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*Review Article*

# Glycerol Acetalisation for Sustainable Biorefineries: A Review on Catalysts and Reaction Parameters

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## ABSTRACT

Glycerol, a renewable by-product of biodiesel production, is an increasingly attractive bio-feedstock for conversion into value-added chemicals. Among its transformations, acetalisation to produce solketal and acetal holds promise due to their use as fuel additives, solvents, and polymer precursors. This review critically examines the properties, synthesis, and applications of glycerol, with a focus on heterogeneous catalytic acetalisation using catalysts such as heteropoly acids, metal oxides, and polymer-supported materials. It also analyzes how reaction parameters such as temperature, molar ratio, water content, and time affect conversion and selectivity. Advancements in this area highlight glycerol's potential in sustainable industrial processes and future biorefineries.

*Keywords*: Acetalisation, biodiesel, glycerol, heterogeneous catalysis, solketal

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## INTRODUCTION

The utilisation of renewable biomass sources to produce fuels and high-value-added chemicals is widespread as a renewable

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method of reducing dependence on finite petroleum resources, decreasing $CO_2$ emissions, and reaching carbon neutrality (He et al., 2023; Lee et al., 2022). Biodiesel, which is generated from organic matter, has been identified as a promising alternative to conventional transportation fuel (Changmai et al., 2020; Nda-Umar et al., 2019). The environmentally friendly aspect of this product is that it is biodegradable and has the potential to reduce chemical emissions, i.e., 100 % sulfur dioxide, 68 % unburned hydrocarbons, and 80 – 90 % polycyclic aromatic hydrocarbons (Fazal et al., 2011). The most widely used biofuel in the European Union (EU) is biodiesel. For instance, biodiesel output in Europe improved significantly from 15 to 430 thousand barrels daily between 2000 and 2012 (Monteiro et al., 2018). Biodiesel production capacity has markedly improved since the European Commission's 2014 report, reaching approximately 26.3 billion litres, with a yearly output of about 10.5 billion litres, or 40% of the total capacity (Nanda et al., 2014).

According to Global Bioenergy Statistics (GBS) data 2018, issued by the World Bioenergy Association (WBA) biodiesel production still shows an upward trend and has reached approximately 32.6 billion litres. According to the Organisation for Economic Cooperation and Development (OECD), global biodiesel output is expected to increase from 36 billion litres in 2017 to 44 billion litres in 2028. The EU is expected to continue dominating the global biodiesel production market. By 2030, the total biodiesel production will reach almost 63 million tonnes (Olson et al., 2023). Consequently, the market is facing an inevitable surplus of glycerol due to the rapid growth of the biodiesel industry. Therefore, it is anticipated that the demand for glycerol would undergo a more accelerated expansion compared to its typical applications, encompassing sectors such as food, cosmetics, and medicines. The observed phenomenon can be attributed to the regular infusion of excess glycerol into a market characterised by a relatively stable demand level (Zahid et al., 2020). On the other hand, catalytic and biological transformation of glycerol provides prospects for value-added chemicals such as propanediols via hydrogenolysis, acrolein via dehydration, dihydroxyacetone via oxidation, poly glycerol via etherification, syngas via reforming (Nda-Umar et al., 2019; Talebian-Kiakalaieh et al., 2018). Glycerol is a platform chemical, with some possibilities being reviewed (Nanda et al., 2016; Nda-Umar et al., 2019; Pirzadi & Meshkani, 2022). Solketal and acetal synthesis through glycerol acetalisation with aldehydes and ketones is an attractive application in fuel, polymers, solvents, intermediates, pharmaceuticals, and foods (Nanda et al., 2016; Talebian-Kiakalaieh et al., 2018; Trifoi et al., 2016). Figure 1 depicts the production of global biodiesel production accompanied by the generation of glycerol (Chilakamarry et al., 2021).

This review paper focusses on the modern methodology of glycerol acetalisation, aiming to advance the technology used in future biorefineries by utilising glycerol as a byproduct. This study tries to compare the efficacy of different developed catalysts and methodologies. Additionally, it involves exploring the chemical reactions that transform

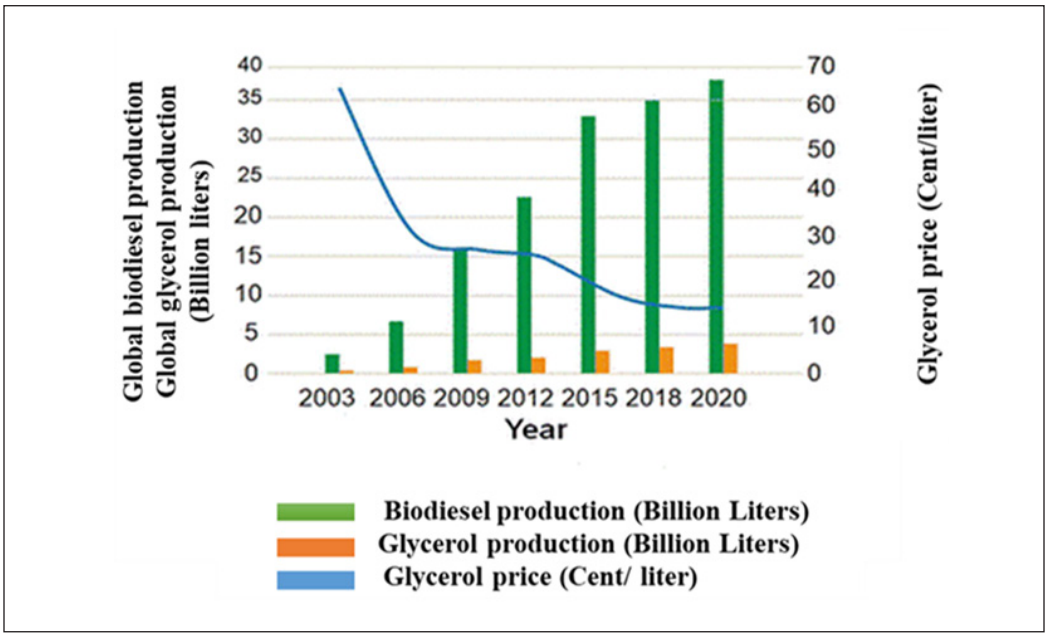


*Figure 1*. Global biodiesel and glycerol production and prices between 2003 to 2020 with acknowledgement of (Chilakamarry et al., 2021)

glycerol into acetal and solketal, paying special attention to the function of a heterogeneous catalyst. The research also targets the complete understanding of the various applications of solketal and acetal in certain industries like fuel additives, polymer manufacture, solvents, chemical intermediates, pharmaceuticals, and foods and beverages. Additionally, the review article aims to discuss the transformation of glycerol to solketal and acetal via different types of catalysts, e.g., zeolite catalysts, hetero-poly acids, metal oxide catalysts, and polymer-based catalysts. The review also aims to examine the impact of different reaction conditions, such as operating temperature, reaction time, solvent, molar ratio, and water, on the acetalisation of glycerol.

## Overview of Glycerol and Its Production

Scientists have been able to transform various wastes into products of greater value. The theme of waste being transformed into a valuable product has kept particular emphasis on the waste produced by the biodiesel sector, for which glycerol has emerged as a major product (Monteiro et al., 2018; Nda-Umar et al., 2019). Glycerol, a coproduct, has been facing oversupply in the global market since 1995, rendering it difficult for the steadily rising production of biodiesel. It was estimated that the production of glycerol was above its consumption by six times (Monteiro et al., 2018). Hence, to avert market saturation and guarantee the long-term sustainability and resilience of the biodiesel sector in general, it

is increasingly necessary to seek out and develop other means of processing the glycerol produced during the production of biodiesel to convert it into products of greater economic value (Cornejo et al., 2019; Monteiro et al., 2018; Nanda et al., 2014).

Glycerol is also widely known as 'glycerine,' a term created by Swedish chemist Carl Wilhelm Scheele in 1779 when he conducted initial tests on the compound with the chemical formula 1,2,3-propanetriol. French chemist Michel Eugène Chevreul standardised the use of glycerine in 1823. The concept "glycerine" originates from the Greek word "glukeros," which means "sweet."Subsequently, in 1855, Charles Adolphe Wurtz established the chemical formula of glycerine as $C_3H_8O_3$ (Zhang et al., 2022).

In its pure state, glycerol exhibits characteristics such as transparency, lack of colour, an absence of odour, a sweet taste, hygroscopicity, and a high viscosity when at room temperature. At standard atmospheric pressure, the substance exhibits a BP of approximately 290 °C and a freezing point of roughly 18 °C. Glycerol is a three-carbon atom, each of which is connected to a hydroxyl group. These groups are entirely miscible with water, methanol, aliphatic alcohols ranging from $C_3$ to $C_5$, and ethanol. Nevertheless, hydrocarbons have been found to exhibit near insolvency to it (Nicol et al., 2012).

The predominant source of glycerol in the worldwide market is derived from transesterification processes, which are employed to produce fatty acid methyl esters (FAME) (Knothe & Razon, 2017). One area of significant scholarly interest revolves around the application of triglycerides derived from plant and animal oils in biodiesel production as a viable fuel source. The production methods generate a substantial quantity of glycerol as the main secondary product, constituting almost 10% of the total biodiesel produced, which can be depicted in Figure 2 (Armylisas et al., 2023; Chol et al., 2018; Kowalska-Kuś et al., 2020).

