An Overview of Recent Research in the Conversion of Glycerol into Biofuels, Fuel Additives and other Bio-Based Chemicals

Usman Idris Nda-Umar 1,2,*, Irmawati Ramli 1,3,*, Yun Hin Taufiq-Yap 1,3 and Ernee Noryana Muhamad 1,3

1 Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, Serdang 43400 UPM, Selangor, Malaysia; taufig@upm.edu.my (Y.H.T.-Y.); ernee@upm.edu.my (E.N.M.)
2 Department of Chemical Sciences, Federal Polytechnic, Bida PMB 55, Niger State, Nigeria
3 Catalysis Science and Technology Research Centre, Faculty of Science, Universiti Putra Malaysia, Serdang 43400 UPM, Selangor, Malaysia
* Correspondence: uindaumar@gmail.com (U.I.N.-U.); irmawati@upm.edu.my (I.R.)

Received: 19 October 2018; Accepted: 19 November 2018; Published: 27 December 2018

Abstract: The depletion of fossil fuels has heightened research and utilization of renewable energy such as biodiesel. However, this has thrown up another challenge of significant increase in its byproduct, glycerol. In view of the characteristics and potentials of glycerol, efforts are on the increase to convert it to higher-value products, which will in turn improve the overall economics of biodiesel production. These high-value products include biofuels, oxygenated fuel additives, polymer precursors and other industrial bio-based chemicals. This review gives up-to-date research findings in the conversion of glycerol to the above high-value products, with a special focus on the performance of the catalysts used and their challenges. The specific products reviewed in this paper include hydrogen, ethanol, methanol, acetin, glycerol ethers, solketal, acetal, acrolein, glycerol carbonate, 1,3-propanediol, polyglycerol and olefins.

Keywords: biodiesel; glycerol; biofuels; oxygenated fuel additives; chemicals; catalysts

1. Introduction

Since the beginning of the industrial revolution, fossil fuels have been the major source of energy and industrial chemicals. At any point in time, the yardstick for development of any country has been attributed to the level of consumption of fossil fuels. It is becoming clearer that fossil fuel reserves are finite in nature. The International Energy Agency (IEA) forecasted that the world maximum oil production will be attained between 1996 and 2035 [1,2]. Some experts have predicted that the current oil may completely be depleted by 2050 [3]. The finite nature, coupled with the challenges of the skyrocketing cost of conventional oil, global warming, and other environmental pollution problems, has led to the current in-depth research into the use of alternative fuels that are renewable and sustainable [4,5].

Renewable energy sources such as solar, wind, geothermal and biomass are considered to be viable alternatives to conventional oil [2]. However, energy from biomass is considered to be more sustainable, especially for the transportation sector. Biofuel is a general name for fuels from biomass, which include bioethanol, biodiesel, biomethanol, biogas, biohydrogen, biodimethylether, bio-ETBE (ethyl-tertiobutyl-ether), bio-MTBE (methyl-tertiobutyl-ether), synthetic biofuels (hydrocarbons) and bio-oil (vegetable) [6–8]. Of all the biofuels, biodiesel is the most researched and it is still work in progress despite the level of its development. This enormous interest by researchers, industrialists and governments worldwide may not be unconnected with the inherent advantages. It is biodegradable,
Biodiesel is a monoalkyl ester of fatty acids obtained from vegetable oil or animal fat through esterification or transesterification reaction with alcohol in the presence of catalyst. This has been reported by several authors [11–15]. Specifically, it is a reversible reaction involving triglyceride with methanol (most commonly) or ethanol (less commonly) in the presence of NaOH, KOH or H₂SO₄ as catalyst. The reaction is shown in Scheme 1. The use of sodium or potassium methoxide (CH₃ONa or CH₃OK) as catalyst has recently become more preferred. This is to substantially minimize or avoid the moisture content associated with biodiesel production [9].

\[
\begin{align*}
\text{Triglyceride from vegetable oil} & \quad + \quad 3\text{CH₃OH} \quad \xrightarrow{\text{Catalyst}} \quad 3\text{R'COOCH₂} \\
& \quad \quad \text{Biodiesel} \quad + \quad \text{Glycerol}
\end{align*}
\]

Scheme 1. Conversion of glyceride to biodiesel and glycerol.

To complement the already-dwindling petroleum products, developed countries have responded to the production and use of biofuels, especially with the directive of European Union (EU) that conventional fuels should have an addition of at least 5.75% biofuels by 2010, with the possibility of increasing it to 20% by 2020 [8]. The foregoing directive, in addition to the compliance with the Kyoto Agreement that member nations should reduce the level of CO₂ emission to below 8% of 1990 level by 2012, has sharply increased the production of biodiesel [16]. Efforts by the EU can be seen from the available data from various sources. Biodiesel production in EU member countries was put at 1.93 million tons in 2004, and after ten years, in 2013, it was put at 10.37 million tons, moving up to 11.58 million tons in 2016, with Germany and France taking the lead [17]. Figure 1 presents a pictorial representation of EU biodiesel production for the period 2004 to 2016, indicating the capacity and actual growth pattern. Similarly, the United States biodiesel production grew from 0.5 million gallons in 1999 to 250 million gallons in 2006 [18], and later to 2.89 billion gallons in 2016 [19]. Figure 2 shows the US biodiesel growth pattern from 2006 to 2016. However, the global status report 2016 [20] indicates that in 2015, the world biodiesel production was 30.1 billion liters, with the United States, Brazil, Germany, France and Argentina being the top five producers. The biodiesel global production of the top 16 countries in 2015 is shown in Figure 3. Some of these countries have already made it mandatory through legislation to have an addition of 2–5% biodiesel to the existing conventional diesel, as stipulated by the EU [3,21]. However, this directive has been reviewed more recently. EU member countries are to ensure that energy from renewable sources forms at least 10% of the transportation fuels by the year 2020 [22]. This is to improve energy efficiency and reduce greenhouse gas emission. It has also been reported in several works that biodiesel production will soar in the coming years and this is evident from the series of diversified global research activities in boosting biodiesel production both in the areas of feedstock and catalysis. On feedstock, research is focused on the use of edible, non-edible and waste oils [23–25]. Recent reviews have shown that more than 350 oil-bearing crops are potential feed stocks for biodiesel production [26,27]. Meanwhile, with regard to catalysis, research is now focused on the use of heterogeneous solid catalysts (acid and base) and enzymes [28,29].
There are also social and environmental concerns when discarded without adequate treatment; hence, biodiesel produced is made up of glycerol. That is, for every 100 kg of biodiesel produced, 10 kg of glycerol is generated [31,32]. The growing biodiesel production will definitely lead to an excess supply of glycerol, which has been described as having a low commercial value because of its low quality [33].

Despite the diversification of research in biodiesel production, the cost is still not favorable when compared to conventional fuels. It was reported that the cost of biodiesel unit price is 1.5–3.0 times higher than that of petroleum-derived diesel fuel, depending on the type of feedstock used [30]. In addition, the high production of biodiesel produces large volumes of waste, with glycerol as the major product. It has been reported in various literature that 10–20% of the total volume of biodiesel produced is made up of glycerol. That is, for every 100 kg of biodiesel produced, 10 kg of glycerol is generated [31,32]. The growing biodiesel production will definitely lead to an excess supply of glycerol, which has been described as having a low commercial value because of its low quality [33]. There are also social and environmental concerns when discarded without adequate treatment; hence,
a lot of research is focused on the conversion of glycerol into high value and useful products. This, in the view of researchers and industrialists, will enhance the economics of biodiesel by lowering its cost of production. The versatility of glycerol is well known in view of its applications in almost all the fields of human endeavors [34,35], as indicated in Table 1. However, for glycerol to be used in food, pharmaceutical, cosmetics and other personal care industries, it must be pure. Unfortunately, the purification process, which involves filtration, chemical treatment and vacuum distillation, is expensive, especially to the small and medium production plants, and therefore not commensurate with its current low market value [21,36]. It is, therefore, not surprising that great attention has recently been directed towards the utilization of crude glycerol or partially-treated raw glycerol in the production of higher-value products. This is expected to promote integrated biodiesel and other chemical production which concept is now known as biorefinery. There are several recent reviews showcasing some of these conversions [35,37–40]; however, some of them are on certain products via bioconversion, while some have emphasized the reaction type or the nature of the glycerol used.

The present review, in addition to providing up-to-date findings of research outcomes, places emphasis on products with applications directed at non-personal care areas, such as biofuels, oxygenated fuel additives, polymers and some industrial bio-based precursor chemicals, with special focus on the performance of the catalysts and techniques used for such conversions. Figure 4 illustrates the applications of the products reviewed in this paper.

**Table 1. Industrial applications of glycerol [31,35,41].**

| Medical, Pharmaceutical and Personal Care Industries | Food Industry | Automotive and Chemical Industries | Other |
|----------------------------------------------------|---------------|-----------------------------------|-------|
| Cough syrups, expectorant and elixirs              | Humidifier/Humectant | Antifreeze                        | Denitrification |
| Mild laxative                                      | Flavor         | hydraulic and lubricating agents  | Enzymatic reagents |
| Allergen treatment                                 | Solvent        | Tannins prevention                | Cryoprotectant   |
| Plasticizer                                        | Emulsifier     | Alcohol free alternatives         | Animal feed     |
| Lubrication                                        | Antioxidant    | Preserving agent                  |                   |
| Flavor                                             | Lubricant      | Explosives                        |                   |
| Additive                                           | Sweetener      | Synthesis of resins and many compound |                   |
| Toothpaste                                         | Preservation   | Polymers and fuels                |                   |
| Mouth washers                                      | Thickening agent |                                   |                   |
| Skin and hair care                                 |                |                                   |                   |
| Moisturizer                                        |                |                                   |                   |
| Softener                                           |                |                                   |                   |
| Soap                                               |                |                                   |                   |

**Figure 4. Applications of some glycerol derivatives.**
2. Glycerol, Its Uniqueness and Availability

Glycerol (propane-1,2,3-triol) is a sweet-tasting oily liquid discovered in 1779 by Swedish chemist Carl Wilhelm Scheele. It was named ‘glycerin’ (Greek: glukeros meaning ‘sweet’) in 1823 by French chemist Michel Eugene Chevreul and was given the formula C₃H₈O₃ in 1855 by Charles-Adolphe Wurtz [42]. When pure, glycerol is water-soluble, clear, almost colorless, odorless, viscous, non-toxic, and hygroscopic, with a high boiling point. Glycerol is a polyhydric alcohol with three hydrophilic hydroxyl groups, each attached to carbon which is responsible for its stable, versatile reactions and applications [43,44]. Some of its major properties are shown in Table 2, as reported by several authors. In the market, there are three categories of glycerol, namely crude glycerol, purified/refined glycerol, and commercially synthesized glycerol. Crude glycerol is of lower purity when compared to the purified and synthesized glycerol. Crude and purified glycerol are products of biodiesel production, while synthesized glycerol is obtained through a different route, commonly from propene [41]. Crude glycerol, unlike purified and synthesized glycerol, cannot be used in sensitive areas such as food, medicine and cosmetics, because of its level of purity (60–80%) [21,39]. Table 3 shows the different categories of glycerol and some of their contents. The composition of crude glycerol varies with the type of catalyst, feedstock employed, the efficiency of the process and the recovery of methanol and/or catalysts used [34]. Several studies have also confirmed this as exhibited in the typical compositions of crude glycerol from different sources [45–47]. Typical composition of different crude glycerol is shown in Tables 4 and 5.

| S/N | Properties | Values Reported by Different Authors |
|-----|------------|-------------------------------------|
| 1   | Form and color | Liquid and colorless na na |
| 2   | Formula weight | 92.09 92.09 92.09 |
| 3   | Specific gravity/Density (20 °C) | 1.260/3 1.261 g/cm³ 1.261 g/cm³ |
| 4   | Melting point | 17.9 °C 18.17 °C 18.0 °C |
| 5   | Boiling point | 290 °C 290 °C 290 °C |
| 6   | Solubility in 100 parts | Water Infinity na na |
|     | Alcohol | Infinity na na |
| 7   | Viscosity of liquid glycerol at 100% purity | 10 cP 1499 cP at 20 °C 1.410 Pa·s |
| 8   | Diffusivity in (DL × 10⁵ sqcm/s) | i-Amyl alcohol 0.32 na na |
|     | Ethanol | 0.56 na na |
|     | Water | 0.94 na 1.33 × 10⁻¹¹ m²/s |
|     | na | 0.0025 mmHg at 50 °C 0.0001 kPa at 20 °C |
|     | na | 0.195 mmHg at 100 °C 0.03 kPa at 100 °C |
| 9   | Vapour pressure | na 4.3 mmHg at 150 °C 0.67 kPa at 152 °C |
|     | na | 46 mmHg at 200 °C 6.67 kPa at 204 °C |
| 10  | Refractive index | na 1.474 1.474 |
| 11  | Surface tension (20 °C) | na 63.4 dyne/cm 63.4 mN/m |
| 12  | Compressibility (28.5 °C) | na 2.1 × 10⁻⁸ MPa 2.1 × 10⁻⁴ MPa |
| 13  | Heat of vaporization | na 21,060 cal/mole at 55 °C 88.2 KJ/mol |
|     | na | 18,170 cal/mole at 195 °C 76.1 KJ/mol |
| 14  | Heat of formation | na 159.6 Kcal/gm mole −669 KJ/mol |
| 15  | Heat of combustion | na 1662 KJ/mole = 18.05 MJ/kg −1662 KJ/mole |
| 16  | Heat fusion (18 °C) | na 47.49 cal/g 18.3 KJ/mole |
| 17  | Heat of solution | na na −5.8 KJ/mole |
| 18  | Thermal conductivity | na 0.29 w/°K 0.29 W/m/°K |
| 19  | Flash point | na 177 °C 177 °C |
| 20  | Fire point | na 204 °C 204 °C |
| 21  | Relative dielectric constant (25 °C) | na na 42.48 |
| 22  | Autoignition temperature on glass | na na 429 °C |
| 23  | Calorific value | na na 18 KJ/g |
| 24  | Specific electrical conductivity (20 °C) | na na 0.1 µS/cm |

na = not available.
Table 3. Quality parameters of different categories of glycerol (adapted from [48]).

| S/N | Parameters         | Crude Glycerol | Purified Glycerol | Refined/Commercial Glycerol |
|-----|--------------------|----------------|-------------------|----------------------------|
| 1   | Glycerol content (%) | 60–80          | 99.1–99.8         | 99.2–99.98                 |
| 2   | Moisture content (%) | 1.5–6.5        | 0.11–0.8          | 0.14–0.29                  |
| 3   | Ash (%)             | 1.5–2.5        | 0.054             | <0.002                     |
| 4   | Soap (%)            | 3–5            | 0.1–0.16          | na                         |
| 5   | Acidity (meq/100 g) | 0.7–1.3        | 0.10–0.16         | 0.04–0.07                  |
| 6   | Chloride (ppm)      | BDL            | 1.0               | 0.6–9.5                    |
| 7   | Color (APHA)        | Dark           | 34–45             | 1.8–10.3                   |

BDL = Below detection limit, na = not available.

Table 4. Elemental analysis of a typical crude glycerol produced in biodiesel industry (adapted from different authors).

| Feedstock  | C (wt%) | H (wt%) | N (wt%) | O (wt%) | Na (ppm) | K (ppm) | P (ppm) | Ca (ppm) | Mg (ppm) | Fe (ppm) | Reference |
|------------|---------|---------|---------|---------|----------|---------|---------|----------|----------|----------|-----------|
| na         | 52.77   | 11.08   | <0.0001 | 36.15   | na       | na      | na      | na       | na       | na       | [49]      |
| SB oil (1) | 24.3    | na      | 0.3     | na      | 11,769   | 118.8   | 38.7    | BDL      | BDL      | 31.6     | [45]      |
| SB oil (2) | 44.3    | na      | 0.6     | na      | 19,361   | 140.5   | 101.3   | 8.4      | 3.7      | 34.2     | [45]      |
| SB oil (3) | 46.8    | na      | 0.7     | na      | 19,108   | 1057    | 24.7    | 4        | BDL      | 52.8     | [45]      |
| WV oil     | 54.2    | na      | 0.9     | na      | 16,263   | 486.2   | 233.8   | 20.5     | 14.2     | 92.1     | [52]      |

BDL = Below detection limit, SB = Soybean oil, WV = Waste vegetable oil, na = not available.

Table 5. Quality of various crude glycerol from biodiesel plants by different authors.

| Feedstock                        | Glycerol Content (%) | Methanol Content (%) | Moisture Content (%) | Ash Content (%) | Soap Content (%) | pH | Appearance         | Reference |
|----------------------------------|----------------------|----------------------|----------------------|-----------------|------------------|----|-------------------|-----------|
| Commercial pure glycerol         | 99.5                 | na                   | 0.5                  | 0               | 0                | 6.7 | Colorless liquid   | [46]      |
| Crude palm oil                   | 88.56                | na                   | 3.41                 | 7.12            | 0.91             | 6.68 | Dark brown liquid  |           |
| RBDF oil (1)                     | 85.2                 | na                   | 8.11                 | 5.26            | 1.43             | 7.73 | Dark brown semi solid |           |
| RBDF oil (2)                     | 93.4                 | na                   | 1.43                 | 3.43            | 1.74             | 12.13 | Dark brown semi solid |           |
| Mixture of vegetable oils        | 71.7                 | 25.7                 | na                   | na              | na               | na  | na                | [50]      |
| SB oil (1)                       | 63                   | 6.2                  | 28.7                 | 2.7             | BDL              | 6.9 | na                |           |
| SB oil (2)                       | 54.8                 | 10.9                 | 18.2                 | 3.0             | 26.2             | 9.7 | na                | [46]      |
| SB oil (3)                       | 33.3                 | 12.6                 | 6.5                  | 2.8             | 26.1             | 9.5 | na                | [45]      |
| WV oil                           | 27.8                 | 8.6                  | 4.1                  | 2.7             | 20.5             | 9.4 | na                |           |
| Waste cooking oil                | 83.4                 | BDL                  | 11.6                 | 2.7             | 1.3              | na  | na                | [51]      |

RBDF = Refined, bleached and deodorized palm oil, BDL = Below detection limit, SB = Soybean oil, na = not available.

Prior to the advent of biodiesel production, glycerol was commonly obtained from fatty acids and soap production, its availability was not commensurate with its demands, hence it had a relatively good market value [38,44]. However, this has now changed. It is believed that since 1995, there has been an oversupply of glycerol in the world market, and the current increase in biodiesel production has further increased the level of glycerol. It has been estimated that by the year 2020, production will be six times higher than demand [41]. It was reported that the worldwide crude glycerol obtained from biodiesel production increased from 200,000 tons in 2004 to 1.224 million tons in 2008 [34]. Garlapati et al. [52] reported that it was forecasted that 4 billion gallons of crude glycerol will be produced as a byproduct of biodiesel by 2016.

From the foregoing, it is clear that the availability of glycerol is not in doubt, in fact, it is generally believed that due to the upsurge in biodiesel production, the glycerol production will continue to grow, hence, the conversion of glycerol into other useful products is timely and of essence due to overall improvement on the economics of biodiesel production.

3. Biofuels from Glycerol

Biofuels may be liquid or gaseous fuels produced from biomass resources to meet energy needs, especially in transportation, electricity and other stationary sectors. These biofuels are considered to be...
efficient, biodegradable, non-toxic or less toxic, and free of sulfur and aromatics [53,54]. Reports have shown that many biofuels have been produced from glycerol via different chemical and biological catalysts. Some of them are reviewed below.

3.1. Hydrogen and Syngas

Hydrogen is considered an ideal fuel for the future; as such, it is of intense interest to researchers and industrialists because of its excellent burning ability and its resultant byproduct, water; hence, it is eco-friendly [38,55]. In addition to the -friendliness, hydrogen has extensive applications in industry for the production of ammonia and methanol, and in petroleum processing. It can also be used to generate electricity in gas turbines and fuel cells for portable electronics [56]. Syngas is considered a versatile intermediate, containing a mixture of hydrogen and carbon monoxide. It is a precursor to many important fuels and chemicals such as methanol and liquid hydrocarbons through Fischer-Tropsch synthesis [32].

The conversion of glycerol into hydrogen and syngas follow a similar protocol. In the past, the conversion was carried out via combustion, but the method was found to be uneconomical, unsafe and technically deficient in view of the high temperature used, obnoxious gas emission and complex product composition [18,36,38,57]. On the contrary, reforming methods have gained acceptance by researchers and industrialists in view of its efficiencies. The reforming methods include steam reforming, partial oxidation, autothermal reforming, aqueous phase reforming and supercritical water reforming [38,56,58–60]. The reforming methods essentially follow a similar basic principle, in line with Scheme 2.

\[
\text{C}_3\text{H}_6\text{O}_3 + x\text{H}_2\text{O} + y\text{O}_2 \xrightarrow{\text{Catalyst}} a\text{CO}_2 + b\text{CO} + c\text{H}_2\text{O} + d\text{H}_2 + e\text{CH}_4 + \ldots
\]

**Scheme 2.** Conversion of glycerol to hydrogen and syngas by catalytic reforming.

Steam reforming is carried out in a gas phase (in Scheme 2, \(x > 0\) and \(y = 0\)), usually at atmospheric pressure and a temperature of 400 °C or above [61]. Aqueous phase reforming (APR) is done with glycerol in the liquid phase at higher pressures (1.6–4.0 MPa) and moderate temperatures (200–250 °C) [62]. In APR, \(x = 0\) and \(y = 0\) in Scheme 2. When a partial oxidation process takes place in the presence of oxygen \(x = 0\), \(y > 0\) in Scheme 2. Autothermal reforming is the combination of both steam and partial reforming, which involves the trio of fuel, air and water [63]. Therefore, in Scheme 2, \(x > 0\), \(y > 0\). Supercritical water reforming is more recent, and the process is carried out at temperature \(\geq 374 °C\) and pressure \(\geq 22.4\) MPa [63–66]. Extensive research on the conversion of glycerol into hydrogen and syngas using the above methods with or without catalyst has been reported. However, it is the general consensus that better and higher yields are obtained in the presence of catalysts particularly transition metal-based catalysts. Some of the recent findings are reviewed below.

Steam reforming of glycerol to hydrogen is the most commonly used method due to simultaneous removal of hydrogen from the water molecule and the resultant high yield from the reaction [59,60,67]. The use of metal-alumina support catalysts in steam reforming has been reported. Demsash and Mohan [68] used the combination of low loading of ceria and nickel (10Ni/Al2O3/5CeO2), and were able to achieve high selectivity of H2 (85.7%) at 650 °C after 16 h of reaction time in a continuous-flow packed-bed reactor. High yield of H2 has also been reported by several researchers using Pt-doped alumina with other metal oxides such as Pt/La2O3/Al2O3 and Pt/CeO2/Al2O3 [69,70]. The use of bimetal-metal oxide support catalysts in steam reforming of glycerol has been reported. Sanchez and Comelli [71] investigated the use of 4Ni/Al2O3, 4Co-4Ni/Al2O3 and 12Co-4Ni/Al2O3 catalysts at three different temperatures, 300, 500, and 700 °C, 0.1 MPa, 10 h⁻¹ WHSV, 6:1 WGMR, 0.17 mL min⁻¹ glycerol solution feed flow rate (FFR) and time-on-stream of 8 h. The main product obtained was H2, which was favored at 300 °C, followed by CO2, CO and CH4 in smaller proportions.

Ni supported on ZrO2, La2O3, SiO2, Al2O3 and MgO catalysts prepared by the wet-impregnation method were used in glycerol steam reforming to produce hydrogen [72]. At reaction conditions of
650 °C, water:glycerol molar ratio of 6 and FFR of 1 mL/min, maximum hydrogen selectivity of 75.1% and glycerol conversion of 80% were exhibited by Ni/Al2O3 catalyst. The good performance was due to the large surface area, small crystal size and high dispersion of Ni on the alumina support material, while the catalyst stability was attributed to the high basicity. Similarly, fly ash (a solid waste of thermal power plants) impregnated with various amounts of nickel were also used as catalyst in hydrogen production [73]. The catalyst containing 7.5 wt% Ni on fly ash showed highest activity and very good stability resulting in the highest hydrogen yield. A maximum yield of 5.8 mol of hydrogen per mole of glycerol fed was produced at 550 °C with steam:glycerol molar ratio of 12:1, and a space-time of 8.4 kg cat h/k mol of glycerol fed. This resulted in glycerol conversion of 98.6%.

