glycerol and ethylene glycol by isobutylene. | Resin Type (Amberlyst 15, 35) As a catalyst | The etherification of glycerol and ethylene glycol with isobutylene was studied by using acid catalysts and exchanges of Amberlyst 15, 35 resins and two H-Y and H-Beta zeolites. The reaction temperature range was 50–90°C. | The highest glycerol conversion rate was achieved in H-Beta, the highest amount of di- and tri-ethers was made from Amberlyst 35 catalysts. In the case of H-Y, the reaction was slower due to its low acidity and the final concentration of di- and tri-ethers was not obtained at the appropriate reaction time. | Glycerol Conversion 88.7% After Eight Hours Using Amberlyst 35 Resin and H-Y Zeolite | Klepacova et al. (2007) |
| 2 Optimization of Microwave-assisted. Etherification of Glycerol to Poly-glycerols by Sodium Carbonate as a Catalyst. | Sodium carbonate catalyst | Etherification of glycerol into poly-glycerol using sodium carbonate catalyst at reaction temperature (220°C and 270°C), catalyst concentration (1 and 3 wt%) and reaction time (0.5, 1.0, 1.5, 2.0, and 3.0 h) | The reaction temperature has the most influence on the etherification of glycerol to poly-glycerol. The reaction temperature at 270°C, the catalyst concentration at 3 wt.% and the reaction time of 1.0 h, which empirically gave the highest glycerol conversion rate, the highest desired product yield and the acceptable selectivity for glycerol at 93%, 70%, and 7%, respectively. | Production of poly-glycerol. With the highest glycerol conversion rate, it was achieved at 93%. | Bookong et al. (2015) |
| 3 Assessment of acid strength in sodium-exchanged resin catalysts: Consequences on glycerol etherification with isobutene in batch and flow reactors | Resin catalysts with sodium exchanges, Glycerol with isobutene, Batch and current reactors. | An IR-based method was proposed to evaluate the strength of Brønsted acid in resin catalysts. | The glycerol selectivity in etherification is strongly correlated with acid strength. Accordingly, the selected product in higher ethers, by limiting isobutene, improves by increasing acid strength. These measurements showed that mono-tert-butyl glycerol ether and di-isobutene are the major products with the Amberlyst 15 catalyst, while di- and tri tert-butyl-glycerol ethers are a primary product in sodium exchange catalysts. | Formation of mono-tert-butyl glycerol ether and di- and tri - tert-butyl glycerol ether | Bozkurt, Baglar, et al. (2019) |

(continued)
Table 6. Continued.

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 4      | Batch reactor coupled with water permselective membrane: Study of glycerol etherification reaction with butanol. | Glycerol etherification reaction with butanol. | The batch reactor coupled with the selective water-displacement membrane was investigated on the glycerol etherification reaction with butanol. The use of a new batch reactor with the help of an absorbable membrane is to improve the conversion of glycerol to etherification with butanol. | Using the A-15 catalyst, the glycerol conversion in the reactor was studied from 70°C to 160°C. At reaction temperatures above 140°C, Selective removal through the membrane and it also facilitates the dehydration and etherification of glycerol. But it creates products that are difficult to separate from the reaction bed. | The formation of ethers and of course some side products that are difficult to separate from the reaction bed. | Cannilla et al. (2015) |
| 5      | Etherification of glycerol with tert-butyl alcohol over sulfonated hybrid silicas. | The etherification of glycerol with tert-butyl alcohol in the liquid phase was obtained from different amounts based on synthetic silicate. | These materials investigated various tissues and acidity properties from 0.3–2.3 mmolg⁻¹. First of all, various experimental variables, including reactant ratio and temperature were tested and all catalysts were tested in optimal conditions | The catalytic performance was very active in the S50TSS0 catalyst at 75°C and the autogenous pressure by resin A-15. The presence of silanol groups on the silicate hybrid prevents the inhibition effect of water. And as a result, with increasing of time, Conversion with catalysts was Increases. | The glycerol conversion obtained in S50TSS0 is greater than that obtained in A-15 (74% and 51%, respectively). | Estevez et al. (2016) |
| 6      | Catalytic etherification of glycerol by tert-butyl alcohol to produce oxygenated additives for diesel fuel | The etherification of glycerol with tert butyl alcohol was investigated by using acid catalysts supported with silica. | The experiment was carried out in batch mode from 303 to 363 K. The catalyst / glycerol ratio was investigated to guarantee high glycerol conversion. | Increasing the reaction temperature is in favor of the formation of alternative ethers. The water formed during the reaction inhibits the etherification of glycerol, and its removal from the reaction bed is essential for the formation of di- and tri- ether. In this regard, designing a reaction medium for the separation of existing water can increase the formation of more ethers. | MTBG (3-Tret-butoxy-1,2-propandiol) | Frusteri et al. (2009) |

(continued)
etherification to short-chain poly-glycerols. The oxidation of Ca–Mg–Al triple compound by various loading rates of Ca was successfully provided by saturating raw materials from calcium citrate solution on Mg–Al formed from LDH oxide. The calcination was performed at 700°C. Results by using the poly-glycerol polymerization method were as follows. Ca–Mg–Al MMO with high-dispersion of Ca²⁺ ions introduced a new semiporous structure. Glycerol conversion and DG correlation performance were well correlated with the amount of MMO catalysts. In 7.5% Ca–Mg–Al MMO, the greatest conversion rate of glycerol (40.4%) and DG selectivity (78.3%) were reported at relatively bottom temperature (220°C) (Sangkhum et al., 2019).

In another study by Zhang et al. (2010), high-energy PEI polymers led poly-glycerol to the delivery of genes. To improve the efficiency of gene transfection and prevent cancer cells, branched polymers, namely PG6-PEI25k and PG6-PEI800, are designed as novel gene pathways.

Currently, a number of poly-glycerols are commercially available in a variety of applications, including cosmetics and pharmaceuticals. Biocompatibility is a prominent feature of these materials in determining their use.
Table 6. Continued.

