Acetalization Catalysts for Synthesis of Valuable Oxygenated Fuel Additives from Glycerol

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Abstract: Biodiesel is one of the most attractive sources of clean energy. It is produced by the transformation of vegetable oils with up to 10% formation of glycerol as a by-product. Therefore, development of new approaches for processing bio-glycerol into such value-added chemical compounds as solketals is necessary. Thus, various six- and five-membered cyclic compounds can be prepared by acetalization of glycerol with aldehyde or ketone. The resulting glycerol oxygenates are excellent fuel additives that increase viscosity, octane or cetane number, and stability to oxidation. In addition, these products significantly reduce carbon monoxide emissions from standard diesel fuel. In this review, we highlight recent advances in the glycerol valorization for the sustainable production of bio-additives. The review includes a discussion of the innovative and potential catalysts to produce solketals.

Keywords: acetalization; glycerol; acetal; ketal; fuel additives

1. Introduction

A constant increase in the consumption of fuels is an important challenge for humanity. At the same time, a strong decline in raw material reserves and high CO₂ emissions from their use and production are observed, which brought about the need to search for a new raw base for the chemical industry. Therefore, the development of new fuel derivatives (fuels, fuel additives, etc.), as well as the synthesis of various chemical products related to “bio-renewable” ones, are gaining momentum worldwide.

Biomass can be considered as a renewable source of energy that does not belong to fossil raw materials, is environmentally friendly, and has extensive reserves with the prospect of expanding [1,2]. Moreover, the use of biomass based on non-edible agricultural and forestry products avoids competition in the food and fuel sectors, and can significantly reduce CO₂ emissions. Although these energy sources cannot immediately replace existing fuel derivatives, they can be used as components in mixtures with fossil fuels. For example, biofuels can be employed as additives for gasoline, heating oil, and diesel fuel [3–6].

Currently, biodiesel, along with bioethanol, offers a great potential to produce liquid biofuels with the increase in world production in the near future [7,8]. Biodiesel is a refined alternative diesel motor fuel synthesized from vegetable oils and animal fats or other renewable resources. It consists of fatty acid esters obtained by transesterification of fats or oils under catalysts containing methanol or other lower alcohols. After secondary treatment including hydrodeoxygenation [9,10], it can be used as a second-generation motor fuel or as an additive.
Transesterification of oils and fats has achieved high levels of production in recent years, yielding about 30.8 million m³ of biodiesel. However, it is worth considering that during the production of methyl esters of fatty acid, about 11% of crude glycerol as the main by-product is generated for every 100 kg of produced biodiesel [11]. It is expected that by 2020, the global production of crude glycerin will reach 7.66 million tons [12]. Therefore, the development of new and economically-viable ways to valorize crude glycerol is necessary.

Several studies on the ways of glycerol transformation have been published in recent years [13–15]. To produce value-added chemical compounds, oxidation, dehydration, acetylation, and ammoxidation can be used. Of special interest are the acetalization reactions of glycerol from biodiesel processes into various oxygenated fuel additives [16–18]. A literature review was conducted to identify the number of articles published in the journals indexed in Web of Science and Scopus using a basic search for the articles containing information about the formation of acetals or ketals from glycerol. Figure 1 clearly shows a constant increase in the number of publications in this area and a sustained increase in the interest of researchers in this subject.

Therefore, this review focuses on the catalytic and non-catalytic processes of glycerol transformation into different fuel additives based on acetal and ketal. The main methods for crude glycerol production using various catalysts and the main methods of its processing will be given below. The third section is devoted to the use of acetals as a fuel and fuel additives is presented. The review also looks at the influence of these oxygenated compounds on the physical and chemical properties of fuel, and their effect on engine characteristics and emissions of exhaust gases. A mechanism for the formation of acetals/ketals is considered. The review also contains detailed information on recent achievements using various types of homogeneous and heterogeneous acetalization catalysts for of glycerol valorization, as well as data about non-catalytic acetalization. The article is aimed at the development of various types of ketals in the fuel industry to increase the production of renewable bio-additives for fuels.

2. Glycerol Production, Consumption and Characterization

The use of plant lipids as a raw material for the production of biofuels has been known for a long time. Thus, for the first time, the diesel engine operation on peanut oil was demonstrated by Rudolf Diesel at the Paris World Exhibition in 1900 [19]. The engine was designed to work not only on oil fuel, but also so that without making any changes in its design, it could work on vegetable oil.

Modern methods of processing vegetable oils into fuels include transesterification in the presence of a catalyst (Figure 2) with ethanol or isopropyl alcohol, as well as methanol, which is mostly used
because of its low cost, and due to its physical and chemical properties [20]. As a result, biodiesel—a mixture of methyl esters of fatty acids—and about 10–11% glycerol as a by-product are formed [11].

Depending on the territory, different oils and fats are used as feedstocks. In Argentina and Brazil, soybean oil is common because it has a low cost [21,22]. Thus, today there are large resource endowments to obtain both biodiesel and crude glycerol.

To obtain biodiesel, various types of catalysts are used. Hydroxides NaOH and KOH, due to their low market value and high catalytic activity at low reaction temperatures (55–75 °C), are the most commonly-used homogeneous basic catalysts [23]. Acidic homogeneous catalysts (HCl and H2SO4) have an advantage when fats with a high content of free fatty acids are processed [24]. However, acid catalysis has a relatively slow reaction rate compared to processes with hydroxides, and requires a higher methanol content [25]. Various types of heterogeneous catalysts, Fe3O4/MCM-41 [26], Mg2Zr5O12 [27], and Ti/SiO2 [28], are used for the transesterification process. Such catalysts can be separated and regenerated after the end of the reaction, which simplifies the purification of products and reuse of the catalytic system. The method of biodiesel production involving enzymatic catalysis such as lipase makes it possible to carry out hydrolysis of insoluble lipids under mild conditions, and helps to avoid the reduction of glycerol during reaction [29].

Generally, the transesterification of vegetable oils is carried out in membrane reactors [30], continuous reactors [31] and batch reactors [32].

The continuous development of biodiesel production technology and funding from the government to use renewable raw materials will lead to a rapid increase in biodiesel production, and glycerin excess production as a by-product will reduce the cost of glycerin.

The crude glycerol produced from transesterification has low quality due to its composition. Usually, this product contains ash, water, organic material, trimethylene glycol, and between 60 and 70 wt % crude glycerol [33]. During the crude glycerol purification process, distillation [34] and ion-exchange purification of crude glycerol derived from biodiesel production process are the most commonly-practiced methods [35]. The first method allows one to obtain 94–97 wt % pure glycerin. The method requires high energy costs, and some components have close boiling points, which makes it difficult to separate them. At the same time, the use of ion exchange resin makes it possible to obtain glycerin with 99% purity; however, the use of this method requires compliance with the requirements for the salt content in the feedstock, which may adversely affect the separation efficiency. In addition, this purification method leads to the formation of large volumes of wastewater. Up to 99.7% purity can
be obtained with a combination of distillation, separation on ion exchange resin, and final purification using adsorption on activated carbon [36].

The resulting glycerin has a variety of applications in the pharmaceutical, food, cosmetic, and polymer industries (Figure 3).

According to its physical characteristics, glycerin (propane-1,2,3-triol) has a molecular formula of C₃H₈O₃ and a molecular weight of 92. The exceptional physical and chemical properties of glycerin are due to the presence of three hydroxy groups, which allows glycerol to be completely dissolved in water and alcohols, soluble in ether and dioxane, but insoluble in hydrocarbon. The arising hydrogen bonds between the three groups cause a high viscosity and a high boiling point of glycerin [38].

A large number of value-added chemicals such as propanediols [39], acrolein [40], dihydroxyacetone [41], glyceric acid [42], hydrogen [43], synthesis gas [44], esters [45,46], etc., can be produced from glycerol using oxidation, reduction and other catalytic reactions (Scheme 1).
Oxidation of primary, secondary, and all three groups yields different molecules of C₃ acids, aldehydes, and ketones [47,48]. Selective hydrogenolysis of glycerol in the presence of metallic catalysts and hydrogen can produce 1,2-propanediol (1,2-PDO) [49], 1,3-propanediol (1,3-PDO), or ethylene glycol (EG). 1,3-PDO has gained industrial importance and value due to its use as a monomer in the synthesis of polymers, such as polyurethanes and polyesters. Recently, a method of fermentation of glycerin, which gives a high yield of the product, has become very popular. For example, the product yield up to 89% can be obtained using Klebsiella pneumoniae [50–52].

Partial oxidation of glycerol at high temperatures with oxygen at sub-stoichiometric ratios or reforming combining the effect of partial oxidation and steam reforming by feeding of glycerol, air, and water together in the reactor can be used to produce hydrogen and synthesis gas [44,53,54]. These processes are exothermic, which leads to high reaction rates and the possibility of not using external heat sources. In addition, the use of oxidizing agents decreases coke deposition, thus increasing the catalyst lifetime. The Schmidt group [55] obtained a 56–79% yield of hydrogen and 27–79% yield of CO over Rh-Ce/Al₂O₃ at a temperature of 1098–1328 K and millisecond contact times in the partial oxidation of glycerol and glycerol/water mixtures.