Good results were also reported with an aqueous phase reforming system that did not require pre-vaporization. Özgür and Uysal [74] used Pt/Al2O3 as catalyst in an aqueous phase reforming system in an autoclave reactor and a continuous fixed-bed reactor. The optimum temperature and FFR were found to be 230 °C and 0.1 mL/min, while hydrogen concentration in the gas product increased with decreasing glycerol concentration in the feed. At less than 45 wt% glycerol concentration, the hydrogen concentration was about 67%. In another study on Pt-based catalysts supported on different oxides (Al2O3, ZrO2, MgO and CeO2), Menezes et al. [75] found all the catalysts to be active in hydrogen production. However, the catalysts supported on MgO showed the highest activity in hydrogen production (71.9%), with low concentration of undesired hydrocarbons. Contrary to the above yields, Seretis and Tsiakaras [76] obtained only 14.1% H2 yield under optimum conditions of 1 g of 5% Pt/Al2O3, 1 wt% glycerol solution, 240 °C and 4 h of reaction time. However, high glycerol conversion of ≈84% was obtained. Other gaseous and liquid compounds were found to be present, such as CO, CH4, CO2, acetaldehyde, acetone, methanol, ethanol, 1-propanol, acetal, lactic acid, propylene glycol and ethylene glycol. From the foregoing, it can be seen that the level of H2 production, as well as glycerol conversion, obtained using aqueous phase reforming were lower when compared to the steam reforming. Aqueous phase reforming also has the challenge of selectivity, in view of the fact that alkane is highly favored due to the low temperature involved. However, aqueous phase reforming is excellent for crude glycerol feedstock because it does not require pre-vaporization of water, thereby saving energy [76]. Table 6 shows the summary of the performance of some catalysts in the conversion of glycerol to hydrogen as recently reported in some literature.

Table 6. Performance of some catalysts in the conversion of glycerol to hydrogen as reported in some literature.

| Catalyst (A) | Operation Parameters | Performance | TOF | Reference |
|-------------|----------------------|-------------|-----|-----------|
| 7.5 wt% Ni/Fly ash (10.4) | T = 550 °C, WGMGR = 12:1, Cat = 1 g | GC = 98.6%, Y = 5.8 mol/mol G, S = na | nd | [73] |
| 10 wt% Ni/Al2O3 (123.4) | T = 630 °C, Cat = 0.3 g, WGMGR = 6:1 | GC = 80%, Y = na, S = 71% | nd | [72] |
| 5% Pt/Al2O3 (na) | T = 240 °C, Cat = 1 g | GC = 84%, Y = 14.1%, S = na | 2.1 | [76] |
| Ni-Co/Al-Mg (na) | T = 680 °C, Cat = 2 g, t = 3 g | GC = 95%, Y = 67 vol%, S = 91% | 58 | [77] |
| 1.44 wt% Pt/MgO (221) | T = 225 °C, P = 2.3 MPa, t = 3 h, Cat = 100 mg | GC = na, Y = 71.9%, S = na | * 24 | [75] |
| 1 wt% Pt/Al2O3 (na) | T = 230 °C, Cat = 2 g, LHSV = 0.73 h<sup>-1</sup> | GC = na, Y = 67 mol%, S = na | nd | [74] |

A = Surface area (m<sup>2</sup>/g), T = Temperature, P = Pressure, Cat = Catalyst load, WGMGR = Water Glycerol Molar Ratio, W/LHSV = Water/Liquid Hourly Space Velocity, t = time, GC = Glycerol Conversion, Y = Yield, S = Selectivity, TOF (mmol g<sup>-1</sup> cat. h<sup>-1</sup>) = Turnover frequency calculated based on the glycerol conversion/* product yield per gram catalyst per total reaction time (h), na = not available, nd = not determined.

The use of microwave plasma in the gasification of biodiesel-derived glycerol to syngas was investigated by Yoon et al. [78]. The results showed high production of syngas (57% H2 and 35% CO) and the composition decreased as the oxygen-to-fuel ratio increased. Similarly, co-gasification of glycerol with other biomass to produce syngas with improved yield has been reported by many researchers. Skoulou and Zabaniotou [79] reported syngas improvement from 0.4 to 1.2 Nm<sup>3</sup>/kg on mixing crude glycerol with olive kernel in a fixed-bed reactor at 750–850 °C. This led to increase in H2 concentration from 19 to 33% (v/v).

Guo et al. [80] also investigated the supercritical water gasification of glycerol in a continuous flow tubular reactor in the range 487–600 °C and 25 MPa over a short residence time (3.9–9.0 s) over different alkali catalysts (NaOH, Na<sub>2</sub>CO<sub>3</sub>, KOH and K<sub>2</sub>CO<sub>3</sub>). The effects of reaction temperature, residence time,.
glycerol concentration and type of catalyst on gasification were also studied. Results revealed that
gasification was favored by higher temperatures, long residence times and lower glycerol concentration.
The alkali catalysts enhanced the water–gas shift reaction, with NaOH being the most active. No char
was observed in any of the experiments. In a similar work, Dianningrum et al. [81] studied the effect
of different operating conditions (temperature (500–650 °C), concentration (5–20 wt%) and residence
time (15–120 min)) on pure glycerol and two different types of crude glycerol in supercritical water
gasification. Results showed decreased hydrogen production in all the feedstocks with increase in
concentration, and increased hydrogen with increase in temperature and residence time. However, the
tar/char was high in crude glycerol when compared with pure glycerol due to the presence of alkali
salts. When the authors used the same feedstocks in a continuous reactor at 650 °C, 5 wt% for different
residence times, complete gasification was achieved.

It is important to note that the syngas produced can be converted to pure hydrogen via the
water–gas shift reaction, as indicated in Scheme 3. Haryanto et al. [82] reported the thermodynamic
analysis for upgrading syngas derived from biomass gasification using the minimization of Gibbs
free energy function. The results indicate that syngas upgrading to hydrogen was best achieved in a
temperature range of 627–827 °C, pressure range of 0.1–0.3 MPa, and at different carbon:steam ratios.
As much as 43–124% hydrogen increment can be achieved with negligible methane yield and coke
formation, as well as decreased production of carbon dioxide.

\[
CO + H_2O \leftrightarrow CO_2 + H_2
\]

Scheme 3. Water-gas shift reaction.

Similarly, the use of partial oxidation and autothermal reforming have been reported in several
other works with >70% H_2 yield and >80% glycerol conversion [59,65,83–86].

The use of microorganisms to produce hydrogen has also been studied and reported over the years,
and findings have shown enhanced crude glycerol utilization without undergoing the high cost of the
purification process associated with having pure glycerol. The use of Enterobacter spH1, Enterobacter
spH2 and Citrobacter freundii H3 [87], Escherichia coli K12 [88], Clostridium freundii H3 [89], Klebsiella
pneumonia TR 17 [90], Thermotoga maritime and Thermotoga neapolitana [91] have shown relatively
large quantities of H_2 (>70%) under varying conditions. However, the details of microbial hydrogen
production are beyond the scope of this review.

3.2. Ethanol

Ethanol is a colorless, flammable oxygenated hydrocarbon [92]. It is a well-known solvent in
industry. It is the largest alternative renewable fuel and/or fuel additive for gasoline.

Efforts have been made to synthesis ethanol from glycerol via a chemical route, but production
via biological means (fermentation) remains the most common. Typically, ethanol is produced from
sugarcane and corn in Brazil and United States, and the argument of food versus fuel has been a
limiting factor [92]. Therefore, with the availability of crude glycerol, its conversion into ethanol will
drastically eliminate the food versus fuel debate, with the advantage being that it will reduce cost.
In fact, Amaral et al. [93] reported that the use of glycerol in ethanol production could reduce the
cost by over 35%, when compared with production from corn, and this was confirmed by the work
of Posada and Cardona [94], which simulated and economically assessed both the production and
purification of ethanol from raw glycerol (60 wt%), crude glycerol (88 wt%) and pure glycerol (98 wt%) using
Escherichia coli. Results showed that the lowest bioconversion cost was obtained when crude
glycerol was diluted at 20 g/L. When purification and global production costs were compared with
the commercial prices of glycerol and fuel ethanol from corn and sugarcane, the purification cost of
raw glycerol was lower than previously reported values due to the methanol recovery.
The fermentation of glycerol using *Escherichia coli* K12 also revealed that a maximum ethanol yield of 0.40 g/g glycerol was obtained when 10 g/L concentration of glycerol was used under membrane headspace conditions [88]. Similarly, Loaces et al. [95] used *E. coli* to improve ethanol production and glycerol conversion using heterologous genes (metagenomic fragment) obtained from anaerobic purge sludge. The LY180 strain carrying G1 fosmid produced the highest concentration (75 g/L) of ethanol at a specific production rate of 0.39 g/h/L after a 24 h fermentation period using 50% crude glycerol dilution. In comparison with other isolates (*Escherichia coli* SS1, *Escherichia coli* BL 21, BW 25113 and *Enterobacter aerogenes* HU101), *E. coli* SS1 gave the highest ethanol yield of 1.0 mol/1.0 mol glycerol, which was found to be higher when glucose was used as substrate [96].

The use of *Klebsiella* strains have also been reported in the efficient conversion of crude glycerol to ethanol. Oh et al. [97] used *Klebsiella pneumoniae* mutant, and 21.5 g/L of ethanol was generated with a productivity of 0.93 g/L/h. While Metsoviti et al. [98] employed *Klebsiella oxytoca* (FMCC-197) to obtain a mixture of 25.2 g/L ethanol, 50.1 g/L 1,3-propanediol and 16.8 g/L lactic acid using fed-batch fermentation. Metsoviti et al. [99] also used an isolated strain of *Citrobacter freundii* (FMCC-207) to produce ethanol from glycerol. Results revealed that 14.5 g/L of ethanol was produced at a yield of 0.45 g/g with a productivity of 0.7 g/L/h.

More recently, researchers have shown the potential of *Enterobacter aerogenes* for ethanol production. Jitrwung and Yargeau [100] showed that under anaerobic conditions, pH 6.4, 500 rpm, fresh feed rate 0.44 mL/min, liquid recycling ratio 0.33 and 18.5 g/L crude glycerol (15 g/L glycerol), ethanol at 0.75 mol/mol glycerol was obtained. However, ethanol enhancement has also been obtained through genetic engineering [101]. The resultant mutant strain *Enterobacter aerogenes* SUM1014 from *Enterobacter aerogenes* ATCC 29007 increased ethanol yield 1.5-fold. 34.22 g/L ethanol was obtained under optimum conditions of fermentation of 34 °C and pH 7.5 after 78 h reaction time by mutant strain, as against 13.09 g/L produced by the wild-type. The use of thermotolerant yeast, namely *Ogataeo polymorpha*, in glycerol conversion to ethanol was reported by Kata et al. [102]. Low concentration of ethanol (0.8 g/L) was obtained with the wild-type strain of *Ogataeo polymorpha*, but on overexpression with the pyruvate decarboxylase (PDC1) gene, it enhanced the ethanol concentration to 2.91 g/L. When the wild-type strain (WT) was overexpressed with both PDC1 and alcohol dehydrogenase (ADH1) genes, the ethanol concentration increased further, to 4.29 g/L at 37 °C and 140 rpm. An increase in temperature to 45 °C slightly improved ethanol production. The summary of the performance of the biocatalysts in the conversion of glycerol to ethanol as recently reported in some literature is shown in Table 7.

| Biocatalyst          | Operating Parameters               | Performance Parameters | Performance | Reference |
|----------------------|-----------------------------------|------------------------|-------------|-----------|
| *Ogataeo polymorpha* | T = 37 °C, pH = na, rpm = 140 h   | C = 0.80 ± 0.100 g/L, Y = 0.077 ± 0.036 g/g, P = 0.007 ± 0.001 g/L/h | [102]       |
| *Ogataeo polymorpha*/PDC1 | t = na               | C = 2.91 ± 0.240, Y = 0.270 ± 0.159 g/g, P = 0.022 ± 0.002 g/L/h |             |
| *Ogataeo polymorpha*/PDC1/ADH1 | t = na        | C = 4.29 ± 0.040, Y = 0.357 ± 0.073 g/g, P = 0.036 ± 0.000 g/L/h |             |
| *Enterobacter aerogenes* ATCC 29007 | T = 34 °C, pH = 7.5, t = 78 h | C = 13.09 g/L, Y = 0.156 g/L, P = 0.161 g/L/h | [101]       |
| *Enterobacter aerogenes* SUM1014 | T = 34 °C, pH = 7.5, t = 78 h | C = 35.44 g/L, Y = 0.428 g/L, P = 0.439 g/L/h |             |
| *Enterobacter aerogenes* SUM12008 | T = 34 °C, pH = 7.5, t = 20–24 h | C = na, Y = 0.75 mol/mol, P = na | [100]       |
| *Escherichia coli* SS1 | T = 37 °C, pH = na, rpm = 120 h | C = 9.23 ± 0.6 g/L, Y = 1.00 mol/mol, P = na | [96]        |
| *Escherichia coli* BL 21 | t = 24 h               | C = 9.50 ± 0.067 g/L, Y = 0.991 mol/mol, P = na |             |
| *Enterobacter aerogenes* HU101 | T = 37.5 °C, pH = 7.9, t = na | C = 3.98 ± 0.27 g/L, Y = 0.594 mol/mol, P = na | [103]       |
| Mixed culture        | Optimization            | C = 6.75 g/L, Y = na, P = na |             |
| *Escherichia coli* MG1655 | T = 37 °C, pH = na, t = 110 h | C = 4.00 g/L, Y = 0.40 g/L, P = na | [88]        |

T = Temperature, t = time, C = Concentration, Y = Yield, P = Productivity.
3.3. Methanol

Methanol is a versatile chemical that has applications in various industries. It can be directly used as fuel or as an additive to gasoline, and can also be used as an intermediate for the production of various chemicals. It has been reported that the use of methanol grew by 1% from 2003 to 2008 and was predicted to have further increased by 2% by 2013 [104]. Currently, methanol is deployed in the production of biodiesel through transesterification of vegetable oil. With the increased production of biodiesel worldwide, it is obvious that the demand for methanol will definitely increase. So if the byproduct of biodiesel production, glycerol, can be converted to methanol, it will amount to recycling back into the transesterification system, thereby saving costs and ultimately reducing the cost of biodiesel. Efforts are on the increase in the conversion of glycerol to methanol via synthesis gas, hydrogenolysis over transition metal catalyst, and steam reforming of oxygenated hydrocarbons over specific catalyst at 380 °C [104].

Haider et al. [105] demonstrated a new potential method for methanol production from crude glycerol. They reacted both refined and crude glycerol separately with water over simple basic and redox oxide catalysts (MgO, CaO, SrO, LaO and CeO$_2$) at 250–407 °C and atmospheric pressure. Results revealed high yield of methanol from both feedstocks with CeO$_2$.

The use of supercritical water conditions of 450 °C and 30 MPa was reported by Carr et al. [106]. After 30 min of reaction, 1 mol of methanol was produced per mole of glycerol fed.

4. Fuel Additives

Fuel additives are substances added or blended with fuels especially gasoline, diesel and or biodiesel to improve their fuel properties leading to excellent performance. When added to fuels it can reduce harmful emissions such as hydrocarbons, particulate, CO$_2$ and NO$_x$ emissions. It improves viscosity, antiknock, octane, cetane and cold flow properties of the fuels as well as improves the thermal stability, cleanliness and prevents corrosion of engines and engine parts [43,107,108].

There are variety of fuel additives that are petroleum and biomass-based; however, the interest in this review is the oxygenated additives that are glycerol-based.

The oxygenated additives produced from glycerol are many and are biodegradable, non-toxic and renewable. They can be classified into three broad groups namely acetin (acetyl glycerol), glycerol ethers and glycerol formal [109]. In view of their importance in improving engine performance, they have the potential to replace the existing petroleum-based additives such as methyl tert-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE). These oxygenated additives are receiving great attention from industrialists and researchers.

4.1. Acetin (Glycerol Esters)

Acetin is the product of glycerol esterification with acetic acid or carboxylic acid in the presence of homogeneous or heterogeneous catalyst [43,107]. Acetin can also be produced through acetylation of glycerol with acetic anhydride as well as direct transesterification of either triglyceride or glycerol with methyl acetate [110,111]. Some of reactions are exemplified in Schemes 4 and 5.
Acetin can be monoacetin, diacetin or triacetin. Monoacetin is a monoacetyl glycerol (2-monoacetyl-1,3-propanediol or 3-monoacetyl-1,2-propanediol), diacetin is a diacetyl glycerol (1,2-diacetyl-3-propanol or 1,3-diacetyl-2-propanol) and triacetin is a triacetyl glycerol (1,2,3-triacetylpropanol) [112]. All the acetins are of versatile application. Monoacetin and diacetin are used in cosmetics, medicines and food industries as humectant and emulsifier. They are also used as monomer for the production of biodegradable polyesters. While triacetin is most basically used as fuel additive to improve viscosity, as an antiknock and to meet the standard flash point and oxidation stability in gasoline [113]. Some authors have also reported the use of diacetin as fuel additive [114]. Triacetin has also been reported to be used as solvents and plasticizers. Series of research in the past have been undertaken with good yield using both homogeneous and heterogeneous catalysts but the heterogeneous catalyst has an edge in view of its advantages.

Acetilation of glycerol with acetic acid over different solid acid catalysts (Amberlyst-15, K-10 montmorillonite, niobic acid, zeolites (H-beta, HZSM-5 and HUSY)) have been investigated by different researchers. Results showed that Amberlyst-15 was the most active catalyst, with over 90% glycerol conversions and selectivity of 31%, 54% and 13% towards mono-, di- and triacetin respectively which was attributed to the strong acid sites on the catalyst surface but low pore size. The poor performance of the zeolites was attributed to diffusion problem of the acylium ion resulting from anhydride by the catalyst unlike the intermediate from acetic acid. Amberlyst-15 acid resin also yielded 100% triacetin, but only after 80 min of reaction at 60 °C. Silva et al. [115] also reported that niobium phosphate (NP) catalyst can also yield 100% triacetin but at a much higher temperature 120 °C. Improved performance in the production of triacetin was also observed with Amberlyst-15 when compared with zeolite HZSM-5 and HUSY in the reaction of glycerol with acetic acid as reported by Zhou et al. [116]. The authors reported that Amberlyst-15 showed high activity as well as high selectivity towards di- and triacetin, corresponding to 98.47% glycerol conversion and 8.65%, 46.56% and 44.79% selectivity towards mono-, di-, and triacetins at optimum conditions of 110 °C and acetic acid:glycerol molar ratio 9:1 as predicted by the non-linear
model, which were found to be closed to the experimental values (97.1% glycerol conversion, 47.7% diacetin and 44.5% triacetin. This performance was attributed to the high acidic sites and sufficient pore volume to contain big molecules such as di- and triacetin. Considerable improvement was also reported when yttrium was incorporated into SBA-3 catalysts [117]. 100% glycerol conversion and selectivity of 34% and 55% towards di- and triacetin were obtained under similar reaction temperature at lower molar ratio of glycerol to acetic acid of 1:4 with 3% Y/SBA-3 catalyst. The catalyst was confirmed to be stable even after being reused three times. The improved triacetin was unconnected with the strong acidity, while the high surface area with large pore size makes the diffusion of both the substrates and products possible. However, the catalyst activity decreased in the fourth cycle with reduction in glycerol conversion to 80% and triacetin reduced to 50% attributing it to reaction conditions and mass transfer limitations.

A two-step method involving esterification and acetylation of glycerol with acetic acid (in the first step) and acidic anhydride (in the second step) over synthesized sulfonic acid functionalized solid acid catalyst which is glycerol-based was reported [118]. Results showed 100% triacetin was obtained after an initial production of 22, 67, and 11% monoacetin, diacetin, and triacetin respectively at 100% glycerol conversion. The authors further showed that the first step was time dependend. The greater the time, the more triacetin was produced. The developed catalyst was found to be highly stable and recyclable. Sun et al. [119] also obtained 100% glycerol conversion and 99.0% selectivity to triacetin using synthesized magnetic solid acid catalyst calcined at 400 °C (Fe-Sn-Ti(SO$_4$)$_2$)-400) with acidic anhydride as the acetylating agent at molar ratio of 6:1 with glycerol at 80 °C within 30 min. The catalyst activity remains unchanged even after reused for three times. This may not be unconnected to the high surface area and pore volume exhibited by the catalyst. However, when acetic acid was used as an acetylating agent at the same reaction conditions, the glycerol conversion was reduced drastically to 32.3% while the selectivity to monoacetin was 100%. When the temperature increased to 140 °C, the conversion improved and the selectivity of 75.7% and 90.3% towards mono- and diacetin were achieved.

The catalytic activities of heteropolyacids were improved with the use of supported materials. Zhu et al. [120] reported complete glycerol conversion (100%) and selectivity of 6.4%, 61.3% and 32.3% towards mono-, di- and triacetin respectively at 120 °C and 4 h of reaction time when zirconia supported H$_4$SiW$_{12}$O$_{40}$ catalyst (HSiW/ZrO$_2$) was used. The catalyst activity was consistent for four consecutive reaction cycles and was resistance to impurities (water, NaCl and methanol) in crude glycerol which was attributed to good surface Bronsted acid sites and hydrothermal stability indicating its good potential for industrial application.

The use of micro and mesoporous structure materials in catalysis has aided catalytic activity in view of their high surface areas. In some, additional treatments of these materials help to increase their selectivity to a particular product as exhibited by some researchers. Khayoon and Hameed [112] developed a solid catalyst by functionalizing β-MoO$_3$ species into the framework of hybrid mesostructured silica by the thermal decomposition of molybdophosphoric acid (MPA) over the mesoporous support. When the resultant catalyst was tested in the esterification of glycerol with acetic acid, the mesoporous support with 15 wt% MPA exhibited a superior catalytic activity with complete conversion of glycerol (100%) with a selectivity of 14%, 67% and 19% towards mono-, di- and triacetin at 110 °C, 6:1 molar ratio of acetic acid to glycerol in 3 h. The catalyst was recycled four times and was found to be stable. The use of supported iron oxide nanoparticle system of a mesoporous aluminosilicate (Fe/Al-SBA-15) catalyst with >99% glycerol conversion to a mixture of 71% di- and 28% triacetin was reported [121]. Though levulinic acid was used as against the conventional acetic acid but the catalyst remains stable even after five consecutive cycles. Dalla Costa et al. [122] compared the catalytic activities of microporous zeolites (H-ZSM-5 and H-Beta) and mesoporous material (SBA-15 functionalized with propylsulfonic groups). The Propyl-SO$_3$H-SBA-15 catalyst performed with high glycerol conversion (96%) and combined selectivity to di- and triacetin (87%) in 2.5 h. The performance was attributed to balance between the level of acid sites and the formation of molecules on the surface
of the mesoporous structure. Unfortunately, the catalyst was not stable because of the leaching of sulfonic group and coke deposition occurring right from the second cycle.

Deployment of metal oxide-based catalysts has shown high selectivity towards oxygenated di- and triacetin. This can be seen in the work of Reddy et al. [123], Reddy et al. [124] and Zhang et al. [125]. Zirconia-based catalysts, namely ZrO$_2$, TiO$_2$–ZrO$_2$, WO$_x$/TiO$_2$–ZrO$_2$ and MoO$_x$/TiO$_2$–ZrO$_2$, were deployed in glycerol acetylation [123]. Results showed that the MoO$_3$/TiO$_2$–ZrO$_2$ catalyst exhibited highest catalytic activity (≈100% glycerol conversion) with a combined selectivity of 49.97% di- and triacetin. It was also noticed that the glycerol conversion and selectivity towards di- and triacetin increased with increased temperature from 40 to 120 °C. The authors further increased the reaction time and observed that as the selectivity of monoacetin decreased, that of di- and triacetin increased. After 60 h of the reaction time, selectivity of ≈80% triacetin was obtained and no more. This was attributed to further conversion of mono- and diacetin to triacetin during the acetylation.

Similarly, SO$_4^{2-}$/CeO$_2$–ZrO$_2$ catalyst exhibited the highest activity with ≈100% glycerol conversion and selectivity of 25.8%, 57.7% and 16.5% towards mono-, di- and triacetin, respectively in a shorter reaction time of 1 h when compared with other cerium-based catalysts (CeO$_2$–ZrO$_2$, CeO$_2$–Al$_2$O$_3$, SO$_4^{2-}$/CeO$_2$–Al$_2$O$_3$) [124]. When SO$_4^{2-}$/CeO$_2$–ZrO$_2$ catalyst was allowed in the acetylation reaction for 40 h, ≈90% selectivity towards triacetin was obtained [124]. On testing the reusability of the catalyst, it was found to be relatively stable but continue to depreciate after each successive run.