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 10     | Experimental study of glycerol etherification with C5 olefins to produce biodiesel additives. | The etherification of glycerol with iso-amylenes was studied by using resin ion exchange catalysts. | Two completely different experimental methods for converting glycerol to biodiesel additives were investigated. These included the use of glycerol (G), tert-amy alcohol (TAA) as well as glycerol or iso-amylenes (IA) in variable molar ratios. | G/IA / TAA compounds preferably allow the production of mono-tet-amy-glycerol and di-tet-amy-glycerol as biodiesel additives with a glycerol conversion of approximately 70%. While mixing glycerol with TAA results in a maximum conversion of glycerol to 51%. The simultaneous presence of isoamylenes and tert-amy alcohol reactants as solvents in the primary compound has a great effect on glycerol conversion. | Production of mono-tet-amy-glycerol and di-amy-glycerol ethers. | Izquierdo et al. (2017) |
| 11     | Glycerol Etherification with Benzyl Alcohol over Sulfated Zirconia Catalysts | Etherification with benzyl alcohol, Zirconia sulfate catalysts. | Two catalysts (S1 / ZrO2 and S2 / ZrO2) were prepared. The catalysts were tested at different temperatures (120-140°C) and the initial mass ratio of the reactants (GLY: BA 1: 1 and 1: 2). | By using BA, the highest conversion was obtained from the highest sulfuric acid (2S/ZrO2) catalyst. Increasing the reaction temperature and the initial mass ratio of GLY: BA, results in an increase in the amount of BA for conversion. Higher acidity of the catalyst, Gains higher activity at any temperature. | The main reaction products were di-benzyl glycerol ether and mono benzyl glycerol ether. | Jaworski et al. (2015) |
| 12     | Glycerol ethers synthesis from glycerol etherification with tert-butyl alcohol in reactive distillation. | Glycerol etherification was investigated with Tert-butyl alcohol and Amberlyst 15 catalysts. | Using simulation calculations based on the regression model, the results of the experiments were investigated. | The Amberlyst 15 catalyst is proven to be an excellent catalyst in the continuous process. The effect of reaction temperature and catalyst content on glycerol conversion and ethers content was significant. However, in the statistical analysis, the ethanol/glycerol molar ratio was not identified as a significant parameter. | The significant conversion was achieved from glycerol and ethers. | Kiatkittipong et al. (2011) |

(continued)

2.1.7. **Glycerol esterification**

Glycerol esterification has been one of the practical methods of converting glycerol into valuable substances. The esterification reaction is carried out by carboxylic acids, carboxylation and adding nitrate to glycerol. By glycerol esterification via acetic acid and catalysts, glycerol is converted to glycerol-monoacetate, glyceryl - diacetate, and glyceryl-tri- acetate. Glycerol conversion can be caused even under the absence of the catalyst in this reaction. Therefore, glycerol esterification is a self-catalyzed reaction, in which the acidic protons present in acetic acid can catalyze this reaction itself (Gao et al., 2015).
Table 6. Continued.

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 13     | Study of glycerol etherification with ethanol in a fixed bed reactor under high pressure. | The etherification of glycerol with ethanol was investigated in a fixed bed reactor with Amberlyst 15 catalyst. | The effect of reaction temperature (180-250°C), ethanol/glycerol molar ratio (4-20.1) and catalyst content (0.80 g) on glycerol conversion and ethers performance was investigated by CCD. | Desirable levels of parameters in ethers performance were included: temperature (238°C), the molar ratio of ethanol/glycerol (16.1) and catalyst content (0.61 g). In these optimum conditions, the yield of ethers was 56%. | Glycerin conversion (97%) and selectivity 56% for ether. | Lemos et al. (2018) |
| 14     | Process design and optimization for etherification of glycerol with isobutene. | The optimization process for the etherification of glycerol with isobutene was investigated. | A process for the production of glycerol ethers with isobutene has been implemented and also the process has been investigated economically. | ME ethers are extracted by glycerol, the remaining glycerol is washed with water and the water, DIB and isobutene are separated by distillation. Optimal design reduces the cost of producing glycerol ethers at 1.201 $ / kg, which also contributes to reducing the cost of isobutene. | Production of ME ethers from glycerol | Liu et al. (2016) |
| 15     | Exploring the impact of zeolite porous voids in liquid phase reactions: The case of glycerol etherification by tert-butyl alcohol. | Etherification of Glycerol by Tert-Butyl Alcohol | The Role of Acidity (Concentration, Strength) and Tissue Characteristics in the Etherification of Glycerol with Tri-Butyl Alcohol for a Range of Acid Catalysts in a Wide Range, such as Amberlyst15, Silica, Alumina, Silica Alumina, and Four Types of Zeolites were evaluated. | Limited BAS (in zeolites) is more active than unlimited BAS (in semi-porous or large porous materials). The etherification of glycerol with tri-butyl alcohol is not sufficient to remove the prediction limit for activity, selectivity, and stability. | – | Miranda et al. (2018) |
| 16     | Enhanced production of high octane oxygenates from glycerol etherification using the desilicated BEA zeolite. | Glycerol etherification using BEA disilicate zeolite. | The improvement of the production of high-octane oxygenated mixtures of the DTBG + TTBG biofuel blend has been investigated with glycerol modified by the BEA catalyst. | With the zeolite (BEA), the pore volume can be more than doubled, so that by etherification, the conversion of glycerol was 98%. And while the selectivity was 99% for di- and tert-butyl glycerol (DTBG + TTBG). | Production of (DTBG + TTBG) | Saxena et al. (2015) |

2.1.8. Carboxylation reaction for glycerol carbonate preparation

In general, glycerol carbonate is synthesized by the reaction between glycerol and fusogen. However, due to the great noxiously of fusogen, trans-esterification-based alternatives to di-alkyl or alkylene carbonates have been investigated. Industrial synthesis of glycerol carbonate requires several stages. Ethylene oxide reacts with carbon dioxide, which results in the production of annular ethylene carbonate. Glycerol is also reacted to produce glycerol carbonate and ethylene glycol. This function includes the utilization of homogeneous basic catalysts, for example, sodium bicarbonate or sodium hydroxide (Figure 18). It has problems such as neutralization and also causes problems in the recovery of the product with low-pressure distillation method (Alvarez et al., 2012).

Trans-esterification of glycerol by annular carbonates or alkyl carbonates is thermodynamically favorable for the production of glycerol carbonate from glycerol. Increasing the temperature may enhance the chemical
Table 6. Continued.

| Target | Materials                  | Method | Results | Products | Ref.                  |
|--------|----------------------------|--------|---------|----------|-----------------------|
| 17     | Cesium exchanged tungstophosphoric acid supported on tin oxide: An efficient solid acid catalyst for etherification of glycerol with tert-butanol to synthesize biofuel additives. | The etherification of glycerol with tert-butanol was investigated using cesium exchange of tungsten phosphoric acid on tin oxide as an acidic catalyst. The activity of the catalysts for the etherification of glycerol with tert-butanol was investigated. The exchange of cesium tungsten phosphoric acid (CsTPA) on tin oxide catalysts was investigated and their physical and chemical properties were obtained by X-ray diffraction, FT-IR, laser spectroscopy. | The etherification activity is related to the acidity of the catalyst. Catalysts containing Cs have stronger catalytic than Cs-free catalysts. The etherification activity depends largely on SnO2-based CsTPA. The catalyst with 20 wt% SnO2 based on CsTPA, showed high catalytic activity with 90% glycerol conversion and 44% higher ethers selectivity. | Glycerol conversion 90% with 44% selectivity. | Srinivas et al. (2015) |

18 Acid zeolites for glycerol etherification with ethyl alcohol: Catalytic activity and catalyst properties. Acid zeolites for etherification of glycerol with ethyl alcohol In order to increase the glycerol value, the catalytic performance of USY, HZSM-5 and H-Beta zeolites in the conversion of glycerol to tert-butyl alcohols was investigated. | For glycerol etherification, the best results were obtained for USY-650-L-2 and H-Beta zeolites, Convert glycerol to ethers 70% | Veiga et al. (2017) |

Figure 15. Conventional monomers for the synthesis of linear poly-glycerol (LPG).