New methods for producing polymeric materials based on glycerol carbonate have been developed recently. Qing et al. [56] used 1,8-diazabicycloundec-7-ene as a catalyst to produce high value-added glycerol carbonate from crude glycerol and dimethyl carbonate with 90% conversion of glycerol and 84% selectivity to glycerol carbonate at a temperature of 40 °C. The carboxylation of glycerol with CO₂ to glycerol carbonate over CeO₂ catalyst was investigated by Liu et al. [57]. It was shown that the yield of glycerol carbonate could reach 78.9% at 150 °C, 4 MPa and 5 h.

Due to the high demand for 1-propanol and 2-propanol, a promising approach is to obtain these alcohols from glycerol. Hydrogenolysis of glycerol usually occurs along the path of dehydration-hydrogenation over metal-acid bifunctional catalysts. Priya et al. [58] studied the effect of various heteropolyacids on the propanol selectivity using the catalysts containing platinum and heteropolyacids (HPA) supported on zirconia in a continuous flow, and a fixed bed reactor at atmospheric pressure. It was found that high activity has been attributed to the dispersion of the metal and acidity of the catalysts. In [39], Priya et al. demonstrated high activity and selectivity of 1–4 wt % Pd/MoO₃-Al₂O₃ in the glycerol hydrogenolysis. In the vapor phase reaction under atmospheric pressure, the catalyst showed 91.3% propanol selectivity at 88.4% glycerol conversion at 210 °C and 100 mL/min H₂ flow rate.

Among the methods of glycerol valorization, two methods have attracted much attention in the academic community and industrial field. Both are used to produce various oxygen-containing fuel additives. One of these methods is transesterification of glycerol with acetic acid, which makes it possible to prepare monoacetylglycerol (MAG), diacetylglycerol (DAG) and triacetylglycerol (TAG) [59–61]. Glycerol esters are widely used in the food, cosmetic, pharmaceutical, and plastics industries. Usually, the esterification of glycerol is carried out using Brønsted acid as a catalyst. However, they have several technical and environmental disadvantages such as high corrosiveness and toxicity. Various heterogeneous porous materials are also used in the transesterification; however, they are characterized by the low selectivity for TAG formation due to a small pore size of the materials that impede the diffusion of the formed TAG in microporous channels [62,63]. The second method includes the acetalization reaction of glycerol with different ketones and aldehydes, which will be discussed in more detail later.

3. Acetals Derived from Glycerin as a New Oxygenated Fuel Additives

The development of new approaches for the conversion of crude glycerol into value-added chemical compounds using various reactions is among the main tasks in the field of biomass processing. One of these may be the production of oxygen-containing fuel additives. Such additives can reduce the density and viscosity of fuels, increase the cetane or octane number, and reduce emissions of exhaust gases and carbon monoxide production due to the presence of oxygen in the additives [64–66]. The most commonly-used additives are bioethanol, biomethanol, and alkyl ethers, such as methyl
tert-butyl ether (MTBE). However, due to environmental concerns associated with the toxicity of some chemicals, the use of eco-friendly bio-additives has aroused great interest over the past few years. Oxygenated glycerin-based compounds are examples of new additives for both biofuels and gasoline. In the initial stages, the development of the additive obtained by esterification of glycerol has greatly advanced. It was shown that such oxygenates lead to an improvement in the viscosity and cold properties of biodiesel, and increase the cetane number [64,65]. Noureddini et al. [66] esterified glycerol using isobutylene and showed that the ethers of glycerol can be effectively added to methyl esters, providing a 5 °C reduction in cloud point and an 8% reduction in viscosity.

Another method for fuel additives production from glycerol is the acetalization reaction with the carbonyl compound, which leads to various six- and five-membered cyclic compounds known as acetals or ketals.

Melero et al. [67] conducted a study of various oxygenated compounds derived from glycerol, including 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (solketal), triacetin, a mixture of tert-butylated glycerol (TBGs), and a mixture of glycerol esters (AGs). The blends with all the oxygenated derivates, except for the ethers, showed higher densities than the pure biodiesel. It is known that the content of unreacted triglycerides in the biodiesel determines its density and viscosity, and can lead to operational problems such as the formation of engine deposits. The addition of solketal or TBGs decreases the value of this property. The best parameter of the pour point (PP) was achieved when solketal and the mixture of TBGs were added to biodiesel at a temperature from −4 °C to −7 °C in the case of the ethers. This means that at −7 °C, the fuel will no longer flow. It was found that the addition of triacetin, as well as AGs, hardly modified the flash point of the pure biodiesel. In contrast, solketal and TBGs significantly decreased the flash point. Thus, solketal proved to be a promising fuel additive.

It was shown by Samoilov et al. [68] that the use of acetals reduces the contribution to air pollution from fuel combustion in engines. For example, the addition of solketal to gasoline increases the octane number and reduces gum formation. In the case of diesel fuel, there is a decrease in harmful emissions, such as oxides of nitrogen, carbon monoxide, hydrocarbons, aldehydes, and particulate matter. The introduction of the glycerol derivatives in a concentration of 0.046–2.25 wt % into hydrocarbon oil improves the antiwear properties by 42%.

Acetals also have antioxidant properties. In the work by Dodson et al. [69], glycerol acetals were successfully obtained with high purity and yields of up to 70–80% by acetalization of glycerol with aromatic aldehydes (benzaldehyde, anisic aldehyde, furfural) using a catalyst Amberlyst-15. In addition, the group showed that the obtained dioxanes and dioxolanes possess antioxidant activity, which was observed in a radical stabilization of the diphenyl-picrylhydrazyl molecule.

In some cases, joint use of different types of fuel additives has a greater effect than the use of individual components. The authors of [70] have shown that adding 5 vol.% of solketal to traditional diesel fuel B100 decreases the viscosity from 4.609 to 4.464 mm²/s, and for a mixture of diesel with biodiesel B50, from 3.699 to 3.65. The flash point of B100 decreases from 159 to 40.5 °C, and for B50 it drops from 76 to 37 °C, which does not satisfy the required standards. At the same time, the cold filter plugging point (CFPP) did not change, and reached −4 °C for B100 and −12 °C for B50. However, the addition of solketal and triacetin (5–10 vol.%) to the biodiesel fuel blend stock (B20) improves the oxidative stability threefold as compared with the oxidative stability for B20, while the viscosity is slightly decreased. Adding the mixture of acetal and triacetin increased the flash point slightly, and corresponded to the standard EN 590. Thus, it can be concluded that the obtained acetals do not improve the low-temperature properties of the fuel, but improve its viscosity and oxidative stability. In addition, the authors developed a new method of triacetin production with a high conversion of glycerin at room temperature without any catalysts.

On the other hand, the use of acetal obtained from butanal and glycerol, instead of solketal, improves the properties of animal fat biodiesel blends. Silva [71] and co-authors found that the addition of 5 vol.% acetal in the biodiesel led to a reduction of 5 °C in the pour point temperature. However, the decanal-based acetal of glycerol was ineffective for reducing the pour point.
Cold flow properties and maintenance of iodine and viscosity values of ketal derivatives with biodiesel blends were studied by De Torres et al. [72]. The addition of ketals to biodiesel improves cold flow properties from $-3^\circ C$ to $-6^\circ C$ and decreases the iodine value, which determines the amount of unsaturation in fatty acids, from 129 mg/100 mg to 107 mg/100 mg. The authors noted that protection of free hydroxyl group in order to improve oxidation stability is required.

Oprescu et al. [73] found that the usage of oxygenated compounds (2 wt % of 2-(ethyl-2-methyl-1,3-dioxolan-4-yl)methyl hexanoate) reduced smoke density. The average smoke reduction in comparison with diesel is about 19.20% for diesel blends with fuel additive. It should be pointed out that blending of diesel with acetal ester increases cetane index from 45.6 to 49.4 and helps in NO\textsubscript{x} reduction because a higher cetane index of the blends leads to a shorter ignition delay and a lower maximum heat release rate, which results in a lower cylinder temperature. A detailed review of oxygenated fuel additives from glycerol valorization was made by Cornejo et al. [74].

Acetalization of glycerol is carried out using homogeneous or heterogeneous catalysts; in some cases, special conditions are used for the reaction without a catalyst. The following sections will be dedicated to these issues.