Zhang et al. [125] also compared a commercial solid acid catalyst, SO$_4^{2-}$/ZrO$_2$–Al$_2$O$_3$, with a prepared diatomite-loaded SO$_4^{2-}$/TiO$_2$ in the esterification of oleic acid with glycerol at 210 °C, 0.1% catalyst loading and oleic acid to glycerol mass ratio of 2:1. The prepared diatomite-loaded SO$_4^{2-}$/TiO$_2$ performed better than the commercial solid acid catalyst, SO$_4^{2-}$/ZrO$_2$–Al$_2$O$_3$ with 59.6% of diacetin in 6 h. The metal oxide-based catalysts were stable, reusable, not expensive and are sustainable over wide range of temperatures.

To save cost in biodiesel production, transesterification of methyl acetate with glycerol was carried out to produce acetin simultaneously with the biodiesel using Ca and Sn mixed metal hydroxides as catalyst [126]. CaSn(OH)$_6$ catalyst performed much better when compared to other hydroxy stannates and metal oxides like MgSn(OH)$_6$, ZnSn(OH)$_6$, SrSn(OH)$_6$, Ca(OH)$_2$, CaO, MgO, etc. The high glycerol conversion (78.2%) was attributed to higher basicity exhibited by the CaSn(OH)$_6$ catalyst contrary to the expectation since it is basic in nature.

More recently, other novel catalysts have been explored in glycerol acetylation. Okoye et al. [127] used crude glycerol as a carbon precursor to synthesize solid acid catalyst via partial carbonization and sulphonation. This in turn was used to catalyze glycerol acetylation with acetic acid to produce mixture of diacetin and triacetin. 99% glycerol conversion and 88% combined diacetin and triacetin selectivity was achieved at 110 °C in 3 h reaction time. Okoye et al. [127] also reported that the catalyst was reused in seven cycles without significant deactivation. The catalyst’s high activity was attributed to high surface acid sites density. Table 8 shows the summary of the performance of some catalysts in the conversion of glycerol to acetin as recently reported in some literature.
| Catalyst (A) | Operation Parameters | Performance (%) | TOF | Reference |
|-------------|---------------------|-----------------|-----|-----------|
| Diatomite loaded 0.3%SO$_2$–/TiO$_2$ (na) | T = 210 °C, P = 0.002 MPa, Cat = 0.1% wt Oleic acid, t = 6 h, 200 rpm, Crude Glycerol/Oleic acid (1:2) | GC = na, MA = na, DA = 59.1 ± 0.6, TA = na | *2955 | [125] |
| 0.3%SO$_2$–/TiO$_2$ (na) | | GC = na, MA = na, DA = 41.4 ± 1.0, TA = na | *2070 | |
| 0.3%SO$_2$–/ZrO$_2$–Al$_2$O$_3$ (na) | | GC = na, MA = na, DA = 39.9 ± 0.7, TA = na | *1995 | |
| Sulphonated glycerol-based carbon catalyst (na) | T = 110 °C, Cat = 2 wt%CG, t = 3 h, Crude Glycerol/Acetic Acid (1:3) | GC = na, MA = na, DA = 59.1 ± 0.6, TA = na | *2955 | [125] |
| Pr-SO$_3$–HSBA-15 (366) | T = 120 °C, Cat = 4 wt% G, t = 2.5 h, Glycerol/Acetic Acid (1:6) | GC = 99, MA = 12, DA+TA = 88 | 165 | [127] |
| CaSn(OH)$_6$ (3.95) | T = 30 °C, Cat = 0.05 g, t = 0.5 h, Glycerol/Acetic Anhydride (1:6) | GC = 58, MA = 83, DA = 7, TA = 0 | 348 | [119] |
| MgO (44.4) | T = 120 °C, Cat = 50 mg/mmol, t = 8 h, 1000 rpm, Glycerol/Levulinic Acid (1:4) | GC = 78.2, MA = 67.3, DA = 32.6, TA = na | 600 | [119] |
| Blank | | GC = 65.4, MA = 66.1, DA = 33.8, TA = na | 594 | [120] |
| 3 wt% Al-SBA-15 (747) | T = 120 °C, Cat = 50 mg/mmol, t = 8 h, 1000 rpm, Glycerol/Levulinic Acid (1:4) | GC = 58, MA = 83, DA = 17, TA = 0 | 600 | [119] |
| 0.63 wt% Fe/Al-SBA-15 (688) | T = 120 °C, Cat = 0.3 g, t = 4 h, 250 rpm, Glycerol/Oleic acid (1:2) | GC = 99, MA = 40, DA = 62.5, TA = 16.5 | 165 | [127] |
| 2 wt% HSiW/ZrO$_2$– (48.7) | T = 110 °C, Cat = 82.86 mmolH$^+$/L, t = 4.5 h, Glycerol/Oleic acid (1:2) | GC = 97, MA = 43.2, DA = 38.3 | 348 | [116] |
| HZSM-5 (368) | T = 110 °C, Cat = 82.86 mmolH$^+$/L, t = 4.5 h, Glycerol/Oleic acid (1:2) | GC = 43.5, MA = 25.7, TA = 7.7 | 348 | |
| HUSY (532) | T = 110 °C, Cat = 82.86 mmolH$^+$/L, t = 4.5 h, Glycerol/Oleic acid (1:2) | GC = 65.4, MA = 20.6, TA = 9.6 | 38 | [119] |
| Blank | T = 30 °C, Cat = 0.2 g, t = 3 h, Glycerol/Oleic acid (1:2) | GC = 82, MA = 54, DA = 26, TA = 68 | 117 | |
| 3% Y/SBA-3 (1568) | T = 110 °C, Cat = 0.2 g, t = 3 h, Glycerol/Oleic acid (1:2) | GC = 100, MA = 11, DA = 34, TA = 83 | 117 | |
| 2% Y/SBA-3 (na) | T = 110 °C, Cat = 0.2 g, t = 3 h, Glycerol/Oleic acid (1:2) | GC = 100, MA = 8.4, DA = 71.8, TA = 19.8 | 217 | |
| Glycerol Based Carbon Catalyst (na) | T = 110 °C, Cat = 0.2 g, t = 3 h, Glycerol/Oleic acid (1:2) | GC = 93.5, MA = 43.2, DA = 38.3 | 348 | |
| Amberlyst-15 (1. 6wt) (37.6) | T = 110 °C, Cat = 0.46 g, t = 1 h, Glycerol/Oleic acid (1:2) | GC = 100, MA = 22, DA = 67, TA = 11 | 217 | |
| Amberlyst-15 (3.2 wt) (37.6) | T = 110 °C, Cat = 0.46 g, t = 1 h, Glycerol/Oleic acid (1:2) | GC = 100, MA = 22, DA = 67, TA = 11 | 217 | |
| Amberlyst-15 (1) (63.2) (37.6) | T = 110 °C, Cat = 0.46 g, t = 1 h, Glycerol/Oleic acid (1:2) | GC = 98.2, MA = 12.0, DA = 62.8, TA = 29.9 | 120 | |
| 20 wt% HPW/ZrO$_2$– (48.7) | T = 110 °C, Cat = 0.46 g, t = 1 h, Glycerol/Acetic Acid (1:10) | GC = 100, MA = 6.4, DA = 56.1, TA = 32.3 | 218 | |
| 20 wt% HPMo/ZrO$_2$– (49.3) | T = 110 °C, Cat = 0.46 g, t = 1 h, Glycerol/Acetic Acid (1:10) | GC = 92.2, MA = 7.3, DA = 62.8, TA = 29.9 | 120 | |

**Table 8.** Performance of some catalysts in the conversion of glycerol to acetin as reported in some literature.
| Catalyst (A) | Operation Parameters | Performance (%) | TOF | Reference |
|-------------|---------------------|-----------------|-----|-----------|
| 0.01 mmol H$_3$PW$_{12}$O$_{40}$ | $T = 60 \, ^\circ$C, $P = 0.101$ MPa, Cat = 0.03 mmol, t = 8 h, Glycerol/Acetic Acid (1:3) | GC = 96, MA = 66, DA = 34, TA = 0 | **5.3 min$^{-1}$** | [128] |
| 0.01 mmol H$_3$PW$_{12}$O$_{40}$-calcined 200 $^\circ$C | | GC = 93, MA = 65, DA = 35, TA = 0 | **4.28 min$^{-1}$** | |
| 0.03 mmol PTSA | | GC = 85, MA = 86, DA = 8, TA = 0 | **3.1 min$^{-1}$** | |
| 0.015 mmol H$_2$SO$_4$ | | GC = 98, MA = 54, DA = 27, TA = Trace | **4.1 min$^{-1}$** | |
| CeO$_2$-Al$_2$O$_3$ (101) | $T = 120 \, ^\circ$C, Cat = 5 wt% G, t = 1 h, Glycerol/Acetic Acid (1:6) | GC = 59.4, MA = 88.1, DA = 11.6, TA = 0.3 | 119 | [124] |
| CeO$_2$-ZrO$_2$ (49) | | GC = 68.1, MA = 75.2, DA = 22.7, TA = 2.1 | 136 | |
| SO$_4^{2-}$/CeO$_2$-Al$_2$O$_3$ (136) | | GC = 79.9, MA = 58.9, DA = 35.5, TA = 5.6 | 160 | |
| SO$_4^{2-}$/CeO$_2$-ZrO$_2$ (92) | | GC = 100, MA = 25.8, DA = 57.7, TA = 16.5 | 200 | |

A = Surface area (m$^2$/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, MA = Monoacetin selectivity, DA = Diacetin selectivity, TA = Triacetin selectivity, TOF (mmol g$^{-1}$ cat. h$^{-1}$) = Turnover frequency calculated based on the glycerol conversion/* product yield per gram catalyst per total reaction time (h), ** TOF as reported in the journals, na = not available, nd = not determined.
4.2. Glycerol Ethers

Glycerol ethers are highly alkylated glycerol with several applications. In addition to being used as oxygenated fuel additives, they are also used as solvents in reactions and as cleaning agent in industry. Glycerol ethers are highly branched and are synthesized through etherification of glycerol with alkenes (most commonly isobutene) and alcohols (most commonly tert-butanol) in the presence of homogeneous or heterogeneous catalyst (Schemes 6 and 7) [107]. For ease of reference, glycerol ethers may be classified as protic (3-alkoxy-1,2-propandiols (monoether) and 1,3-dialkyoxy-2-propanols (diether)) and non-protic (1,2,3-trialkxyoxypropanes (triether)) [129].

![Scheme 6](image.png)

**Scheme 6.** Conversion of glycerol to glycerol ethers by etherification with alkene (isobutene) (MTBG: mono-tert-butylglycerol, DTBG: di-tert-butylglycerol, TTBG: tri-tert-butylglycerol).

![Scheme 7](image.png)

**Scheme 7.** Conversion of glycerol to glycerol ethers by etherification with alcohol (tert-butanol).

In view of its usage as oxygenated fuel, etherification of glycerol has received massive attention over the years and several studies involving different catalysts have been reported.

Goncalves et al. [130] prepared sulfonated carbon-based catalysts from agro-industrial wastes (sugar cane bagasse, coconut husk, and coffee grounds), and they proved to be highly efficient. In fact, the sugar cane bagasse-based catalyst was more effective than the commercially available Amberlyst-15. Glycerol conversion and selectivity to di-tertiary butyl glycerol and tri-tertiary butyl ether glycerol of 80.9% and 21.3%, respectively, were achieved after 4 h. The performance of the catalysts was attributed to the sulfonic groups present.

When different homogeneous alkali catalysts (LiOH, NaOH, KOH and Na₂CO₃) were tested in the glycerol etherification, complete glycerol conversion were achieved but after 8 h reaction time. Selectivity of 33% towards di-tertiary butyl glycerol was achieved with LiOH, while others gave lower selectivity despite the longer reaction time and was attributed to the exhibition of very high alkalinity in the reaction mixture [131].
The use of SiO$_2$-supported tungstophosphoric acid (H$_3$PO$_4$W$_{12}$, HPW) catalyst was excellent, with 97.1% conversion of glycerol with formation of mono, di and tri-ethers at 160 $^\circ$C and ethanol:glycerol molar ratio of 6:1 compared to other catalysts (H-ZSM5, H-$\beta$, tungstophosphoric acid (H$_3$PO$_4$W$_{12}$, HPW), FeCl$_3$, AlCl$_3$, and H$_2$SO$_4$) under the same conditions [132]. However, deactivation of the SiO$_2$-supported HPW was reported due to leaching.

The use of zeolites and sulfonic group containing resin catalysts appear to be more stable and generally more acceptable in view of their performance and ease of separation as exemplified by several research works. When Viswanadham and Saxena [133] compared variously prepared resins (Amberlyst-15 and Amberlyst-35), zeolites (Beta-BEA and USY) and mordenite (MOR)-based catalysts in batch and fixed-bed reactor, it was discovered that the resin catalysts exhibited higher glycerol conversion and ether selectivity at relatively lower reaction temperature (75 $^\circ$C) than the zeolite-based catalysts (90 to 110 $^\circ$C). However, the zeolite-based catalysts performed better in terms of stability to produce high amounts of di-tertiary butyl glycerol and TTBG of glycerol. At optimized conditions, nano-beta (N-BEA) zeolite catalyst exhibited above 95% conversion of glycerol with more than 45% and 54% selectivity to di-tertiary butyl glycerol and tri-tertiary butyl ether glycerol in a fixed-bed reactor. This behavior has been attributed to the pore structure of zeolites. Bigger porosity favors large molecule formation. Similarly, Veiga et al. [134] reported the performance of USY, HZSM-5 and H-Beta zeolites after calcination. H-Beta and USY-650-L-2 zeolites showed higher activity with glycerol conversion of up to 74 and 75% with tert-butyl alcohol and 67 and 81% with ethyl alcohol with selectivity towards mono- and di-substituted ethers which was attributed to the fact that these catalysts exhibit higher hydrophobicity (low hydrophilicity). However, the earlier findings of Pinto et al. [135] showed that Amberlyst-15 acid resin exhibited the best performance with 96% of glycerol conversion and 80% selectivity to the ethyl ethers at 180 $^\circ$C at ethanol:glycerol molar ratio of 3:1 and within the reaction time of 4 h when it was compared with clays and zeolites catalysts which was attributed to higher acid strength of the Amberlyst-15 acid resin catalyst. The catalyst also showed good stability because there was no any significant deactivation noticed after three consecutive reuses.

In another study, Estevez et al. [136] reported the use of silica-based and organosilica-based hybrid materials as catalysts in glycerol etherification with tert-butyl alcohol. Of all the hybrid materials, S$_{50}$TS$_{50}$O catalyst performed better than the highly active commercial sulfonic resin (Amberlyst-15) with glycerol conversion of 98% after 24 h reaction time at 75 $^\circ$C. The high performance was attributed to the high density of acid sites, textural and chemical properties of the catalyst as well as its ability to prevent the effect of water due to silanol groups on the hybrid silicas. Table 9 shows the summary of the performance of some catalysts in the conversion of glycerol to glycerol ethers as recently reported in some literature.
Table 9. Performance of some catalysts in the conversion of glycerol to glycerol ethers as reported in some literature.

| Catalyst (A)          | Operation Parameters                                      | Performance (%)       | TOF     | Reference |
|-----------------------|-----------------------------------------------------------|-----------------------|---------|-----------|
| USY-650-L-2 (741)     | T = 200 °C, Cat = 3.5 wt% G, t = 6 h, Glycerol/Ethyl alcohol (1:9) | GC = 67, ME = 73, DE = 25, TE = 2 |         |           |
| HZSM-5 (337)          | T = 90 °C, Cat = 7.6 wt% G, t = 4 h, Glycerol/tert-butyl alcohol (1:4) | GC = 74, ME = 79, DE = 21, TE = 0 | nd [134]|
| H-Beta (623)          | T = 180 °C, Cat = none, t = 8 h, Glycerol/Ethanol (1:6)       | GC = 92, ME = 71, DE = 17, TE = 12 | 6       |           |
| Blank                 | T = 180 °C, Cat = 2.1 g, t = 4 h, Glycerol/Ethanol (1:6)      | GC = 59, ME = 72, DE = 18, TE = 10 | 8       |           |
| K-10 (260)            | T = 180 °C, Cat = 2.5 g, t = 6 h, Glycerol/Ethanol (1:3)      | GC = 61, ME = 94, DE = 4, TE = 2 | 4       |           |
| HZSM-5 (408)          | T = 180 °C, Cat = 1.9 g, t = 8 h, Glycerol/Ethanol (1:3)      | GC = 40, ME = 95, DE = 3, TE = 2 | 5 [135]|
| H-Beta (564)          | T = 180 °C, Cat = 1.1 g, t = 4 h, Glycerol/Ethanol (1:6)      | GC = 99, ME = 75, DE = 14, TE = 10 | 12      |           |
| Amberlyst-15 (53)     | T = 180 °C, Cat = 0.32 g, t = 8 h, Glycerol/Ethanol (1:6)     | GC = 95, ME = 65, DE = 19, TE = 16 | 6       |           |
| K-10 (260)            | T = 180 °C, Cat = 2.1 g, t = 4 h, Glycerol/Ethanol (1:6)      | GC = 60, ME = 79, DE = 14, TE = 7 | 5       |           |
| HZSM-5 (337)          | T = 180 °C, Cat = 1.9 g, t = 4 h, Glycerol/Ethanol (1:3)      | GC = 61, ME = 94, DE = 4, TE = 2 | 4       |           |
| Amberlyst-15 (53)     | T = 180 °C, Cat = 0.32 g, t = 8 h, Glycerol/Ethanol (1:6)     | GC = 95, ME = 79, DE = 12, TE = 9 | 12      |           |
| Amberlyst-15 (53)     | T = 180 °C, Cat = 0.32 g, t = 8 h, Glycerol/Ethanol (1:6)     | GC = 95, ME = 79, DE = 12, TE = 9 | 12      |           |
| S90T50O (538)         | T = 75 °C, Cat = 5 wt% G, t = 17 h, Glycerol/tert-butyl alcohol (1:4) | GC = 6, ME = 97, DE + TE = 0.2 | nd [136]|
| S90T50O (18)          | T = 75 °C, Cat = 2.1 g, t = 6 h, Glycerol/Ethanol (1:3)      | GC = 32, ME = 87, DE + TE = 4.0 | nd       |
| Amberlyst-15 (39)     | T = 75 °C, Cat = 2.5 g, t = 6 h, Glycerol/Ethanol (1:3)      | GC = 51, ME = 65, DE + TE = 18.0 |         |           |
| Amberlyst-15 (53)     | T = 75 °C, Cat = 5 wt% G, t = 24 h, Glycerol/tert-butyl alcohol (1:4) | GC = 98, ME = 71, DE + TE = 28.0 |         |           |
| Amberlyst-35 (50)     | T = 75 °C, Cat = 5 wt% G, t = 24 h, Glycerol/tert-butyl alcohol (1:4) | GC = 98, ME = 71, DE + TE = 28.0 |         |           |
| Zedite-BEA (450)      | T = 90 °C, Cat = 0.38 g, t = 4 h, Glycerol/tert-butyl alcohol (1:4) | GC = 97.8, ME = 94.2, DE = 5.8, TE = na | 35      |           |
| Mordenite (400)       | T = 90 °C, Cat = 0.38 g, t = 4 h, Glycerol/tert-butyl alcohol (1:4) | GC = 97.7, ME = 94.8, DE = 5.2, TE = na | 35      |           |
| Ultra-Stable Y (USY) (614) | T = 120 °C, Cat = 5 wt% G, t = 4 h, Glycerol/tert-butyl alcohol (1:4) | GC = 61.5, ME = 60.5, DE + TE = 21.8 |         |           |
| Sulfonated sugar cane bagasse (<10) | T = 240 °C, P = atm. press., Cat = 2 wt% G, t = 8 h, Glycerol, no solvent used | GC = 100, ME = na, DE = na, TE = na | nd [131]|
| Sulfonated coconut husk (<10) | T = 120 °C, Cat = 5 wt% G, t = 4 h, Glycerol/tert-butyl alcohol (1:4) | GC = 61.5, ME = 60.5, DE + TE = 21.8 |         |           |
| Sulfonated coffee grounds (<10) | T = 240 °C, P = atm. press., Cat = 2 wt% G, t = 8 h, Glycerol, no solvent used | GC = 100, ME = na, DE = na, TE = na | nd [131]|
| LiOH (na)             | T = 240 °C, P = atm. press., Cat = 2 wt% G, t = 8 h, Glycerol, no solvent used | GC = 100, ME = na, DE = na, TE = na | nd [131]|
| NaOH (na)             | T = 240 °C, P = atm. press., Cat = 2 wt% G, t = 8 h, Glycerol, no solvent used | GC = 100, ME = na, DE = na, TE = na | nd [131]|
| Na2CO3 (na)           | T = 240 °C, P = atm. press., Cat = 2 wt% G, t = 8 h, Glycerol, no solvent used | GC = 100, ME = na, DE = na, TE = na | nd [131]|

GC = glycerol, ME = methyl ether, DE = diethyl ether, TE = triethyl ether.
Table 9. Cont.

| Catalyst (A)        | Operation Parameters | Performance (%) | TOF | Reference |
|---------------------|----------------------|-----------------|-----|-----------|
| Blank               |                       | GC = 0, ME = na, DE = -, TE = na | -   |           |
| HZSM5-20 (na)       | T = 160 °C, P = 3.0 MPa N\(_2\), Cat = 1 g, t = 20 h, Glycerol/Ethanol (1:6) | GC = 7.3, ME = 80, DE = 7.9, TE = 12.1 | 2   |           |
| HZSM5-100 (na)      |                       | GC = 1.1, ME = 100, DE = 0, TE = 0 | 3   |           |
| H-β (na)            |                       | GC = 5.7, ME = 100, DE = 0, TE = 0 | 2   |           |
| H\(_2\)PO\(_4\)W\(_{12}\) (na) |               | GC = 68.9, ME = 79, DE = 14.8, TE = 6.2 | 19  | [132]     |
| H\(_2\)SO\(_4\) (na) |                       | GC = 70, ME = 78.6, DE = 14.9, TE = 6.5 | 19  |           |
| FeCl\(_3\) (na)     |                       | GC = 19.2, E = 72.4, DE = 16.3, E = 11.3 | 5   |           |
| AlCl\(_3\) (na)     |                       | GC = 10.2, ME = 79.6, DE = 9.4, TE = 11 | 3   |           |
| H\(_3\)PO\(_4\)W\(_{12}\) (na) | T = 160 °C, Cat = 3.3 g, t = 20 h, Glycerol/Ethanol (1:6) | GC = 97.1, ME = 61.9, DE = 28.1, =10.0 | 26  |           |

A = Surface area (m\(^2\)/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, ME = Monoglycerolether selectivity, DE = Diglycerolether selectivity, TE = Triglycerolether selectivity, STSO = Sulfonated organosilicas, TOF (mmol g\(^{-1}\) cat. h\(^{-1}\)) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined.
4.3. Glycerol Formal

Glycerol formal is a mixture of both solketal (4-hydroxymethyl-1,3-dioxolane) and acetal (5-hydroxy-1,3-dioxane) and is synthesized by the condensation of glycerol with aldehydes or ketones over homogeneous and/or heterogeneous catalysts (Scheme 8). The predominant acetal or ketal in the mixture depends on the conditions of the reaction especially the catalyst used [43,115,137].

\[
\text{Glycerol} + \text{Aldehyde/Ketone} \xrightarrow{\text{Catalyst}} \text{Solketal} + \text{H₂O}
\]

Scheme 8. Conversion of glycerol to solketal and acetal by acetalization with aldehyde or ketone.

4.3.1. Solketal

Solketal is a colorless and odorless 5-membered ring compound liquid that is completely soluble in water [107]. In addition to reducing particulate emission and improving cold flow properties, solketal can also reduce gum formation, improve oxidation stability and can be used as solvent and plasticizer in a polymer industry [138,139]. Solketal production has also received considerable attention as reported in the literature.