Figure 16. Synthesis of linear poly-glycidol with high molar mass.

Figure 17. Polymerization of Ethoxy Ethyl Glycidyl ether.
Figure 18. Preparation of glycerol carbonate from reaction between glycerol and di-alkyl carbonate.

Moreover, glycerol carbonate can be produced by the following methods (Figures 19–21) (Li & Wang, 2011). The production of glycerol carbonate by using aluminum waste as a low-cost catalyst resulted in the highest conversion of glycerol at 500°C (Das & Mohanty, 2019). Glycerol carbonate is polar, colorless, non-toxic and has high boiling temperature. Another method for the production of carbonate derivatives of glycerol results from the reaction between urea and glycerol. In this process, glycerol carbonate is separated from glycerol by 90% yield (with 100% purity) and the reaction provides more conversion and more energy savings, 29.1%, and 37.1% respectively (Lertlukkanasuk et al., 2013).

Alvarez et al. (2012) investigated the synthesis of glycerol carbonate by trans-esterification of glycerol in a continuous system using hydrotalcites as a catalyst. Glycerol esterification method, as an efficient method to obtain the hydrotalcite used in α-Al₂O₃ or γ-Al₂O₃, was employed. They are active in converting glycerol to glycerol carbonate and glycerol di-carbonate.

In addition, it was demonstrated that activated catalysts led to greater production of glycerol dicarbonate manufactured in glycerol carbonate. An enhancement in Mg amount in the catalyst resulted in better glycerol conversion and better glycerol dicarbonate yield, although the HTr4-Alpha catalyst was less stable than the HTr2-Alpha catalyst. This was maybe due to the presence of excess MgO (H) in the catalyst. Therefore, it was deduced that hydrotalcite combinations were promising for the continuous trans-esterification reaction (Alvarez et al., 2012).

Zheng et al. (2015) investigated the trans-esterification of glycerol with calcined Ca–Al hydrocalumite dimethyl carbonate. Ca–Al hydrocalumite (Ca/Al = 2–6) was synthesized by high crystallization using a conventional Coprecipitation technique in N₂ space. According to results, calcined Ca–Al hydrocalumite was an efficient catalyst for glycerol trans-esterification with dimethyl glycerol carbonate and had high selectivity of glycerol carbonate compared with usual conditions. The highest conversion rates of glycerol and GC selectivity were 93% and 97%, respectively.

Different studies on the carboxylation reaction for glycerol carbonate were performed (Alvarez et al., 2012; Alvarez et al., 2012; Das & Mohanty, 2019; dos Santos et al., 2019; Elhaj et al., 2019; Gao et al., 2015; Goncalves et al., 2015; Gonzalez-Arellano et al., 2015; Lertlukkanasuk et al., 2013; Li & Wang, 2011; Sangkhum et al., 2019; Wang et al., 2017; Zhang et al., 2010; Zheng et al., 2015) (Table 7). The carboxylation reaction results in the production of glycerol carbonate, which is used as a solvent for plastics and resins, for example, cellulose acetate, nitro-cellulose, and poly-acrylonitrile. Besides, this compound has the adhering property to metal surfaces and resistant to oxidation, hydrolysis, and pressure, and has a lubricating effect. According to the results of the above table, various studies have been carried out to produce glycerol carbonate. Among them, Wang et al. (2017) reported the highest amount of glycerol carbonate production. The Na₂SiO₃ solid base catalyst at 200°C was a noteworthy example for industrial applications in GC synthesis that illustrated glycerol conversion of 97.7%. This comparison is expressed based on the highest amount of glycerol carbonate production efficiency.

2.1.9. Reaction of adding nitrate to glycerol
Glycerol can be treated by using nitrating material to form di-nitro-glycerol solution. This solution is converted to glycidyl nitrate by an annular agent from di-nitro-glycerol, which is also polymerized to poly (glycidyl...
Poly (glycidyl nitrate) is known as a high-energy polymer appropriate for utilization in propellants, explosive materials, gas generators and pyrotechnics (Zheng et al., 2008). Besides, the glycerol nitrate reaction can produce glycerol carbonate. In this method, glycerol reacts with urea to produce glycerol carbonate (Figure 22).

In Ashok et al. (2013), under anaerobic conditions, 3-HP production of glycerol by KpC (Klebsiella pneumonia ΔglpKΔdhaT) resulted in an increase of NADH cell levels and decrease of glycerol consumption. Adding nitrate enables KpC to successfully regenerate NAD\(^+\), but the active presence of the enzymes was effective in reducing the carbon flow pathway to produce 3-HP and 1,3-PDO. A heavy compound of KpCΔglpKΔdhaT, which contained both GlpK and DhaT, ran a large amount of glycerol toward the generation of 3-HP in the presence of nitrate under anaerobic conditions.

Glycerol can be polymerized into poly-glycidyl nitrate using nitrating factors. This polymer has the potential to be used in fire-cracking materials and propulsions.

Table 7. Studies on carboxylation reaction for glycerol carbonate preparation.

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 1 | Functionalized quaternary ammonium salt ionic liquids (FQAILs) as an economic and efficient catalyst for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate | A compound (FQAILs) was prepared from various functional groups such as hydroxyl, carboxyl, ether and amino groups, then used as a catalyst for glycerol carbonate synthesis. | Under mild conditions, the reaction was investigated at temperature, time and molar ratio of DMC/GL and catalyst rate (based on GL) for GL and GLC conversion. | There is a strong interaction between the hydroxyl molecule and the dimethyl carbonate molecule and between the OH\(^-\) anion and the glycerol molecule. Under mild conditions, reaction temperature of 80°C, 90 min time, in molar ratio DMC/GL = 3 and 0.9 mol% catalyst (based on GL). Using the {[HPTPA]} OH catalyst, the conversion rate of GL was 96.2%. While the production rates of GLC was 87.2%. | The production rates of GLC was 87.2%. | Elhaj et al. (2019) |
| 2 | Synthesis of glycerol carbonate from biodiesel by-product glycerol over calcined dolomite. | Trans-esterification of glycerol was performed with dimethyl carbonate and with the CaO-MgO catalyst. | At 800°C, mixed CaO-MgO oxide was used as the catalyst for the conversion of glycerol to GC. | The calcination process has stability and strength and improves GC production. Changing the temperature and tissue of the surface results in the trans-esterification of glycerol and GC production. CaO-MgO catalyst increases glycerol conversion to 97% and GC production to 94%. This result is obtained at 75°C and DMC/glycerol ratio of 3 and a catalyst dose of 6 wt%. | GC production reaches 94%. | Algoufi et al. (2016) |
| 3 | Synthesis of oxygenated fuel additives via the solventless etherification of glycerol | Synthesis of oxygen-containing fuel additives by glycerol etherification method. | The etherification of glycerol to DG was successfully investigated by using different alkaline pretreatments (LiOH, NaOH, KOH, and Na2CO3). | LiOH catalyst showed unique activity in glycerol trans-esterification reaction, the best reaction conditions were in temperature of 240°C, catalyst/glycerol mass ratio of 0.02 and reaction time of 6 h. | Production of 33% DG | Ayoub et al. (2012) |