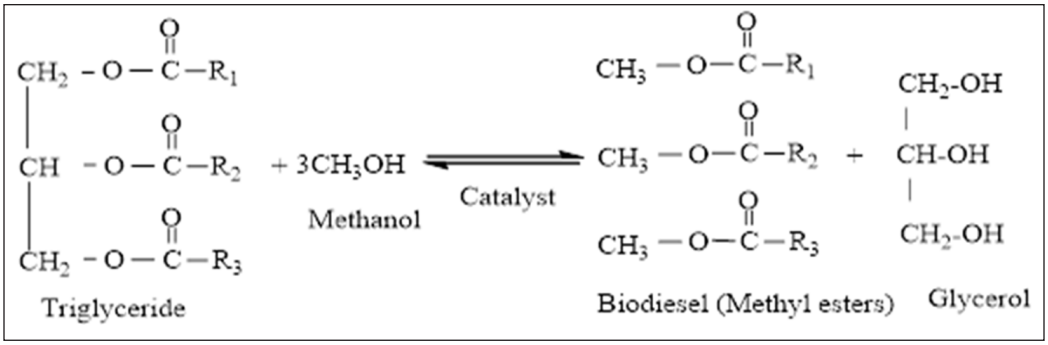


*Figure 2*. Transesterification reaction of triglyceride

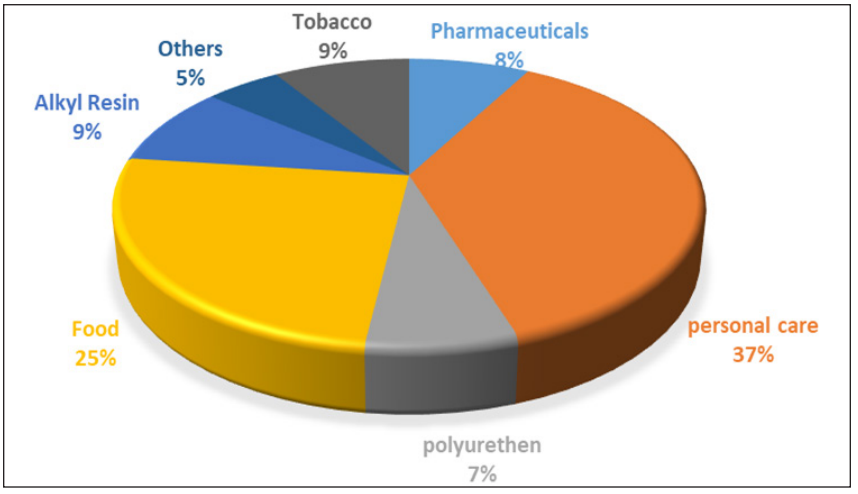


*Figure 3*. Percentage distribution of glycerol application in different fields (Bagnato et al., 2017; Quispe et al., 2013)

Glycerol is utilised in various applications as a precious good in sectors including personal hygiene, beauty products, pharmaceutical, and food industries that necessitate high levels of pure glycerol as a raw material (Armylisas et al., 2023). Figure 3 illustrates the primary areas of glycerol application, along with their percentage distribution. Glycerol is utilised as a food preservative, in creams, and as a sweetener. Due to its non-poisonous properties, glycerol is widely applied in beauty products and hygiene. In addition, glycerol is also employed in the paper and printing industries to soften and reduce contraction in the papermaking process, in the tobacco business to minimise the occurrence of breakage and crumbling during cigarette manufacture, while simultaneously enhancing the flavour of tobacco (Figure 4) (Doukeh et al., 2023; Kowalska-Kus et al., 2017). Table 1 gives the physicochemical properties of glycerol.

Table 1
*Physicochemical properties of glycerol*

| Properties | Standard value |
|---|---|
| Chemical formula | $CH_2OH$-CHOH-$CH_2OH$ |
| Form and Colour | Colourless Liquid |
| Molecular weight | 92.09 |
| Melting point | 18.17℃ |
| Boiling point (760 mmHg) | 290℃ |
| Density (20 ℃) | 1.261g/cm3 |
| Vapour pressure | 0.0025 mmHg at 50℃ |
| | 0.195 mmHg at 100℃ |

Table 1 *(continued)*

| Properties | Standard value |
|---|---|
| Refractive index | 1.474 |
| Surface tension (20 ℃) | 63.4 dyne/cm |
| Compressibility (28.5 ℃) | 2.1 × 10 MPa |
| Viscosity | 1499cP at 20℃° |
| Specific heat | 2.42J/gm at 26℃ |
| Heat of vapourisation | 21060 cal/mole at 55℃<br>18170 cal/mole at 195℃ |
| Vapour pressure in 760mmgh | 290℃ |
| Heat of the formation | 159.5 kilocalories/gram mole |
| Heat of combustion | 1661 KJ/mole = 18.04 MJ/kg |
| Heat fusion | 18.2 kilojoule/mole |
| Thermal conductivity | 0.29 w/ °K |
| Flash point | 177℃ |
| Fire point | 204℃ |

Source: Gupta & Kumar (2012)

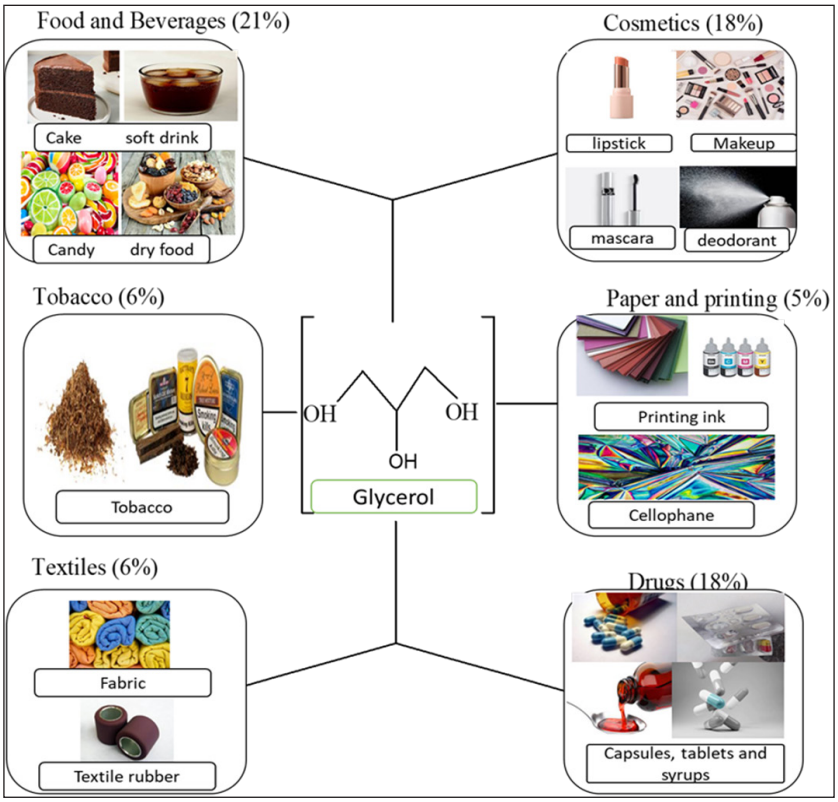


*Figure 4*. Some applications of glycerol production to other products

## Transformation of Glycerol into a High-value Chemical

Various catalytic methods, well-documented in the literature, have consistently demonstrated success in converting glycerol into valuable chemicals. In Figure 5, the procedures involve the following steps: oxidation to generate glyceric acid, dihydroxyacetone, and tartaric acid; hydrogenolysis to produce 1,2-propanediol; dehydration for the synthesis of acrolein; reforming for the generation of synthesis gas; etherification for the production of ethers; acetalisation for the formation of solketal and acetals; and acetylation for the output of acetins (Liu & Gao, 2018; Okoye et al., 2017; Smirnov et al., 2018). These byproducts serve as intermediates in many processes, with some being used as final products. They have diverse applications across various industries, including polymers, beauty products, food additives, pharmaceuticals, colorants, fine chemicals, tobacco, and fuel stabilisers (Liu & Gao, 2018; Okoye et al., 2017; Smirnov et al., 2018). However, the transition of glycerol to solketal and acetal through the acetalisation process is a significant topic extensively discussed in this paper. One of the most pivotal applications involves converting glycerol into a gasoline additive, which enhances the properties of biofuels. Glycerol, solketal, and acetal are important in biodiesel and diesel blends. According to earlier studies (Talebian-Kiakalaieh et al., 2018; Zahid et al., 2020), Solketal, a gasoline additive, has been identified as a promising option for mitigating emissions generated by combustion engines. Table 2 presents the summary table of all major glycerol transformation reactions, key products, and industrial applications.