The reaction of glycerol and acetone in a glass reactor was catalyzed with p-toluenesulfonic acid under reflux for 12 h. Findings from the experiment showed that with increased acetone to glycerol molar ratio, the conversion toward solketal increased. At the end of 12 h, 1:6 molar ratio gave the highest conversion (82.7%) followed by 1:4 molar ratio (70.9%) and 1:2 molar ratio (54.9%) [140]. Higher yield of over 90% solketal and high selectivity has been previously reported by Vicente et al. [141] using the same catalyst with a high molar ratio of glycerol:acetone of 1:6.

To know the possibility of using other ketones in the condensation, De Torres et al. [142] used several linear, branched and cyclic ketones (acetone, butanone, cyclopentanone, 4-methyl-2-pentanone and 3,3-dimethyl-2-butanone) over several catalysts. Results revealed that on using sulfuric acid as catalyst, the yield was strongly depending on the structure of the starting ketone. Yields above 80% were obtained for ketals using acetone, butanone and cyclopentanone in 1 h. While moderate yield of about 60% were obtained for ketals using 4-methyl-2-pentanone and 3,3-dimethyl-2-butanone due to the steric hindrance caused by isobutyl and tert-butyl groups. However, in the case of 3,3-dimethyl-2-butanone it took a longer reaction time of 4 h. The use of some heterogeneous catalysts has revealed better performance as exhibited by De Torres et al. [142]. Excellent yield of 100% and 81.4% solketal were obtained when fluorosulfonic resins (NR-50 and SAC-13) and K10-montmorillonte were used as catalysts in the condensation of glycerol and cyclopentanone at a molar ratio 1:1, 60 °C in reaction time of 2 h.

Similarly, excellent yield of solketal was also obtained with increase in the molar ratio of acetone/crude glycerol irrespective of the heterogeneous catalysts used in a new continuous-flow process [143]. Among all the solid acid catalysts tested (Amberlyst wet, zeolite, Amberlyst dry, zirconium sulfate, montmorillonite and polymyx), the use of Amberlyst Wet produced the maximum solketal yield at 40 °C, 4.1 MPa and weight hour space velocity (WHSV) of 4 h⁻¹ (being 88% at the acetone/crude glycerol molar ratio of 6.0). However, all the catalysts, except polymyx, showed a slight decrease in its activity for up to 24 h on-stream, which may be due to the loss of acidity. The above process was further optimized using response surface methodology based on Box-Behnken design at optimal conditions (temperature of 25 °C, acetone/crude glycerol molar ratio of 4 and weight
hour space velocity (WHSV) of 2 h\(^{-1}\)) and maximum yield of 94 ± 2% solketal was obtained [144]. The catalyst, Amberlyst Wet, demonstrated that it could be regenerated and reused for 24 h with little or no sign of deactivation. Furthermore, [145] was able to show the spontaneous of the reaction using thermodynamic and kinetic studies. The authors concluded that the rate of the reaction increased with increase in temperature, quantity of catalyst and acetone:glycerol molar ratio, with the effect of pressure and agitation was negligible.

Molybdenum phosphate catalysts supported on SBA-15 with varying MoPO loadings (5–50 wt%) showed excellent yield [146]. 40 wt% MoPO/SBA-15 catalyst exhibited the best activity with 98% selectivity towards solketal and 100% glycerol conversion within the reaction time of 2 h due to high Bronsted acid sites. However, leaching of the catalyst was observed leading to decreased activity. The authors further reported that the glycerol conversion and selectivity during acetalization strongly depends on catalyst loading, glycerol to acetone molar ratio and the reaction time.

The use of acid-treated zeolite has also shown great performance. Acid (hydrochloric acid, nitric acid and oxalic acid)-treated beta zeolite showed enhanced catalytic activity with the nitric acid-treated beta zeolite exhibiting the highest glycerol conversion with 94.26% and 94.21 wt% solketal yield [147]. The excellent performance of the nitric acid-treated beta zeolite was attributed to the higher specific surface area, mesoporosity and strong acidity. Similarly, when ammonium-treated beta zeolites catalysts (H-Beta-1 small crystallite size) were tested and compared with other zeolites (H-Beta-2, H-ZSM-5 H-Y and H-Mordenite) and other catalysts (Amberlyst-15, K-10, CsHPW and MoO\(_3\)), 5 wt% H-Beta-1 zeolite catalyst was the most active with 86% glycerol conversion and 98.5% selectivity towards solketal [148]. The catalysts were reusable without any significant loss in their activities. The excellent performance was attributed to the presence of high number of strong acid site on small crystal of the zeolites (H-Beta-1).

Metal, bimetals and trimetals supported catalysts have also shown good potentials in solketal production as reported by Khayoon and Hameed [149], de Carvalho et al. [150], Rodrigues et al. [151] and Kapkowski et al. [152] with low to high glycerol conversion (33–100%) and high solketal selectivity (98–100%).

4.3.2. Acetal

Glycerol acetal is a viscous six-membered ring liquid. In addition to being used as fuel additive, it is also used as solvent in paint and pesticide industries. Acetalization of glycerol to predominant product of acetal has been reported in the literature.

Acetalization of glycerol with benraldehyde was carried out using solid catalyst, mesoporous MoO\(_3\)/SiO\(_2\) with varying MoO\(_3\) loadings (1–20 mol%) [153]. Results indicate that 20 mol% MoO\(_3\) loading was found to be the most active catalyst at 100 °C for 8 h with a maximum conversion of benraldehyde to be 72% and 60% selectivity towards the six-membered acetal. Further studies of using various aldehydes (\(p\)-tert-butylbenzaldehyde, 2-hydroxy-5-nitrobenzaldehyde, anisaldehyde, \(o\)-chlorobenzaldehyde, benzaldehyde \(n\)-heptaldehyde, \(n\)-butyaldehyde, \(trans\)-cinnamaldehyde and phenylacetaldelyde) by the same authors revealed that with substituted benzaldehydes under the same reaction conditions, the conversion of aldehydes decreased with increase in selectivity to acetal. They concluded that aliphatic aldehydes gave comparatively higher conversions when compared to aromatic aldehydes which were attributed to the level of unsaturation. However, Da Silva et al. [3] reported higher yield (95%) with 70% selectivity towards 6-membered ring when zeolites were used as catalyst. Zeolite beta was found to be the most active within a shorter reaction time of 1 h compared to the foregoing. Furthermore, a shorter reaction time of 30 min was enough to achieve good performance when solid acid metal oxides supported catalysts were used as reported below. Sudarsanam et al. [154] investigated the use of ZrO\(_2\), TiO\(_2\)-ZrO\(_2\), MoO\(_x\)/ZrO\(_2\) and MoO\(_x\)/TiO\(_2\)-ZrO\(_2\) catalysts using benzaldehyde and its mono substituted derivatives (\(o\)-chloro benzaldehyde, \(p\)-chloro benzaldehyde, \(p\)-anisaldehyde, \(o\)-nitrobenzaldehyde and \(p\)-nitrobenzaldehyde). The MoO\(_x\)/TiO\(_2\)-ZrO\(_2\) catalyst exhibited the highest glycerol conversion (74%) with 51% selectivity towards1,3-dioxane product
within the reaction time of 30 min with benzaldehyde attributable to the presence of a greater number of acidic sites. Lower conversion of glycerol and high selectivity towards 1,3-dioxane were reported with the mono substituted derivatives of benzaldehyde due to steric hindrance. However, temperature (60–100 °C) exhibited significant effect on the glycerol conversion when compared with the use of solvents (aldehydes listed above).

The use of supported iron oxide nanoparticle system of a mesoporous aluminosilicate heterogeneous catalyst (Fe/Al-SBA-15) in acetalization of glycerol with paraformaldehyde, benzaldehyde, furfural and acetone was investigated at 100 °C [121]. All the reactions gave very good conversion and selectivity to glycerol formal. With paraformaldehyde, up to 90% conversion was achieved with dioxane and dioxolane selectivity of 66 and 34% within 8 h reaction time. However, when the glycerol:paraformaldehyde molar ratio increased to 1:2, the glycerol conversion increased up to 100% with increase in dioxane selectivity (76%). The catalyst, Fe/Al-SBA-15, was found to be highly active, stable and reusable despite the long hours of reaction which was attributed to the large number of active sites.

Chen et al. [155] reported the use of different heterogeneous acid functionalized catalysts (mesoporous organosilicas (PMOs), zeolite ZSM-5, heteropoly compound Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ and Amberlyst-15) in the acetalization of glycerol with aqueous formaldehyde to glycerol formal. Cs$_{2.5}$H$_{0.5}$PW$_{12}$O$_{40}$ exhibited the best performance with glycerol conversion of 70% within 1 h of reaction time. The authors also reported that catalyst load, glycerol to formaldehyde molar ratio and temperature play critical roles in the distribution of the two isomers of acetal (5- and 6-membered rings). Table 10 shows the summary of the performance of some catalysts in the conversion of glycerol to solketal and acetal as recently reported in some literature.
### Table 10. Performance of some catalysts in the conversion of glycerol to solketal and acetal as reported in some literature.

| Catalyst (A)                      | Operation Parameters                                                                 | Performance (%)          | TOF   | Reference |
|-----------------------------------|---------------------------------------------------------------------------------------|--------------------------|-------|-----------|
| β-Zeolite (467.4)                 | T = 60 °C, Cat = 10 wt% G, t = 4 h, Bioglycerol/Acetone (1:6)                         | GC = 70.13, SK = 64.65, AT = 5.48 | nd    | [147]    |
| HNO3-treated β-Zeolite (597.15)   | T = 60 °C, Cat = 10 wt% G, t = 4 h, Bioglycerol/Acetone (1:6)                         | GC = 86.32, SK = 83.71, AT = 2.61 | nd    |           |
| HCl-treated β-Zeolite (607.22)    | T = 60 °C, Cat = 10 wt% G, t = 4 h, Bioglycerol/Acetone (1:6)                         | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Oxalic acid-treated β-Zeolite (527.09) | T = 60 °C, Cat = 10 wt% G, t = 4 h, Bioglycerol/Acetone (1:6)                | GC = 92.45, SK = 89.60, AT = 2.85 | nd    |           |
| Blank                             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 0.6, SK = 100, AT = na, OT = 0 | nd    |           |
| SiO2 (na)                         | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 0.3, SK = 100, AT = na, OT = 0 | nd    |           |
| Mo (na)                           | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 92.6, SK = 94.6, AT = na, T = 5.4 | nd    |           |
| OXalic acid-treated Mo (na)       | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Blank                             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| MoO3/SiO2 (na)                    | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Blank                             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| 1% Re/SiO2 (na)                   | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Blank                             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| 1% Ru/Mo (na)                     | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Blank                             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| 10 wt% MoPO/SBA-15 (573)          | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Amberlyst-15 (na)                 | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| K-10 Clay (na)                    | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| CsHPW (na)                        | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| MoO3/SiO2 (na)                    | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| HZSM-5 Zeolite (na)               | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| H-mordenite Zeolite (na)          | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| H-Y Zeolite (na)                  | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| H-Beta-1 Zeolite (na)             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Amberlyst-35 Dry (35)             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Amberlyst-35 Wet (35)             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Amberlyst-35 Wet (35)             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Zeolite (480)                     | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Montmorillonite (264)             | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Polymax (na)                      | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
| Zirconium Sulphate (na)           | T = 55 °C, Cat = 50 mg, t = 1.5 h, Glycerol/Butanone (1:10), under N2 flow          | GC = 94.26, SK = 94.21, AT = 0.05 | nd    |           |
Table 10. Cont.

| Catalyst (A) | Operation Parameters | Performance (%) | TOF | Reference |
|--------------|----------------------|-----------------|-----|-----------|
| Amberlyst-35 Dry (35) | T = 40 °C, P = 4.1 MPa, WHSV = 4/h, Glycerol/Acetone (1:6) | GC = 88 ± 3, SK = 86 ± 3, AT = na, OT = na | 4396 | |
| Amberlyst-35 Wet (35) | | GC = 89 ± 3, SK = 88 ± 4, AT = na, OT = na | 4446 | |
| Zeolite (480) | | GC = 85 ± 2, SK = 84 ± 2, AT = na, OT = na | 4246 | |
| Montmorillonite (264) | T = 100 °C, Cat = 5 wt%, t = 30 min, Glycerol/Benzaldehyde (1:1) | GC = 58, SK = 47, AT = 53 | 252 | [154] |
| Polymax (na) | | GC = 64, SK = 47, AT = 53 | 278 | |
| Zeolite Sulphate (na) | | GC = 70, SK = 47, AT = 53 | 304 | |
| ZrO₂ (42) | | GC = 74, SK = 49, AT = 51 | 321 | |
| TiO₂-ZrO₂ (30) | | GC = 28, SK = 75, AT = 6, OT = 25 | - | |
| 10 wt% MoOₓ/ZrO₂ (94) | | GC = 33, SK = 81, AT = 0, OT = 19 | 30 | |
| Blank Activated Carbon (AC) (780) | T = 45 °C, Cat = Nil, t = 3 h, Glycerol/Acetone (1:8), 530 rpm, under N₂ flow | GC = 83, SK = 62, AT = 26, OT = 12 | 75 | [149] |
| 1% Ni/AC (na) | | GC = 98, SK = 86, AT = 10, OT = 4 | 89 | |
| 3% Ni/AC (na) | | GC = 54, SK = 77, AT = 23, OT = 0 | 49 | |
| 5% Ni/AC (582) | | GC = 57, SK = 66, AT = 32, OT = 0 | 51 | |
| 1% Zr/AC (799) | T = 45 °C, Cat = 0.2g, t = 3 h, Glycerol/Acetone (1:8), 530 rpm, under N₂ flow | GC = 57, SK = 66, AT = 37, OT = 0 | 61 | |
| 5% Zr/AC (na) | | GC = 67, SK = 63, AT = 30, OT = 0 | 61 | |
| 5% Ni-1% Zr/AC (612) | | GC = 100, SK = 74, AT = 26, OT = 0 | 90 | |
| 1% Ni-5% Zr/AC (74.9) | | GC = 74, SK = 61, AT = 39, OT = 0 | 67 | |

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, SK = Solketal selectivity, AT = Acetal selectivity, OT = Other product(s), TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), ** TOF as reported in the journals, na = not available, nd = not determined.
5. Other Precursor Bio-Based Chemicals from Glycerol

5.1. Acrolein

Acrolein, also known as propenal, is the simplest unsaturated aldehyde, and it is a versatile intermediate compound obtained via the dehydration of glycerol (Scheme 9). This intermediate is usually manipulated via suitable catalyst and reaction conditions to yield polymers, acrylic acid esters, super absorbers, adhesive and detergents [34].

\[
\text{HO} \text{CH} \text{CH} \text{OH} \xrightarrow{\text{Acid catalyst}} 2\text{H}_2\text{O}
\]

Scheme 9. Conversion of glycerol to acrolein by dehydration.

In acrolein selectivity, the choice of catalyst is critical and research have shown over the years that the presence of Bronsted acid sites favors high acrolein production [156]. So many catalysts have been employed in acrolein production over the years. Some of these catalysts include sulfuric acid, niobic acid, alumina, silica, metal oxides on different support materials, zeolites, heteropoly acids, hydrotalcite-type compounds, organic acids, etc. Some of these research works are reviewed below.

Sulfuric acid has been used as catalyst to convert glycerol in hot compressed water to acrolein. Rajan et al. [157] obtained up to 74% selectivity to acrolein under supercritical conditions with the sulfuric acid catalyst within reaction time of 12 s. TiO_2 and WO_3/TiO_2 in supercritical water at 400 °C and 33 MPa was examined using a fixed-bed flow reactor [158]. It was observed that the supercritical condition changed the structure of TiO_2 from anatase to rutile type. However, the rate of reaction was found to increase with increase in WO_3 content of the catalyst, which was attributed to higher surface area and stronger acidity of WO_3/TiO_2 catalysts. The use of supercritical conditions was attributed to the fact that at lower temperatures other products such as acetaldehyde, propionaldehyde, methanol, allyl alcohol, carbon monoxide, carbon dioxide, hydrogen, etc. were also formed [158].

Gu et al. [159] used supported nickel sulfate catalyst prepared at lower calcination temperature (350 °C) and moderate loading (17NiSO_4-350). More than 90% glycerol conversion was obtained with acrolein selectivity higher than 70 mol% even after 10 h of reaction. However, it was noticed that the catalyst became deactivated due to oxidation and loss of sulfur. Several catalysts and support materials (dodecatungstophosphoric acid (DTP) supported on hexagonal mesoporous silica (HMS), K-10 clay and octahedral molecular sieves (OMS)) were investigated [160]. Results showed that HMS acted as a better support material for acrolein selectivity compared to K-10 clay and OMS. 20% w/w DTP/HMS catalyst resulted in 94% of glycerol conversion and 80% of acrolein selectivity at 225 °C. The catalyst deactivation was not reported after six times reuse. However, subsequently the catalyst suffered deactivation due to coke deposition. In a similar vein, using the deactivation data obtained from the 20% w/w DTP/HMS catalyst above, a new robust one, MUICat-5 catalyst (W-Zr-Al/HMS composition) was synthesized and on testing, gave 86% glycerol conversion and 60% selectivity to acrolein. Unlike the DTP/HMS catalyst, the MUICat-5 was not deactivated even after reuse up to six times and did not affect the glycerol conversion and acrolein selectivity.

The use of Cs heteropoly salt as the catalyst at 275 °C and 1bar gave excellent results [161]. 100% glycerol conversion and 98% selectivity of acrolein were achieved. However, when Wells–Dawson and Keggin-type phosphotungstic acids supported on MCM-41 catalysts (H_3PW_12O_40/MCM-41 and H_9P_2W_18O_62/MCM-41) were synthesized and used in the gas phase dehydration of glycerol to acrolein, not much was achieved [162]. H_9P_2W_18O_62/MCM-41 catalyst gave 51.3% while H_3PW_12O_40/MCM-41 gave 43.8% acrolein respectively. The low catalytic activity was attributed to the leaching of heteropolyacids (HPW) and coke deposition.
The catalyst performance was attributed to its micro-mesoporous nature with high pore volume as well. The decrease in the activity of the catalysts after 5 cycles with time was negligible. The method of preparing catalysts also plays a great role in acrolein production. The use of zeolite-based catalysts has also shown great potential in acrolein production from glycerol. The use of nanocrystalline HZSM-5 catalyst with a Si/Al ratio of 65 was compared with the bulk HZSM-5 catalyst [164]. The nanocrystalline HZSM-5 catalyst showed enhanced catalytic performance in glycerol dehydration even at very high space velocity (GHSV) of 1438 h⁻¹ with excellent glycerol conversion and selectivity even with crude glycerol. When glycerol was dehydrated over ZSM-5 zeolite treated with NaOH, oxalic acid or HCl and later impregnated with vanadium oxides (V₂O₅), over 65% glycerol conversion was achieved with high selectivity towards acrolein [165]. The catalyst performance was attributed to its micro-mesoporous nature with high pore volume as well as the presence of redox-active sites.

Glycerol conversion of 54.2% and acrolein yield of 44.9 wt% were achieved over the montmorillonite catalyst activated by aqueous sulfuric acid (10 wt%) at optimum conditions of 320 °C, liquid hourly space velocity (LHSV) of 18.5 h⁻¹ and 10 wt% glycerol solution [166]. Table 11 shows a summary of the performance of some catalysts in the conversion of glycerol to acrolein as recently reported in some literature.

### Table 11. Performance of some catalysts in the conversion of glycerol to acrolein as reported in some literature.

| Catalyst (A)                      | Operation Parameters                                                                 | Performance (%) | TOF   | Reference |
|----------------------------------|--------------------------------------------------------------------------------------|-----------------|-------|-----------|
| H₃PWₓO₂ₓOₙ/MCM-41 (615)          | T = 320 °C, P = atm. press., t = 1–5 h, Cat = 0.5 g, 10 wt% glycerol solution, FFR = 3 mL/h, under 10 mL/min N₂ flow | GC = >95, S = 43.8 ** | 103.7 | [162]     |
| H₃PWₓO₂ₓOₙ/H₂/MCM-41 (601)       | T = 300 °C, P = atm. press., t = 4 h, Cat = 100 mg, 20 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 90, S = 33 | 900   |           |
| ZSM-5 (NaOH-treated) (na)        | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = >95, S = 24 | 890   |           |
| ZSM-5 (H₂C₂O₄·H₂O-treated) (na) | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 29 | 1000  |           |
| ZSM-5 (HCl-treated) (na)         | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 35 | 1000  |           |
| 10 wt% V₂O₅/ZSM-5 (na)           | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 35 | 1000  |           |
| (NaOH-treated) (na)              | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 89, S = 24 | 890   |           |
| 10 wt% V₂O₅/ZSM-5 (HCl-treated) (na) | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 35 | 1000  |           |
| 10 wt% V₂O₅/ZSM-5 (HCl-treated) (na) | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 35 | 1000  |           |
| 10 wt% CuO/CeO₂-ZrO₂ (na)        | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 89, S = 24 | 890   |           |
| 10 wt% CuO/CeO₂-ZrO₂ (na)        | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 35 | 1000  |           |
| 10 wt% CuO/CeO₂-ZrO₂ (na)        | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 100, S = 35 | 1000  |           |
| SO₃H-Activated                    | T = 300 °C, P = atm. press., t = 1 h, Cat = 100 mg, 10 wt% glycerol solution, FFR = 0.05 mL/min, under 30 mL/min N₂ flow | GC = 89, S = 24 | 890   |           |

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, W/GHSV = Water/Gas Hourly Space Velocity, FFR = Feed Flow Rate, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), ** TOF as reported in the journals, nd = not determined.
5.2. Glycerol Carbonate

Glycerol carbonate (GC), also named as 4-hydroxymethyl-2-oxo-1,3-dioxolane, is a liquid compound that has huge applications in the polymer and chemical industries to produce polyurethanes, polyesters, polycarbonates and polyamides. Generally, GC is considered to be a green substitute for important petro-derivative compounds such as ethylene carbonate or propylene carbonate. It is used as solvent in the paint, battery and detergent industries as well as in the synthesis of very valuable intermediates such as glycidol, which is used in textile, plastics, pharmaceutical and cosmetics industries [167].

GC is prepared by reacting glycerol with urea or dimethyl carbonate or by directly reacting it with carbon dioxide under supercritical conditions (Schemes 10–12). In view of the versatile applications of glycerol for the production of GC via catalysis, it has generated a lot of interest over the years as reviewed below.

**Scheme 10.** Conversion of glycerol to glycerol carbonate via glycerolysis with urea.

**Scheme 11.** Conversion of glycerol to glycerol carbonate via transesterification with dimethyl carbonate.

**Scheme 12.** Conversion of glycerol to glycerol carbonate by direct carboxylation with carbon dioxide.

The use of oxides as catalyst proved to be excellent. The transesterification reaction of glycerol with ethylene carbonate over basic oxides (MgO and CaO) and mixed oxides (Al/Mg, Al/Li) derived from hydrotalcites were studied [168]. Results showed that calcined Al/Ca-mixed oxide (AlCaMO) was the optimum catalyst in terms of activity and selectivity due to its strong basic character. The advantage of this catalyst is that low reaction temperature (35 °C) and low catalyst loading (0.5 wt%) was able to give high glycerol conversion with 98% selectivity to GC.

The use of copper (II) complexes as catalysts in the synthesis of glycerol carbonate via oxidative carbonylation was reported with above 92% glycerol conversion and over 93% selectivity towards GC.
Catalysts within 4 h reaction time [169]. The best reaction condition was found to be CuCl₂:pyridine in a 1:0.5 molar ratio catalyst in DMA as the solvent, at 130 °C and 4 MPa of CO₂:O₂ (5:1 as molar ratio). However, the use of nanoparticle-sized Cu/La₂O₃ catalysts could not give as much GC as expected, despite the use of moderate temperature and pressure conditions. The glycerol conversion and selectivity to GC of 33.4 and 45.5% were obtained at 150 °C, 7.0 MPa and 12 h reaction time [170]. The authors also reported that monoaceton was formed during the reaction with selectivity of 52.9%.