(continued)
Table 7. Continued.

| Target                                                                 | Materials                                                                 | Method                                                                                                                                     | Results                                                                                                                                  | Products                                                                                      | Ref.                      |
|------------------------------------------------------------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------|--------------------------|
| 4. Batch reactor coupled with water perm-selective membrane: Study of glycerol etherification reaction with butanol. | The etherification of glycerol with butanol in a batch reactor coupled with a perm-selective water membrane was investigated. | Due to maximizing glycerol conversion with A-15 resin, Solid acid catalysts were used at a reaction temperature of 70–160°C. Water formed during the reaction was continuously removed by rotating the gas through the membrane to increase the reaction kinetics. | Reaction temperature above 140°C. Selective removal through the membrane as well as dehydration actions, facilitate the glycerol etherification process. But on the one hand, it creates other products that are difficult to separate from the reaction ambiance. It was observed that by removing the water with the membrane, the reaction equilibrium changes. | Creating products that are difficult to separate from the reaction ambiance. Cannilla et al. (2015) |                         |
| 5. KNO3/CaO as a cost-effective heterogeneous catalyst for the synthesis of glycerol carbonate from glycerol and dimethyl carbonate. | KNO3 / CaO as a heterogeneous catalyst                                      | Different heterogeneous KNO3 / CaO catalysts with different amounts of KNO3 were used to synthesize glycerol carbonate from glycerol and dimethyl carbonate. | Under molar ratio of dimethyl carbonate / glycerol = 3, reaction temperature 70°C and reaction time 2 h, glycerol conversion for KNO3 / CaO catalyst (15%) can reach to 99.23%. | GC produced Hu et al. (2015)                             |                         |
| 6. Production of Glycerol Carbonate from Glycerol with Aid of Ionic Liquid as Catalyst | Trans-esterification of glycerol with ammonium and imidazolium-based ionic liquids (ILs) catalysts | The effects of reaction temperature, time, Di-ethyl carbonate (DEC) / glycerol molar ratio and catalyst loading on glycerol conversion and GC performance have been investigated. | After 2 h, in the 120°C temperature and DEC/glycerol = 2 molar ratio and 0.5 mol catalyst loading, IL, 1-ethyl-3-methylimidazolium acetate (emim [Ac]), showed the highest yield under solvent-free conditions, with glycerol conversion and GC production of 93.5% and 88.7%, respectively. | Glycerol conversion 93.5% and GC production 88.7% Ishak et al. (2016) |                         |
| 7. Lipase-catalyzed synthesis of glycerol carbonate from renewable glycerol and dimethyl carbonate through trans-esterification. | Enzymatic synthesis with Candida Antarctica (CALB, Novozym 435). | The enzymatic synthesis of glycerol carbonate from renewable raw materials (glycerol and dimethyl carbonate) was performed with lipase collected from Candida Antarctica (CALB, Novozym 435). | The enzymatic synthesis was successful. After optimization, the simultaneous use of glycerol and dimethyl carbonate in the catalytic reaction of Novozym 435 results in the production of low-yield glycerol carbonate. | Low glycerol carbonate production Kim et al. (2007) |                         |

Researches showed that successful production of 3-HP from glycerol required maintaining an appropriate inhibitory balance and optimal enzyme activity related to glycerol metabolism. However, not many researches have been reported on glycerol nitration and therefore more studies need to be done.

2.1.10. Selective oxidation of glycerol

The catalytic conversion of glycerol into high-value products has attracted scientists’ attention. Among various methods, the selective oxidation of glycerol via oxygen molecule to di-hydroxy-acetone, glycric acid, glyceryl aldehydes, and tartaric acid are challenging in research...
and industrial applications. Extensive catalysts for the selective oxidation of hydroxyl groups in glycerol have been reported, for example, single metals Au, Pt, and Pd NPs and bimetallic Au–Pt, Au–Pd, Pt–Bi, Pt–Sb and Cu–Pt (Yang et al., 2019). Glycerol oxidation consists of four basic steps: Di-hydrogenation of OH group, Di-hydrogenation of CH group, aldehyde oxidation and C-C bond cleavage. Studies showed that the increased catalytic activity of glycerol oxidation to carboxylic acids (mainly glycyrrhizic acid and Tartronic acid) was possible by polarizing the Pt surface and forming Pt–OH. From a thermodynamic point of view, high-energy

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 8 | Sustainable Valorisation of Glycerol via Acetalization as well as Carboxylation Reactions over Silicotungstates Anchored to Zeolite Hmbeta | Catalysts consisting of silicotungstates Anchored to Hβ zeolites, were used to synthesize glycerin. | A highly stable, recyclable and efficient catalyst, of silicotungstates that attach to Hβ, was used as a heterogeneous catalyst for the synthesis of important industrial chemicals. | Glycerol carbonate production 73% | Narkhede and Patel (2016) |
| 9 | Review on recent progress in catalytic carboxylation and acetylation of glycerol as a byproduct of biodiesel production. | Investigation of homogeneous and heterogeneous catalysts for carboxylation and glycerol acetylation with DMC and acetic acid | Acetylation and carboxylation pathways for promoting glycerol to appropriate chemicals were investigated by using various catalysts. | GC | Okoye and Hameed (2016) |
| 10 | Microbial removal of carboxylic acids from 1,3-propanediol in glycerol anaerobic digestion effluent by PHAs-producing consortium. | Conversion of glycerol to 1,3-propanediol (1,3-PDO) | Microbial removal of carboxylic acids from 1,3-PDO in glycerol ADE was performed by poly-hydroxy alkanoates (PHAs). | 1,3-propanediol (1,3-PDO) | Pan et al. (2016) |
| 11 | Production of glycerol carbonate using crude glycerol from biodiesel production with DBU as a catalyst. | Crude glycerol containing DBU and ionic compounds DBU / glycerol / CO₂ (DGC), reacts directly with dimethyl carbonate (DMC). | The synthesis of glycerol carbonate (GC) was investigated by trans-esterification of glycerol with dimethyl carbonate (DMC), using ionic compounds DBU and DGC as catalysts at 30–80°C. | Conversion of 90% glycerol and selectivity 84% to GC. | Qing et al. (2017) |
Table 7. Continued.