Table 2
*Summary table of all major glycerol transformation reactions, key products, and industrial applications*

| Glycerol Transformation Reactions/ Process | Product | Industrial Applications |
|---|---|---|
| Oxidation | Glyceraldehyde Dihydroxyacetone | Cosmetics (e.g., tanning agents), pharmaceuticals, and biochemical intermediates |
| Reforming | Syngas | Feedstock for Fischer–Tropsch synthesis, methanol production, and hydrogen generation |
| Dehydration | Acrolein, Acetol | Acrolein is used in acrylic acid production; acetol is a precursor in fine chemicals and solvents |
| Carbonylation | Glycerol carbonate | Used in polymers, coatings, batteries, and as a green solvent |
| Hydrogenolysis | Propane 1,2 -diol Propane 1,3 -diol Ethylene glycol | Used as antifreeze, solvents, and in unsaturated polyester resins and cosmetics |
| Acetylation | Mono acetin, Di acetin and Tri acetin | Used as plasticisers, solvents, and fuel additives |
| Acetalisation | Solketal, Acetal | Solketal is a fuel additive, solvent, and intermediate in fine chemicals |
| Etherification | Polyglycerol | Used in food emulsifiers, cosmetics, pharmaceuticals, and surfactants |

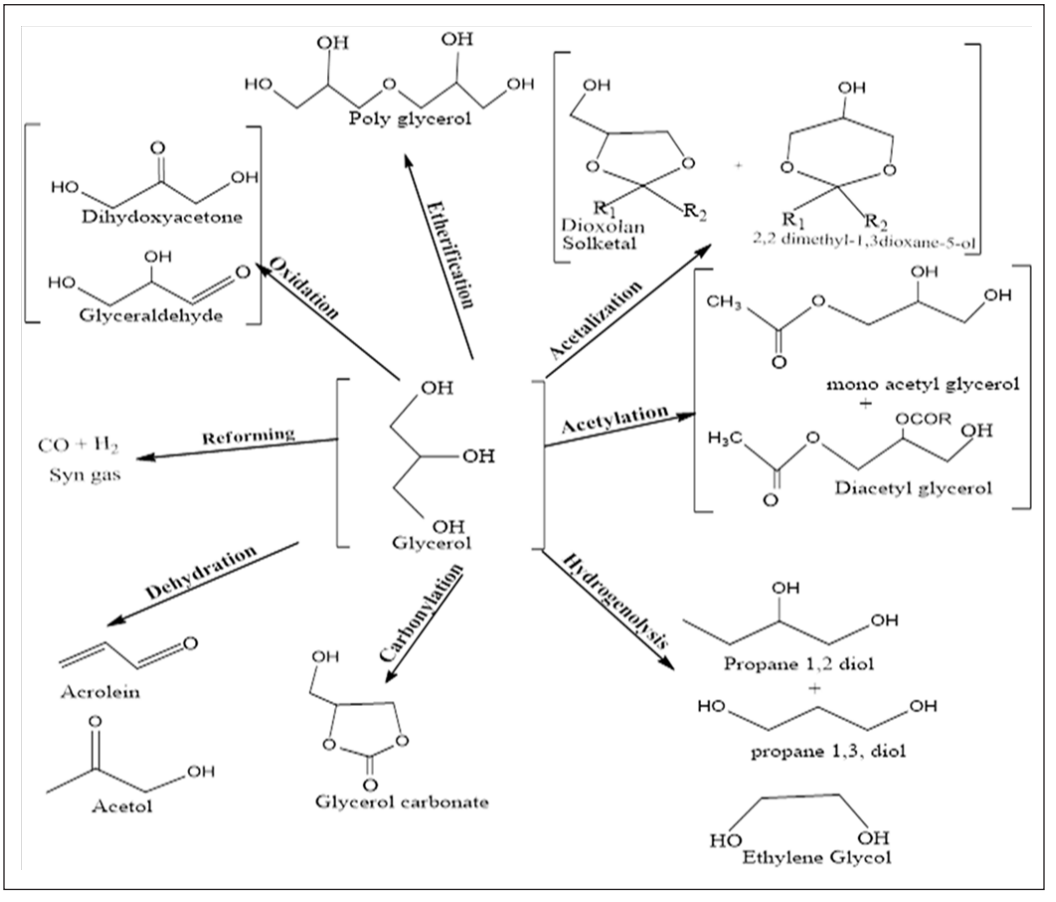


*Figure 5*. Schematic catalytic transformations of glycerol to high-value chemicals

## Glycerol Acetalisation to Solketal and Acetal

### *Solketal*

Solketal is a transparent and scentless cyclic compound (2,2-dimethyl-1,3-dioxan-5-ol) consisting of a five-membered ring, which can dissolve entirely in water (García et al., 2014). The compound has a mass by volume of 1.063 $gmL^{-1}$, a boiling point of 188 $^{o}C$, a viscosity of 11 centipoise at 20 $^{o}C$, and a small vapour pressure at 25 °C (an estimated value = 0.16 Torr). In conformity with the MSDS (material safety data sheet), the substance has an $LD_{50}$ value of 7 grams per kilogramme. Under the influence of an acid catalyst, glycerol and acetone undergo an acetalisation process to produce solketal (Figure 6). Irrespective of the catalyst and reaction conditions employed, only a 5-membered cyclic ketal is produced in this scenario (García et al., 2014; Khayoon & Hameed, 2013).

However, regardless of the catalyst employed, solketal is typically the only product in practice. This is because the proximity of hydroxyl groups on glycerol favours attack from

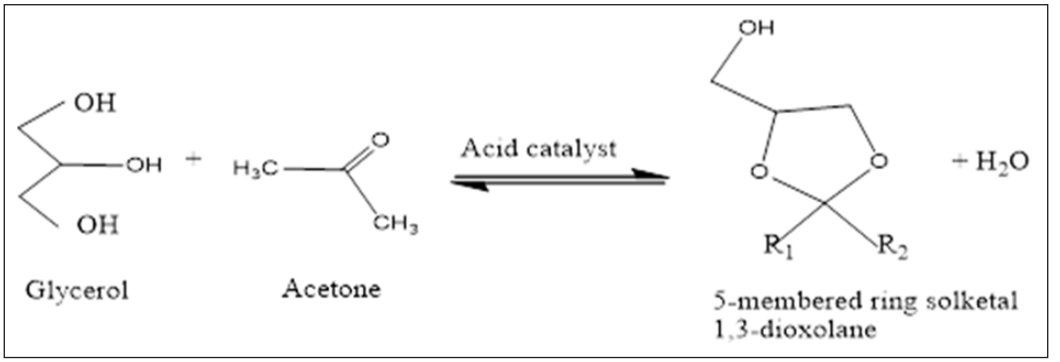


*Figure 6*. Production of solketal via acetalisation of glycerol with acetone

the secondary -OH (central carbon), which is spatially closer to the first -OH involved in hemiacetal formation. This makes the 5-membered ring formation (solketal) kinetically more accessible. Five-membered rings have minimal ring strain and are typically more stable than six-membered rings involving glycerol's three-carbon backbone. The steric barrier of solketal formation involves fewer atoms in the ring and less crowding, especially under high glycerol concentrations (Rodrigues et al., 2014). For example, Khayoon and Hameed (2013) demonstrated that glycerol could be efficiently acetalised with acetone in a solvent-free system, producing solketal (a five-membered ring molecule) as the predominant product with a selectivity of 74% yield.

The study conducted by Gadamsetti et al. (2015), showed that MoPO/SBA-15 catalysts with different loadings (5-50 wt%) had a remarkable yield. The catalyst containing 40-weight percent MoPO/SBA-15 demonstrated the maximum activity due to its abundant Bronsted acid sites. The reaction exhibited very good selectivity toward solketal at 98% and the complete conversion of glycerol within a time span of 2 hours. Furthermore, the utilisation of acid-treated zeolite has also proved to be outstanding. Acid treatment of beta zeolite using acids like HCl, $HNO_3$, and $C_2H_2O_4$ (oxalic acid) has led to enhanced catalytic activity. Among these beta zeolites treated with acids, $HNO_3$ showed the greatest glycerol conversion (GC) rate of 94.26% and solketal yield of 94.21 wt.% (Jamil et al., 2017). The superior performance of the $HNO_3$-treated beta zeolite is due to its high surface area, mesoporosity, and enhanced acidity. Manjunathan et al. (2015) conducted a comparison of the performance of different zeolites and catalysts. Amongst the zeolites screened, the beta zeolite catalyst with a smaller crystallite size (designated as H-Beta-1) treated with ammonium was found to be the most catalytically active. This gave an 86% gas chromatography (GC) efficiency and 98.5% selectivity to the product solketal. Further zeolites (H-beta-2, H-ZSM-5, and acidic mordenite) and some catalysts (Amberlyst-15, KSF MMT, CsHPW, and $MoO_3$) performed poorly. The catalysts showed the potential for

reuse with consistent activity without any notable degradation. This excellent activity can be ascribed to the excellent availability of effective acid sites on the minute crystals of zeolites (H-beta-1). In a separate study by M. J. da Silva et al. (2017), A solid stannous fluoride ($SnF_2$) catalyst was employed for glycerol acetalisation with propanone to yield solketal. Under the best settings of glycerol to propanone MR of 1:8, a catalyst stannous fluoride ($SnF_2$), and a solvent $CH_3CN$, the GC to solketal reached 97 % selectivity at a glycerol conversion rate of 97%. These reactions were applied at room temperature using 21.0 mmol of glycerol and 168.0 mmol of propanone. Significantly, this catalyst demonstrated remarkable durability even after undergoing recycling and reuse four times, maintaining nearly constant reaction conversion and solketal selectivity.