Zuhaimi et al. [171] reported the use of both calcined and uncalcined gypsum (CaSO₄) as catalysts. The calcined ß-CaSO₄ phase showed the highest activity with 92.8% glycerol conversion, 90.1% selectivity and 83.6% yield of GC. The catalyst was found to be stable and easily recoverable. The performance of the calcined catalyst was attributed to the presence of Lewis acid sites (Ca²⁺) and conjugate base sites (SO₄²⁻). The catalyst preparation method was taken into consideration and good glycerol conversion and selectivity towards GC were obtained. Wu et al. [172] prepared 0.2CeNiO-400 by co-precipitation method and when used in the transesterification of glycerol with diethyl carbonate at optimum conditions (5 wt% catalyst loading, 85 °C, glycerol:diethyl carbonate molar ratio of 1:3 and 8 h), 94.14% glycerol conversion and 90.95% GC selectivity were achieved. The catalyst demonstrated high potential when reused up to three times without deactivation or decreased GC yield. The performance was attributed to the presence of strong basic sites and a well dispersed NiO species.

Zeolites are known to be inactive in the carbonation of glycerol. However, when they were impregnated with metals, the resultant catalysts were seen to be active and produced some quantity of GC. This was reported by Ozorio et al. [173], where AgY, ZnY and SnY zeolite catalysts were synthesized and tested in the direct carbonation of glycerol with CO₂ at 180 °C, 100 bar in 3 h. All of the catalysts produced some quantity of GC as against the parent zeolite (NaY). The ZnY yield was the highest with about 5.8% GC. The activity exhibited by the metal-impregnated zeolites was attributed to the presence of large volume of active metal oxide phase.

When waste boiler ash was used as catalyst in the direct synthesis of GC from glycerol and urea, it exhibited high-activity 93.6 ± 0.4% glycerol conversion with GC selectivity and yield of 90.1 ± 1.0% and 84.3 ± 1.1% [174].

The use of organocatalyst in the production of GC has been explored, with good glycerol conversion and selectivity being obtained. Naik et al. [175] obtained as much as 93% GC after 5 h with a low catalyst loading of 5 mol% 1-n-butyl-3-methylimidazolium-2-carboxylate. The interesting thing about this catalyst was that no byproduct was formed, and catalyst loading as low as 1% was sufficient to yield quantitative conversions. The catalyst performance was found to strongly contrast the K₂CO₃ catalyst commonly used, which requires pure glycerol. Similarly, when selected ammonium and imidazolium-based ionic liquids were used as catalysts in the transesterification reaction, 1-ethyl-3-methylimidazolium acetate recorded the highest activity, with glycerol conversion of 93.5%, selectivity 94.9% and GC yield of 88.7% at optimum conditions of 120 °C, 0.5 mol% catalyst loading, diethyl carbonate/glycerol molar ratio of 2 and reaction time of 2 h [176]. There was no significant deactivation even when the catalyst was used three times, which was attributed to excellent interaction between the ionic liquid and the reactant. Table 12 shows a summary of the performance of some catalysts in the conversion of glycerol to GC as recently reported in some literature.

Table 12. Performance of some catalysts in the conversion of glycerol to glycerol carbonate as reported in some literature.

| Catalyst (A) | Operation Parameters | Performance (%) | TOF | Reference |
|-------------|----------------------|-----------------|-----|-----------|
| NiO-400 (56.07) | T = 80 °C, P = na, t = 6 h, Cat = 5 wt% G, | GC = 17.3, S = 100 | 6 | |
| 0.2CeNiO-400 (30.49) | | GC = 76.95, S = 100 | 28 | [172] |
| 0.6CeNiO-400 (41.10) | | GC = 66.51, S = 100 | 24 | |
| 1.0CeNiO-400 (71.80) | Glycerol/DEC (≈1:3) | GC = 67.5, S = 100 | 27 | |

Zuhaimi et al. [171] reported the use of both calcined and uncalcined gypsum (CaSO₄) as catalysts. The calcined ß-CaSO₄ phase showed the highest activity with 92.8% glycerol conversion, 90.1% selectivity and 83.6% yield of GC. The catalyst was found to be stable and easily recoverable. The performance of the calcined catalyst was attributed to the presence of Lewis acid sites (Ca²⁺) and conjugate base sites (SO₄²⁻).
Several catalysts involving noble metals have been employed in 1,3-PD synthesis in the presence of hydrogen. Due to alcohol’s resistance to hydrogenation, modified metals supported by different materials have been employed as catalysts in hydrogenolysis of glycerol with low to moderate product yields as reviewed below.

### Table 12. Cont.

| Catalyst (A)                              | Operation Parameters                                                                 | Performance (%) | TOF  | Reference |
|-------------------------------------------|--------------------------------------------------------------------------------------|-----------------|------|-----------|
| Methylammonium nitrate                    | GC = <10, Y = <10                                                                   |                 |      |           |
| Ethylammonium nitrate                     | GC = <10, Y = <10                                                                   |                 |      |           |
| 2-hydroxyethylammonium formate            | GC = 24.08, Y = 240                                                                  |                 |      |           |
| 1-ethyl-3-methylimidazolium dimethyl phosphate | GC = 22.20, Y = 22                                                                 |                 |      |           |
| 1-butyl-3-methylimidazolium diisocyanide  | GC = 45, Y = 45                                                                      |                 |      |           |
| 1-butyl-3-methylimidazolium chloride      | GC = <10, Y = <10                                                                   |                 |      |           |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | GC = <5, Y = <5                                                                   |                 |      |           |
| 1-ethyl-3-methylimidazolium acetate       | GC = 93.5, Y = 88.7                                                                |                 |      |           |
| Gypsum (CaSO\(_3\)\_2\_H\(_2\)O) (10.8) | GC = 92.5, S = 64.8, Y = 59.9                                                      | ** 89.7         |      |           |
| Gypsum-150 (2.6)                          | GC = 92.8, S = 90.1, Y = 83.6                                                      | ** 110.5        |      |           |
| Gypsum-800 (1.4)                          | GC = 90.1, Y = 93.8, S = 39.8                                                      | ** 59.6         |      |           |
| Blank                                     | GC = 78.7, S = 32.8, Y = 25.8                                                    |                 |      |           |
| Waste boiler ash-110 (8.05)               | GC = 91.1, S = 83.5, Y = 76.2                                                      | ** 136.7        |      |           |
| Waste boiler ash-700 (na)                 | GC = 94.1, S = 88.6, Y = 83.4                                                      | ** 141.2        |      |           |
| Waste boiler ash-900 (2.00)               | GC = 93.6, S = 90.1, Y = 84.3                                                      | ** 140.4        |      |           |
| Waste boiler ash-1100 (na)                | GC = 89.8, S = 85.6, Y = 77.0                                                      | ** 134.7        |      |           |
| Blank                                     | GC = 78.7, S = 32.8, Y = 25.8                                                    |                 |      |           |
| La\(_2\)O\(_3\) (21)                     | GC = 0.8, S = 6.3, Y = 0.05                                                       | 0.1             |      |           |
| 0.7% Cu/La\(_2\)O\(_3\) (21)              | GC = 19.3, S = 47.7, Y = 9.2                                                      | 4               |      |           |
| 2.3% Cu/La\(_2\)O\(_3\) (20)              | GC = 33.4, S = 45.4, Y = 15.2                                                      | 6               |      |           |
| 4.6% Cu/La\(_2\)O\(_3\) (20)              | GC = 30.6, S = 44.2, Y = 13.5                                                      | 6               |      |           |
| 13.4% Cu/La\(_2\)O\(_3\) (na)             | GC = 1.7, S = 35.3, Y = 0.6                                                       | 4               |      |           |
| Blank                                     | GC = 0.4, S = 5.0, Y = 0.02                                                        | -              |      |           |
| Na\(_2\)V-Zeolite (760)                   | GC = na, Y = 0.0, S = na                                                          | 0               |      |           |
| 5.9 wt% Ag\(_2\)V-Zeolite (289)           | GC = na, Y = 5.6, S = na                                                          | 10              |      |           |
| 6.0 wt% Zn\(_2\)V-Zeolite (407)            | GC = na, Y = 5.8, S = na                                                          | 11              |      |           |
| 10.3 wt% Sm\(_2\)V-Zeolite (442)          | GC = na, Y = 5.1, S = na                                                          | 9               |      |           |
| AgNO\(_3\) (na)                           | GC = na, Y = 3.5, S = na                                                          | 6               |      |           |
| SnCl\(_2\) (na)                           | GC = na, Y = 2.7, S = na                                                          | 5               |      |           |
| Cu\(_2\)Cl\(_2\) (na)                     | GC = na, Y = 2.6, S = na                                                          | 5               |      |           |
| CuBr\(_2\) (na)                           | GC = na, Y = 89                                                                  |                 |      |           |
| Cu\(_2\)I\(_2\) (na)                      | GC = na, Y = 89                                                                  |                 |      |           |
| CuO\(_2\)SO\(_3\) (na)                    | GC = na, Y = 89                                                                  |                 |      |           |
| Cu(OTf\(_2\)) (na)                        | GC = na, Y = 89                                                                  |                 |      |           |
| Cu(OCl\(_2\)) (na)                        | GC = na, Y = 89                                                                  |                 |      |           |

A = Surface area (m\(^2\)/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, GC = Glycerol Conversion, Y = Yield, S = Selectivity, DEC = Diethylcarbonate, DMA = Dimethylcarbonate, TOF (mmol g\(^{-1}\) cat. h\(^{-1}\)) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), ** TOF as reported in the journals, na = not available, nd = not determined.

### 5.3. 1,3-Propanediol

1,3-propanediol (1,3-PD) is an important chemical compound considered to be a monomer in the production of polyesters, polyethers and polyurethanes [3]. It is also used as an intermediate in the production of cosmetics, lubricants, engine coolants, water-based inks, adhesives, wood paints, coatings, antifreeze, and heterocyclic compounds [177,178]. The versatility of 1,3-PD was tremendously enhanced with the development of new biodegradable polyester, polytrimethylene terephthalate (PTT) because of its great potential in carpet, fiber and textile industries [179]. 1,3-PD is obtained via hydrogenolysis of the secondary OH of glycerol with the type of catalyst and conditions of the reaction playing critical roles (Scheme 13).

![Scheme 13. Conversion of glycerol to 1,3-propanediol by hydrogenolysis.](image-url)

Several catalysts involving noble metals have been employed in 1,3-PD synthesis in the presence of hydrogen. Due to alcohol’s resistance to hydrogenation, modified metals supported by different materials have been employed as catalysts in hydrogenolysis of glycerol with low to moderate product yields as reviewed below.
Qin et al. [180] reported the hydrogenolysis of glycerol over Pt/WO$_3$/ZrO$_2$ as catalyst in a fixed-bed continuous-flow reactor at 130 °C under 4.0 MPa. 70% glycerol conversion with 32% yield and 46% selectivity towards 1,3-PD was attained after 24 h reaction time. In another report, silica supported catalyst, Pt/WO$_3$/TiO$_2$/SiO$_2$ in several solvents and in a batch reactor was found to be effective and selective in the conversion of glycerol to 1,3-PD when compared to Pt/WO$_3$/TiO$_2$ catalyst. The authors concluded that the reaction was influenced by the type of solvent, catalyst loading, temperature and hydrogen pressure [181]. At slightly higher temperature and pressure of 220 °C and 4.5 MPa, higher selectivity to 1,3-PD was obtained (38.5%) when alumina was used as support, Pt/WO$_x$/Al$_2$O$_3$, after a reaction time of 16 h [182]. Similarly, under the same conditions, but with a longer reaction time of 24 h, glycerol conversion and selectivity towards 1,3-PD increased to 51.9% and 53.1% with 9 Pt/8WO$_x$/Al$_2$O$_3$ catalyst [183]. This great improvement was attributed to the highly dispersed polytungstate species responsible for Bronsted acidity, the closeness of platinum oxide and tungsten oxide as well as the electronic interactions between the acid and metallic sites.

In order to further improve 1,3-PD yield, selectivity and glycerol conversion, mesoporous catalysts were deployed in the hydrogenolysis. Longjie et al. [184] compared the hydrogenolysis of glycerol to 1,3-PD over the prepared mesoporous tungsten trioxide (m-WO$_3$) catalyst with the commercial WO$_3$ catalyst. The Pt/m-WO$_3$ catalyst performed better with 18.0% glycerol conversion and 39.2% selectivity under the reaction conditions of 180 °C, 5.5 MPa H$_2$, and within a reaction time of 12 h. The Pt/m-WO$_3$ catalyst activity was attributed to the presence of a larger surface area and the highly dispersed Pt particles on the support.

Good improvement was noticed when alkaline metals (Li, K, Rb and Cs) were added to Pt–H$_4$SiW$_{12}$O$_{40}$/ZrO$_2$ catalysts (heteropolyacids). The addition was found to greatly enhance the catalysts’ acidic property (both in terms of Bronsted acid sites and Lewis acid sites), thereby improving glycerol hydrogenolysis [185]. The Pt–Li H$_4$SiW$_{12}$O$_{40}$/ZrO$_2$ catalyst promoted the reactivity most pronouncedly with 43.5% glycerol conversion and selectivity of 53.6% towards 1,3-PD at 180 °C and 5 MPa. In a comparative study using zirconia supported bifunctional catalysts containing Pt and heteropoly acids (H$_4$SiW$_{12}$O$_{40}$, H$_3$PW$_{12}$O$_{40}$ and H$_3$PMO$_{12}$O$_{40}$) as active compounds; the results indicate that heteropoly acids modified Pt/ZrO$_2$ catalysts were effective due to the enhanced acidity [186]. The Pt–H$_4$SiW$_{12}$O$_{40}$/ZrO$_2$ catalyst, which exhibited the highest selectivity towards 1,3-PD (48.1%), also showed the highest Bronsted acid sites and thermal stability. Zhu et al. [186] also revealed that independent of the heteropolyacid type used, the concentration of Bronsted acid sites guide the glycerol hydrogenolysis to 1,3-PD, while the concentration of Lewis acid sites direct to the formation of 1,2-PD.

To further improve 1,3-PD selectivity, SiO$_2$ modified Pt–WO$_x$/ZrO$_2$ catalysts prepared via deposition–precipitation method were employed in the hydrogenolysis of glycerol [187]. The SiO$_2$ doping greatly improved Pt dispersion and acidity, which led to improved activity as well as 1,3-PDO selectivity. The highest glycerol conversion of 54.3% and the best selectivity of 52% were achieved with 5 wt% Pt–WO$_x$/ZrO$_2$–SiO$_2$. However, it was noticed that the excessive introduction of SiO$_2$ led to decline in the glycerol conversion and 1,3-PD selectivity.

Deng et al. [188] employed a series of synthesized different particle sizes of Pt-Re/carbon nano tube (CNT) catalysts and found that smaller particle sizes were better in hydrogenolysis due to increase in the surface acidic areas. However, sizes below 1.5 nm suffered severe coking, leading to decreased activity.

The use of Pt and Ru supported on ZrO$_2$ and WO$_3$/ZrO$_2$ as catalyst in the hydrogenolysis of glycerol did not improve its conversion nor selectivity to 1,3-PD as such [189]. Maximum selectivity achieved were 30.6% for Pt/ZrW and 9.5% for Ru/ZrW after 18 h of reaction time, while the glycerol conversion was 10.4%. The wide difference in the activity of the catalyst was traced to the fact that the metals exhibited different electron density on ZrO$_2$.

The use of zeolite as support material was explored in hydrogenolysis. Single and bimetals of Zr, Ni, Cu, and Zn supported on H-beta zeolite were prepared by wet impregnation method and used in the hydrogenolysis of glycerol under aqueous conditions at different reaction temperatures.
(150–250 °C), times (5–15 h) and H₂ pressures (2.1–8.3 MPa) [190]. Zr-Ni/H-beta catalyst (bimetallic) showed high activity with 77% glycerol conversion and 14% selectivity towards 1,3-PD, which was associated with its strong Bronsted acidity. Furthermore, the authors also reported that longer reaction time, higher temperature, and higher H₂ pressure had positive effects on the efficiency of glycerol hydrogenolysis. However, propanol and 1,2-PD were also obtained in reasonable quantity.

The production of 1,3-PD remains a challenge in view of the difficulties to high selectivity towards the CO cleavage of the secondary hydroxyl group in glycerol. So many researchers over the years have also explored, and are still exploring, the use of biocatalysts, usually from microorganisms, in 1,3-PD production.

It has been reported that bacteria, namely *Bacillus*, *Lactobacillus*, *Klebsiella*, *Citrobacter*, *Ilyobacter*, *Enterobacter* and *Clostridium*, have been used in the fermentation of glycerol to 1,3-PD using batch and/or continuous operation system [58]. The use of these organisms in 1,3-PD production is beyond the scope of this review. Table 13 shows the summary of the performance of some catalysts in the conversion of glycerol to 1,3-PD as recently reported in some literature.

| Catalyst (A) | Operation Parameters | Performance (%) | TOF | Reference |
|-------------|----------------------|-----------------|-----|-----------|
| H-beta (484) |                      |                 |     |           |
| 5 wt% Zr/H-beta (445) | $T = 200^\circ C$, $P = 4.1$ MPa, $H_2$, $t = 10$ h, Cat = 0.5 g, 600 rpm, 50 wt% glycerol solution | GC = 85, S = 0.2, Y = 0.2 | 85 | [190] |
| 10 wt% Zr/H-beta (434) |                      |                 |     |           |
| 5 wt% Ni-Zr/H-beta (407) |                      |                 |     |           |
| 5 wt% Cu-Zr/H-beta (417) |                      |                 |     |           |
| 5 wt% Zn-Zr/H-beta (420) |                      |                 |     |           |
| 2 wt% Pt/ZrO₂ (34.2) |                      |                 |     |           |
| 2 wt% Pt/ZrO₂-WO₃ (76.3) | $T = 180^\circ C$, $P = 8$ MPa, $t = 18$ h, Cat = 1 g, 1000 rpm, 10 wt% glycerol solution (in 40 mL H₂O) | GC = 100, S = 0.3 | 2.4 | [189] |
| 2 wt% Pt/ZrO₂-WO₃ (34.4) |                      |                 |     |           |
| 2 wt% Pt/ZrO₂-WO₃ (81.5) |                      |                 |     |           |
| 1 wt% Pt-WO₃/Al₂O₃ (95) | $T = 220^\circ C$, $P = 4.5$ MPa, $H_2$, $t = 16$ h, Cat = 0.35 g, 550 rpm under H₂ atm. | GC = 105, S = 0.3 | 7 | [182] |
| 1 wt% Pt-WO₃/Al₂O₃ (128) |                      |                 |     |           |
| 1 wt% Pt-WO₃/Al₂O₃ (104) |                      |                 |     |           |
| 4 wt% Pt-WO₃/Al₂O₃ (na) |                      |                 |     |           |
| 9 wt% Pt-WO₃/Al₂O₃ (81) | $T = 200^\circ C$, $P = 4.5$ MPa, $H_2$, $t = 24$ h, Cat = 0.35 g, 550 rpm, 5 wt% glycerol solution | GC = 53, S = 51.9 | 3 |           |
| 2 wt% Pt-WO₃/Al₂O₃ (35.1) |                      |                 |     |           |
| 2 wt% Pt-WO₃/Al₂O₃ (35.2) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 3 g, WHSV = 1.0 g/g cat/h | GC = 30, S = 44.3 | 5.8 | [190] |
| 2 wt% Pt-WO₃/Al₂O₃ (35.3) |                      |                 |     |           |
| 2 wt% Pt-WO₃/Al₂O₃ (35.4) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 3 g, WHSV = 1.0 g/g cat/h | GC = 41.5, S = 46.3 | 5.8 | [187] |
| 2 wt% Pt-WO₃/Al₂O₃ (35.5) |                      |                 |     |           |
| 2 wt% Pt-WO₃/Al₂O₃ (113.3) |                      |                 |     |           |
| 2 wt% Pt-WO₃/Al₂O₃ (121.2) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 3 g, WHSV = 1.0 g/g cat/h | GC = 40.1, S = 46.7 | 5.8 | [187] |
| 2 wt% Pt-WO₃/Al₂O₃ (152.4) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 3 g, WHSV = 1.0 g/g cat/h | GC = 32.1, S = 47.1 | 5.8 | [187] |
| 1 wt% Pt-20 wt% HSiWO₄/ZrO₂ (46.9) |                      |                 |     |           |
| 1 wt% Pt-LiSiWO₄/ZrO₂ (50.5) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 2 g, WHSV = 0.9/ h | GC = 43.5, S = 53.6 | 5.8 | [185] |
| 1 wt% Pt-KSiWO₄/ZrO₂ (51.8) |                      |                 |     |           |
| 1 wt% Pt-RbSiWO₄/ZrO₂ (53.3) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 2 g, WHSV = 0.9/ h | GC = 42.0, S = 43.6 | 5.8 | [185] |
| 1 wt% Pt-CsSiWO₄/ZrO₂ (53.8) |                      |                 |     |           |
| 2 wt% Pt/ZrO₂ (61.0) |                      |                 |     |           |
| 2 wt% Pt-WO₃/Al₂O₃ (54.8) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 2 g, WHSV = 0.9/ h | GC = 42.1, S = 48.1 | 5.8 | [186] |
| 2 wt% Pt-WO₃/Al₂O₃ (57.0) |                      |                 |     |           |
| 2 wt% Pt-WO₃/Al₂O₃ (59.3) | $T = 180^\circ C$, $P = 5$ MPa, Cat = 2 g, WHSV = 0.9/ h | GC = 25.5, S = 32.9 | 5.8 | [186] |
| 2 wt% Pt-WO₃/Al₂O₃ (55.3) |                      |                 |     |           |
| Pt/mesoporous-WO₃ (22) | $T = 180^\circ C$, $P = 5$ MPa, $H_2$, $t = 12$ h, Cat = 1 g, 10 wt% glycerol solution | GC = 18.0, S = 39.3 | 1.5 | [184] |
| Pt/commercial-WO₃ (9.0) |                      |                 |     |           |

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, t = time, WHSV = Water Hourly Space Velocity, GC = Glycerol Conversion, S = Selectivity, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined.

5.4. Polyglycerol (Oligomers)

Polyglycerol (PG) is simply the coming together of more than one glycerol, which is also known as oligomerization. PG is classified as an ether in view of its C-O-C bond formation and may be linear, branched or cyclic [191]. PG has numerous applications in the cosmetic, pharmaceutical, food and detergent industries [42,192].

PG can also be diglycerol, triglycerol, tetragelycerol, hexaglycerol and deca glycerol depending on the number of glycerol and the hydroxyl group of the glycerol (primary or secondary) involved in
the reaction, as well as the conditions of the reaction. PG is prepared by condensing glycerol with glycidol; however, self-condensation of glycerol has recently become more preferred (Scheme 14) using an appropriate catalyst.

Scheme 14. Conversion of glycerol to polyglycerol by self-condensation.

Several catalytic conversions of glycerol to PG have been undertaken, with the big challenge of controlling the oligomerization to the desired oligomer, and so more and more research is being undertaken in the area of catalysis with a view to improving yield and selectivity [193].

Researchers have shown that the use of homogeneous catalyst such as sulfuric acid results in high quantities of PG with preference to linear and/or cyclic oligomers. However, several disadvantages are associated with these catalysts, some of which include lack of effective selectivity in the oligomerization and difficulty in separating the catalyst from the product, as well as the burden involved in purification of the process. These foregoing reasons made scientists shift attention to solid heterogeneous catalysts, finding that they are more selective and easier to separate, but the quantity is not as great as their homogeneous counterpart. Heterogeneous catalysts yield more branched oligomers [192].

Different alkaline earth metal oxides (MgO, CaO, SrO, and BaO) were tested as potential heterogeneous catalysts [194]. Results showed that the glycerol conversion increased with increasing catalyst basicity in the order: MgO<CaO<SrO<BaO. The best selectivity values for di- and triglycerol (>90% at 60% conversion) were obtained over CaO, SrO, and BaO. Further study also showed that catalysts activity depends on the strength of both basic and Lewis acid sites.

The catalyst preparation method also improves glycerol conversion and product yield. García-Sancho et al. [195] investigated the use of MgAl mixed oxides as base catalysts (prepared by coprecipitation and urea hydrolysis) at 220 °C in a batch reactor. The catalyst prepared by coprecipitation exhibited the highest glycerol conversion of 50.7% with full selectivity to diglycerol with 43% yield and was attributed to highest specific surface area.

Hydrotalcite catalysts prepared using combustion method was investigated [196]. The catalyst showed 12.3% glycerol conversion at 450 °C with high selectivity to diglycerol (97.7%). However, with calcination of the catalyst at 650 °C in 16 h, the catalyst activity increased with glycerol conversion of 77.7% after 16 h. However, at higher temperature of 850 °C, the catalyst was affected, thereby affecting the conversion.