| Target | Materials | Method | Results | Products | Ref. |
|--------|-----------|--------|---------|----------|------|
| 12     | Heterogeneous synthesis of glycerol carbonate from glycerol and dimethyl carbonate catalyzed by LiCl/CaO. | The CaO-based catalyst by saturate chloride salts on CaO was used to prepare a highly efficient heterogeneous catalyst for the synthesis of glycerol carbonate (GC) from glycerol and dimethyl carbonate. | LiCl / CaO catalysts were prepared and the catalytic activity was tested by glycerol and DMC with trans-esterification. For the catalysts, the amount of calcination, temperature, and loading value were investigated. | The highest yield of 94.19% glycerol carbonate was achieved at 65°C in 10% LiCl-loaded CaO after 1 h. And the catalyst was highly stable for reuse. | 94.3% production of glycerol carbonate | Tang et al. (2019) |
| 13     | A review on the performance of glycerol carbonate production via catalytic trans-esterification: Effects of influencing parameters. | Use of various catalysts including pure and mixed metal oxides, ionic liquids and lipases to produce glycerol carbonate from glycerol | The production performance of glycerol carbonate with catalytic trans-esterification was investigated to investigate the influence of the effective parameters to produce high GC content using different catalysts. | High GC values can be obtained by glycerol trans-esterification using various catalysts including pure and mixed metal oxides, ionic liquids and lipases. Organic solvents, surfactants, and silica gel can be used to increase GC. | Generates a high amount of GC | Teng et al. (2014) |
| 14     | Synthesis of Glycerol Carbonate from Glycerol and Dimethyl Carbonate Catalyzed by Calcined Silicates | Several silicates were prepared at 400°C and investigated as solid base catalysts for glycerol carbonate (GC) synthesis. | Synthesis of glycerol in the form of glycerol carbonate and dimethyl carbonate using calcifed silicate catalysts was used to trans-esterification of glycerol with DMC. | Glycerol conversion 97.7%. | | Wang et al. (2017) |

**Figure 22.** Production of glycerol carbonate via reaction of glycerol and urea.

molecule oxygen reacted exothermically with organic compounds. Most organic compounds were stable in the vicinity of oxygen due to their high activation energy. Hydroxylated molecules and oxygen were activated on the surface of the solid catalyst and the hydrogen removal reaction was carried out and converted to the carbonyl group. Figure 23 is adapted and reproduced from (Yan et al., 2019).

Hydrotalcite catalyst supported by platinum catalyst (Pt/HT) was determined as an extremely active heterogeneous catalyst for the oxidation of glycerol in net water under atmospheric oxygen pressure and at a high

**Figure 23.** Main products of glycerol oxidation.
glycerol-metal molar ratio. Moreover, the high selectivity of glyceric acid (78%) was attained at 25°C and 1 atm. The Pt/HT catalyst also selectively oxidized the hydroxyl groups 1,2-propylene glycol to obtain carboxylic acid from glycerol (Tsuij et al., 2011). Selective oxidation of glycerol requires a temperature of 60-80°C. Generally, platinum and palladium are highly active catalysts for oxidation of glycerol. Di-hydroxy-acetone is obtained by aerobic oxidation of glycerol in the vicinity of Pt-Bi-C and in high acidic ambiance. More research is needed to attain comprehensive results.

2.2. Important compounds derived from glycerol

A list of important compounds that can be synthesized from glycerol is shown in Table 8.

2.3. Effects of modified glycerol on engine performance and emissions

After having described methods of producing valuable substances from glycerol, the effects of the utilization of these materials as diesel fuel additives in diesel engines are investigated. The purpose of this research is to investigate the consequence of these additives on engine performance and emissions, which are identified by examining the results of reported studies. Clearly, an additive that can improve engine performance while decreasing emissions is paramount. In Table 9, the role of these additives on engine performance and emissions is investigated.

3. Discussion about effects of additives on the performance and emissions of diesel engines

The use of glycerin in the production of a valuable additive is very economical due to the use of 10% of the production of the transesterification process material besides the 90% biodiesel. But some parameters can influence the economic condition. Therefore, depending on the type of production equipment and available primary resources for biodiesel production, the economic parameter is slowly changing, but in general, the use of glycerin as waste material and its conversion into a suitable and valuable additive to reduce diesel engine pollution and improve engine performance is very important. It is observed that most research has been performed on acetone, isopropanol, propanol, diethyl ether and poly-oxy-methylene dimethyl ethers. In the following, the effects of these additives are discussed. Adding acetone to diesel and biodiesel fuel and using it in diesel engine reduces the emissions and most NOx reduction occurs. Therefore, adding this substance can solve one of the problems (i.e. the production of high NOx) caused by the use of biodiesel. The main reason for this decrease is due to the low heat value of acetone, which reduces heat and therefore reduces NOx production. On the other hand, the addition of this substance reduces the soot, which can be due to the presence of oxygen in the acetone combination. Therefore, oxidation can reduce soot. Besides, the reduction of CO, PAH (aromatic hydrocarbons) and PM occur. Adding acetone to diesel has a better effect on soot reduction compared to butanol and ethanol. It adds acetone effect on engine performance because it improves braking thermal efficiency. Moreover, adding acetone improves energy efficiency and productivity. Acetone delays the combustion time and improves the required temperature for combustion, which is due to the endothermic properties of acetone. Therefore, the use of this additive can be effective in providing engine benefits and reducing emissions. Adding isopropanol to diesel and biodiesel fuel and using it in diesel engine reduces CO and THC. However, according to most of the reported research in Table 9, it increases NOx, which can be one of the major disadvantages of isopropanol. Although a study reported that changing the type of injecting and double injecting could reduce NOx production, NOx increase, especially at full load, is generally greater. The high thermal value of isopropanol, which releases high heat, is the main parameter in increasing NOx production. Another study also reported that using the EGR method could reduce NOx and soot simultaneously. By using isopropanol, most reduction is observed in UBHC and CO emission. Adding isopropanol to the diesel engine increases BSEC. This combination delays combustion and reduces the peak pressure. It also reduces BTE but increases the brake thermal efficiency. Injector penetration results in higher fuel injection than diesel fuel. Therefore, it can be concluded that the use of isopropanol in engines containing EGR due to NOx reduction can be recommended. But compared to acetone, it has a low performance in reducing emissions and engine performance.