4. Catalyst-Free Acetalization of Glycerol

Typically, catalyst-free acetalization leads to low glycerol conversion. At the same time, the choice of a substrate is of particular importance, as are the ratio at which the initial reagents are taken and the solvent that is used. Currently, special attention is paid to carrying out the acetalization reaction under special conditions, for example, microwave or subcritical ones. Table 1 summarizes the results of glycerol acetalization with various oxygen-containing reagents under various conditions. A more detailed description of the observed results will be presented below.

| Entry | Substrate | Sub/Gly Molar Ratio | Condition | Time (min) | X \textsuperscript{1} (%) | Select. 6-M/5-M \textsuperscript{2} (%) | Ref. |
|-------|-----------|---------------------|-----------|------------|----------------|-------------------|------|
| 1     | acetone   | 1:1                 | 110 °C, 150 rpm | 360        | 0.01          | NA                | [75] |
| 2     | benzaldehyde | 0:1.0:11            | 100 °C, toluene | 480        | 20            | 49/51             | [76] |
| 3     | formaldehyde | 1:1                | 75 °C, 1200 rpm | 120        | 21            | NA                | [77] |
| 4     | benzaldehyde | 1:2                 | 600 W microwave, 140 °C | 15      | 95            | 44/56             | [78] |
| 5     | chlorobenzaldehyde | 1:2               | 600 W microwave, 140 °C | 15     | 84            | 46/54             | [78] |
| 6     | 3,4-dimethoxybenzaldehyde | 1:2      | 600 W microwave, 140 °C | 15      | 96            | 47/53             | [78] |
| 7     | cyclohexanone | 1:2                 | 600 W microwave, 140 °C | 15     | 90            | 2/98              | [78] |
| 8     | 2-methylcyclohexanone | 1:2      | 600 W microwave, 140 °C | 15      | 60            | 78/22             | [78] |
| 9     | butanal   | 22.8:21.7           | 70 °C, dimethylsulfoxide | 120    | 20            | NA                | [71] |
| 10    | hexanal   | 22.8:21.7           | 70 °C, dimethylsulfoxide | 120    | 10            | NA                | [71] |
| 11    | decanal  | 22.8:21.7           | 70 °C, dimethylsulfoxide | 120    | 5             | NA                | [71] |
| 12    | isopropenyl acetate | 1:1              | 180 °C, 0.8 MPa | 300      | 73            | 0/44              | [79] |
| 13    | isopropenyl acetate | 5:1               | 180 °C, 0.8 MPa | 300      | 73            | 0/29              | [79] |
| 14    | acetone   | 2.1                 | 250 °C, 8 MPa | 240        | 13.5          | 0/75              | [80] |
| 15    | acetone   | 3.6                 | 250 °C, 8 MPa | 240        | 23            | 0/81              | [80] |
| 16    | acetone   | 10.8                | 250 °C, 8 MPa | 240        | 28.2          | 0/80              | [80] |

\textsuperscript{1} Conversion of the glycerol (Sub/Gly $\geq$ 1) or substrate (Sub/Gly < 1). \textsuperscript{2} The ratio of selectivity of the 5-membered (5-M) and 6-membered (6-M) cyclic products formation.

Carvalho et al. [72] have shown low activity with 0.01% conversion of glycerol in the catalyst-free acetalization reaction of glycerol with acetone (1:1) in a 50 mL batch reactor with stirring at 150 rpm under nitrogen flow at 110 °C for 6 h. In contradiction with these data, a blank experiment on acetalization conducted by Umbarkar et al. [76] without any catalysts led to 20% benzaldehyde.
conversion with 49 and 51% selectivity for the 6-membered cyclic products and 5-membered cyclic products, respectively, at 100 °C, 0.11 mol of glycerol, 0.1 mol of benzaldehyde, 8 h of reaction time, and toluene as the solvent. Such a difference in conversion values is probably due to the different nature of reagents (aldehyde and ketone) and the presence of a solvent in the second case.

The effect of catalyst loading on the conversion of glycerol at 1200 rpm, temperature 348 K and glycerol/formaldehyde molar ratio of 1:1 was studied by Hasabnis and Mahajani [77]. In this condition, the catalyst-free reaction led to a 21% conversion of glycerol, while in the presence of Amberlyst-15 (10 wt %), the conversion increased to 50%.

Radheshyam R. Pawar et al. [78] performed acetylation of glycerol with carbonyl compounds using a microwave-assisted processing. The main feature is that the reaction is catalyst- and solvent-free and high yields of cyclic acetals/ketals, including commercially-valuable compounds and precursors of the fuel additive, were observed. About 95% conversion of benzaldehyde was achieved using a twofold excess of glycerol. The obtained high activity confirms the high efficiency of microwave irradiation, which excludes the use of solvents, expensive catalysts, and subsequent separation thereof. As shown in Table 1, various aldehydes showed high activity, with the formation of 5-membered (5-M) and 6-membered (6-M) cyclic products in a ratio close to 50:50, while ketones showed a significantly lower conversion value with a high selectivity for the formation of 5-M solketal. It was found that an electron donating or electron withdrawing substituent on the aromatic ring affects the conversion and selectivity. Thus, the introduction of the methyl group leads to a slight increase in the selectivity (65%) for the 5-M product with a slight decrease in the conversion (59%). The use of chlorine or bromine as a substitute did not have a strong effect. The authors also found that with increasing chain length of aliphatic aldehydes, a decrease in conversion was observed. For example, the conversion in the case of butanal was 90% at 80 °C, whereas in the case of decanal it was 17% at 140 °C.

To prove the effect of diffusion of aldehyde molecules inside the structure of porous catalysts on the conversion of glycerol, Silva et al. [71] carried out the reaction without a catalyst. The results showed that in the absence of a catalyst, the same dependence was observed as with the presence of a catalyst. Conversion of glycerol decreases with increasing size of the aldehyde chain. The authors agreed that parameters of the catalyst pores have no effect on the conversion of acetone. Probably, aldehyde aggregation in the reaction medium occurs. Glycerin and solvent form a reaction medium that is not as effective for dissolving aldehydes. Thus, aldehyde molecules combine to minimize repulsive interactions between the non-polar hydrocarbon chain and the polar reaction medium. In this case, the longer the aldehyde hydrocarbon chains, the less interaction between glycerol and aldehyde.

The reaction of glycerol with acetates in the absence of any catalyst can also lead to solketals formation. Calmanti et al. [79] performed batch reactions by using the mixtures of glycerol and methyl or isopropenyl acetates in a molar ratio variable between 1 and 20. Autoclave tests were carried out at 120–220 °C (Scheme 2).

![Scheme 2. Scheme of batch reactions using mixtures of glycerol and methyl or isopropenyl acetates. Adapted from Ref. [79].](image-url)
It was shown that at 180 °C and acetate/glycerol ratios of 1:1 and 5:1, the reactions of glycerol with isopropenyl acetate yield multicomponent mixtures, including solketal (32% and 22%, respectively) and its methyl ester (12 and 7, respectively). A higher excess of isopropenyl acetate up to 20 molar ratio substantially inhibits the acetalization reaction. The authors explain the formation of solketales as a result of competitive acetalization of glycerol with acetone formed during transesterification with isopropenyl acetate. To confirm this, acetalization of a mixture of glycerol and acetone (in a molar ratio of 1:10) at 180 °C for 5 h was carried out. The conversion achieved 70% with 100% selectivity for solketal formation. In the case of methyl acetate, the ketone does not occur and solketales are not formed.

At standard conditions, acetalization of acetone and glycerol poorly occurs. In experiments of Royon et al. [80], the reaction was performed under supercritical conditions, i.e., at high pressure and temperature, making this reaction possible without acid catalysts. High rates of conversion and selectivity under supercritical conditions can be explained by a combination of several factors. It is known that under supercritical conditions, the solubility of acetone in glycerol increases, which contributes to an increase in the reaction rate. In addition, acetone can play the role of a catalyst, since upon reaching supercritical conditions, the acidic property of alpha-hydrogen of acetone will increase through the keto-enol tautomerism. Thus, supercritical acetone at 508 K and pressure 8 MPa can simultaneously be a solvent, catalyst, and reaction reagent in acetalization reaction. The maximal glycerol conversion was 28% with 80% selectivity to solketal, and was achieved at 240 min and 10.8 of acetone/glycerol molar ratio.

5. Homogeneous Catalysts for Acetalization

Generally, acetalization of glycerol is performed over homogeneous mineral acids such as H₃PO₄ and H₂SO₄ [81,82], as well as other strong organic acids like p-toluenesulfonic acid. Ch et al. [83] studied the formation of glycerol acetals during the reaction of 200 g of aqueous glycerol with 63 g of acetone. The reaction was initiated with the addition of the catalyst. The reaction was carried out at refluxing temperature for 4 h, after which the toluene solvent was used for the extraction of the acetal. The study showed that the conversion of glycerol to acetal increases with increasing concentration of glycerol in the reaction medium. At the same time, the degree of conversion reduced in the series H₂SO₄ > p-toluene sulfonic acid > Amberlyst-15 > methyl sulfonic acid with the highest glycerol conversion for sulfuric acid, which is 90%. It was found that toluene is the most effective extracting solvent.