### *Acetal*

A compound acetal with the molecular formula $C_4H_8O_2$ is 1,3-dioxane, which is a viscous six-membered ring compound found in glycerol called acetals. A clear, colourless fluid that dissolves in ethanol $C_2H_5OH$, $CH_3COCH_3$ (acetone), $C_6H_6$ (benzene), and water. 1.3 Dioxane has a variety of useful applications as a solvent and stabiliser. Moreover, 1,3-dioxane is used as a surfactant base in the paint and pesticide industries, as a flavouring or aroma in food, and as an additive for diesel fuels. The acetalisation of glycerol to acetal has been reported in some kinds of literature (Güemez et al., 2013; Kulkarni & Arvind, 2021; Nda-Umar et al., 2019).

The acetalisation of glycerol with $C_7H_6O$ (benzaldehyde) (Figure 7) was performed using a solid catalyst, mesoporous $MoO_3/SiO_2$. The catalyst had different loadings of $MoO_3$ ranging from 1 to 20 mol%. This experiment was performed by Umbarkar et al. (2009). The findings demonstrate that a catalyst with a 20 mol % $MoO_3$ loading exhibited the highest level of activity at a temperature 100 °C for 8 hours. This catalyst achieved a maximum GC rate of 72% for benzaldehyde and a selectivity of 60% towards the formation of the six-membered acetal compound.

Additional investigations conducted by the same researchers Umbarkar et al. (2009) explored the utilisation of different aldehydes, including phenylacetaldehyde, p-tert-butylbenzaldehyde, anisaldehyde, n-butyraldehyde, benzaldehyde n-heptaldehyde, trans-cinnamaldehyde, and o-chlorobenzaldehyde. These studies demonstrated that when substituted benzaldehydes were subjected to similar reaction settings, the conversion of aldehydes decreased while the acetal's selectivity increased. The researchers determined that aliphatic aldehydes exhibited higher conversion rates than aromatic aldehydes, which was attributable to the degree of unsaturation.

Sudarsanam et al. (2013) accomplished a study of $C_7H_6O$ and its mono-substituted by-products namely o-chlorobenzaldahyde, p-chloro- benzaldehyde, p-anisaldehyde, o-nitrobenzaldehyde, and p-nitrobenzaldehyde) over $ZrO_2$, $TiO_2$ –$ZrO_3$, $MoOx/ZrO_2$, and

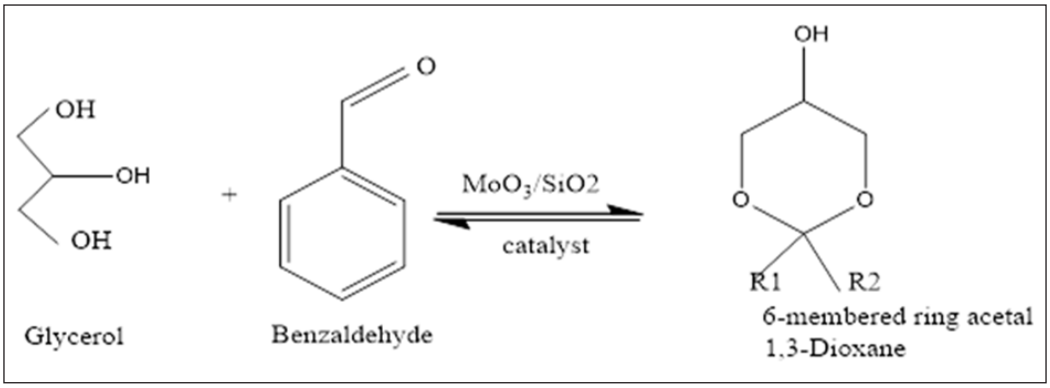


*Figure 7*. Synthesis of acetal by acetalisation of glycerol with benzaldehyde

$MoOx/TiO_2–ZrO_2$ catalysts achieved a GC rate of 74%, with a 51% preference for the production of 1,3-dioxane.

The method of glycerol acetalisation was investigated at a temperature of 100 ℃ utilising iron oxide nanoparticles as a support for a mesoporous alumino-silicate heterogeneous catalyst. The aldehydes used in the reaction were paraformaldehyde, benzaldehyde, and furfural, along with acetone. The procedures exhibited excellent conversion and selectivity while utilising glycerol formal (Gonzalez-arellano et al., 2014). Achieving a conversion rate of 90% for paraformaldehyde required 8 hours of processing, but dioxane and dioxolane only achieved 66% and 34% conversion rates, respectively. Nevertheless, altering the molar ratio of glycerol to paraformaldehyde to 1:2 resulted in a complete GC, accompanied by a significant enhancement in dioxane selectivity of approximately 76%. Despite the lengthy reaction period, Fe/Al-SBA-15 catalysts were shown to be very steady, reusable, and effective.

Several heterogeneous acid-enhanced catalysts, such as mesoporous organosilica (PMOs), zeolite ZSM-5, hetero-poly compound $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, and Amberlyst-15, were employed in a study by Chen et al. (2015) to create solketal and acetal in the glycerol acetalisation reaction with aqueous formaldehyde. The catalyst that exhibited the highest performance was $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, achieving a glycerol conversion rate of 70% within a one-hour time frame. The catalyst load, the MR of glycerol to formaldehyde, and temperature are known to influence the distribution of the two isomers of solketal, which has a 5-membered ring, and acetal of a 6-membered ring.

## Application of Solketal and Acetal

Solketal has the prospects to serve as a fuel supplement for increasing the octane rating, improving the ignition quality, and decreasing the gum formation and oxidation resistance of gasoline. In diesel fuels, it reduces the release of destructive chemicals, including

hydrocarbons, nitrogen oxides, carbon monoxide, aldehydes, and particulate matter. Solketal and acetal are utilised to minimise the impact of air contamination caused by gasoline-burning engines (Corrêa et al., 2021; Samoilov et al., 2016; Talebian-Kiakalaieh et al., 2018). In numerous other uses, such as drug and fine chemical synthesis, solketal is a green, non-hazardous solvent that can be substituted for toxic and hazardous solvents (Corrêa et al., 2021). Ketal can be utilised as solvents in various chemical reaction processes of different natures (Talebian-Kiakalaieh et al., 2018). Solketal can be utilised as intermediates to produce a plethora of mixtures, such as glyceric acid, which is widely utilised for the production of food additives, cosmetics, drug research, and suspending agents (Cychy et al., 2022). Some biodegradable and biocompatible polymers are produced via acetal derived from glycerol. Such polymers find application in biomedical materials like drug carriage systems, tissue engineering scaffolds, and wound-covering agents (Cychy et al., 2022). For eco-friendly plastics, acetal polymers derived from glycerol can be used as a substitute for traditional petrochemical-based plastics, which are non-biodegradable and environmentally polluting (Goyal et al., 2021). Glycerol-based acetals and ketals have potential applications as food additives and flavour enhancers, providing a range of aromas and flavours in food and beverages. (Trifoi et al., 2016) reported that acetals and ketals obtained from the acetalisation of glycerol have a nutty flavour and are used as flavouring agents in food and beverage manufacturing. According to a report by Corrêa et al. (2021), the food and beverage business uses solketal, a cyclic glycerol ketal produced through the reaction of glycerol with acetone, as a flavour enhancer.

## Acetalisation of Glycerol on Different Heterogeneous Catalysts

### *Heteropoly Acid-based Catalysts*

Heteropolyacid (HPA) usage in the biodiesel industry and synthesis of some highly reviewed glycerol derivatives have also been extensively worked out. In contrast to the results of Martin et al. (2012), HPAs are highly stable in humidity and air without deliquescence or slow oxidation reactions at room temperature, show low toxicity with good water solubility like organic acids but generate fewer residues than mineral acids and have lower corrosiveness as well as more safety compared to other catalysts.