Adding propanol to diesel fuel and biodiesel mixture reduces some of the diesel engine emissions. Most studies show that the addition of propanol reduces NOx and soot emissions. Adding this substance reduces the temperature of the exhaust gas (EGT). Lower temperature and lower heat value are the main reasons for the reduction of NOx emissions. However, adding propanol increases some of the emissions such as SOF, THC and CO. Therefore, higher monoxide production can be negative factors for propanol use. The addition of propanol also affects the engine performance. Its addition reduces the combustion time. At low injection pressure, the BSFC value also decreases. Important and effective factors in the addition of propanol are the decrease in viscosity and density.
Table 8. Important compounds derived from glycerol.

| Name                  | Chemical formula | Chemical structure | Name                  | Chemical formula | Chemical structure | Name                  | Chemical formula | Chemical structure |
|-----------------------|------------------|--------------------|-----------------------|------------------|--------------------|-----------------------|------------------|--------------------|
| Glycerol (L)          | C₃H₈O₃           | ![Glycerol](image)  | Solketal (L)          | C₆H₁₂O₃          | ![Solketal](image)  | Pyruvic acid (L)      | C₃H₄O₃          | ![Pyruvic Acid](image) |
| Tartronic acid (S)    | C₃H₃O₅           | ![Tartronic Acid](image) | Acrolein (L)         | C₃H₄O            | ![Acrolein](image)   | Propylene glycol (L)  | C₃H₈O₂           | ![Propylene Glycol](image) |
| Dihydroxyacetone (S)  | C₃H₆O₃           | ![Dihydroxyacetone](image) | Allyl alcohol (L)    | C₃H₅O            | ![Allyl Alcohol](image) | Glycidol (L)         | C₃H₆O₂           | ![Glycidol](image) |
| Mesoxalic acid (S)    | C₃H₂O₅           | ![Mesoxalic Acid](image) | Propionaldehyde (L)  | C₃H₆O            | ![Propionaldehyde](image) | Propionic acid (L)   | C₃H₆O₂           | ![Propionic Acid](image) |
| Glyceraldehyde (L)    | C₃H₅O₃           | ![Glyceraldehyde](image) | Propylene oxide (L)   | C₃H₆O            | ![Propylene Oxide](image) | Lactic acid (L)      | C₃H₆O₃           | ![Lactic Acid](image) |
| Glyceric acid (L)     | C₃H₆O₄           | ![Glyceric Acid](image) | Acetone (L)           | C₃H₆O            | ![Acetone](image)    | Acrylic acid (L)      | C₂H₅O₂           | ![Acrylic Acid](image) |
| Malonic acid (S)      | C₂H₄O₄           | ![Malonic Acid](image) | Isopropanol (L)       | C₃H₈O            | ![Isopropanol](image) | Hydroxypyruvic acid (L) | C₂H₄O₄       | ![Hydroxypyruvic Acid](image) |
### Table 9. Effects of additives from glycerin on engine performance and emission.

| Row | Research | Glycerin additives | Functional Results on emission | Engine performance results | Ref. |
|-----|----------|--------------------|---------------------------------|---------------------------|------|
| 1   | Algayyim et al. (2017) | iso-butanol and n-butanol of butanol - acetone | The combination of diesel fuel with n-butanol has lower UHC and NOx production. The combination of diesel fuel and ISO-BA produces much less CO. | In n-butanol and iso-BA combined with diesel fuel, the spray penetration is slightly higher than that of pure diesel fuel. Combining iso-BA with diesel improves the peak of cylinder pressure and braking power. | Algayyim et al. (2017) |
| 2   | Algayyim et al. (2018) | Acetone | NOx, CO and EGT emissions were reduced for all diesel combinations with BA. | Brake thermal efficiency (BTE) was significantly increased in all BA compounds. | Algayyim et al. (2018) |
| 3   | Changa et al. (2013) | acetone | The combination of W-ABE can significantly reduce the emission of PM, NOx, and PAH. | W-ABE can increase the energy efficiency of a diesel engine. | Changa et al. (2013) |
| 4   | Chang et al. (2013) | acetone | ABE can solve NOx and PM problems when using biodiesel. Also, the amount of PAH (polycyclic aromatic hydrocarbons) can be reduced further. | Adding ABE to biodiesel and diesel mixtures can increase energy efficiency. | Chang et al. (2013) |
| 5   | Luo et al. (2017) | acetone | The diesel blend with ABE has less soot emission than the butanol blend. Amount of soot production: acetone-diesel > butanol-diesel > ethanol-diesel. | - | Luo et al. (2017) |
| 6   | Wu et al. (2016) | Acetone | ABE is able to achieve much cleaner combustion than diesel. ABE is low in soot due to its good chemical composition in reaction. | - | Wu et al. (2016) |
| 7   | Han et al. (2017) | acetone | Adding ABE to diesel fuel reduces soot production. | Diesel combinations with ABE have longer combustion delay and faster burning speed than diesel. Small explosions occur at the end of the flame in all tests of combining diesel fuel with ABE. | Han et al. (2017) |
| 8   | Tsai et al. (2013) | acetone | Biodiesel containing 1-3% acetone and 1% IPA can reduce the emission of PM, CO, and PAH. | - | Tsai et al. (2013) |
| 9   | Fu et al. (2017) | Acetone | By reducing the oxygen concentration to 16%, the highest ABE soot mass increases to 25%. | - | Fu et al. (2017) |
| 10  | Zhou et al. (2013) | acetone | Combining ABE with diesel fuel can reduce soot. | The combustion process gets better. The temperature in the combustion chamber is lower. | Zhou et al. (2013) |
| 11  | Wu et al. (2014) | acetone | ABE and diesel combinations can reduce soot production under different conditions. | With a moderate ratio of ABE composition, the ignition delay occurs at a lower temperature. The additional acetone in the ABE and diesel combinations improve the combustion properties. | Wu et al. (2014) |
| 12  | Alptekin (2017) | isopropanol | The combination of diesel fuel and alcohol increases the emission of THC, NOx, and CO compared to pure diesel fuel. | BSFC values are higher in the combination of diesel fuel with alcohol than with pure diesel fuel. Depending on the type of fuel, the injection characteristics are varied in engine speed and load. | Alptekin (2017) |