The acidity of the catalyst has a significant impact on the reaction rate of acetalization and the yield of products since H⁺ is involved in activating the carbonyl group. Scheme 3 shows the reaction mechanism of glycerol acetalization of with aldehydes or ketones with the participation of homogeneous acid catalysts proposed according to [84–86].

According to the literature, the proposed reaction mechanism involves the formation of a protonated intermediate (a positively charged carbonyl carbon of the carbonyl compound) when the oxygen atom of the carbonyl group interacts with a hydrogen cation H⁺. The obtained cation interacts with one of the free primary -OH groups of glycerol with the further formation of hemiacetal, followed by the removal of water molecules to form a carbenium ion. Subsequently, this ion will be attacked by a single pair of electrons of neighboring hydroxyl group with a tertiary carbon atom, which leads to the formation of a 5-membered acetal. The formation of a 6-membered acetal occurs when electron pair on -OH group interacts with a tertiary carbon atom [87]. It is worth noting that acetal formation strongly depends on electronic and steric factors. The reaction medium must have high acidity to promote effective protonation of any hemiacetal formation, and should be sufficiently polar to ensure the stabilization of the cationic intermediate [88]. In the case of the interaction of glycerol and aldehyde, 1,3-dioxane (6-membered ring) and 1,3-dioxolane (5-membered ring) structures are formed.
Recently, scientists have paid much attention to organic acids as homogeneous catalysts, which are less aggressive to metals, and can be removed from the substrate by distillation. Also, ionic liquids (ILs), which are at the intersection of homogeneous and heterogeneous catalysts, got high popularity. In this work, we consider that ILs are homogeneous catalysts sometimes involved in heterophase catalysis. Garcia et al. [70] used p-toluenesulfonic acid (0.27 mol) as a catalyst for acetalization of glycerol (2.74 mol) by acetaldehyde (8.22 mol) (Scheme 4). The reaction was carried out by heating to reflux for 16 h. The yield of the target product (2,2-dimethyl-1,3-dioxolan-4-yl methanol) under the above conditions was 90%. Such a high parameter is connected with minimization of water content in the substrate. The formation of water as a by-product is the main problem with the acetalization reaction. Even a small amount of water creates a thermodynamic and kinetic barrier for glycerol conversion. During acetalization, wet acetone was dried and introduced to the reactor. The obtained 2,2-dimethyl-1,3-dioxolan-4-yl-methanol was used as a reagent for the 2,2-dimethyl-1,3-dioxolane-4-yl methyl acetate preparation to modify its structure, introducing an acyl group into the -OH. It was an effective solution to get a viscosity improver. The obtained acetals were used as an additive to diesel fuel and its mixture with biodiesel. Although 2,2-dimethyl-1,3-dioxolane-4-yl methyl acetate did not improve cold properties, it did not exert a negative effect either.

Scheme 3. Mechanism of acetals formation for the reaction of acetone/ketone and glycerol.

Scheme 4. Scheme for the formation of 2,2-dimethyl-1,3-dioxolan-4-yl methanol and 2,2-dimethyl-1,3-dioxolan-4-yl methyl acetate. Adapted from Ref. [70].
p-Toluenesulfonic acid was used as a homogeneous catalyst in [89] for furfural and polyvinyl alcohol acetalization. The reaction (Scheme 5) was carried out in water or dimethyl sulfoxide (DMSO) at room temperature with stirring for 12 h. The reagents (furfural and polyvinyl alcohol) were mixed in the required proportion, and then the catalyst was added. In the case of water, the pH reached 1.7 and with DMSO amount of acid was about 1 vol.%. The yield of acetals under the above conditions was about 50% in the case of water and 55% in the presence of DMSO.

![Scheme 5](image)

**Scheme 5.** Scheme of polyvinyl alcohol acetalization with furfural in the presence of p-toluenesulfonic acid. Adapted from Ref. [89].

p-Toluenesulfonic acid was also used in the reaction of acetalization of glycerol with benzaldehyde (Scheme 6) by Radheshyam et al. [78]. The process was carried out using SIclo M-II microwaves with variable frequency and temperature. It was shown that the optimal reaction conditions in terms of benzaldehyde conversion and product yield are as follows: 140 °C, reaction time 15 min, power of microwave waves 600 W, ratio glycerol:benezaldehyde = 1:1. Under these conditions, the benzaldehyde conversion was 67%, while the selectivity for dioxolane and dioxane was 47% and 53%, respectively.

![Scheme 6](image)

**Scheme 6.** Reaction scheme for acetalization of glycerol with benzaldehyde with the formation of (a) 2-benzyl-4-hydroxymethyl-1,3-dioxolane and (b) 2-benzyl-5-hydroxy-1,3-dioxane. Adapted from Ref. [78].

Currently, ionic liquids (ILs) are of interest and are widely used in many catalytic applications due to their adjustable structure and physicochemical properties; in addition, they are
environmentally-friendly solvents and catalysts that are active at room temperature. Such liquids have also been used in the acetalization reaction. For example, Li et al. [90] showed that acetalization of propionaldehyde with ethanediol, catalyzed by an acid functional IL, makes it possible to obtain acetals in a yield of up to 99%.

Acetalization of glycerol with benzaldehyde was carried out in the presence of an acidic IL with HSO$_4^-$ as an anion in [91]. It was shown that the acetal yield was 66–73% in this case.

Wang at al. [91] used ionic liquids represented by imidazole cations containing sulfonate and sulfanilamide groups synthesized according to [92]. The process was carried out in a batch reactor equipped with a magnetic stirrer. Glycerol (2.6 g), benzaldehyde (2.0 g) and ionic liquid (0.88 g) were placed in the reactor. The reaction mixture was heated to 70 °C with vigorous stirring at atmospheric pressure, and was kept at this temperature for 2 h. It was shown that the highest yield of acetals was observed in the presence of [BPy]HSO$_4^-$ and was 74% (Table 2). The activity of ILs decreased in the series [BPy]HSO$_4^-$ > [BSPy]HSO$_4^-$ > [BSMim]CF$_3$SO$_3^-$ > [BSMim]HSO$_4^-$ > [HMim]HSO$_4^-$ . Mineral and organic acids were also used along with IL, but their activity was lower.

Table 2. The composition of acetalization products of glycerol and benzaldehyde in the presence of various catalysts. According to Ref. [91].

| Entry | Catalyst          | Yield 5-M, % | Yield 6-M, % |
|-------|-------------------|--------------|--------------|
| 1     | No catalyst       | 12           | 4            |
| 2     | [BSPy]HSO$_4^-$   | 26           | 44           |
| 3     | [BSMim]CF$_3$SO$_3^-$ | 22         | 46           |
| 4     | [BSMim]HSO$_4^-$  | 26           | 42           |
| 5     | [Bpy]HSO$_4^-$    | 28           | 47           |
| 6     | [HMim]HSO$_4^-$   | 29           | 35           |
| 7     | H$_2$SO$_4$       | 21           | 34           |
| 8     | HCl               | 20           | 33           |
| 9     | NH$_2$SO$_3$H     | 21           | 38           |
| 10    | 4-toluenesulfonic acid | 14         | 17           |

The most active catalyst, [BPy]HSO$_4^-$, was used to optimize parameters in order to increase the yield of target products. It was shown that 99.8% yield of acetal was observed after 2 h at 25 °C, and that the molar ratio of glycerol and benzaldehyde was 1:3. The authors attribute the high activity of ILs to the formation of a micro water-removing system constituted by the ionic liquid by virtue of its special solubility.

In [17], the authors used sulfonic ILs in the acetalization reaction of cyclohexanone and glycerin. They showed that the sample [MeSO$_3$bmim][MeSO$_4$] is capable of achieving glycerol conversion of up to 86% (Table 3), with a selectivity for six-membered acetal of 28%. Usually, an ionic liquid consists of an organic cation and an inorganic or organic anion. Therefore, it has a more branchy structure than traditional homogeneous inorganic acid catalysts (such as sulfuric and hydrochloric acids). Particularly, such a branched structure significantly complicates the cyclization of hydroxyl groups in positions 1 and 2 of glycerol, leading to the formation of dioxolane; nevertheless, in positions 1 and 3 of glycerol, such cyclization is able to form dioxane. Thus, the authors consider that significant steric difficulties characteristic of this type of ILs have a positive effect on the selectivity for six-membered acetal. The reaction parameters were optimized: catalyst [MeSO$_3$bmim][MeSO$_4$] in the amount of 0.5 mmol; process temperature was 120 °C; 0.12 mol of cyclohexanone and 0.10 mol of glycerin were used; 20 mL of toluene as a solvent; reaction time was 2 h. Combining such parameters, the glycerol conversion was 87%, the acetal yield was 85%, while the selectivity for products A and B were 31 and 61%, respectively.