Three of the most famous commercially available HPAs are silicotungstic acid (SiWA), phosphomolybdic acid (PMA), and tungstophosphoric acid (PWA). PWA is the most often utilised hetero polyacid. HPA catalysts exhibit a significant capacity for modification by introducing various chemicals to their core atoms. Scientists have endeavoured to improve catalysts' catalytic efficiency and durability to maximize fuel additives. The Cs/HPW catalyst demonstrated exceptional potential as a catalyst for glycerol acetalisation, achieving a remarkable 98% selectivity towards solketal and roughly 95% conversion of glycerol, as reported by Talebian-Kiakalaieh et al. (2018). The Keggin structure is possessed by HPA

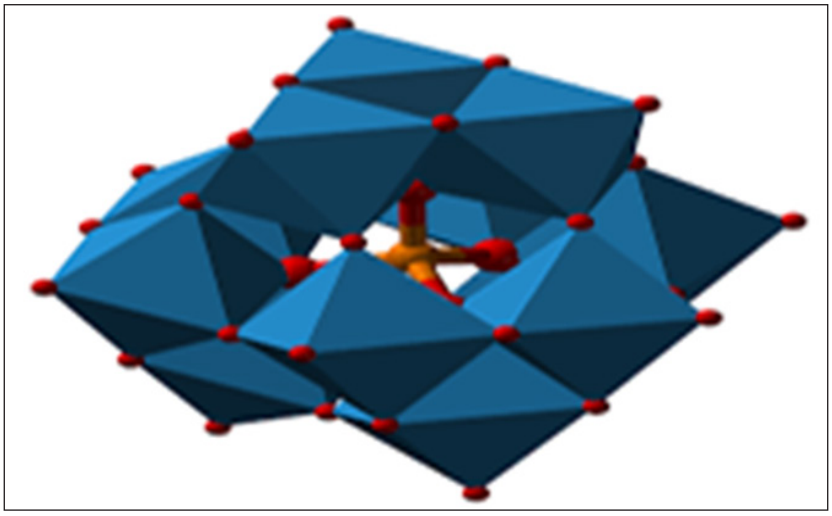

*Figure 8*. Keggin form of hetero-poly acid catalysts (Talebian-Kiakalaieh et al., 2018)

as shown in Figure 8. The α-Keggin anions exhibit a structural configuration characterised by the formula $[XM_{12}O_{40}]_n -$, where X, M, and O correspond to the heteroatoms.

Using a sequence of promoted heteropolyacid (PWA, PMA, SiWA, and SiMA) bound in silica catalysts by utilising a sol-gel method, the glycerol acetalisation process was investigated (Paiva et al., 2022). Under ideal reaction conditions of temperature 70 °C, catalyst load of 0.2 g, and a G/A MR of 1:6, all catalysts demonstrated remarkable solketal selectivity of 98% for near-complete conversions. The reaction time was 4 hours. Moreover, the catalytic activities decreased in the following sequence: PWA-S less than SiWA-S less than PMA-S less than SiMA-S. The catalysts demonstrated remarkable stability, maintaining 90-87% of their initial activity after the fourth successive run.

In a different work by Narkhede and Patel, (2014), they utilised 30% silicotungstic acid (SiWA) supported on MCM-41 catalysts with benzaldehyde as a solvent. This method led to a high degree of selectivity towards solketal. The outcomes demonstrate that the 30%-SiW11/MCM-41 catalyst obtained 82% selectivity to solketal with a GC of 85% at room temperature (30 °C). These conditions were achieved by utilising MR of glycerol to benzaldehyde (1:1.2), catalyst weight 100 mg, and response time 1 hour. Additionally, the adjustment of the acidic character of the parent silicotungstic (SiWA) led to increased specificity toward solketal. The high acidity, high specific surface area, and broad pore diametres are responsible for the outstanding performance of these catalysts.

### *Metal Oxide-based Catalysts*

Metal oxides (MO) have been utilised as gasoline additives through their application in the glycerol acetalisation reaction. Common MO catalysts, like ($SiO_2$), ($WO_3$), and

($Nb_2O_5$), are widely applied in numerous chemical reactions. Synthesis procedure impacts the physicochemical properties of metal oxide catalysts, particularly the temperature of thermal decomposition and the application of double or triple component mixtures (Talebian-Kiakalaieh et al., 2014).

Bewana et al. (2021) carried out the acetalisation process of glycerol with acetone over bimetallic oxide catalysts, $Co_3O_4/SnO_2$. They reported that glycerol conversion (GC) was above 90%, with 100% total selectivity towards the formation of solketal. They achieved these results at the optimal reaction conditions, i.e., a temperature of 60 ℃.

In a different independent study by Reddy et al. (2011), a sequences of zirconia-based catalysts were explored to examine their performance in the acetalisation reaction. The findings revealed that the catalytic activity was enhanced in a stepwise manner in the following order: $ZrO_2$ less than $WOx/ZrO_2$ less than $MoOx/ZrO_2$ less than $SO_4^{2-}/ZrO_2$. Notably, employing a sulfated zirconia catalyst led to a remarkable enhancement, with 98% GC and 97% solketal.

In another study described by Britto et al. (2023) and Fan et al. (2012) for the conversion of glycerol up to 95 % with $TiO_2$-$SiO_2$ catalyst, which mostly contains Lewis acid sites, may also generate Bronsted acidic sites upon water adsorption.

**Polymer-based Catalysts**

Green chemistry is essential for creating innovative and cost-effective catalysts using affordable materials (Kobayashi & Miyamura, 2010). Recently, micro-encapsulation has become a promising method for immobilising metal catalysts to polymers (Akiyama & Kobayashi, 2009). Furthermore, these carbon constituents demonstrated excellent efficacy as catalysts for solid acid in the process of glycerol acetalisation, surpassing the performance of commercially available acid exchange resins, such as Amberlite RIR120 and Amberlyst R70, with ease. The solketal achieved selectivity of ≥ 99.5%, 53%, and 51% when acetone, methyl 4-oxopentanoate acid, and 2-Furaldehyde were present. In batch procedures with nearly complete glycerol conversion.

In their initial study, Qing et al. (2017) employed a catalytically active membrane created using nonsolvent-induced phase separation to enhance the rate of GC in an acetalisation reaction by continually eliminating water. A very porous and absorbent catalytic layer, resembling a sponge, was affixed with $Zr\ SO_4^{2-}4H_2O$ catalyst and applied over a PVA layer on a pervapouration membrane. The catalytic activities were compared in a simultaneous vessel, a catalysed active membrane vessel, and an inert membrane vessel. The results demonstrated that there was no equilibrium restrictions observed in the active membrane reactor and the inert membrane reactor during glycerol conversion. An assessment was conducted to determine the influence of various operative circumstances on the synthesis output of the catalytically active membrane reactor. The outcomes demonstrated that

an increase in the ratio of feed volume (A/V) and temperature led to improved glycerol conversion, which was primarily attributed to the enhanced water removal rate. The maximum GC of 93% was reached under the optimal conditions of 5 percent by weight catalysts, a membrane area to A/V ratio of 50/108, a MR of cyclohexanone to glycerol of 1.2:1, a temperature of 75 °C, and a response time 25 hours.

Recently, the use of organometallic complexes, specifically the cationic oxorhenium(v) complexes with phenolate-oxazoline ligands and [2-(2′-hydroxyphenyl)-2-oxazolinato(-2)] oxorhenium(v), has been confirmed for the reaction between glycerol and 2-furaldehyde. 70% solketal was achieved with 80% GC at a temperature of 100 °C for 4 hours (Wegenhart & Abu-omar, 2010). Table 3 shows the summary comparison table of heteropolyacid-based, metal oxide-based, and polymer-based catalysts in the transformation of glycerol to solketal and acetal as reported by some researchers.

### *Reaction Pathway and Mechanistic Acetalisation of Glycerol*

Based on multiple reports, it has been observed that acetalisation of glycerol with aldehyde/ketone can lead to plausible reactions (Maksimov et al., 2011; Nanda et al., 2014; Nda-Umar et al., 2019). As depicted in Figure 9, The reaction begins with protonation of the oxygen atom in the carbonyl group of acetone by an acid catalyst ($H^+$), increasing the electrophilicity of the carbonyl carbon. This generates a resonance-stabilised oxonium ion, making the carbonyl carbon more susceptible to nucleophilic attack by a primary hydroxyl group of glycerol, leading to the formation of a hemiacetal intermediate. The hemiacetal is stabilised by hydrogen bonding and the polar nature of the reaction medium. Under continued acidic conditions, dehydration of the hemiacetal occurs via protonation of the hydroxyl group followed by elimination of water, resulting in the generation of carbenium ion. This reactive intermediate undergoes intramolecular nucleophilic attack by a neighboring secondary hydroxyl group of glycerol, typically the central –OH, due to its favourable spatial proximity to the intermediate. This intramolecular cyclisation yields solketal, a five-membered ring, as the predominant product. In contrast, the formation of a six-membered acetal requires cyclisation between terminal –OH groups, which involves greater torsional strain and less favourable conformations, making it a minor product under typical reaction conditions. The preference for solketal formation over the six-membered acetal is attributed to both kinetic and thermodynamic factors. The five-membered ring pathway is kinetically favoured due to reduced steric hindrance and favourable geometric orientation of the participating groups. Thermodynamically, five-membered rings exhibit minimal ring strain and are generally more stable than six-membered analogs in the context of glycerol's three-carbon backbone.