(continued)
| Row | Research | Glycerin additives | Functional Results on emission | Engine performance results | Ref. |
|-----|----------|-------------------|--------------------------------|---------------------------|------|
| 13  | Lee et al. (2019) | isopropanol | Combining diesel with isopropanol reduces soot emission. | Diesel combinations with IBE are able to maintain the combustion properties and operate similar to diesel. However, at lower temperatures and higher oxygen concentrations, diesel combinations with IBE show higher combustion delays. | Lee et al. (2019) |
| 14  | Li, Lee, et al. (2019) | isopropanol | Double spraying reduces NOx emissions and increases soot emissions. | Peak pressure and HRR are reduced when using pilot spraying. | Li, Lee, et al. (2019) |
| 15  | Li, Liu, et al. (2018) | isopropanol | The potential for soot emission reductions is significantly increased by the IBE ratio. IBE30 combined with EGR is capable of simultaneously reducing NOx and soot emissions. | The brake thermal efficiency of IBE15 is higher than pure diesel. | Li, Liu, et al. (2018) |
| 16  | Shaafi and Velraj (2015) | isopropanol | The presence of oxygen in soybean biodiesel, as well as better incorporation of nanoparticles, significantly reduces the amount of CO and UBHC. However, under full load conditions, there is a slight increase in NOx. | The braking thermal efficiency is higher in the case of the D80SBD15E4S1 alumina fuel mixture. | Shaafi and Velraj (2015) |
| 17  | Sen (2019) | propanol | The addition of propanol to diesel fuel resulted in reduced NOx emission and soot. | The combustion duration of the propanol mixture is shorter than diesel fuel. And with increasing spray pressure, the combustion time is slightly reduced. The lowest BSFC is found at low spray pressure. | Sen (2019) |
| 18  | Bencheikh et al. (2019) | propanol | Propanol reduces carbon monoxide (CO), exhaust gas temperature (EGT), nitrogen oxides (NOx) and soot. | The DSC and TGA results confirm that Propanol reduces the starting temperature of the mixtures. Propanol increases specific brake energy consumption (BSEC). Also, it increases brake specific fuel consumption (BSFC). | Bencheikh et al. (2019) |
| 19  | Dhanasekaran et al. (2018) | propanol | N-Propanol decreases NOx, soot, CO and CO2 compared to diesel. | Triple compounds of WCO, n-propanol, and diesel can reduce the viscosity. Adding n-propanol to D50-WCO50 increases BSFC for all compounds. BTE improves at all times by adding n-propanol to D50-WCO50. | Dhanasekaran et al. (2018) |
| 20  | Atmanli (2016) | propanol | All high alcohol compounds increase CO emissions, while reducing NOx emissions from the combination of diesel and biodiesel. | The cloud-point properties for diesel and biodiesel compounds are improved by adding more alcohols. | Atmanli (2016) |
| 21  | Pinzi et al. (2017) | propanol | Increasing alcohol in the composition reduces nitrogen oxides (NOx) and soot emissions, While the soluble organic fraction (SOF) increases the total hydrocarbons (THC) and carbon monoxide (CO). | At a similar concentration of alcohol mixed with diesel fuel (10%), propanol exhibits lower emission and noise than ethanol. | Pinzi et al. (2017) |
| Row | Research | Glycerin additives | Functional Results on emission | Engine performance results | Ref. |
|-----|----------|-------------------|-------------------------------|---------------------------|-----|
| 22  | Gómez-Cuenca et al. (2013) | propylene glycol ethers | These compounds are useful for achieving cleaner combustion in a diesel engine. Compounds with less than 2.5% oxygen reduce CO, HC and NOx emissions, but increase soot. Ethylene glycol and ethyl acetate can reduce NOx and soot emissions. | A combination with less than 4% oxygen does not change the quality of diesel fuel. Generally at full load, there is a slight reduction in fuel consumption compared to pilot diesel fuel. The performance of the ethylene glycol motor is quite comparable to ethanol and ethyl acetate. There was no significant difference in brake specific fuel consumption and exhaust gas temperature for the compounds. | Gómez-Cuenca et al. (2013) |
| 23  | Hongwei et al. (2017) | ethylene glycol | | | Hongwei et al. (2017) |
| 24  | Dumitrescu et al. (2015) | Tri-propylene-glycol mono-methyl ether (TPGME) | TPGME inhibits soot formation or increases soot oxidation during and after the end of fuel injection. And effectively eliminates the smoke from the engine. | Alone TPGME is not sufficient to enable long flame combustion. | Dumitrescu et al. (2015) |
| 25  | Imtenan et al. (2015) | diethyl ether | The performance and variability of greenhouse gas emissions from compounds modified from basic fuels (biodiesel blend from Jatropha and diesel) improved slightly compared to diesel. | The physical and chemical properties of the mixtures are improved by additives. 10% of the additive was better than 5% of the additive. Diethyl ether works better in terms of engine performance than n-butanol. | Imtenan et al. (2015) |
| 26  | Beatrice et al. (2014) | glycerol ethers | Under moderate load conditions, there is a maximum of 70% reduction in PM emissions. In contrast, there is a slight increase in NOx. At low load conditions, a maximum increase of HC and CO is observed at about 50%. | Combustion of diesel combinations with GEM does not have a significant effect on combustion characteristics and efficiency. | Beatrice et al. (2014) |
| 27  | Gómez-Cuenca et al. (2011) | ethylene glycol ethers | Mixing with 1 and 2.5 wt% oxygen reduces CO and HC emission but does not reduce smoke. | The addition of DEGEE increases the cetane number of pilot diesel fuel, but EGEE and EGBE reduce it. | Gómez-Cuenca et al. (2011) |
| 28  | Jeevanantham et al. (2019) | two ether additives: diethyl ether (DEE) methyl third-butyl ether (MTBE) | 15.08% of carbon monoxide emission is reduced by adding 5% ether. A 45% reduction in NOx emission is achieved by adding 10% diethyl ether. All triple compounds of biodiesel, ether, and diesel, reduce the emission of HC. | 5% Diethyl ether in triple composition, Increases brake thermal efficiency. | Jeevanantham et al. (2019) |
| 29  | Ibrahim (2018) | diethyl ether | The heat emission was lower. And the duration of combustion for diesel is higher than other fuels at different engine loads. | By combining diesel with biodiesel, minimum brake specific fuel consumption (BSFC) increases by 8.1%. And the maximum thermal efficiency is reduced by 6.8%, respectively, compared to diesel fuel. | Ibrahim (2018) |
| 30  | Garcia et al. (2018) | 1-octanol and di-n-butyl ether (DNBE) | Significant decrease in soot and NOx emissions compared to diesel. | Oxygen biofuels improve the efficiency of fuel conversion to mechanical work. In general, compared to diesel, combustion losses are reduced. | Garcia et al. (2018) |