Despite their high activity, the use of homogeneous catalysts in the acetalization process is limited by some technical and environmental aspects, such as catalyst separation, product purity, reactor corrosion, and the formation of large amounts of waste. Therefore, there is the task to develop highly efficient heterogeneous solid acid catalysts that have several advantages over homogeneous ones:
they are easier to separate from products, stable at high temperatures, and less toxic. In addition, heterogeneous catalytic systems provide better selectivity for the desired products as compared to the homogeneous catalysts.

### Table 3. The composition of acetalization products of glycerol and cyclohexanone in the presence of various sulfonic ILs. Adapted from Ref. [17].

| Entry | Catalyst | Conversion of glycerol, % | Yield of ketals, % | Selectivity, (6-M/5-M) |
|-------|----------|---------------------------|-------------------|------------------------|
| 1     | [MeSO$_3$bmim][MeSO$_4$] | 86                         | 84                | 28/69                  |
| 2     | [MeSO$_3$Py][MeSO$_4$] | 83                         | 80                | 26/70                  |
| 3     | [MeSO$_3$bm$_3$N][MeSO$_4$] | 86                         | 83                | 26/71                  |
| 4     | [EtSO$_3$bmim][EtSO$_4$] | 81                         | 78                | 27/70                  |
| 5     | [HSO$_3$bmim][HSO$_4$] | 84                         | 81                | 24/73                  |
| 6     | [bmim][MeSO$_4$] | 80                         | 78                | 17/80                  |
| 7     | [bmim][EtSO$_4$] | 73                         | 71                | 16/82                  |
| 8     | [MeSO$_3$bmim][MeSO$_4$] | 85                         | 85                | 29/69                  |
| 9     | [MeSO$_3$bmim][MeSO$_4$] | 87                         | 83                | 28/69                  |

### 6. Heterogeneous Catalysts for Glycerol Acetalization

As noted earlier, the use of heterogeneous catalysts has a number of advantages, such as the ability to control the selectivity for the formation of ketals and acetals by varying some characteristics of the catalyst and its support. Heterogeneous catalysts can easily be separated from the reaction medium, do not require neutralization, and are suitable for multiple uses.

The mechanism of acetalization using heterogeneous catalysts is similar to the scheme presented in Scheme 3 for homogeneous catalysts, only instead of H$^+$, there may be coordination centers (metal sites, acid sites) of a heterogeneous catalyst, which very often have bifunctional nature. Gomes et al. [93] studied a catalyst containing PtO$_x$ and chlorined-Pt species dispersed on the alkali trititanate nanotube phase (TNT) in acetalization of glycerol with acetone. The authors proposed a reaction mechanism by which acetalization is initiated by the attack of the carbonyl group of acetone on Pt nanoparticles dispersed on the TNT structure. Thus, the Pt particles are coordinated with the carbonyl group of acetone and glycerin to form an intermediate which interacts with the proton of the TNT structure to produce acetal and solketal. Reaction parameters of different studies using of catalysts containing noble metals are presented in Table 4. Catalytic testing was carried out in a batch reactor at 150 rpm and temperature range 50–110 °C. It is noted that the increase in the acetone to glycerol molar ratio from 1:1 to 4:1 enhances glycerol conversion from 40 to 86.5%, respectively, but it also decreases ketal selectivity from 30 to 20, respectively. However, the catalytic parameter was higher for Pt-containing catalyst than for Ni- or Co-containing TNT samples. Ruiz with colleagues [94] obtained up to 94% yield of acetals for 4 h with AuCl$_3$ as Lewis acid catalysts under mild reaction conditions. The gold catalyst has been made recoverable by preparing a cationic Au(I) complex (AuPPh$_3$NTf$_2$) that can be separated and reused up to seven times with >90% yield of acetal. Catalytic reactions were carried out in a closed glass reactor. To the catalyst (2 mol%), a mixture of glycerol (1 mmol), trioxane as a source of formaldehyde (1 mmol), and dioxane as a solvent was added. The reaction mixture was stirred at 80 °C. Kapkowski et al. [95] screened the Re-, Ru-, Ir-, and Rh-containing catalysts supported on nano-silica in glycerol acetalization with acetone or butanone. It was discovered that 1.0% Re/SiO$_2$ catalyst produced five-membered cyclic compounds in the main. The yield of 2,2-dimethyl-1,3-dioxolane-4-methanol reached 98% at 30 °C, 1 h, 200 rpm, using 1.23 mol/L of glycerol in the reaction mixture (glycerol/acetone molar ratio 1:10), inert reaction atmosphere (N$_2$), and ultrasounds for 10 min. The activity level for Mo supported catalysts was lower than for the SiO$_2$ supported ones, which illustrates the importance of the SiO$_2$ support, which can provide the acidity needed in acetalization. In addition, the use of a Mo support destroyed high selectivity of the Re catalyst, and both five- and six-membered products were observed.
The obtained acetals can be used for blending with petroleum diesel oil to obtain valuable biofuels and protect the environment [96].

**Table 4.** Reaction parameters reported by different studies for the glycerol acetalization with catalysts containing noble metals.

| Entry | Catalyst | Substrate | Sub/Gly Molar Ratio | Condition | Time (h) | X (%) | Select. 6-M/5-M (%) | Ref. |
|-------|----------|-----------|---------------------|-----------|----------|-------|---------------------|------|
| 1     | Pt-TNT   | acetone   | 1:1                 | 50 °C, 0.1 MPa, 150 rpm, \(m_{\text{cat}} = 130 \text{ mg}\) | 6        | 40    | 0/30               | [93] |
| 2     | Pt-TNT   | acetone   | 4:1                 | 50 °C, 0.1 MPa, 150 rpm, \(m_{\text{cat}} = 130 \text{ mg}\) | 6        | 87    | 0/20               | [93] |
| 3     | Pt-TNT   | acetone   | 8:1                 | 50 °C, 0.1 MPa, 150 rpm, \(m_{\text{cat}} = 130 \text{ mg}\) | 6        | 78    | 0/0                | [93] |
| 4     | AuCl₃    | trioxane  | 1:1                 | 80 °C, 0.1 MPa, dioxane as a solvent, 5 mol% of cat. | 4        | NA    | 3 (93)             | [94] |
| 5     | AuCl₃    | trioxane  | 1:1                 | 80 °C, 0.1 MPa, dioxane as a solvent, 2 mol% of cat. | 7        | NA    | 3 (61/31)          | [94] |
| 6     | AuCl₃    | formaldehyde | 3:1              | 60 °C, 0.1 MPa, dioxane as solvent, 2 mol% of cat. | 3        | NA    | 3 (37/13)          | [94] |
| 7     | AuPPh₃NTf₂ | n-heptanal | 1:1              | 22 °C, 0.1 MPa, 75 mol% of acetonitrile, 5 mol% of cat., after 7 times of the use. | 24       | NA    | 3 (90)             | [94] |
| 8     | 1.0% Re/SiO₂ | acetone   | 10:1               | 30 °C, 0.1 MPa, 200 rpm, ultrasounds for 10 min, \(m_{\text{cat}} = 20 \text{ mg}\) | 1        | 100   | 2/97               | [95] |
| 9     | 1.0% Re/SiO₂ | acetone   | 10:1               | 55 °C, 0.1 MPa, 200 rpm, ultrasounds for 10 min, \(m_{\text{cat}} = 50 \text{ mg}\) | 3        | 100   | 3/94               | [95] |
| 10    | 1.0% Re/Mo | acetone   | 10:1               | 55 °C, 0.1 MPa, 200 rpm, ultrasounds for 10 min, \(m_{\text{cat}} = 50 \text{ mg}\) | 3        | 20    | 25/48              | [95] |

1 Glycerol (Sub/Gly ≥ 1) or substrate (Sub/Gly < 1) conversion. 2 The ratio of selectivity for 5-membered (5-M) and 6-membered (6-M) cyclic products formation. 3 Glycerol conversion and acetal selectivity not available, the yield of acetals is presented.

Despite the high activity of catalysts based on noble metals, their high cost does not make them widely used. Therefore, studies are underway on the development of new catalysts with high acidity. Currently, catalysts based on zeolite, acid resins, and mineral clay are being developed (Table 5). Acetalization of glycerol with butanal has been investigated over a range of zeolites such as USY with different Si/Al ratio, BEA, ZSM-5 and Dowex resin, with different pore structures and acidity by Serafim et al. [88]. The results showed that BEA zeolite presented the highest catalytic activity (75.6 mmol/h \(g_{\text{cat}}\)). All catalysts exhibited high selectivity (77–82%) to five-membered ring acetal product. The five-membered ring acetal is more probable kinetically than the formation of six-membered ring acetal. Similar results were also observed by Silva et al. [71] using Amberlyst-15 acid resin as a catalyst. In work [88], it also was shown that the initial activity of USY increases with an increase in the Si/Al ratio up to 30. Further increase in the ratio leads to a decrease in catalytic activity. This behavior can be explained by the fact that with an increase in the Si/Al ratio, hydrophobicity of the catalyst increases, which improves the diffusion of reagents in the zeolite pores, while the number of acid sites decreases.