When acid-treated montmorillonite K-10 (Clay MK-10) was modified with LiOH (Clay Li/MK-10) and used as catalyst at 240 °C, high glycerol conversion of 98% and selectivity of 53% towards diglycerol were achieved after 12 h of reaction time [197].

Recent research has also shown the etherification of glycerol in a solventless process. Heterogeneous mesoporous basic catalysts were synthesized by wet impregnation of MCM-41 with
calcium nitrate and lanthanum nitrate and used in the solventless etherification of glycerol to produce diglycerol at 250 °C for 8 h [198]. Results showed that 20% Ca$_{1.6}$La$_{0.6}$/MCM-41 catalyst resulted in the highest glycerol conversion of 91%, with diglycerol yield of 43%. However, leaching of the metal was reported. It was also previously reported that metal oxide composite catalyst (Ca$_{1+x}$Al$_{1-x}$La$_x$O$_3$) calcined at 560 °C with La:Ca ratio of 1:2.7 produced 91% glycerol conversion and 53.2% diglycerol selectivity after 8 h reaction at 250 °C and catalyst loading of 2 wt% [199]. The catalytic performance was attributed to synergic mixed oxide complex resulting from the interaction between La, Ca, and Al oxides. Similarly, Guerrero-Urbaneja et al. [200] prepared MgFe mixed oxides with a molar ratio ranging from 1 to 4, which were tested in a batch reactor at 220 °C. All the catalysts performed well without solvent, but the selectivity was lower than previously reported by [199]. The catalyst with Mg/Fe molar ratio of 4 produced the highest glycerol conversion of 41% with >90% selectivity to diglycerol. This was attributed to the excellent textural properties, with specific surface areas close to 200 m$^2$ g$^{-1}$ of the catalyst. However, in addition to diglycerol, triglycerol was also detected after 24 h of the reaction. While the use of lithium-exchanged zeolite Y (Li-ZeY) catalyst at 240 °C was found to be highly active and thermally stable, with glycerol conversion of 99% after 8 h of reaction, which was much higher than homogenous LiOH catalyst [201].

The use of crude glycerol via microwave irradiation was explored in PG synthesis and interestingly 94.94% was obtained at 250 °C in 1 h despite soap content of 12.5% [46].

In the optimization reaction (temperature of 270 °C, catalyst concentration of 3 wt%, and reaction time of 1.0 h) of etherification of glycerol to PG without solvent using Na$_2$CO$_3$ as catalyst and microwaves as a source of heat yield 93%, 70%, and 7% diglycerol, triglycerol and tetruglycerol respectively [202]. The values obtained correlated with the predicted values of 84%, 63%, and 9%. The authors also reported that increased in the parameters studied (temperature, catalyst concentration and reaction time) led to higher amount of the product.

In other to improve the etherification reaction of glycerol towards di- to pentaglycerol (lower glycerols), Pérez-Barrado et al. [203] prepared several MgAl and CaAl layered double hydroxides (LDH) catalysts and tested them after calcinations at 450 °C. Results showed that catalysts with lower acidity resulted in lower glycerol conversion (24% for calcined MgAl-LDH and 40% for calcined CaAl-LDH) but showed higher selectivity (100% and 64%) towards di- and triglycerol. While higher-acidity catalysts exhibited higher glycerol conversion (96% for calcined MgAl-LDH and 75% for calcined CaAl-LDH) as well as higher selectivity towards other undesired products (88% for calcined MgAl-LDH and 58% for a calcined CaAl-LDH) with acrolein been the major contributor. The authors also reported that as the calcination temperature increased, the acidity decreased and the number of strong basic sites increased, resulting in higher selectivity to triglycerol (20%), tetruglycerol (15%) and pentaglycerol (6%) and decreased formation of acrolein.

Up to 75% PG yield and about 80% glycerol conversion were obtained with Aquivion® PFSA PW98 catalyst (solid super acid, perfluoro polymer with in cooperated sulfonic acid (-SO$_3$H) [204]. The catalyst was so stable that it was recycled 10 times without apparent decrease in activity or selectivity and makes it ahead of other conventional solid acid catalysts such as Nafion NR 50 and Amberlyst-70.

Galy et al. [205] reported the use of K$_2$CO$_3$ catalyst in a continuous flow reactor improved the formation of glycerol dimer with 20 wt%, glycerol trimer 21 wt%, glycerol tetramer 16 wt% and glycerol pentamer 11 wt%.

A novel idea of using eggshell waste (raw and calcined) as catalyst was investigated in glycerol etherification and under optimal reaction conditions of 2 wt% catalyst loading, 220 °C temperature and reaction time of 24 h gave 85% glycerol conversion with 43% oligomers (di-and triglycerol) yield [206]. However, the catalyst was not stable because it leached into the reaction medium. Table 14 shows the summary of the performance of some catalysts in the conversion of glycerol to PG as recently reported in some literature.
Table 14. Performance of some catalysts in the conversion of glycerol to polyglycerol as reported in some literature.

| Catalyst (A)                      | Operation Parameters | Performance (%) | TOF   | Reference |
|-----------------------------------|----------------------|-----------------|-------|-----------|
| Calcined Eggshell (29)            | T = 245 °C, Cat = 2 wt% G, t = 6 h, under N₂ flow | GC = 80, DG = 40, TG = 2.5, Oth = 57.5 | 72    | [206]     |
|                                   | T = 220 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 85, DG = 35, TG = 8, Oth = 57   | 19    |           |
| K₂CO₃ (na)                        | T = 250 °C, Cat = 18 g, 4.69 mol glycerol (in 50 mL H₂O) | G = 59.9 ± 2.7, DG = 18 ± 0.2, CDG = 1.5 ± 0.2, TG = 8.4 ± 1.2, CTG = 1.0 ± 0.2, TtG = 4.4 ± 1.0, PG = 3.1 ± 0.1, HG = 1.0 ± 0.5 | [205] |
| Aquivion PW 98 (na)               | T = 150 °C, Cat = 0.45 mmol, t = 6 h | GC = 82, YDG = 21, YTG = 17, Y-TTG = 33, Yo = 87 | nd    |           |
| Amberlyst 70 (na)                 | T = 150 °C, Cat = 1 wt% G, t = 1 h | GC = 76, YDG = 31, YTG = 15, Y-TTG = 26, Yo = 81 | nd    |           |
| Naion NR 50 (na)                  | T = 150 °C, Cat = 0.45 mmol, t = 7 h | GC = 78, YDG = 14, YTG = 21, Y-TTG = 24, Yo = 76 | nd    |           |
| Aquivion PW 98 (na)               | T = 270 °C, P = atm. press., Cat = 1 wt% G, t = 1 h | GC = 85.26, Y(DDG-TG+G) = 59.13, SGC = 11.44, SCDG = 7.18 | [202] |
| Na₂CO₃ (na)                       | T = 270 °C, P = atm. press., Cat = 3 wt% G, t = 1 h | GC = 96.03, Y(DDG-TG+G) = 66.83, SPC = 12.50, SCDG = 12.94 | [208] |
|                                   | T = 270 °C, P = atm. press., Cat = 3 wt% G, t = 3 h | GC = 96.12, Y(DDG-TG+G) = 47.33, SPC = 37.53, SCDG = 8.33 | nd    |           |
|                                   | T = 270 °C, P = atm. press., Cat = 3 wt% G, t = 1 h | GC = 92.83, Y(DDG-TG+G) = 70.13, SPC = 9.06, SCDG = 6.50 | [205] |
|                                   | T = 270 °C, P = atm. press., Cat = 3 wt% G, t = 3 h | GC = 96.20, Y(DDG-TG+G) = 53.30, SPC = 13.33, SCDG = 12.63 | [205] |
| MgAl-LDH₁₋₋₂₋₋₂ (237)            | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 96, SDC = 9, SPC = 3, SCDG = 88, Yo = 12 | 22    |           |
| MgAl-LDH₁₋₋₂₋₋₂ (188)            | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 24, SDC = 89, SPC = 11, SCDG = 0, Yo = 24 | 5     |           |
| CaAl-LDH₁₋₋₂₋₋₂ (15)             | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 75, SDC = 56, SPC = 6, SCDG = 58, Yo = 32 | 17    |           |
| CaAlL-MDH₁₋₋₂₋₋₂ (3)             | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 60, SDC = 44, SPC = 11, SCDG = 45%, Yo = 33 | 14    |           |
| CaAlL-MDH₁₋₋₂₋₋₂ (3)             | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 59, SDC = 38, SPC = 13, SCDG = 49, Yo = 35 | 13    |           |
| Blank                             | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 84, SDC = 29, SPC = 20, SCDG = 51%, Yo = 59 | 19    |           |
| MCM-41 (938)                      | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 2, SDC = 3, YDC = 0, SPC = 0, SCDG = 97, Yo = 2. | -     |           |
| CaO (14)                          | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 2, SDC = 4, YDC = 0, SPC = 0, SCDG = 96, Yo = 2. | 1     |           |
| La₂O₃ (na)                        | T = 235 °C, Cat = 2 wt% G, t = 24 h, under N₂ flow | GC = 72, SDC = 27, YDC = 20, SPC = 10, YTG = 7, Yo = 63, Yo = 6. | 49    |           |
| Ca₁₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋₋值得一 |
5.5. Olefins

Olefin, simply referred to as alkene, is a verse class of unsaturated hydrocarbons with at least a carbon-to-carbon double bond (\(-\text{C} = \text{C}\)). Lower olefins have short chains with 2 to 4 carbon atoms. The higher olefins have chains of up to 20 or more [207]. In view of the presence of the double bond, olefins are very reactive; hence, their ability to form many derivatives.

The light olefins such as ethylene, propylene, butadiene and their derivatives are considered to be the most sought after because of their industrial applications, which include production of plastics and industrial solvents [208].

Research into the conversion of glycerol into olefins is still in its infancy. The possibility of reducing cost via the use of glycerol against the current method of production, thermal cracking of natural gas and crude oil, is being investigated using heterogeneous catalysts [207,209].

Catalyst screening of various metals (Cr, Ca, Cu, Ni and Al)-impregnated ZSM-5 (zeolite) for catalytic conversion of glycerol to olefins in a fixed-bed reactor was investigated by Zakaria et al. [206]. Results showed that metal-doped ZSM-5 increased its activity and olefin yield. CuZSM-5 exhibited the best result with 17.76% glycerol conversion and 3.55% olefin yield. The authors also indicated that methanol and other unidentified compounds were also produced. Similarly, Zakaria et al. [210] modified ZSM-5 into HZSM-5, Al/ZSM-5, Ca/ZSM-5, Cr/ZSM-5, Cu/ZSM-5, Li/ZSM-5, Mg/ZSM-5 and Ni/ZSM-5, and these were tested as catalysts for the conversion of glycerol to light olefins at 600 °C. Results revealed that olefin and paraffin were produced by all the catalysts, with olefin being the superior product. The turnover frequencies (TOF) for Cu/ZSM-5 and Cr/ZSM-5 catalysts were significantly high, which possibly informed the high yield, with up to a 15% improvement in olefin production. It could also be attributed to the synergistic effect of the physico-chemical properties between the parent ZSM-5 and the metals. In terms of olefin product, ethylene is the most produced (2.61–18.62%), followed by propylene (0.07–2.60%) and butylene (0.56–0.96%). Of the paraffin, methane (4.74–9.63%) was produced by all the catalysts. Other products, such as CO, CO\(_2\) and H\(_2\), were also observed from all the catalysts.

Blass et al. [211] also explored the conversion of glycerol to olefins in a reactor using different catalyst at different stages of dehydration and hydrogenation. In the first step, glycerol, co-fed with H\(_2\) over HZSM-5 catalyst at 400 °C, was dehydrated to mixture of acetaldehyde, acrolein, and hydroxypropanone. In the second step, acrolein was hydrogenated to propanal over Pd/\(\alpha\text{-Al}_2\text{O}_3\) catalyst, and in the third step, propanal was converted to light olefins over HBEA at 500 °C with minimal CO production, but with catalyst deactivation occurring, leading to a decrease in propanal conversion with time on stream. The authors further showed that varying degrees of olefins can be produced by varying the temperature and the zeolite pore size. Product distribution was shifted to \(\text{C}_{2−3}\) olefins at higher temperatures and \(\text{C}_{4−5}\) olefins at lower temperatures. \(\text{C}_{6−9}\) products were formed when the zeolite pore size increased from 10-MR in HZSM-5 to 12-MR in HBEA due to the fact that larger pores can accommodate larger products.

Using the Gibbs free energy minimization method, the thermodynamic equilibrium analysis of glycerol steam reforming to light olefins was investigated at temperature range (300–1000 °C), glycerol/water ratio (1:12–2:1) and pressure (0.1–1.2 MPa). Results revealed that light olefins formation was not spontaneous but experimental work involving catalyst proved that ethylene selectivity could be improved on in a heterogeneous reaction. The amount of ethylene produced was very small, but improved at higher pressure and temperatures between 600 and 750 °C. Results further revealed that coking depends on the glycerol/water ratio and temperature [212]. Table 15 shows the summary of the performance of some catalysts in the conversion of glycerol to olefins as recently reported in some literature.
Table 15. Performance of some catalysts in the conversion of glycerol to olefins as reported in some literature.

| Catalyst (A) Operation Parameters | Performance (%) | TOF | Reference |
|-----------------------------------|-----------------|-----|-----------|
| HZSM-5 (~400) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Ethene S = 7.94, Y = 3.99, Propene S = 0.35, Y = 0.18, Butene S = 0.00, Y = 0.00, Methane S = 4.75, Y = 2.38, Ethene S = 6.45, Y = 5.26, Propene S = 0.07, Y = 0.06, | nd | [210] |
| 30%Al/ZSM-5 (~350) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Butene S = 0.00, Y = 0.00, Methane S = 9.63, Y = 7.85, Ethene S = 3.95, Y = 1.93, Propene S = 0.83, Y = 0.41, | nd | [210] |
| 30%Ca/ZSM-5 (~215) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Butene S = 0.00, Y = 0.00, Methane S = 9.95, Y = 2.90, Ethene S = 15.20, Y = 14.82, Propene S = 2.60, Y = 2.53, Butene S = 0.96, Y = 0.93, Methane S = 8.16, Y = 7.96, Ethene S = 18.62, Y = 14.97, Propene S = 1.06, Y = 0.86, Butene S = 0.56, Y = 0.45, Methane S = 5.60, Y = 4.50, Ethene S = 2.61, Y = 0.90, Propene S = 1.76, Y = 0.61, | [207] |
| 30%Cr/ZSM-5 (~230) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Butene S = 0.96, Y = 0.33, Methane S = 6.04, Y = 2.10, Ethene S = 6.142, Y = 4.19, Propene S = 0.271, Y = 0.19, Butene S = 0.00, Y = 0.00, Methane S = 5.457, Y = 3.72, Ethene S = 3.27, Y = 3.20, Propene S = 0.5, Y = 0.5, | nd | [207] |
| 30%Li/ZSM-5 (~230) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Butene S = 0.00, Y = 0.00, Methane S = 7.21, Y = 7.05, Ethene S = 3.27, Y = 3.20, Propene S = 0.5, Y = 0.5, | [207] |
| 30%Mg/ZSM-5 (~250) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Ethene S = 2.61, Y = 0.90, Propene S = 1.76, Y = 0.61, | nd | [207] |
| 30%Mn/ZSM-5 (~270) T = 600 °C, P = 0.1 MPa, WHSV = 105/h, Cat = na | Ethene S = 3.27, Y = 3.20, Propene S = 0.5, Y = 0.5, | | |
| HZSM-5 T = 700 °C, P = 0.1 MPa | GC = 11.62, Olefin S = 1.20 | | |
| 10 w% Cr-ZSM-5 (na) | GC = 10.65, Olefin S = 0.63 | | |
| 10 w% Al-ZSM-5 (na) | GC = 10.44, Olefin S = 1.09 | | |
| 10 w% Ca-ZSM-5 (na) | GC = 15.02, Olefin S = 1.34 | | |
| 10 w% Cu-ZSM-5 (na) | GC = 17.72, Olefin S = 3.55 | | |
| 10 w% Ni-ZSM-5 (na) | GC = 16.07, Olefin S = 1.84 | | |

A = Surface area (m²/g), T = Temperature, P = Pressure, Cat = Catalyst load, WHSV = Water/Liquid Hourly Space Velocity, FFR = Feed Flow Rate, t = time, GC = Glycerol Conversion, S = Selectivity, Y = Yield, TOF (mmol g⁻¹ cat. h⁻¹) = Turnover frequency calculated based on the glycerol conversion per gram catalyst per total reaction time (h), na = not available, nd = not determined.

Though it must be stated that there are scanty literature available in this area of conversion of glycerol to olefin, which can be attributed to the fact the area is relatively new hence the need for more research in this direction.

6. Prospects and Conclusions

As the environmental impact of petroleum-based fuels and chemicals continues to tear the world apart, research into the alternatives is growing at an interesting rate, to the extent that some the products have already been commercialized. Today, many countries in the world are already, interestingly, using biodiesel as fuel or as a fuel additive. The major byproduct in biodiesel production, glycerol, has grown to the extent that ways of valorization are not only being contemplated, but are necessary and already underway. This is to guard against immediate and future consequences of the byproduct, as well as to ameliorate the cost of biodiesel production. Glycerol is being converted into many value-added products via several reactions. These products include fuels, fuel additives and other precursor chemicals.

Though some of the reactions leading to the production of the above products have been patented, only a few of the products have reached commercial production stage. Specifically, epichlorohydrin obtained from glycerol-based dichloropropanol is already being produced at commercial level by the Solvay, Dow and Shandong Chemical Companies of Belgium, United States and China, respectively, and have been found to be economically and environmentally friendlier than the usual conventional method which is based on petroleum oil. Similarly, DuPont company developed the production of 1,3-PD through fermentation of glycerol with recombinant Escherichia coli, with the process saving 40% of the energy expended by its petroleum-based counterpart. Polyglycerols also has been commercialized by Sakamoto Company in Japan, along with very few others. However, a lot of research efforts are ongoing to overcome some of the challenges hindering commercialization of other products, as well as exploring new frontiers in order to discover new products.

Some of the challenges include overcoming catalyst selectivity to some of the products, deactivation of catalyst occasioned by reuse, the use of harsh conditions such as high temperature and/or pressure, as well as difficulty in separation of catalyst from the desired products, long hours of reaction and low product yields. Overcoming impurities in crude glycerol, if it must be used directly, is also a big challenge for industry.
To address some of the above challenges, scientists, technologists and engineers must explore new process technologies, integrated process systems, highly tolerant and novel catalysts, improved activation methods, improved reactor systems, synergizing chemical and biological catalysis to improve certain inherent weaknesses associated with each of the catalyst.

Finally, if some of these barriers are broken, biodiesel production and usage will become cost effective and sustainable, and glycerol will, no doubt, become a great feedstock that will replace most petroleum-based chemicals.

Author Contributions: All authors contributed in either sourcing materials, writing, reviewing and or editing the article.

Funding: This research was funded by the University Putra Malaysia IPS grant, grant number 9619500.