Table 3
*Comparison table of heteropolyacid, metal oxide, and polymer-based catalysts in the transformation of glycerol to solketal and acetal as reported by some researchers*

| Type | Catalysts | Optimum Condition | Selectivity (%) | | GC (%) | Cost | Scalability | Environmental Impact/ Reusability | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sol. | Acet. | | | | | |
| Heterogenous Heteropolyacid | $[HMIm]_3(PW_{12}O_{40})$ @MOF-Fe | | 100 | 0 | 100 | | | MOF supports and ionic liquids are expensive; hazardous solvents and synthesis complex with reusability at 7th cycle | Ali and Siddiqui (2023) |
| | $HMIm]_3(PMo_{12}O_{40})$ @MOF-Fe | Glycerol/Acetone {1:4}, T= 25°C, t = 1 hr, Catalyst = 5 wt.% | 96.84 | 3.16 | 95 | High | Moderate | | |
| | $HMIm]_3(SiW_{12}O_{40})$ @MOF-Fe | | 93.33 | 6.67 | 90 | | | | |
| | UAV-63(MOF) | Glycerol/Acetone {1:10}, T = 55°C, t = 2 hr, Catalyst = 10wt.% | 96 | 4 | 84 | High | Moderate | More friendly among MOFs, requires high temp/time and 10 wt%; reusability only up to 3 times | Santos-Vieira et al. (2021) |
| | UiO-66(MOF) | Glycerol/Acetone {1:4}, T= 30°C, t = 2 hr, Catalyst = 10 wt. % | 73 | 27 | 2 | High | Moderate | More friendly among MOFs with 4 times reused | Bakuru et al. (2019) |
| | $SnSiW_{12}O_{40}$ | Glycerol/Acetone {1:4}, T= 25°C, t = 2 hr, Catalyst = 0.010mol | 97 | 3 | 75 | Moderate | Good | Contain tungstate species which can persist in environment. High selectivity and 4-cycle reusability | Jose et al. (2020) |

Table 3 *(continued)*

| Type | Catalysts | Optimum Condition | Selectivity (%) | | GC (%) | Cost | Scalability | Environmental Impact/ Reusability | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sol. | Acet. | | | | | |
| | HR/Y-$W_{20}$ | Glycerol/Acetone {1:10}, T= 20°C, t = 1.5 hr, Catalyst = 10% wt. | 67.7 | 23.3 | 93.59 | Moderate | Good | Contain tungstate species which can persist in environment and reusability not reported | Talebian and Tarighi (2019) |
| | PWS | Glycerol/Acetone {1:16}, T= 70°C, t = 2.5 hr, Catalyst = 0.2 g | 97 | 3 | 98 | Moderate | Good | Good selectivity (97%), moderate reusability at 4 times reused contain tungstate/ phosphate species which can persist in the environment | Ferreira et al. (2010) |
| Metal oxide-based | γ-$Al_2O_3$/ $FeCl_3$ | Glycerol/Acetone (1:10), T =25°C, t = 30 min, Catalyst = 0.2 mol | 98.36 | 1.67 | 99.89 | Low | High | Simple, low-cost materials with minimal toxic byproducts; environmentally benign and excellent reusability (6 cycles) | Zhang et al. (2022) |
| | $WO_3/SnO_2$ | Glycerol/Acetone (1:1), T = 60°C, t = 30 min, Catalyst = 0.125g | 97 | 3 | 100 | Moderate | High | Highly active and stable (7 cycles) with low toxic byproducts; easy to scale up | Shen et al. (2022) |

Table 3 *(continued)*

| Type | Catalysts | Optimum Condition | Selectivity (%) | | GC (%) | Cost | Scalability | Environmental Impact/ Reusability | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sol. | Acet. | | | | | |
| | $SO_4^{2-}/CeO_2–ZrO_2$ | Glycerol/Benzaldehyde (1:3), T = 100°C, t = 8 hr, Catalyst = 9wt.% | 87.2 | 12.8 | 91.8 | Moderate-High | Moderate | Sulfated oxides may cause mild acid leaching if not stabilised. Reusability NR | Kulkarni and Arvind (2021) |
| | HC-SZ ($SO_4^{2-}/ZrO_2$ | Glycerol/Acetone (1:3), T = 60°C, t = 100 min Catalyst = 0.2g | 94 | 6 | 96 | Moderate | High | Excellent reusability at 6 time reused without loss of activity, low cost, simple prep. | Vasantha et al. (2018) |
| | $SO_4/SnO_2$ | Glycerol/Furfural (1:1), T = 100°C, t = 30 min, Catalyst = 5 wt.% | 84 | 26 | 99 | Moderate | High | Generally regarded as safe and reusability NR | Mallesham et al. (2016) |
| | MoPO/SBA-15 | Glycerol/Acetone (1:3), T = 30°C, t = 2 hr, Catalyst = 50 mg | 98 | 2 | 100 | High | Moderate | SBA-15 support synthesis is costly and time-intensive with 4 times reused | Gadamsetti et al. (2015) |
| | $NbO_2(OH)$ | Glycerol/Acetone (1:4), T° = 40°C, t = 1 hr, Catalyst = 200 mg | 65 | 35 | 74 | High | Moderate | Good activity but expensive and less common. Reusability NR | Souza et al. (2014) |
| | $TiO_2$-$ZrO_2$ | Glycerol/Benzaldehyde (1:1), T = 100°C, t = 30 min, Catalyst =5 wt.% | 47 | 53 | 64 | Low | Moderate | Generally stable and inert Low GC and selectivity; limited applicability and reusability NR | Sudarsanam et al. (2013) |

Table 3 *(continued)*

| Type | Catalysts | Optimum Condition | Selectivity (%) | | GC (%) | Cost | Scalability | Environmental Impact/ Reusability | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sol. | Acet. | | | | | |
| | $Nb_2O_5$ | Glycerol/Acetone (1:1.5), T = 70°C, t = 6 hr, Catalyst = 6.4 wt.% | 92 | 8 | 80 | High | Moderate | Good activity, but expensive and less common and generally stable and inert, but Nb sourcing has environmental implications, with 4 times reused | Nair et al. (2012) |
| Polymer-based | Purulite CT275 | Glycerol/Acetone (1:12), T = 50°C, t = 5 hr, Catalyst = 5wt.% | 99.5 | 0.5 | 91 | Moderate | High | Non-toxic, but disposal may contribute to microplastic pollution, and commercially available; reusability not reported | Cornejo et al. (2019) |
| | PSF Polymer | Glycerol/Acetone (1:5), T = 60°C, t = 4 hr, Catalyst = 8 wt.% | 100 | - | 97 | Low-Moderate | High | Non-toxic with the 4$^{th}$ cycle reused | Ikbal and Rajkumari (2018) |
| | Amberlyst-46 | Glycerol/Acetone (1:2), T = 60°C, t = 30 min, Catalyst = 1 wt.% | 64 | 36 | 84 | Moderate | High | Widely used ion-exchange resins, non-biodegradable; excellent reusability (up to 9 cycles) | Ilgen et al. (2017) |

Table 3 *(continued)*

| Type | Catalysts | Optimum Condition | Selectivity (%) | | GC (%) | Cost | Scalability | Environmental Impact/ Reusability | References |
|---|---|---|---|---|---|---|---|---|---|
| | | | Sol. | Acet. | | | | | |
| | Amberlyst- 15 | Glycerol/Acetone (1:1.2), T = 60°C, t = 2 hr, Catalyst = 31 wt.% | 90 | 10 | 87.41 | Moderate | High | Non-biodegradable, may cause long-term microplastic waste and reusability not reported | Dqg et al. (2020) |
| | Nafion N150 | Glycerol/Acetone (1:43), T = 30°C, t = 18 hr, Catalyst = 20 wt.% | 88 | 12 | 90 | Very high | Moderate | Expensive; limited large-scale use due to cost; persistent fluoropolymer with high environmental footprint. Reusability NR | Cucciniello and Cavani (2018) |
| | CS/KIT-6 | Glycerol/Acetone (1:4), T = 25°C, t = 15 hr, Catalyst = 5wt.% | 98 | 2 | 95 | Moderate | Moderate | Chitosan-based systems are environmentally friendly reusability not reported | Chen et al. (2018) |

*Note.* T = Temperature; t = Time; Sol = Solketal; Acet = Acetal, GC = Glycerol conversion, NR = Not reported