Deutsch et al. [97] carried out the catalytic condensation of glycerol with benzaldehyde, formaldehyde, and acetone over acid polymers Amberlyst-36 and Nafion-H NR-50, zeolite H-BEA (Si/Al = 25), and mineral Montmorillonite K-10 to obtain cyclic acetals of glycerol. High yields, i.e., up to 94%, can be achieved for Amberlyst-36 in the reaction of glycerol with benzaldehyde. Six-membered cyclic acetal with a ratio of 78% is observed for formaldehyde as a reaction partner for glycerol. It is...
worth noting that Amberlyst-36 has high acidity compared with other catalysts, and the number of acid sites is 5.4 mmol/g, whereas for others catalysts it does not exceed 0.8 mmol/g. Researchers found that acetalization is more difficult in the absence of a solvent due to the strong adsorption of polar reactants on the catalyst surface, which deactivates the active sites.

The effect of catalyst acidity on its activity in the formation of acetals can be observed in the work by Nandan et al. [98]. They synthesized sulfonated carbon–silica-meso composite materials using glucose as a carbon source as well as a precursor. The highly acidic (2.25 mmol/g) composite gave the higher glycerol conversion of 82% and 99% selectivity for solketal. For the reaction, 0.25 g of the catalyst (5% of glycerol weight) was taken in a round bottom flask; 18.91 g of acetone and 5 g of glycerol with glycerol to acetone molar ratio 1:6 were added to it and refluxed at 70 °C for 30 min.

Faria et al. [99] reported a study about the acetalization reaction between acetaldehyde and glycerol to produce glycerol ethyl acetal. The screening of the catalysts demonstrated that acid ion-exchange resins present higher activities than zeolites. The Amberlyst-15 wet resin was found to be a suitable catalyst for this reaction. At the reaction conditions T = 293.15 K, P = 1.0 bar, initial acetaldehyde/glycerol molar ratio = 1:1, and mass of catalyst = 1 wt %, the conversion of glycerol reached 70–80%. Agirre et al. [100] investigated the kinetics of the reaction between glycerol and acetaldehyde. The study showed that this reaction is not a thermodynamically-limited, reversible one. As a result, the presence of water in the initial reactant mixture does not have a negative effect on the reaction kinetics because of dilution.

Nanda and co-worker [101] optimized the catalytic conversion of glycerol to an oxygenated fuel additive in a continuous flow reactor over Amberlyst in accordance with their previous research [84]. A maximum yield of solketal reached 94 ± 2% at temperature 25 °C, acetone equivalent 4, and WHSV 2 h⁻¹. They showed that the presence of impurities like salt and water in glycerol reduced the yield significantly. Similar values of the yield (95%) and the selectivity of 100% solketal formation were achieved using heterogeneous Purolite® PD206 [102]. The optimum conditions were temperature 20 °C, pressure 120 bar, acetone/glycerol ratio 5, feed flowrate 0.1 mL-min⁻¹, and the catalyst mass 0.77 g. Despite the satisfactory yield, the reaction pressure was very high.

Ferreira et al. [103] observed that the catalytic activity in acetalization of glycerol in a stirred batch reactor using heteropolyacids as catalysts at 70 °C decreases in the series: tungstophosphoric (PW) > tungstosilicic (SiW) > molybdophosphoric (PMo) > molybdosilicic (SiMo) acids immobilized in silica by sol-gel method. It was reported that more than 99% conversion of glycerol with 97% selectivity toward solketal was observed.

Three types of water-tolerant heterogeneous catalysts were studied in the reaction of glycerol with aqueous formaldehyde by Chen et al. [104]. The activity of Cs₂.₅H₀.₅PW₁₂O₄₀ was found to be over 70% within 60 min of reaction time, which was higher compared with using of acid functionalized periodic mesoporous organosilicas (PMOs), zeolite ZSM-5 and Amberlyst-15. The better activity of Cs₂.₅H₀.₅PW₁₂O₄₀ is due to its high acid strength and surface area. On the second stage, Chen et al. [105] studied Cs₂.₅H₀.₅PW₁₂O₄₀ supported on mesoporous silica in glycerol acetalization with formaldehyde. They found that the mesopore volume affects the activity: the higher the pore value, the better access to acid sites of the catalyst.

Mixed oxide TiO₂–SiO₂ as Lewis acid was synthesized by the sol-gel method by Fan et al. [106]. The results show that after adsorbing water molecules by Ti–Si mixed oxides, Bronsted acid sites can be produced, leading to the highest catalytic property. Under the optimum conditions (2.2 g catalyst per 100 g glycerol, acetone/glycerol molar ratio 4 and reaction temperature 90 °C), the glycerol conversion and 5-membered ring ketal selectivity can reach up to 95 and 90%, respectively. The authors concluded that the glycerol acetalization with acetone to ketals occurred on the Bronsted acid sites of TiO₂–SiO₂ catalysts.

Arias et al. [107] valorized glycerol and 5-hydroxymethylfurfural by acetalization reaction in the presence of large pore zeolites HY and Beta, a laminar zeolite ITQ-2, a mesoporous aluminosilicate (MCM-41), and p-toluenesulfonic acid. The research team showed that the homogeneous catalyst
mainly promotes polymerization reactions, while HY and Beta are more active catalysts but are less selective and deactivate more rapidly than mesoporous MCM-41 and ITQ-2, whose balance between number of acid sites and adequate surface polarity provides high yield (98%) and selectivity (100%) to the acetals.

### Table 5. Reaction parameters reported by different studies for the glycerol acetalization with acidic heterogeneous catalysts containing noble metals.

| Entry | Catalyst | Acidity (mmol/g) | Substrate | Sub/Gly Molar Ratio | Conditions | Time (h) | X (%) | 6-M/5-M | Select. |
|-------|----------|------------------|-----------|---------------------|------------|---------|-------|---------|---------|
| 1     | USY1     | 2.68             | butanal   | 0.11:0.04           | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.3 g. | 4        | 45    | 19/81   | [88]    |
| 2     | USY2     | 1.28             | butanal   | 0.11:0.04           | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.3 g. | 4        | 76    | 23/77   | [88]    |
| 3     | USY3     | 0.53             | butanal   | 0.11:0.04           | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.3 g. | 4        | 84    | 22/78   | [88]    |
| 4     | USY4     | 0.2              | butanal   | 0.11:0.04           | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.3 g. | 4        | 72    | 20/80   | [88]    |
| 5     | BEA      | 0.41             | butanal   | 0.11:0.04           | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.3 g. | 4        | 87    | 21/79   | [88]    |
| 6     | Amberlyst-15 | 1.5        | butanal   | 1:1.05               | 85 °C, 0.1 MPa, dimethylsulfoxide as a solvent, m<sub>cat</sub> = 0.36 g | 2        | 80    | 21/79   | [71]    |
| 7     | Amberlyst-36 | 5.4        | benzaldehyde | 0.1:0.011          | 61.2 °C, 0.1 MPa, refluxing chloroform as a solvent, m<sub>cat</sub> = 0.1 g | 4        | NA    | NA      | (57/37) |
| 8     | Nation-H | 0.8             | benzaldehyde | 0.1:0.011          | 61.2 °C, 0.1 MPa, refluxing chloroform as a solvent, m<sub>cat</sub> = 0.1 g | 4        | NA    | NA      | (49/45) |
| 9     | Amberlyst-36 | 5.4        | benzaldehyde | 0.1:0.011          | 20 °C, 0.1 MPa, dichloromethane and methanol as a solvent, m<sub>cat</sub> = 0.1 g | 8        | NA    | NA      | (48/33) |
| 10    | Nation-H | 0.8             | benzaldehyde | 0.1:0.011          | 20 °C, 0.1 MPa, dichloromethane and methanol as a solvent, m<sub>cat</sub> = 0.1 g | 8        | NA    | NA      | (-/-)   |
| 11    | SCS1/2   | 1.35            | acetone   | 6:1                  | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.25 g | 0.5     | 75    | 0/90    | [98]    |
| 12    | HSCS1/2  | 2.25            | acetone   | 6:1                  | 70 °C, 0.1 MPa, m<sub>cat</sub> = 0.25 g | 0.5     | 82    | 0/99    | [98]    |
| 13    | Amberlyst-15 | 5.5        | acetone   | 4:1                  | 25 °C, 0.1 MPa, WHSV = 2 h<sup>-1</sup>, m<sub>cat</sub> = 0.25 g | -       | NA    | NA      | 0/94    |
| 14    | Purolite® PD206 | NA        | acetone   | 5:1                  | 20 °C, m<sub>cat</sub> = 0.77 g | -       | 95    | 0/100   | [102]   |
| 15    | TiO<sub>2</sub>-SiO<sub>2</sub> | 0.11     | acetone   | 4:1                  | 90 °C, 0.1 MPa, m<sub>cat</sub> = 0.22 g | 3       | 95    | 0/90    | [106]   |
| 16    | HBet     | NA              | 5-hydroxymethyl furfural | 1:2          | 83 °C, 0.1 MPa, 1000 rpm, m<sub>cat</sub> = 0.025 g | 8       | 60    | 22/71   | [107]   |
| 17    | USY      | NA              | 5-hydroxymethyl furfural | 1:2          | 83 °C, 0.1 MPa, 1000 rpm, m<sub>cat</sub> = 0.025 g | 8       | 68    | 22/78   | [107]   |
| 18    | ITQ-2    | NA              | 5-hydroxymethyl furfural | 1:2          | 83 °C, 0.1 MPa, 1000 rpm, m<sub>cat</sub> = 0.025 g | 3       | 98    | 26/74   | [107]   |
| 19    | MCM-41   | NA              | 5-hydroxymethyl furfural | 1:2          | 83 °C, 0.1 MPa, 1000 rpm, m<sub>cat</sub> = 0.025 g | 8       | 94    | 20/80   | [107]   |
| 20    | 80LS20PS 450H+ | 3.49    | furfural   | 4:1                  | 100 °C, 0.1 MPa, 300 rpm, m<sub>cat</sub> = 0.5 wt % | 1       | 100   | 49/51   | [108]   |