Acknowledgments: The authors deeply appreciate the University Putra Malaysia for the Putra IPS research grant. The sponsorship received from the Tertiary Education Trust Fund (TETFund) through the Federal Polytechnic Bida, Nigeria is also gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Liu, H.; Su, L.; Shao, Y.; Zou, L. Biodiesel production catalyzed by cinder supported CaO/KF particle catalyst. Fuel 2012, 97, 651–657. [CrossRef]
2. Akia, M.; Yazdani, F.; Motae, E.; Han, D.; Arandiyan, H. A review on conversion of biomass to biofuel by nanocatalysts. Biofuel Res. J. 2014, 1, 16–25. [CrossRef]
3. Da Silva, G.P.; Mack, M.; Contiero, J. Glycerol: A promising and abundant carbon source for industrial microbiology. Biotechnol. Adv. 2009, 27, 30–39. [CrossRef] [PubMed]
4. Markočič, E.; Kramberger, B.; van Bennekom, J.G.; Heeres, H.J.; Vos, J.; Knez, Ž. Glycerol reforming in supercritical water; a short review. Renew. Sustain. Energy Rev. 2013, 23, 40–48. [CrossRef]
5. Yang, C.-Y.; Fang, Z.; Li, B.; Long, Y.-F. Review and prospects of Jatropha biodiesel industry in China. Renew. Sustain. Energy Rev. 2012, 16, 2178–2190. [CrossRef]
6. Balat, M. Potential alternatives to edible oils for biodiesel production—A review of current work. Energy Convers. Manag. 2011, 52, 1479–1492. [CrossRef]
7. Thanh, L.T.; Okitsu, K.; Boi, L.V.; Maeda, Y. Catalytic technologies for biodiesel fuel production and utilization of glycerol: A review. Catalysts 2012, 2, 191–222. [CrossRef]
8. EU-Commission. Directive 2003/30/EC of the European Parliament and of the Council of 8 May 2003 on the promotion of the use of biofuels or other renewable fuels for transport. Off. J. Eur. Union 2003, 5. Available online: http://data.europa.eu/eli/dir/2003/30/oj (accessed on 22 September 2017).
9. Knothe, G.; Razon, L.F. Biodiesel fuels. Prog. Energy Combust. Sci. 2017, 58, 36–59. [CrossRef]
10. Fan, X.; Burton, R. Recent development of biodiesel feedstocks and the applications of glycerol: A review. Open Fuels Energy Sci. J. 2009, 2, 100–109. [CrossRef]
11. Babajide, O. Sustaining biodiesel production via value-added applications of glycerol. J. Energy 2013, 2013. [CrossRef]
12. Refaat, A. Different techniques for the production of biodiesel from waste vegetable oil. Int. J. Environ. Sci. Technol. 2010, 7, 183–213. [CrossRef]
13. Banerjee, N.; Ramakrishnan, R.; Jash, T. Biodiesel production from used vegetable oil collected from shops selling fritters in Kolkata. Energy Procedia 2014, 54, 161–165. [CrossRef]
14. Zhang, F.; Fang, Z.; Wang, Y.-T. Biodiesel production direct from high acid value oil with a novel magnetic carbonaceous acid. Appl. Energy 2015, 155, 637–647. [CrossRef]
15. Neumann, K.; Werth, K.; Martin, A.; Görak, A. Biodiesel production from waste cooking oils through esterification: Catalyst screening, chemical equilibrium and reaction kinetics. Chem. Eng. Res. Des. 2016, 107, 52–62. [CrossRef]
16. Dimitratos, N.; Lopez-Sanchez, J.A.; Hutchings, G.J. Green catalysis with alternative feedstocks. Top. Catal. 2009, 52, 258–268. [CrossRef]
17. European Biodiesel Board. European Biodiesel Board Statistics on Biodiesel Production. Available online: http://www.ebb-eu.org/stats.php# (accessed on 22 September 2017).
18. Stelmachowski, M. Utilization of glycerol, a by-product of the transesterification process of vegetable oils: A review. *Ecol. Chem. Eng.* 2011, 18, 9–30. [CrossRef]
19. National Biodiesel Board, U.S. Biodiesel Production Statistics. Available online: http://biodiesel.org/production/production-statist (accessed on 22 September 2017).
20. Ren21. Renewables 2016 Global Status Report. Available online: http://www.ren21.net/status-of-renewables/global-status-report/ (accessed on 23 September 2017).
21. Comelli, R.A. Glycerol, the co-product of biodiesel: One key for the future bio-refinery. In *Biodiesel-Quality, Emissions and By-Products*; InTech: Rijeka, Crotia, 2011. [CrossRef]
22. Union, E. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC. *Off. J. Eur. Union* 2009, 5. Available online: http://data.europa.eu/eli/dir/2009/28/oj (accessed on 22 September 2017).
23. Kawentar, W.A.; Budiman, A. Synthesis of biodiesel from second-used cooking oil. *Energy Procedia* 2013, 32, 190–199. [CrossRef]
24. Kumar, A.; Shukla, S.; Tierkey, J. A review of research and policy on using different biodiesel oils as fuel for CI engine. *Energy Procedia* 2016, 90, 292–304. [CrossRef]
25. Kurnia, J.C.; Jangam, S.V.; Akhtar, S.; Sasmito, A.P.; Mujumdar, A.S. Advances in biofuel production from oil palm and palm oil processing wastes—a review. *Biofuel Res. J.* 2016, 3, 332–346. [CrossRef]
26. Mofijur, M.; Atabani, A.; Masjuki, H.A.; Kalam, M.; Masum, B. A study on the effects of promising edible and non-edible biodiesel feedstocks on engine performance and emissions production: A comparative evaluation. *Renew. Sustain. Energy Rev.* 2013, 23, 391–404. [CrossRef]
27. Aransiola, E.; Ojumu, T.; Oyekola, O.; Madzimbamuto, T.; Ikhu-Omoregbe, D. A review of current technology for biodiesel production: State of the art. *Biomass Bioenergy* 2014, 61, 276–297. [CrossRef]
28. Galadima, A.; Muraza, O. Biodiesel production from algae by using heterogeneous catalysts: A critical review. *Energy* 2014, 78, 72–83. [CrossRef]
29. Gaurav, A.; Ng, F.T.; Rempel, G.L. A new green process for biodiesel production from waste oils via catalytic distillation using a solid acid catalyst—Modeling, economic and environmental analysis. *Green Energy Environ.* 2016, 1, 62–74. [CrossRef]
30. Demirbas, A. Importance of biodiesel as transportation fuel. *Energy Policy* 2007, 35, 4661–4670. [CrossRef]
31. Singhabhandhu, A.; Tezuka, T. A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock. *Energy* 2010, 35, 2493–2504. [CrossRef]
32. Quispe, C.A.; Coronado, C.J.; Carvalho, J.A., Jr. Glycerol: Production, consumption, prices, characterization and new trends in combustion. *Renew. Sustain. Energy Rev.* 2013, 27, 475–493. [CrossRef]
33. Yazdani, S.S.; Gonzalez, R. Anaerobic fermentation of glycerol: A path to economic viability for the biofuels industry. *Curr. Opin. Biotechnol.* 2007, 18, 213–219. [CrossRef] [PubMed]
34. Yang, F.; Hanna, M.A.; Sun, R. Value-added uses for crude glycerol—a byproduct of biodiesel production. *Biotechnol. Biofuels* 2012, 5, 13. [CrossRef] [PubMed]
35. Bagheri, S.; Julkapli, N.M.; Yehye, W.A. Catalytic conversion of biodiesel derived raw glycerol to value added products. *Renew. Sustain. Energy Rev.* 2015, 41, 113–127. [CrossRef]
36. Gupta, M.; Kumar, N. Scope and opportunities of using glycerol as an energy source. *Renew. Sustain. Energy Rev.* 2012, 16, 4551–4566. [CrossRef]
37. Luo, X.; Ge, X.; Cui, S.; Li, Y. Value-added processing of crude glycerol into chemicals and polymers. *Bioresource Technol.* 2016, 215, 144–154. [CrossRef] [PubMed]
38. Anitha, M.; Kamarudin, S.K.; Kofli, N.T. The potential of glycerol as a value-added commodity. *Chem. Eng. J.* 2016, 295, 119–130. [CrossRef]
39. Gholami, Z.; Abdullah, A.Z.; Lee, K.-T. Dealing with the surplus of glycerol production from biodiesel industry through catalytic upgrading to polyglycerols and other value-added products. *Renew. Sustain. Energy Rev.* 2014, 39, 327–341. [CrossRef]
40. Len, C.; Luque, R. Continuous flow transformations of glycerol to valuable products: An overview. *Sustain. Chem. Process.* 2014, 2, 1. [CrossRef]
41. Christoph, R.; Schmidt, B.; Steinberner, U.; Dilla, W.; Karinen, R. Glycerol. *Ullmann’s Encycl. Ind. Chem.* 2006. [CrossRef]
42. Kenar, J.A. Glycerol as a platform chemical: Sweet opportunities on the horizon? Lipid Technol. 2007, 19, 249–253. [CrossRef]
43. Rahmat, N.; Abdullah, A.Z.; Mohamed, A.R. Recent progress on innovative and potential technologies for glycerol transformation into fuel additives: A critical review. Renew. Sustain. Energy Rev. 2010, 14, 987–1000. [CrossRef]
44. Ayoub, M.; Abdullah, A.Z. Critical review on the current scenario and significance of crude glycerol resulting from biodiesel industry towards more sustainable renewable energy industry. Renew. Sustain. Energy Rev. 2012, 16, 2671–2686. [CrossRef]
45. Hu, S.; Luo, X.; Wan, C.; Li, Y. Characterization of crude glycerol from biodiesel plants. J. Agric. Food Chem. 2012, 60, 5915–5921. [CrossRef] [PubMed]
46. Din, N.; Idris, Z.; Kian, Y.S.; Hassan, H.A. Preparation of polyglycerol from palm-biodiesel crude glycerin. J. Oil Palm Res. 2013, 25, 289–297.
47. Xiao, Y.; Xiao, G.; Varma, A. A universal procedure for crude glycerol purification from different feedstocks in biodiesel production: Experimental and simulation study. Ind. Eng. Chem. Res. 2013, 52, 14291–14296. [CrossRef]
48. Hazimah, A.; Ooi, T.; Salmiah, A. Recovery of glycerol and diglycerol from glycerol pitch. J. Oil Palm Res. 2003, 15, 1–5.
49. You, Y.-D.; Shie, J.-L.; Chang, C.-Y.; Huang, S.-H.; Pai, C.-Y.; Yu, Y.-H.; Chang, C.H. Economic cost analysis of biodiesel production: Case in soybean oil. Energy Fuels 2007, 22, 182–189. [CrossRef]
50. Moita, R.; Freches, A.; Lemos, P. Crude glycerol as feedstock for polyhydroxyalkanoates production by mixed microbial cultures. Water Res. 2014, 58, 9–20. [CrossRef] [PubMed]
51. Liu, Y.; Koh, C.M.J.; Ji, L. Bioconversion of crude glycerol to glycolipids in Ustilago maydis. Bioreour. Technol. 2011, 102, 3927–3933. [CrossRef] [PubMed]
52. Garlapati, V.K.; Shankar, U.; Buddhira, A. Bioconversion technologies of crude glycerol to value added industrial products. Biotechnol. Rep. 2016, 9, 9–14. [CrossRef] [PubMed]
53. Demirbas, A.; Dincer, K. Sustainable green diesel: A futuristic view. Energy Sources Part A 2008, 30, 1233–1241. [CrossRef]
54. Balat, H.; Kirtay, E. Hydrogen from biomass—Present scenario and future prospects. Int. J. Hydrog. Energy 2010, 35, 7416–7426. [CrossRef]
55. Wei, Z.; Sun, J.; Li, Y.; Dayte, A.K.; Wang, Y. Bimetallic catalysts for hydrogen generation. Chem. Soc. Rev. 2012, 41, 7994–8008. [CrossRef] [PubMed]
56. Avasthi, K.S.; Reddy, R.N.; Patel, S. Challenges in the production of hydrogen from glycerol—A biodiesel byproduct via steam reforming process. Procedia Eng. 2013, 51, 423–429. [CrossRef]
57. Hu, H.; Wood, T.K. An evolved Escherichia coli strain for producing hydrogen and ethanol from glycerol. Biochem. Biophys. Res. Commun. 2010, 391, 1033–1038. [CrossRef] [PubMed]
58. Leonetti, A.B.; Aragão-Leonetti, V.; De Oliveira, S.V.W.B. Glycerol as a by-product of biodiesel production in Brazil: Alternatives for the use of unrefined glycerol. Renew. Energy 2012, 45, 138–145. [CrossRef]
59. Lin, K.-H.; Chang, A.C.-C.; Lin, W.-H.; Chen, S.-H.; Chang, C.-Y.; Chang, H.-F. Autothermal steam reforming of glycerol for hydrogen production over packed-bed and Pd/Ag alloy membrane reactors. Int. J. Hydrog. Energy 2013, 38, 12946–12952. [CrossRef] [PubMed]
60. Schwegner, C.A.; Alves, H.J.; Schaffner, R.A.; da Silva, F.A.; Sequinel, R.; Bach, V.R.; Ferracin, R.J. Overview of glycerol reforming for hydrogen production. Renew. Sustain. Energy Rev. 2016, 58, 259–266. [CrossRef]
61. Dou, B.; Rickett, G.L.; Dupont, V.; Williams, P.T.; Chen, H.; Ding, Y.; Ghadiri, M. Steam reforming of crude glycerol with in situ CO\textsubscript{2} sorption. Bioreour. Technol. 2010, 101, 2436–2442. [CrossRef] [PubMed]
62. Lin, Y.-C. Catalytic valorization of glycerol to hydrogen and syngas. Int. J. Hydrog. Energy 2013, 38, 2678–2700. [CrossRef]
63. Fan, X.; Burton, R.; Zhou, Y. Glycerol (byproduct of biodiesel production) as a source for fuels and chemicals mini review. Open Fuels Energy Sci. J. 2010, 3. [CrossRef]
64. Tan, H.; Aziz, A.A.; Aroua, M. Glycerol production and its applications as a raw material: A review. Renew. Sustain. Energy Rev. 2013, 27, 118–127. [CrossRef]
65. Omwudilli, J.A.; Williams, P.T. Hydrothermal reforming of bio-diesel plant waste: Products distribution and characterization. Fuel 2010, 89, 501–509. [CrossRef]
66. Tapah, B.; Santos, R.; Leeke, G. Processing of glycerol under sub and supercritical water conditions. *Renew. Energy* **2014**, *62*, 353–361. [CrossRef]

67. Bepari, S.; Pradhan, N.C.; Dalai, A.K. Selective production of hydrogen by steam reforming of glycerol over Ni/Al2O3 monolithic catalysts. *Catal. Today* **2017**, *291*, 36–46. [CrossRef]

68. Özgür, D.O.; Uysal, B.Z. Hydrogen production by aqueous phase catalytic reforming of glycerine. *Biomass Bioenergy* **2011**, *35*, 822–826. [CrossRef]

69. Menezes, A.O.; Rodrigues, M.T.; Zimmaro, A.; Borges, L.E.; Fraga, M.A. Production of renewable hydrogen from aqueous-phase reforming of glycerol over Pt catalysts supported on different oxides. *Renew. Energy* **2011**, *36*, 595–599. [CrossRef]

70. Seretis, A.; Tsaiakaras, P. Aqueous phase reforming (APR) of glycerol over platinum supported on Al2O3 catalyst. *Renew. Energy* **2016**, *85*, 1116–1126. [CrossRef]

71. Sanchez, E.A.; Comelli, R.A. Hydrogen production by glycerol steam-reforming over nickel and nickel-cobalt impregnated on alumina. *Int. J. Hydrog. Energy* **2014**, *39*, 8650–8655. [CrossRef]

72. Zamzuri, N.H.; Mat, R.; Amin, N.A.S.; Talebian-Kiakalaieh, A. Hydrogen production from catalytic steam reforming of glycerol over various supported nickel catalysts. *Int. J. Hydrog. Energy* **2017**, *42*, 9087–9098. [CrossRef]

73. Liu, S.-K.; Lin, Y.-C. Autothermal partial oxidation of glycerol to syngas over Pt-, LaMnO3-, and Pt/LaMnO3-coated monoliths. *Ind. Eng. Chem. Res.* **2012**, *51*, 16278–16287. [CrossRef]

74. Rennard, D.C.; Kruger, J.S.; Michael, B.C.; Schmidt, L.D. Long-time behavior of the catalytic partial oxidation of glycerol in an autothermal reactor. *Ind. Eng. Chem. Res.* **2010**, *49*, 8424–8432. [CrossRef]

75. Dianningrum, L.W.; Choi, H.; Kim, Y.; Jung, K.-D.; Susanti, R.F.; Kim, J.; Sang, B.-I. Hydrothermal gasification in a continuous flow tubular reactor. *Int. J. Hydrog. Energy* **2013**, *38*, 5559–5568. [CrossRef]

76. Chaudhary, N.; Ngadi, M.O.; Simpson, B.K.; Kassama, L.S. Biosynthesis of ethanol and hydrogen by glycerol fermentation using Escherichia coli. *Adv. Chem. Eng. Sci.* **2011**, *1*, 83. [CrossRef]

77. Mangayil, R.; Karp, M.; Santala, V. Bioconversion of crude glycerol from biodiesel production to hydrogen. *Int. J. Hydrog. Energy* **2012**, *37*, 12198–12204. [CrossRef]

78. Adhikari, S.; Fernando, S.D.; Haryanto, A. Hydrogen production from glycerol: An update. *Energy Convers. Manage.* **2009**, *50*, 2600–2604. [CrossRef]

79. Manfro, R.L.; Ribeiro, N.F.; Souza, M.M. Production of hydrogen from steam reforming of glycerol using nickel catalysts supported on Al2O3, CeO2 and ZrO2. *Catal. Sustain. Energy* **2013**, *1*, 60–70. [CrossRef]

80. Liu, S.; Guo, Y.; Cao, C.; Yin, J.; Lu, Y.; Zhang, X. Hydrogen production from glycerol by supercritical water gasification: A thermodynamic analysis. *Renew. Energy* **2009**, *35*, 822–826. [CrossRef]

81. Mano, B.T.; Constanti, M.; Stchigel, A.M.; Medina, F.; Sueiras, J.E. Biohydrogen production by dark fermentation of glycerol using Enterobacter and Citrobacter sp. *Biotechnol. Prog.* **2013**, *29*, 31–38. [CrossRef] [PubMed]

82. Haryanto, A.; Fernando, S.D.; Pordesimo, L.O.; Adhikari, S. Upgrading of syngas derived from biomass gasification of crude glycerol with lignocellulosic biomass for enhanced hydrogen production. *Biomass Bioenergy* **2009**, *33*, 353–361. [CrossRef]
90. Lo, Y.-C.; Chen, X.-J.; Huang, C.-Y.; Yuan, Y.-J.; Chang, J.-S. Dark fermentative hydrogen production with crude glycerol from biodiesel industry using indigenous hydrogen-producing bacteria. *Int. J. Hydrog. Energy* **2013**, *38*, 15815–15822. [CrossRef]

91. Maru, B.T.; Bielen, A.; Kengen, S.; Constanti, M.; Medina, F. Biohydrogen production from glycerol using *Thermotoga* spp. *Energy Procedia* **2012**, *29*, 300–307. [CrossRef]

92. Nomanbhay, S.; Hussain, R.; Rahman, M.M.; Palanisamy, K. Review paper integration of biodiesel and bioethanol processes: Conversion of low cost waste glycerol to bioethanol. *Adv. Nat. Appl. Sci.* **2012**, *6*, 802–818.

93. Amaral, P.F.F.; Ferreira, T.F.; Fontes, G.C.; Coelho, M.A.Z. Glycerol valorization: New biotechnological routes. *Food Bioprod. Process.* **2009**, *87*, 179–186. [CrossRef]

94. Posada, J.; Cardona, C. Design and analysis of fuel ethanol production from raw glycerol. *Energy* **2010**, *35*, 5286–5293. [CrossRef]

95. Loaces, I.; Rodríguez, C.; Amarelle, V.; Fabiano, E.; Noya, F. Improved glycerol to ethanol conversion by *E. coli* using a metagenomic fragment isolated from an anaerobic reactor. *J. Ind. Microbiol. Biotechnol.* **2016**, *43*, 1405–1416. [CrossRef] [PubMed]

96. Suhaimi, S.; Phang, L.-Y.; Maeda, T.; Abd-Aziz, S.; Wakisaka, M.; Shirai, Y.; Hassan, M.A. Bioconversion of glycerol for bioethanol production using isolated *Escherichia coli* SS1. *Braz. J. Microbiol.* **2012**, *43*, 506–516. [CrossRef] [PubMed]

97. Oh, B.-R.; Seo, J.-W.; Heo, S.-Y.; Hong, W.-K.; Luo, L.H.; Joe, M.-H.; Park, D.-H.; Kim, C.H. Efficient production of ethanol from crude glycerol by a *Klebsiella pneumoniae* mutant strain. *Bioresour. Technol.* **2011**, *102*, 3918–3922. [CrossRef] [PubMed]

98. Metsoviti, M.; Paraskevaidi, K.; Koutinas, A.; Zeng, A.-P.; Papanikolaou, S. Production of 1,3-propanediol, 2,3-butanediol and ethanol by a newly isolated *Klebsiella oxytoca* strain growing on biodiesel-derived glycerol based media. *Process. Biochem.* **2012**, *47*, 1872–1882. [CrossRef]

99. Metsoviti, M.; Paramithiotis, S.; Drosinos, E.H.; *Klebsiella pneumoniae* SS1. *J. Ind. Microbiol. Biotechnol.* **2012**, *39*, 3871–3876. [CrossRef] [PubMed]

100. Jitrwung, R.; Yargeau, V. Biohydrogen and bioethanol production from biodiesel-based glycerol by *Enterobacter aerogenes* in a continuous stir tank reactor. *Int. J. Mol. Sci.* **2015**, *16*, 10650–10664. [CrossRef] [PubMed]

101. Thapa, L.P.; Lee, S.J.; Yang, X.; Lee, J.H.; Choi, H.S.; Park, C.; Kim, S.W. Improved bioethanol production from metabolic engineering of *Enterobacter aerogenes* ATCC 29007. *Process. Biochem.* **2015**, *50*, 2051–2060. [CrossRef]

102. Kata, I.; Semkiv, M.V.; Ruchala, J.; Dmytruk, K.V.; Sibirny, A.A. Overexpression of the genes *PDC1* and *ADH1* activates glycerol conversion to ethanol in the thermotolerant yeast *Ogataea* (*Hansenula*) *polymorpha*. *Yeast* **2016**, *33*, 471–478. [CrossRef] [PubMed]

103. Varrone, C.; Fiocchetti, F.; Giussani, B.; Izzo, A.; Marone, A.; Massini, G.; Patriarca, C.; Rosa, S.; Signorini, A.; Wang, A. Bio-Conversion of Biodiesel-Derived Glycerol into Hydrogen and Ethanol: Beyond Second-Generation Biofuels. In Proceedings of the 20th European Biomass Conference & Exhibition, Milan, Italy, 18–22 June 2012; pp. 713–716, ISBN 978-88-89407-54-7.

104. Sankaranarayanan, S.; Srinivasan, K. Carbon dioxide—A potential raw material for the production of fuel, fuel additives and bio-derived chemicals. *Indian J. Chem. A* **2012**, *51*, 1252–1262.

105. Haider, M.H.; Dummer, N.F.; Knight, D.W.; Jenkins, R.L.; Howard, M.; Moulijn, J.; Taylor, S.H.; Hutchings, G.J. Efficient green methanol synthesis from glycerol. *Nat. Chem.* **2015**, *7*, 1028. [CrossRef] [PubMed]

106. Carr, A.G.; Shi, X.; Domene, C.; Leung, A.K.; Green, W.H. Methanol formation from the treatment of glycerol in supercritical water and with ethylsulfide. *J. Supercrit. Fluids* **2016**, *117*, 80–88. [CrossRef]

107. García, J.L.; García-Marín, H.; Pires, E. Glycerol based solvents: Synthesis, properties and applications. *Green Chem.* **2014**, *16*, 1007–1033. [CrossRef]

108. Cornejo, A.; Barrio, I.; Campoy, M.; Lázaro, J.; Navarrete, B. Oxygenated fuel additives from glycerol valorization. Main production pathways and effects on fuel properties and engine performance: A critical review. *Renew. Sustain. Energy Rev.* **2017**, *79*, 1400–1413. [CrossRef]
109. Farinha, J.; Caiado, M.; Castanheiro, J. Valorisation of glycerol into biofuel additives over heterogeneous catalysts. In Materials and Processes for Energy: Communicating Current Research and Technological Developments; Méndez-Vilas, A.S., Ed.; Formatex Research Center Country: Badajoz, Spain, 2013; pp. 422–429, ISBN 978-84-939843-7-3. Available online: http://hdl.handle.net/10174/10317 (accessed on 29 May 2017).

110. Usai, E.; Gualdi, E.; Solinas, V.; Battistel, E. Simultaneous enzymatic synthesis of FAME and triacetyl glycerol from triglycerides and methyl acetate. Bioresour. Technol. 2010, 101, 7707–7712. [CrossRef] [PubMed]

111. Morales, G.; Paniagua, M.; Melero, J.A.; Vicente, G.; Ochoa, C. Sulfonic acid-functionalized catalysts for the valorization of glycerol via transesterification with methyl acetate. Ind. Eng. Chem. Res. 2011, 50, 5898–5906. [CrossRef]

112. Khayoon, M.; Hameed, B. Synthesis of hybrid SBA-15 functionalized with molybdophosphoric acid as efficient catalyst for glycerol esterification to fuel additives. Appl. Catal. A Gen. 2012, 432, 152–161. [CrossRef]

113. Liao, X.; Zhu, Y.; Wang, S.-G.; Li, Y. Producing triacetylglycerol with glycerol by two steps: Esterification and acetylation. Fuel Process. Technol. 2009, 90, 988–993. [CrossRef]

114. Gonzalez-Arellano, C.; De, S.; Luque, R. Selective glycerol transformations to high value-added products catalysed by aluminosilicate-supported iron oxide nanoparticles. Catal. Sci. Technol. 2014, 4, 4242–4249. [CrossRef]

115. Silva, L.N.; Gonçalves, V.L.; Mota, C.J. Catalytic acetylation of glycerol with acetic anhydride. J. Ind. Eng. Chem. 2010, 16, 1036–1039. [CrossRef]

116. Zhu, L.; Al-Zaini, E.; Adesina, A.A. Catalytic characteristics and parameters optimization of the glycerol acetylation over solid acid catalysts. Fuel 2013, 103, 617–625. [CrossRef]

117. Khayoon, M.; Triwahyono, S.; Hameed, B.; Jalil, A. Improved production of fuel oxygenates via glycerol acetylation with acetic acid. Chem. Eng. J. 2014, 243, 473–484. [CrossRef]

118. Sandesh, S.; Kristachar, P.K.R.; Manjunathan, P.; Halgeri, A.; Shanbhag, G.V. Synthesis of biodiesel and acetins by transesterification reactions using novel CaSn (OH) 6 heterogeneous base catalyst. Appl. Catal. A Gen. 2016, 523, 1–11. [CrossRef]

119. Okoye, P.; Abdullah, A.; Hameed, B. Synthesis of oxygenated fuel additives via glycerol esterification with acetic acid over bio-derived carbon catalyst. Fuel 2017, 209, 538–544. [CrossRef]

120. Khayoon, M.; Triviňahyono, S.; Hameed, B.; Jalil, A. Improved production of fuel oxygenates via glycerol acetylation with acetic acid. Chem. Eng. J. 2014, 243, 473–484. [CrossRef]

121. Dalla Costa, B.; Decolatti, H.; Legnoverde, M.; Querini, C. Influence of acidic properties of different solid acid catalysts for glycerol acetylation. Catal. Today 2017, 289, 222–230. [CrossRef]

122. Reddy, P.S.; Sudarsanam, P.; Raju, G.; Reddy, B.M. Synthesis of bio-additives: Acetylation of glycerol over zirconia-based solid acid catalysts. Catal. Commun. 2010, 11, 1224–1228. [CrossRef]

123. Reddy, P.S.; Sudarsanam, P.; Raju, G.; Reddy, B.M. Selective acetylation of glycerol over CeO₂–M and SO₄²⁻/CeO₂–M (M = ZrO₂ and Al₂O₃) catalysts for synthesis of bioadditives. J. Ind. Eng. Chem. 2012, 18, 648–654. [CrossRef]

124. Zhang, Z.; Huang, H.; Ma, X.; Li, G.; Wang, Y.; Sun, G.; Teng, Y.; Yan, R.; Zhang, N.; Li, A. Production of diacylglycerols by esterification of oleic acid with glycerol catalyzed by diatomite loaded SO₄²⁻/TiO₂. J. Ind. Eng. Chem. 2017, 53, 307–316. [CrossRef]

125. Sandesh, S.; Kristachar, P.K.R.; Manjunathan, P.; Halgeri, A.; Shanbhag, G.V. Synthesis of biodiesel and acetins by transesterification reactions using novel CaSn (OH) 6 heterogeneous base catalyst. Appl. Catal. A Gen. 2016, 523, 1–11. [CrossRef]

126. Okoye, P.; Abdullah, A.; Hameed, B. Synthesis of oxygenated fuel additives via glycerol esterification with acetic acid over bio-derived carbon catalyst. Fuel 2017, 209, 538–544. [CrossRef]

127. Morales, G.; Paniagua, M.; Melero, J.A.; Vicente, G.; Ochoa, C. Sulfonic acid-functionalized catalysts for the valorization of glycerol via transesterification with methyl acetate. Ind. Eng. Chem. Res. 2011, 50, 5898–5906. [CrossRef]