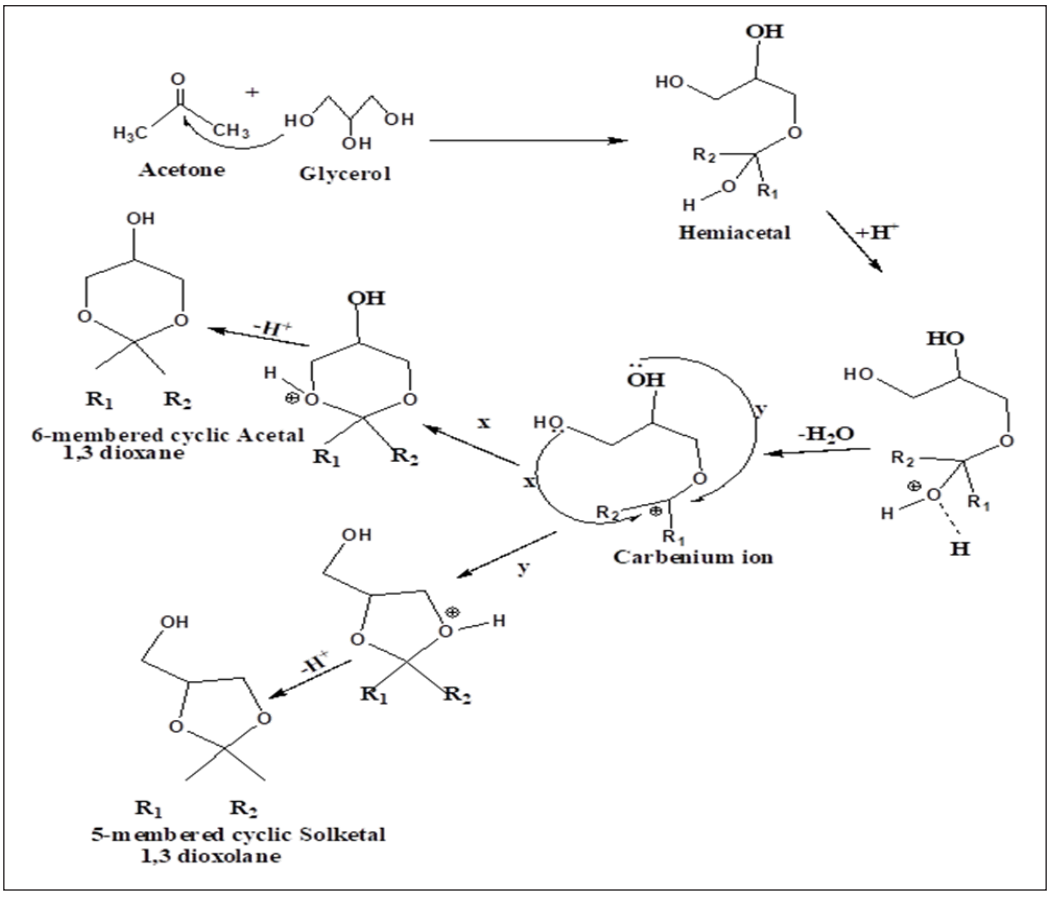


*Figure 9*. Plausible mechanistic reactions for solketal and acetal by glycerol acetalisation

## Influence of Reaction parameters on Acetalisation of Glycerol

### *Temperature*

Temperature is one of the significant factors for the acetalisation of glycerol, deciding the reaction strength and an increase in glycerol conversion (Kulkarni & Arvind, 2021). The influence of temperature on the efficacy of catalysts in the process of glycerol acetalisation is contingent upon the particular reaction conditions and catalyst employed. The relationship between glycerol conversion and temperature was positively correlated in certain research, whereby a temperature rise led to an increase in GC. However, other studies looked into the impact of temperature on reaction rate, selectivity, and conversion. The acetalisation of glycerol with acetone over the UAV 59 catalyst was investigated (Santos-Vieira et al., 2021). The temperature significantly impacted the catalytic activity of the UAV-59 catalyst in the acetalisation of glycerol and acetone. The conversion rate peaked at 94% after the temperature rose from 25-55°C.

Another study explored the impact of temperature on the glycerol conversion with benzaldehyde, utilising a ferromagnetic hetero polyacid catalyst. The results revealed that the transformation rate increased as the temperature rose to 80-120 °C (Trifoi et al., 2016). Serafim et al. (2011) demonstrated that rising the temperature from 30℃ to 70℃ significantly improved glycerol conversion rate with butanal, raising it from 40-87%. Khayoon and Hameed (2013) reported a reasonable rise in temperature, which resulted in a surge in GC and efficient solketal formation.

In line by the outcomes mentioned earlier and reports from different researchers, several researchers found that a rise in reaction temperature may cause a reduction in product selectivity. Nanda et al. (2014) on the acetalisation of glycerol with acetone found that the product yield decreased with temperature in exothermic processes. More precisely, the temperature rise impacted only the early reaction rate.

**Reaction Time**

The reaction time for which a chemical reaction proceeds can substantially affect the yield, reaction rate, conversion, and selectivity. Several researchers addressed the influence of reaction time on the yield, conversion, and selectivity of glycerol acetalisation reactions. Ali and Siddiqui (2023) determined the impact of response time on the selective acetalisation of glycerol to solketal using $[HMIm]_3[PW_{12}O_{40}]$@MOF-Fe, indicated that extending the response time to 60 minutes resulted in the complete GC, achieving a solketal selectivity and yield of 100%. The findings remained consistent as the reaction time was extended to 90 minutes and further disclosed that the solketal selectivity was unaffected by the reaction time.

Kulkarni and Arvind (2021) observed the influence of time in the acetalisation of glycerol with benzaldehyde using $SO_4^{2-}/CeO_2–ZrO_2$ catalyst, showing that the reaction rate and yield increased with the rise in reaction time from 60 to 120 min. Employment of heteropolyacid, specifically $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, as catalysts for the acetalisation of glycerol with acetone to produce solketal revealed that both reaction rate and solketal yield were affected by reaction time. Notably, the highest selectivity of solketal was achieved following 5 hours of reaction time (Chen et al., 2018).

Glycerol acetalisation with acetone in the presence of BEA zeolite as a catalyst was investigated. The findings on how the response time affects the result of glycerol acetalisation indicate that the GC improved as the response time was lengthened from 5 up to 30 minutes. Furthermore, GC readings kept on rising, finally peaking at about 40 minutes (Venkatesha & Bhat, 2016). Diana and Fatima (2022) investigated the acetalisation of glycerol with benzaldehyde in the presence of a Phosphotungstic (PW4-KIT-6) catalyst. The highest yield of solketal was achieved after 6 hours of response time.

## Mole Ratio

Most researchers have determined that the molar ratio of glycerol acetalisation significantly affects reaction conversion and product selectivity. Researchers examined the variation of the G/A molar ratio using metal-modified SBA-15 catalysts and the effect of this variation on GC (Ammaji et al., 2018; Oliveira et al., 2016). Based on Ammaji et al. (2018), GC was greater when the G/A ratio was increased from 1:2 to 1:3. Nonetheless, no significant difference in GC was observed when the G/A molar ratio was raised to 1:4.

Using the Amberlyst-47 catalyst, Agirre et al. (2011) investigated different molar ratios of formaldehyde to glycerol. The reaction was carried out at 80 °C by adjusting the molar ratio of glycerol to formaldehyde using ratios of (1:1), (1:2), and (1:3). The rise in the molar ratio of glycerol was accompanied by an increase in the equilibrium conversion of formaldehyde. Ferreira et al. (2010) observed the impact of an excess of acetone on glycerol conversion in another study. The selectivity to solketal remained unaffected, though, whereas the GC rose with a rise in the G/A mole ratio from (1:3-1:12).

The 5% Ni addition to 1% Zr/AC was found to improve glycerol transformation and enhance acetal synthesis, as reported by Khayoon and Hameed (2013). This improvement was observed by increasing the G/A mole ratio from (1:4-1:8). Serafim et al. (2011) investigated the impact of the glycerol-to-butanal molar ratio on GC using BEA zeolite as a catalyst at 80 °C. With a 1:1 molar ratio, a GC of 71% was achieved after 4 hours. Increasing the ratio to 1:2.5 enhanced the conversion to 88%. However, further increasing the ratio to 1:6 did not result in any significant improvement in conversion.

## Influence on Interaction between Parameters

3D surface model plots were employed to assess the impact of the four independent variables (catalyst loading [CL], temperature, time, and G/A mole ratio) on glycerol conversion using response surface methodology (RSM) as shown in Figure 10. Devasan et al. (2024) reported that it is possible to observe the interaction of two variables on the model graphs. The interactive effect of the G/A mole ratio with parameters such as catalyst concentration and time (Figure 10a and b) demonstrates a linear relationship, and the glycerol conversion is observed to decline after the maximum point is reached. Temperature variations, ranging from 55 to 75°C, were examined during the conversion of glycerol. Figure 10 c shows the combined effect of reaction temperature and the G/A molar ratio on glycerol conversion over a 12 min reaction time with a catalyst loading of 7 wt%. An increase in reaction temperature and the G/A mole ratio increased the solketal concentration, and the study showed that optimal conditions for temperature and the G/A mole ratio resulted in the highest conversion of glycerol. Nevertheless, the glycerol conversion increased until the specified reaction temperature and G/A mole ratio value. Higher G/A mole ratio values result in lower glycerol conversion, which makes product

separation more challenging. Similarly, production also decreased with the increase in temperature above 65 °C. Despite using a pressure environment, acetone still evapourates, resulting in decreased conversion (Devasan et al., 2024).

The combined effect of temperature and time on glycerol conversion is depicted in Figure 10d. Glycerol conversion increased significantly as the reaction temperature and time were linearly related. An increase in the conversion up to 12 min might be because of the increase in the number of reacting molecules causing the formation of new bonds after cleaving the pre-existing bonds (Devasan et al., 2024; Khayoon & Hameed, 2013). As time progressed, the product may have hydrolyzed by forming water, explaining the drop in conversion (Churipard et al., 2017). Therefore, for the 12 min optimal reaction time, a reaction temperature of 65°C was more favourable.