<sup>1</sup> Glycerol (Sub/Gly ≥ 1) or substrate (Sub/Gly < 1) conversion.  <sup>2</sup> The ratio of selectivity for 5-membered (5-M) and 6-membered (6-M) cyclic products formation.  <sup>3</sup> Glycerol conversion not available, the yield of acetals is presented.

Continuous solketal production at atmospheric pressure, 0.5 wt % catalyst, 100 °C with 50 mL/min N₂ flow and 300 rpm stirring using strongly acidic solid meso/macroporous carbon catalysts obtained
from Na-lignosulfonate (LS) was studied by Konwar et al. [108]. High activity (glycerol conversion ≥ 91%), even after 90 h time on stream, was observed. A strong performance of LS-derived materials is linked with a macro/mesoporous and highly functionalized heteroatom-doped carbon structure with large amounts of -OH, -COOH and -SO$_3$H groups on the surface.

Catalysts based on transition metals demonstrate good catalytic performance in glycerol condensation with ketones and aldehydes. In Table 6, the main results in use of catalysts containing transition metals are summarized. Among the modified metal oxides, AlPO$_4$ has attracted considerable attention. Zhang with colleagues [109] doped M-AlPO$_4$ with Zn, Cu, Ni, and Co. The obtained catalysts exhibit good thermal stability and mesoporous structures. In the solvent-free acetalization of glycerol with acetone at 80 °C with M-NiAlPO$_4$, a yield of 75.44% and a selectivity of 75.12% were observed. Corresponding to the specific surface area, the yield increased in the following order: M-AlPO$_4$ < M-ZnAlPO$_4$ < M-CoAlPO$_4$ < MCuAlPO$_4$ < M-NiAlPO$_4$.

A series of ZrMo-KIT-6 solid acid catalysts were designed and synthesized by one-pot synthesis to study in the solvent-free conversion of glycerol to solketal in the work by Li et al. [110]. The results indicate that when the content of Zr and Mo species incorporated into the skeleton of material is below 7%, they are in the highly-dispersed state on a mesostructural KIT-6 material with excellent textural properties. If the content of Zr and Mo is higher than 5%, highly-dispersed Zr and Mo species aggregate and form crystalline ZrO$_2$ and MoO$_3$, thus decreasing the catalytic activity. The ZrMo-KIT-6 material with the Zr/Si and Mo/Si ratio equal to 5 showed the optimal catalytic performance. The conversion of glycerol was 85.8% and the selectivity for solketal was 97.8% at the following conditions: solid acid catalyst (0.05 g); glycerol (1 g); acetone (5 g); stirred at 50 °C for 4 h. In addition, there was no decline in activity even after five cycles.

The isostructural metal-organic frameworks of the families MIL-100(M) and MIL-53(M) with different M = V, Al, Fe, and Cr were investigated in acetalization of acetone and glycerol [111]. MIL-100(V) possesses high activity and selectivity at 25 °C. It was demonstrated that glycerol conversion decreases in the following order: V$^{3+}$ > Al$^{3+}$ > Fe$^{3+}$ > Cr$^{3+}$. It was suggested, that catalytic parameters depend on the length of the M-O bond and type of metal ion.

Li et al. [112] found that a Co.$\text{II}$[Co.$\text{III}$xAl$_{2-x}$]$\text{O}_4$ catalyst prepared via controlled decomposition of layered double hydroxide is highly active and selective in acetalization of glycerol with acetone. The conversion of solketal reached 69.2% and correlated with the catalyst acidity; the glycerol selectivity was 98.6% at 130 °C and 3.0 h using the presented catalyst.

Khayoon and coworker developed Ni-based catalyst with a different amount of the active component and using activated carbon (AC) [113] and multi-walled carbon nanotubes (MWCNT’s) [114]. The conversion of glycerol through acetalization process with acetone catalyzed by mesoporous 5%Ni–1%Zr/AC catalyst was 100%, with the corresponding selectivity of 26% and 74% toward the 5-membered ring and 6-membered ring components, respectively [113]. The reaction was carried out under nitrogen flow conditions using 0.20 g of the catalyst at 45 °C, the molar ratio of glycerol/acetone of 1:8, and a reaction time of 3 h. The catalytic activity was mainly attributed to the NiO and ZrO$_2$ species intercalated into the AC structure. Using MWCNTs as a support for Ni [114], the conversion of glycerol reduced (96%) compared with AC. The selectivity at 40 °C, 3 h, and the molar ratio of glycerol/acetone 1:6 reached 72% and 28% to 5-M and 6-M formation, respectively.

Priya et al. [115] used microwave irradiation as a heating method for the solvent-free synthesis of solketal. Mordenite promoted with transition metal ions (Fe, Co, Ni, Cu and Zn) was chosen as a catalyst. The effect of various operating parameters on catalytic activity was examined. Amongst all tested catalysts, Cu-mordenite had excellent activity due to the presence of a large number of acid sites and better interaction of Cu with the mordenite support. Conversion of glycerol during a microwave-assisted (500 W) reaction time of 15 min over Cu-mordenite catalyst and acetone/glycerol at a molar ratio of 3:1 achieved 95% with 98% selectivity to solketal.

Different types of solid acids based on Mo have been reported as the catalysts for glycerol acetalization. Umbarkar et al. [76] prepared a series of MoO$_3$/SiO$_2$ catalysts with different MoO$_3$
loadings from 1 to 20 mol% by sol-gel technique. Among the series of mesoporous catalysts, MoO$_3$(20 mol%)/SiO$_2$ was found to be the most active catalyst in acetalization, with 72% benzaldehyde conversion in 8 h at 100 °C and 60% selectivity for the 6-M acetal. According to the physicochemical method, the formation of amorphous phase occurred up to 10 mol% of MoO$_3$, whereas at a higher loading, the crystalline MoO$_3$ on amorphous silica was observed. It was shown that the presence of an electron-donating or electron-withdrawing substitution on phenyl ring led to a decrease in glycerol conversion, but with an increase in selectivity for six-membered acetal under same reaction conditions.

The Reddy group [116] also reported that the addition of 10 wt% of MoO$_3$ promoter to TiO$_2$-ZrO$_2$ catalyst improves the surface acidic properties, and slightly increases glycerol conversion to 74% within the reaction time of 30 min. They also showed that activity in the promoted zirconia catalysts increased in the order of ZrO$_2$ < WO$_3$/ZrO$_2$ < MoO$_3$/ZrO$_2$ < SO$_4^{2-}$/ZrO$_2$ [117] with the selectivity of 97% towards solketal. It was discussed that the addition of promoters strongly influences the surface acidity of ZrO$_2$ and enhances the tetragonal zirconia phase. Reddy et al. [118] prepared SnO$_2$ catalysts promoted by molybdenum and tungsten. According to XRD and Raman data, the formation of nanocrystalline SnO$_2$ solid solutions doped by Mo$^{6+}$ and W$^{6+}$ was observed. Also, the prepared catalysts contained large amounts of oxygen vacancy defects. Using FTIR studies, the presence of higher amounts of Brønsted acid sites in the promoted catalysts was confirmed. As the SnO$_2$ has a small level of surface acid sites and a low specific surface area, it is low active. The addition of Mo$^{6+}$ in SnO$_2$ improved the catalytic activity and selectivity for the products. In the case of promoted SnO$_2$ catalysts, similar with ZrO$_2$, the activity of the catalysts was found to increase in the following order: SnO$_2$ < WO$_3$/SnO$_2$ < MoO$_3$/SnO$_2$ < SO$_4^{2-}$/SnO$_2$. The glycerol conversions with acetone and furfural achieved ~98 and 99% on the SO$_4^{2-}$/SnO$_2$ catalyst, respectively [119]. Thus, a catalyst based on Mo and Sn can be considered as a promising system for the production of fuel additives from glycerol.