(continued)
| Row | Research | Glycerin additives | Functional Results on emission | Engine performance results | Ref. |
|-----|----------|-------------------|--------------------------------|----------------------------|------|
| 31  | Ibrahim (2016) | diethyl ether | - | Using DEE as a fuel additive improves engine performance significantly. The thermal efficiency of the motor is increased and the fuel consumption of the motor is reduced. | Ibrahim (2016) |
| 32  | Kakoe and Gharaghani (2019) | diethyl ether | In addition, hydrogen increases nitrogen oxides. It also reduces unauthorized hydrocarbons and carbon monoxides. | Diesel has a faster combustion start in comparison to dimethyl ether and has less combustion time. Hydrogen was more effective in natural gas/dimethyl ether case studies. | Kakoe and Gharaghani (2019) |
| 33  | Krishnamoorthi et al. (2019) | diethyl ether | In comparison to diesel, the combination of carbon monoxide (CO), nitrogen oxides (NOx) and hydrocarbon (HC) decreased by 12.8, 4.19 and 9.61, respectively. | The maximum braking thermal efficiency (29.3%) is achieved in the without EGR state. | Krishnamoorthi et al. (2019) |
| 34  | Krishnamoorthi and Malayalamurthi (2017a) | diethyl ether | 4.7% reduction in nitrogen emission oxides occurs at full load. | As the engine load increases, the exhaust gases are reinforced and the exergy efficiency is increased by increasing the load. When the engine was running with a B2 blend (60% D + 30% + 10% DEE), the brake thermal efficiency increased by 3.5%. | Krishnamoorthi and Malayalamurthi (2017a) |
| 35  | Liu, Wang, et al. (2017) | Poly-oxymethylene Dimethyl Ethers | Significantly reduces greenhouse gas emissions. Non-soot combustion is achieved using P20 and P30. A significant reduction in CO emissions occurs without a significant impact on NOx emissions. | PODE-4/diesel combinations can improve efficiency. Diesel engines are capable of normal operation with a combined fuel ratio of less than 30% PODE. | Liu, Wang, et al. (2017) |
| 36  | Liu, Sun, et al. (2017) | Poly-oxymethylene Dimethyl Ethers | PODE diesel compounds can reduce the amount of smoke, CO and HC. PODE diesel compounds reduce particle concentrations. | PODE diesel blends have high oxygen and high cetane numbers. Adding PODE can improve the combustion process and brake thermal efficiency. | Liu, Sun, et al. (2017) |
| 37  | Roy et al. (2016) | diethyl ether | Mixed biodiesel with additives has much lower carbon dioxide emissions than diesel. The additives were effective in reducing NOx. Ethanol additives significantly reduce the amount of HC release in the B100 mixture. | In the biodiesel blend, B20 with ethanol additive, the cloud point is below 25°C. | Roy et al. (2016) |
| 38  | Barro et al. (2018) | Poly-oxymethylene Dimethyl Ethers | All HC emissions contain significant amounts of methane. NOx emission is strongly dependent on the amount of EGR applied. | The operating conditions of the engine are highly dependent on the EGR. | Barro et al. (2018) |
| 39  | Krishnamoorthi and Malayalamurthi (2017b) | diethyl ether | Reduction of greenhouse gas emissions such as hydrocarbons (HC), carbon monoxide (CO) and smoke occurs. | When operating the diesel engine with B2, the brake thermal efficiency (BTE) of the engine is better at 4.3%. The exergy efficiency of fuel reaches 63.88%, lead to a reduction in brake specific energy consumption (BSEC). | Krishnamoorthi and Malayalamurthi (2017b) |
Table 9. Continued.

| Row | Research | Glycerin additives | Functional Results on emission | Engine performance results | Ref.        |
|-----|----------|--------------------|--------------------------------|---------------------------|------------|
| 40  | Benajes et al. (2018) | dimethyl-ether | The non-sooting property of DME is crucial for NOx control. | DME improves engine performance by 6.9% compared to the pilot fuel engine. | Benajes et al. (2018) |
| 41  | Liu et al. (2015) | Poly-oxymethylene Dimethyl Ethers | It reduces engine emissions especially soot emissions. PM decreases with an increasing level of DMC compound, NOx emissions increased by 3.2% and 3.1% for compounds above 20% and 30%, respectively. | Diesel combinations with PODE3-4 increase engine efficiency. Compared to diesel fuel, BSFC has increased with increasing DMC mixing levels. | Liu et al. (2015) |
| 42  | Yang et al. (2016) | dimethyl carbonate |                            |                            | Yang et al. (2016) |

Besides, cloud point improves with the addition of this material. On the other hand, adding propanol reduces the noise of the diesel engine. Adding diethyl ether to biodiesel and diesel fuel reduces some of the emission parameters. In general, THC and CO engines emissions increase with blending this material in diesel fuel. These pollutants are especially increased in EGR engines, due to the reduced inlet oxygen to the combustion chamber. The rate of heat emission is reduced by diethyl ether. Therefore, NOx production is reduced due to the addition of this substance and this decrease has been reported at higher loads. The addition of diethyl ether to blend of diesel fuel and hydrogen increases NOx because hydrogen fuel has a high heat value, which increases temperature and NOx emission. Besides, the use of diethyl ether in fuel blend up to 10% improves the engine performance. The addition of diethyl ether has better engine performance in comparison to that of butanol. The addition of diethyl ether increases BSFC and thermal efficiency. Compared to diesel, it has a longer combustion delay. Cloud point temperature occurs at below 25°C. With the addition of diethyl ether, it has been reported an increase in BTE, which is due to the high thermal efficiency of this material. However, this action reduces BSEC. Adding poly-oxymethylene diethyl ethers reduces the emission of soot, CO, and HC. The effect of adding this substance to diesel fuel is much more severe in reducing HC, which is due to its high oxygen concentration. Yet, adding it does not have much effect on NOx. If EGR is used, NOx emissions are high due to the increase in inlet air temperature to the combustion chamber. Therefore, the disadvantages of using this additive are its non-efficiency in reducing NOx. Adding poly-oxymethylene diethyl ethers improves engine efficiency. This additive improves the combustion process due to the high oxygen concentration in it, and also increases the brake thermal efficiency. Adding this material also increases the cetane number of fuels. Therefore, it is found that this additive performs very well on the diesel engine combustion process.

4. Conclusion

The global production of glycerol is increasing significantly and leading to its economic evaluation in the market. Since the generation of new glycerol is quicker than the market demand, the value of glycerol decreases significantly due to overproduction. The production capacity and demand for biodiesel fuel have been increasing in recent years and consequently, global production of glycerol is on the increase. It has little direct utilization and its fuel value is low. Glycerol is a suitable molecule for the synthesis of various products, for example, surfactants, emulsifiers, solvents, lubricants, cosmetics, etc. Besides, glycerol is non-toxic, edible, and biodegradable and has a very different structure that enables the synthesis of a wide array of valuable derivatives using different methods. Among various methods of producing valuable materials from glycerol, the choice of the best method depends on criteria such as the desired product, equipment required and other economic and environmental parameters. Therefore, depending on these parameters, the required method to produce the desired product is chosen. The methods of etherification, carboxylation, and glycerol carbonate preparation have been more widely used, respectively. This is due to being more industrial and producing different products. The use of derived additives from glycerin (with a variety of ways) shows that it plays a role in engine performance and emission parameters. For this reason, different studies on these materials should be carried out under different engine operating conditions. In most study cases, the use of these additives has reduced several emissions parameters, which proved their importance. The presence of hydroxyl groups can reduce NOx. Using glycerin additives to improve the properties of biodiesel can be important. Therefore, they must be added to the base fuel under different engine conditions and in different amounts. Among these additives, acetone is one of the most important additives in the blend of diesel and biodiesel fuel due to the maximum reduction of emissions. Diethyl
ether additive is also a useful additive due to its increased thermal efficiency and BSFC. Hence, wide experimental investigations will be needed to obtain an appropriate additive.

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