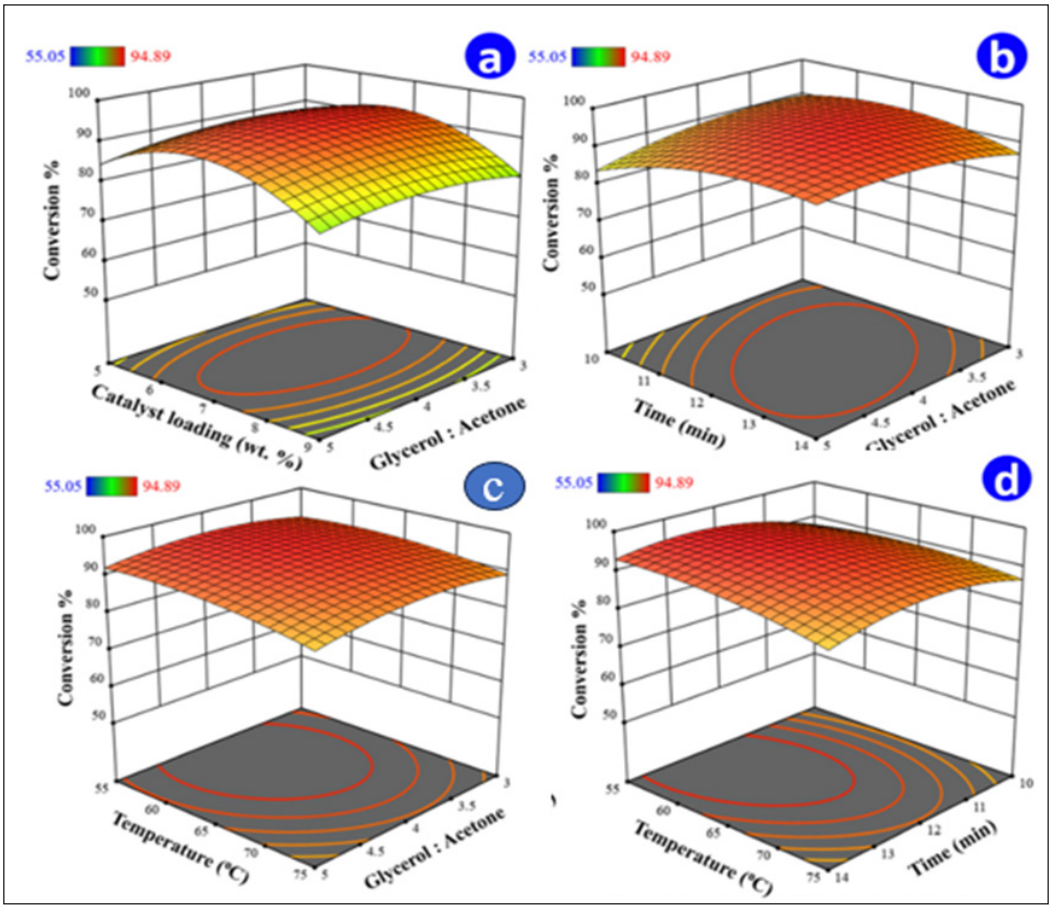


*Figure 10*. 3D surface plot depicting the interaction of the independent variables A–D and their effect on the efficiency of microwave-assisted solketal synthesis from glycerol (Devasan et al., 2024)

## Influence on Water

The acetalisation reaction has been noted to show a low equilibrium constant, as described by Corrêa et al. (2021). The presence of water in the acetalisation procedure can reverse the reaction and render the acid sites of the catalyst inactive, resulting in a decrease in the production yield and conversion of glycerol. Two approaches have been suggested for this purpose. One, the continual removal of water produced throughout the reactions, and two, introducing an excess amount of acetone into the reactor. However, the former method is described to be more active in overcoming the thermodynamic obstacles. Entrainers have been employed in various processes to get rid of water from the reaction mixture (Kale et al., 2016; Talebian-Kiakalaieh et al., 2018; Zahid et al., 2020). Examples include petroleum ethers, chloroform, and benzene. Although these compounds can be effective, their boiling points are higher than that of acetone, which can lead to co-distillation of acetone and reduce the efficacy of azeotropic water removal. For instance, the use of petroleum ether as an entrainer presented certain limitations (Chen et al., 2005). To address moisture in the system, phosphorus pentoxide and sodium sulfate have also been used as catalysts and desiccants (Talebian-Kiakalaieh et al., 2018; Zahid, et al., 2021).

But, the high catalyst consumption in these situations raises the operating costs (Kale et al., 2016; Talebian-Kiakalaieh et al., 2018). Increasing the use of acetone, which can be an entrainer and a reactant, is one way to deal with these problems. Furthermore, the ability to regenerate and reuse the extra acetone in the same or various processes offers a more sustainable method for the acetalisation reaction.

## Application of Crude Glycerol

The use of crude glycerol in industrial processes is highly constrained by its low purity, which directly affects both reaction efficiency and catalyst stability. Crude glycerol, a major by-product of biodiesel production, typically contains a complex mixture of contaminants, including methanol, water, esters, fatty acids, soaps, and inorganic salts collectively known as MONG (matter organic non-glycerol) (Rosas et al., 2017). These impurities not only reduce the effectiveness of downstream chemical conversions but also present severe challenges for catalyst performance, particularly in heterogeneous catalytic systems.

Purity is still the foremost prerequisite for glycerol use in high-value applications like solketal production, polymer synthesis, and pharmaceutical intermediates. Although the large biodiesel manufacturers tend to have the facilities to purify crude glycerol, most commonly through multi-step processes involving neutralisation, phase separation, vacuum distillation, and activated carbon treatment, the small and medium-scale industries tend to lack the financial and technical resources to install such purification systems. Therefore, they might be compelled to either discard crude glycerol as waste or burn it for low-grade energy, incurring economic loss and environmental burden (Wilson, 2002).

Pre-treatment technologies are critical in establishing process feasibility. Basic techniques like acid-base neutralisation and phase separation are economically effective at removing soaps and free fatty acids, but are generally not enough to achieve the levels of purity necessary for sensitive catalytic reactions. More sophisticated methods, such as ion exchange resins, membrane separations, and adsorption-based systems (e.g., activated carbon or zeolites), are more effective at removing polar organics, salts, and water, but may have capital and operating costs that are not economically justified for smaller-scale operations. Vacuum distillation is effective for methanol removal but is very energy-intensive.

Impurities in crude glycerol have a dramatic effect on long-term catalyst activity and stability. Fatty acids and esters can lead to coke formation, while salts (e.g., $Na^+$, $K^+$, $Cl^-$) can poison active sites or alter surface acidity by ion exchange. Methanol and water compete for adsorption sites, reducing glycerol conversion and selectivity. Over time, these interactions may cause irreversible deactivation through sintering, pore blockage, or chemical fouling of active sites. Though there is increased interest in valorising crude glycerol for chemical synthesis, the majority of research has used refined glycerol because of the added complexity from impurities. More systematic studies are urgently needed on using crude glycerol directly as a feedstock, particularly regarding the mechanism of catalyst deactivation, regeneration methods, and process optimization under realistic conditions. Filling these knowledge gaps may create economically viable options for small biodiesel producers while enhancing circular resource use.

C. X. A. da Silva and Mota (2011) analysed the influence of impurities on the synthesis of solketal in a batch reactor system to utilise crude glycerol instead of the purified one. They examined the influences of typical impurities (e.g., 1% methanol, 10% water, and 15% NaCl) in the acetalisation of crude glycerol over different heterogeneous catalysts such as H-beta zeolite and Amberlyst-15. The substitution of refined glycerol with crude glycerol resulted in a spectacular decline in reaction conversion to 47% and 50% over Amberlyst-15 and H-beta zeolite catalysts, respectively, from the 95% reaction conversion using refined glycerol over analogous catalysts. They indicated methanol to be less influential than water and NaCl.

Vicente et al. (2010) demonstrated the application of acid-functionalised SBA-15 catalysts for glycerol acetalisation of crude glycerol (85.8 wt.%). They obtained 81% glycerol conversion. However, high Na+ content in crude glycerol strongly deactivated the sulfonic acid sites through a cation exchange reaction between H+ and Na+.

## CONCLUSION AND FUTURE PROSPECTS

In the past decade, the acetalisation of glycerol to solketal has become a promising process for the value addition of glycerol by converting it into high-value products. Solketal, in

particular, has advantages as a fuel additive in octane rating, combustion efficiency, and engine performance, and is additionally utilised for the production of polymers, coatings, and perfumery. This review has explained heterogeneous catalytic systems, such as heteropoly acids, metal oxides, and supported polymer catalysts, and assessed the influence of significant reaction parameters, such as temperature, molar ratio, reaction time, and the influence of water.

Despite considerable advances, problems persist. Catalyst deactivation, lengthy reaction times, low product yields, and the negative influence of water continue to hamper process effectiveness because of an inherently low equilibrium constant. Another gap is that most of the researchers in the literature utilise pure glycerol, while crude glycerol from the biodiesel process contains impurities that deactivate catalysts and necessitate stronger changes in the process.

Research in the future must focus on the use of continuous flow systems, recyclable catalysts and reactor systems with enhanced features. Methods such as azeotropic water removal techniques through in situ water removal or using acetone in excess can enhance selectivity and yield. Further, the adoption of green synthesis routes to catalysts and the acceptance of crude glycerol as a feedstock are imperative for large-scale and sustainable operations. Overcoming these challenges can enable glycerol acetalisation to play a crucial role in life circle analysis (LCA), and circular bioeconomy approaches that integrate environmental benefits with economic value in the transition toward renewable, bio-based industrial processes.

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