Table 6. Reaction parameters reported by different studies for the glycerol acetalization with catalysts containing transition metals.

| Entry | Catalyst                  | Substrate | Sub/Gly Molar Ratio | Condition                          | Time (h) | X$^1$ (%) | Select. 6-M/5-M$^2$ (%) | Ref.   |
|-------|--------------------------|-----------|---------------------|------------------------------------|----------|-----------|------------------------|-------|
| 1     | M-NiAlPO$_4$             | acetone   | 8:1                 | 80 °C, $m_{\text{cat}} = 0.2$ g   | 1        | NA        | NA (0/75)              | [109] |
| 2     | M-CuAlPO$_4$             | acetone   | 8:1                 | 80 °C, $m_{\text{cat}} = 0.2$ g   | 1        | NA        | NA (0/69)              | [109] |
| 3     | M-CoAlPO$_4$             | acetone   | 8:1                 | 80 °C, $m_{\text{cat}} = 0.2$ g   | 1        | NA        | NA (0/67)              | [109] |
| 4     | M-ZnAlPO$_4$             | acetone   | 8:1                 | 80 °C, $m_{\text{cat}} = 0.2$ g   | 1        | NA        | NA (0/66)              | [109] |
| 5     | M-AlPO$_4$               | acetone   | 8:1                 | 50 °C, $m_{\text{cat}} = 0.05$ g  | 4        | 86        | 0/98                   | [110] |
| 6     | ZrMo-KIT-6               | acetone   | 8:1                 | 70 °C, acetonitrile as a solvent, $m_{\text{cat}} = 0.2$ g | 1.25 | 85 | 2/98 | [111] |
| 7     | MIL-100(V)               | acetone   | 10.2:2.17           | 70 °C, acetonitrile as a solvent, $m_{\text{cat}} = 0.2$ g | 1.25 | 85 | 2/98 | [111] |
| 8     | MIL-100(Al)              | acetone   | 10.2:2.17           | 70 °C, acetonitrile as a solvent, $m_{\text{cat}} = 0.2$ g | 1.25 | 44 | 6/94 | [111] |
| 9     | MIL-100(Fe)              | acetone   | 10.2:2.17           | 70 °C, acetonitrile as a solvent, $m_{\text{cat}} = 0.2$ g | 1.25 | 19 | 14/86 | [111] |
| 10    | MIL-100(Cr)              | acetone   | 10.2:2.17           | 70 °C, acetonitrile as a solvent, $m_{\text{cat}} = 0.2$ g | 1.25 | 4 | 22/78 | [111] |
| 11    | Co.[II](Co.[II]Al$_{0.75}$)$_{25}$[Cr$_2$][Cr$_{0.4}$]O$_4$ | acetone   | 10:1                | 130 °C, $m_{\text{cat}} = 0.1$ g | 3 | 69 | 1/99 | [112] |
| 12    | Co.[II](Co.[II]Al$_{0.8}$)$_{25}$[Cr$_2$][Cr$_{1.4}$]O$_4$ | acetone   | 10:1                | 130 °C, $m_{\text{cat}} = 0.1$ g | 3 | 32 | 3/97 | [112] |
Table 6. Cont.

| Entry | Catalyst          | Substrate | Sub/Gly Molar Ratio | Condition | Time (h) | X 1 (%) | Select. 6-M/5-M 2 (%) | Ref. |
|-------|-------------------|-----------|---------------------|-----------|----------|---------|----------------------|------|
| 13    | 1% Ni/AC          | acetone   | 8:1                 | 45 °C, 530 rpm, \(m_{cat} = 0.2 \) g | 3        | 65      | 3/91                 | [113]|
| 14    | 5% Ni/AC          | acetone   | 8:1                 | 45 °C, 530 rpm, \(m_{cat} = 0.2 \) g | 3        | 98      | 10/86                | [113]|
| 15    | 5% Ni–1%Zr/AC     | acetone   | 8:1                 | 45 °C, 530 rpm, \(m_{cat} = 0.2 \) g | 3        | 100     | 26/74                | [113]|
| 16    | Ni(1.8)/MWNTs     | acetone   | 6:1                 | 40 °C, 530 rpm, \(m_{cat} = 0.3 \) g | 3        | 96      | 28/72                | [114]|
| 17    | Cu-mordenite      | acetone   | 3:1                 | 100 °C, 500 W, \(m_{cat} = 0.3 \) g | 0.25     | 95      | 0/98                 | [115]|
| 18    | 1% MoO₃/SiO₂      | benzaldehyde | 0.1:0.11       | 100 °C, toluene as a solvent, \(m_{cat} = 10 \) wt % | 8        | 37      | 63/37                | [76]|
| 19    | 10% MoO₃/SiO₂     | benzaldehyde | 0.1:0.11       | 100 °C, toluene as a solvent, \(m_{cat} = 10 \) wt % | 8        | 43      | 63/37                | [76]|
| 20    | 20% MoO₃/SiO₂     | benzaldehyde | 0.1:0.11       | 100 °C, toluene as a solvent, \(m_{cat} = 10 \) wt % | 8        | 72      | 60/40                | [76]|
| 21    | 10% MoO₃/TiO₂-ZrO₂ | benzaldehyde | 1:1            | 100 °C, \(m_{cat} = 5 \) wt % | 0.5      | 74      | 51/49                | [116]|
| 22    | SnO₂              | furfural   | 1:1                 | 20 °C, \(m_{cat} = 5 \) wt % | 0.5      | 51      | 38/62                | [118]|
| 23    | WO₃/SnO₂          | furfural   | 1:1                 | 20 °C, \(m_{cat} = 5 \) wt % | 0.5      | 67      | 37/63                | [118]|
| 24    | MoO₃/SnO₂         | furfural   | 1:1                 | 20 °C, \(m_{cat} = 5 \) wt % | 0.5      | 75      | 36/64                | [118]|
| 25    | SO₄²⁻/SnO₂        | acetone   | 1.5:1               | 20 °C, \(m_{cat} = 5 \) wt % | 4        | 98      | NA                   | [119]|

1 Glycerol (Sub/Gly ≥ 1) or substrate (Sub/Gly < 1) conversion. 2 The ratio of selectivity for 5-membered (5-M) and 6-membered (6-M) cyclic products formation. 3 Glycerol conversion and acetals selectivity not available, the yield of acetals is presented.

7. Conclusions

Over the past ten years, various types of catalytic systems have been investigated in the processing of glycerol into oxygen-containing fuel additives: homogeneous catalysts based on mineral acids and ionic liquids, and heterogeneous catalysts based on noble metals, zeolites, resins or systems including transition metals. The obtained results show a high potential for using acetals and ketals as fuel additives, while the developed catalysts make it possible to obtain high product yields close to 100% under optimal conditions. According to this review of catalysts for glycerol acetalization, the following conclusions can be drawn:

- The use of microwave-assisted reaction or supercritical conditions makes it possible to obtain high acetal formation rates without using a catalyst.
- The formation of water during acetalization decreases the rate of acetal formation, which requires the development of methods for drying the substrate or the use of heterogeneous catalysts that are resistant to water adsorption on the surface.
- The use of ionic liquids with a complex structure makes it possible to vary the selectivity for the formation of a 5-membered cycle or six-membered cyclic acetals.
- Brønsted acid sites promote the acetalization of glycerol with acetone higher than Lewis acidic sites.
- The acetalization reaction is a reversible process. In order to shift the reaction equilibrium to the formation of acetal or ketal, it is necessary to use an excess of the reagent with respect to glycerol.
- The nature of the reagent and the presence of a solvent can affect the reaction rate. For example, electron donating or electron withdrawing substituent on the molecule and the size of reagent...
affect the conversion and selectivity. The presence of a solvent can lead to a decrease in the viscosity of the reaction components and increase their diffusion to the active sites.

- For acetalization of glycerol, textural characteristics of the catalyst, such as acidity, pore size, and influence of the promoter, play an important role.

Thus, it can be concluded that glycerol can be converted into fuel additives by acetalization with high yields and conversion values under mild conditions, without the use of solvents, and even without a catalyst under certain conditions. It was shown that acetals improve the octane number and cold flow properties of gasoline and biodiesel. In the near future, this will make possible the creation of a new series of ECO-additives derived from the products of renewable raw materials such as crude glycerol and acetone, formaldehyde, and furfural. The direct production of such additives in biodiesel plants will make the technology for fuel additives production cheaper than the existing analogs, and will increase the production volumes of biodiesel.

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