128. García, J.I.; García-Marín, H.; Mayoral, J.A.; Pérez, P. Green solvents from glycerol. Synthesis and physico-chemical properties of alkyl glycerol ethers. Green Chem. 2010, 12, 426–434. [CrossRef]
130. Gonçalves, M.; Souza, V.C.; Galhardo, T.S.; Mantovani, M.; Figueiredo, F.V.C.; Mandelli, D.; Carvalho, W.A. Glycerol conversion catalyzed by carbons prepared from agroindustrial wastes. *Ind. Eng. Chem. Res.* 2013, 52, 2832–2839. [CrossRef]

131. Ayoub, M.; Khayoon, M.; Abdullah, A.Z. Synthesis of oxygenated fuel additives via the solventless etherification of glycerol. *Bioresour. Technol.* 2012, 112, 308–312. [CrossRef] [PubMed]

132. Yuan, Z.; Xia, S.; Chen, P.; Hou, Z.; Zheng, X. Etherification of biodiesel-based glycerol with bioethanol over tungstophosphoric acid to synthesize glyceryl ethers. *Energy Fuels* 2011, 25, 3186–3191. [CrossRef]

133. Viswanadham, N.; Saxena, S.K. Etherification of glycerol for improved production of oxygenates. *Fuel* 2013, 103, 980–986. [CrossRef]

134. Veiga, P.M.; Gomes, A.C.; Veloso, C.O.; Henriques, C.A. Acid zeolites for glycerol etherification with ethyl alcohol: Catalytic activity and catalyst properties. *Appl. Catal. A Gen.* 2017, 548, 2–15. [CrossRef]

135. Pinto, B.P.; de Lyra, J.T.; Nascimento, J.A.; Mota, C.J. Ethers of glycerol and ethanol as bioadditives for biodiesel. *Fuel* 2016, 168, 76–80. [CrossRef]

136. Estevez, R.; Lopez, M.; Jimenez-Sanchidrián, C.; Luna, D.; Romero-Salgueiro, F.; Bautista, F. Etherification of glycerol with tert-butyl alcohol over sulfonated hybrid silicas. *Appl. Catal. A Gen.* 2016, 526, 155–163. [CrossRef]

137. Agirre, I.; Garcia, I.; Requies, J.; Barrio, V.; Güemez, M.; Cambra, J.; Arias, P. Glycerol acetals, kinetic study of the reaction between glycerol and formaldehyde. *Biomass Bioenergy* 2011, 35, 3636–3642. [CrossRef]

138. Mota, C.J.; da Silva, C.X.; Rosenbach, N., Jr.; Costa, J.; da Silva, F.V. Glycerin derivatives as fuel additives: The addition of glycerol/acetone ketal (solketal) in gasolines. *Energy Fuels* 2010, 24, 2733–2736. [CrossRef]

139. Maksimov, A.; Nekhaev, A.; Ramazanov, D.; Arinicheva, Y.A.; Dzyubenko, A.; Khadzhiev, S. Preparation of high-octane oxygenate fuel components from plant-derived polyols. *Pet. Chem.* 2011, 51, 61–69. [CrossRef]

140. Suriyaprapadilok, N.; Kitiyanan, B. Synthesis of solketal from glycerol and its reaction with benzyl alcohol. *Energy Procedia* 2011, 9, 63–69. [CrossRef]

141. Vicente, G.; Melero, J.A.; Morales, G.; Paniagua, M.; Martin, E. Acetalisation of bio-glycerol with acetone to produce solketal over sulfonic mesostructured silicas. *Green Chem.* 2010, 12, 899–907. [CrossRef]

142. De Torres, M.; Jimenez-Oses, G.; Mayoral, J.A.; Pires, E.; de los Santos, M. Glycerol ketals: Synthesis and profits in biodiesel blends. *Fuel* 2012, 94, 614–616. [CrossRef]

143. Nanda, M.R.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Poirier, M.-A.; Xu, C.C. A new continuous-flow process for catalytic conversion of glycerol to oxygenated fuel additive: Catalyst screening. *Appl. Energy* 2014, 123, 75–81. [CrossRef]

144. Nanda, M.R.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Poirier, M.-A.; Xu, C.C. Catalytic conversion of glycerol to oxygenated fuel additive in a continuous flow reactor: Process optimization. *Fuel* 2014, 128, 113–119. [CrossRef]

145. Nanda, M.R.; Yuan, Z.; Qin, W.; Ghaziaskar, H.S.; Poirier, M.-A.; Xu, C.C. Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive. *Fuel* 2014, 117, 470–477. [CrossRef]

146. Gadamsetti, S.; Rajan, N.P.; Rao, G.S.; Chary, K.V. Acetalization of glycerol with acetone to bio fuel additives over supported molybdenum phosphate catalysts. *J. Mol. Catal. A Chem.* 2015, 410, 49–57. [CrossRef]

147. Jamil, F.; Saxena, S.K.; Al’a’a, H.; Baawain, M.; Al-Abri, M.; Viswanadham, N.; Kumar, G.; Abu-Jrai, A.M. Valorization of waste “date seeds” bio-glycerol for synthesizing oxidative green fuel additive. *J. Clean. Prod.* 2017, 165, 1090–1096. [CrossRef]

148. Manjunathan, P.; Maradur, S.P.; Halgeri, A.; Shanbhag, G.V. Room temperature synthesis of solketal from acetalization of glycerol with acetone: Effect of crystallite size and the role of acidity of beta zeolite. *J. Mol. Catal. A Chem.* 2015, 396, 47–54. [CrossRef]

149. Khayoon, M.; Hameed, B. Solventless acetalization of glycerol with acetone to fuel oxygenates over Ni-Zr supported on mesoporous activated carbon catalyst. *Appl. Catal. A Gen.* 2013, 464, 191–199. [CrossRef]

150. De Carvalho, D.C.; Oliveira, A.C.; Ferreira, O.P.; Josué Filho, M.; Tehuacanero-Cuapa, S.; Oliveira, A.C. Titanate nanotubes as acid catalysts for acetalization of glycerol with acetone: Influence of the synthesis time and the role of structure on the catalytic performance. *Chem. Eng. J.* 2017, 313, 1454–1467. [CrossRef]

151. Rodrigues, R.; Mandelli, D.; Gonçalves, N.S.; Pescarmona, P.P.; Carvalho, W.A. Acetalization of acetone with glycerol catalyzed by niobium-aluminum mixed oxides synthesized by a sol–gel process. *J. Mol. Catal. A Chem.* 2016, 422, 122–130. [CrossRef]
152. Kapkowski, M.; Ambrożkiewicz, W.; Siudyga, T.; Sitko, R.; Szade, J.; Klimontko, J.; Balin, K.; Lelątko, J.; Polanski, J. Nano silica and molybdenum supported Re, Rh, Ru or Ir nanoparticles for selective solvent-free glycerol conversion to cyclic acetalts with propanone and butanone under mild conditions. *Appl. Catal. B Environ.* 2017, 202, 335–345. [CrossRef]

153. Umbarkar, S.B.; Kotbagi, T.V.; Biradar, A.V.; Pasricha, R.; Chanale, J.; Dongare, M.K.; Mamede, A.-S.; Lancelot, C.; Payen, E. Acetalization of glycerol using mesoporous MoO3/SiO2 solid acid catalyst. *J. Mol. Catal. A Chem.* 2009, 310, 150–158. [CrossRef]

154. Sudarsanam, P.; Mallesham, B.; Prasad, A.N.; Reddy, P.S.; Reddy, B.M. Synthesis of bio–additive fuels from acetalization of glycerol with benzaldehyde over molybdenum promoted green solid acid catalysts. *Fuel Process. Technol.* 2013, 106, 539–545. [CrossRef]

155. Chen, L.; Nohair, B.; Kaliaguine, S. Glycerol acetalization with formaldehyde using water-tolerant solid acids. *Appl. Catal. A Gen.* 2016, 509, 143–152. [CrossRef]

156. Possato, L.G.; Diniz, R.N.; Garetto, T.; Pulcinelli, S.H.; Santilli, C.V.; Martins, L. A comparative study of glycerol dehydration catalyzed by micro/mesoporous MFI zeolites. *J. Catal.* 2013, 300, 102–112. [CrossRef]

157. Rajan, N.P.; Rao, G.S.; Pavankumar, V.; Chary, K.V. Vapour phase dehydration of glycerol over VPO catalyst supported on zirconium phosphate. *Catal. Sci. Technol.* 2014, 4, 81–92. [CrossRef]

158. Akizuki, M.; Oshima, Y. Kinetics of glycerol dehydration with WO3/TiO2 in supercritical water. *Ind. Eng. Chem. Res.* 2012, 51, 12253–12257. [CrossRef]

159. Gu, Y.; Liu, S.; Li, C.; Cui, Q. Selective conversion of glycerol to acrolein over supported nickel sulfate catalysts. *J. Catal.* 2013, 301, 93–102. [CrossRef]

160. Yadav, G.D.; Sharma, R.V.; Katole, S.O. Selective dehydration of glycerol to acrolein: Development of efficient and robust solid acid catalyst MUICaT-5. *Ind. Eng. Chem. Res.* 2013, 52, 10133–10144. [CrossRef]

161. Alhanash, A.; Kozhevnikova, E.F.; Kozhevnikov, I.V. Gas-phase dehydration of glycerol to acrolein catalysed by caesium heteropoly salt. *Appl. Catal. A Gen.* 2010, 378, 11–18. [CrossRef]

162. Ma, T.; Ding, J.; Shao, R.; Xu, W.; Yun, Z. Dehydration of glycerol to acrolein over Wells–Dawson and Keggin type phosphotungstic acids supported on MCM-41 catalysts. *Chem. Eng. J.* 2017, 316, 797–806. [CrossRef]

163. Dar, B.A.; Dadhwal, S.; Singh, G.; Garg, P.; Sharma, P.; Singh, B. Vapour phase conversion of glycerol to acrolein over supported copper. *Arab. J. Sci. Eng.* 2013, 38, 37–40. [CrossRef]

164. Jia, C.-J.; Liu, Y.; Schmidt, W.; Lu, A.-H.; Schüth, F. Small-sized HZSM-5 zeolite as highly active catalyst for gas phase dehydration of glycerol to acrolein. *J. Catal.* 2010, 269, 71–79. [CrossRef]

165. Possato, L.G.; Chaves, T.F.; Cassinelli, W.H.; Pulcinelli, S.H.; Santilli, C.V.; Martins, L. The multiple benefits of acetalization of glycerol conversion to acrolein and acrylic acid catalyzed by vanadium oxides supported on micro-mesoporous MFI zeolites. *Catal. Today* 2017, 289, 20–28. [CrossRef]

166. Zhao, H.; Zhou, C.H.; Wu, L.M.; Lou, J.Y.; Li, N.; Yang, H.M.; Tong, D.S.; Yu, W.H. Catalytic dehydration of glycerol to acrolein over sulfuric acid-activated montmorillonite catalysts. *Appl. Clay Sci.* 2013, 74, 154–162. [CrossRef]

167. Ochoa-Gómez, J.R.; Gómez-Jiménez-Aberasturi, O.; Maestro-Madurga, B.; Pesquera-Rodríguez, A.; Ramírez-López, C.; Lorenzo-Ibarreta, L.; Torrecilla-Soria, J.; Villarán-Velasco, M.C. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate by transesterification: Catalyst screening and reaction optimization. *Appl. Catal. A Gen.* 2009, 366, 315–324. [CrossRef]

168. Climent, M.J.; Corma, A.; De Frutos, P.; Ibura, S.; Noy, M.; Velty, A.; Concepción, P. Chemicals from biomass: Synthesis of glycerol carbonate by transesterification and carbonylation with urea with hydrotalcite catalysts. The role of acid–base pairs. *J. Catal.* 2010, 269, 140–149. [CrossRef]

169. Casiello, M.; Monopoli, A.; Cotugno, P.; Milella, A.; Dell’Anna, M.M.; Ciminale, F.; Nacci, A. Copper (II) chloride-catalyzed oxidative carbonylation of glycerol to glycerol carbonate. *J. Mol. Catal. A Chem.* 2014, 381, 99–106. [CrossRef]

170. Zhang, J.; He, D. Surface properties of Cu/La2O3 and its catalytic performance in the synthesis of glycerol carbonate and monoacetin from glycerol and carbon dioxide. *J. Colloid Interface Sci.* 2014, 419, 31–38. [CrossRef] [PubMed]

171. Zuhaimi, N.A.S.; Indran, V.P.; Deraman, M.A.; Mudrikah, N.F.; Maniam, G.P.; Taufiq-Yap, Y.H.; Rahim, M.H.A. Reusable gypsum based catalyst for synthesis of glycerol carbonate from glycerol and urea. *Appl. Catal. A Gen.* 2015, 502, 312–319. [CrossRef]
172. Wu, Y.; Song, X.; Cai, F.; Xiao, G. Synthesis of glycerol carbonate from glycerol and diethyl carbonate over Ce-NiO catalyst: The role of multiphase Ni. J. Alloys Compd. 2017, 720, 360–368. [CrossRef]
173. Ozorio, L.P.; Pianzolli, R.; da Cruz Machado, L.; Miranda, J.L.; Turci, C.C.; Guerra, A.C.; Souza-Aguiar, E.F.; Mota, C.J. Metal-impregnated zeolite Y as efficient catalyst for the direct carbonation of glycerol with CO2. Appl. Catal. A Gen. 2015, 504, 187–191. [CrossRef]
174. Indran, V.P.; Zuhami, N.A.S.; Deraman, M.A.; Maniam, G.P.; Yusoff, M.M.; Hin, T.-Y.Y.; Rahim, M.H.A. An accelerated route of glycerol carbonate formation from glycerol using waste boiler ash as catalyst. RSC Adv. 2014, 4, 25257–25267. [CrossRef]
175. Naik, P.U.; Petitjean, L.; Refes, K.; Picquet, M.; Plasseraud, L. Imidazolium-2-carboxylate as an Efficient, Expeditious and Eco-Friendly Organocatalyst for Glycerol Carbonate Synthesis. Adv. Synth. Catal. 2009, 351, 1753–1756. [CrossRef]
176. Ishak, Z.I.; Sairi, N.A.; Alias, Y.; Aroua, M.K.T.; Yusoff, R. Production of glycerol carbonate from glycerol with aid of ionic liquid as catalyst. Chem. Eng. J. 2016, 297, 128–138. [CrossRef]
177. Saxena, R.; Anand, P.; Saran, S.; Isar, J. Microbial production of 1,3-propanediol: Recent developments and emerging opportunities. Biotechnol. Adv. 2009, 27, 895–913. [CrossRef] [PubMed]
178. Ten Dam, J.; Hanefeld, U. Renewable chemicals: Dehydroxylation of glycerol and polyols. ChemSusChem 2011, 4, 1017–1034. [CrossRef] [PubMed]
179. Zeng, A.-P.; Sabra, W. Microbial production of diols as platform chemicals: Recent progresses. Curr. Opin. Biotechnol. 2011, 22, 749–757. [CrossRef] [PubMed]
180. Qin, L.-Z.; Song, M.-J.; Chen, C.-L. Aqueous-phase deoxygenation of glycerol to 1,3-propanediol over Pt/WO3/ZrO2 catalysts in a fixed-bed reactor. Green Chem. 2010, 12, 1466–1472. [CrossRef]
181. Gong, L.; Lu, Y.; Ding, Y.; Lin, R.; Li, J.; Dong, W.; Wang, T.; Chen, W. Selective hydrogenolysis of glycerol to 1,3-propanediol over a Pt/WO3/TiO2/SiO2 catalyst in aqueous media. Appl. Catal. A Gen. 2010, 390, 119–126. [CrossRef]
182. García-Fernández, S.; Gandarias, I.; Requies, J.; Soulimani, F.; Arias, P.L.; Weckhuysen, B.M. The role of tungsten oxide in the selective hydrogenolysis of glycerol to 1,3-propanediol over Pt/WO3/Al2O3. Appl. Catal. B Environ. 2017, 204, 260–272. [CrossRef] [PubMed]
183. García-Fernández, S.; Gandarias, I.; Requies, J.; Güemez, M.; Bennici, S.; Auroux, A.; Arias, P. New approaches to the Pt/WO3/Al2O3 catalytic system behavior for the selective glycerol hydrogenolysis to 1,3-propanediol. J. Catal. 2015, 323, 65–75. [CrossRef]
184. Longjie, L.; Zhang, Y.; Aiqin, W.; Zhang, T. Mesoporous WO3 supported Pt catalyst for hydrogenolysis of glycerol to 1,3-propanediol. Chin. J. Catal. 2012, 33, 1257–1261. [CrossRef]
185. Zhu, S.; Gao, X.; Zhu, Y.; Zhu, Y.; Xiang, X.; Hu, C.; Li, Y. Alkaline metals modified Pt-H3SiW12O40/ZrO2 catalysts for the selective hydrogenolysis of glycerol to 1,3-propanediol. Appl. Catal. B Environ. 2013, 140, 60–67. [CrossRef]
186. Zhu, S.; Qiu, Y.; Zhu, Y.; Hao, S.; Zheng, H.; Li, Y. Hydrogenolysis of glycerol to 1,3-propanediol over bifunctional catalysts containing Pt and heteropolyacids. Catal. Today 2013, 212, 120–126. [CrossRef]
187. Zhu, S.; Gao, X.; Zhu, Y.; Cui, J.; Zheng, H.; Li, Y. SiO2 promoted Pt/WO3/ZrO2 catalysts for the selective hydrogenolysis of glycerol to 1,3-propanediol. Appl. Catal. B Environ. 2014, 158, 391–399. [CrossRef]
188. Deng, C.; Duan, X.; Zhou, J.; Chen, D.; Zhou, X.; Yuan, W. Size effects of Pt-Re bimetallic catalysts for glycerol hydrogenolysis. Catal. Today 2014, 234, 208–214. [CrossRef]
189. Zhou, W.; Zhao, Y.; Wang, S.; Ma, X. The effect of metal properties on the reaction routes of glycerol hydrogenolysis over platinum and ruthenium catalysts. Catal. Today 2017, 298, 2–8. [CrossRef]
190. Kant, A.; He, Y.; Jawad, A.; Li, X.; Rezaei, F.; Smith, J.D.; Rownaghi, A.A. Hydrogenolysis of glycerol over Ni, Cu, Zn, and Zr supported on H-ß. Chem. Eng. J. 2017, 317, 1–8. [CrossRef]
191. Sivahia, M.; Robles-Manuel, S.; Valange, S.; Barrault, J. Recent developments in acid and base-catalyzed etherification of glycerol to polyglycerols. Catal. Today 2012, 198, 305–313. [CrossRef]
192. Beltramini, J.N.; Zhou, C.-H.C. Catalytic conversion of glycerol to valuable commodity chemicals. In Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals; Crocker, M.S., Ed.; RSC Publishing: London, UK, 2010; pp. 435–467, ISBN 978-1-84973-035-8. [CrossRef]
193. Martin, A.; Checinski, M.P.; Richter, M. Tuning of diglycerol yield and isomer distribution in oligomerization of glycerol supported by DFT-calculations. Catal. Commun. 2012, 25, 130–135. [CrossRef]
194. Ruppert, A.M.; Meeldijk, J.D.; Kuipers, B.W.; Erné, B.H.; Weckhuysen, B.M. Glycerol Etherification over Highly Active CaO-Based Materials: New Mechanistic Aspects and Related Colloidal Particle Formation. Chem.-A Eur. J. 2008, 14, 2016–2024. [CrossRef] [PubMed]
195. García-Sancho, C.; Moreno-Tost, R.; Mérida-Robles, J.M.; Santamaría-González, J.; Jiménez-López, A.; Torres, P.M. Etherification of glycerol to polyglycerols over MgAl mixed oxides. Catal. Today 2011, 167, 84–90. [CrossRef]
196. Anuar, M.R.; Abdullah, A.Z.; Othman, M.R. Etherification of glycerol to polyglycerols over hydrotalcite catalyst prepared using a combustion method. Catal. Commun. 2013, 32, 67–70. [CrossRef]
197. Ayoub, M.; Abdullah, A.Z. Diglycerol synthesis via solvent-free selective glycerol etherification process over lithium-modified clay catalyst. Chem. Eng. J. 2013, 225, 784–789. [CrossRef]
198. Gholami, Z.; Abdullah, A.Z.; Lee, K.-T. Heterogeneously catalyzed etherification of glycerol to diglycerol over calcium-lanthanum oxide supported on MCM-41: A heterogenous basic catalyst. Appl. Catal. A Gen. 2014, 479, 76–86. [CrossRef]
199. Gholami, Z.; Abdullah, A.Z.; Lee, K.-T. Glycerol etherification to polyglycerols using Ca$\text{}_{1+x}$Al$\text{}_{1-x}$La$\text{x}$O$_\text{3}$ composite catalysts in a solventless medium. J. Taiwan Inst. Chem. Eng. 2013, 44, 117–122. [CrossRef]
200. Guerrero-Urbaneja, P.; García-Sancho, C.; Moreno-Tost, R.; Mérida-Robles, J.; Santamaría-González, J.; Jiménez-López, A.; Maireles-Torres, P. Glycerol valorization by etherification to polyglycerols by using metal oxides derived from MgFe hydrotalcites. Appl. Catal. A Gen. 2014, 470, 199–207. [CrossRef]
201. Ayoub, M.; Abdullah, A.Z.; Ahmad, M.; Sultana, S. Performance of lithium modified zeolite Y catalyst in solvent-free conversion of glycerol to polyglycerols. J. Taibah Univ. Sci. 2014, 8, 231–235. [CrossRef]
202. Bookong, P.; Ruchirawat, S.; Boonyaratnamaklin, S. Optimization of microwave-assisted etherification of glycerol to polyglycerols by sodium carbonate as catalyst. Chem. Eng. J. 2015, 275, 253–261. [CrossRef]
203. Pérez-Barrado, E.; Pujol, M.C.; Aguiló, M.; Llorca, J.; Cesteros, Y.; Díaz, F.; Pallarès, J.; Marsal, L.E.; Salagre, P. Influence of acid–base properties of calcined MgAl and CaAl layered double hydroxides on the catalytic glycerol etherification to short-chain polyglycerols. Chem. Eng. J. 2015, 264, 547–556. [CrossRef]
204. Karam, A.; Sayoud, N.; Vigier, K.D.O.; Lai, J.; Liebens, A.; Oldani, C.; Jérôme, F. Heterogeneously-acid catalyzed oligomerization of glycerol over recyclable superacid Aquivion® PFSA. J. Mol. Catal. A Chem. 2016, 422, 84–88. [CrossRef]
205. Galy, N.; Nguyen, R.; Blach, P.; Sambou, S.; Luart, D.; Len, C. Glycerol oligomerization in continuous flow reactor. J. Ind. Eng. Chem. 2017, 51, 312–318. [CrossRef]
206. Barros, F.; Moreno-Tost, R.; Cecilia, J.; Ledesma-Muñoz, A.; de Oliveira, L.; Luna, F.; Vieira, R. Glycerol oligomers production by etherification using calcined eggshell as catalyst. Mol. Catal. 2017, 433, 282–290. [CrossRef]
207. Zakaria, Z.; Mohamad, N.; Amin, N. Catalysts Screening for Catalytic Conversion of Glycerol to Olefins. J. Appl. Sci. 2010, 10, 1166–1170. [CrossRef]
208. Li, X.; Shen, B.; Guo, Q.; Gao, J. Effects of large pore zeolite additions in the catalytic pyrolysis catalyst on the light olefins production. Catal. Today 2007, 125, 270–277. [CrossRef]
209. Masih, M.; Algahtani, I.; De Mello, L. Price dynamics of crude oil and the regional ethylene markets. Energy Econ. 2010, 32, 1435–1444. [CrossRef]
210. Zakaria, Z.Y.; Linnekoski, J.; Amin, N. Catalyst screening for conversion of glycerol to light olefins. Chem. Eng. J. 2012, 207, 803–813. [CrossRef]
211. Blass, S.D.; Hermann, R.J.; Persson, N.E.; Bhan, A.; Schmidt, L.D. Conversion of glycerol to light olefins and gasoline precursors. Appl. Catal. A Gen. 2014, 475, 10–15. [CrossRef]
212. Zakaria, Z.Y.; Amin, N.A.S.; Linnekoski, J. Thermodynamic analysis of glycerol conversion to olefins. Energy Procedia 2014, 61, 2489–2492. [CrossRef]