Recent Advances in the Valorization of Biodiesel By-Product Glycerol to Solketal

Supongsenla Ao and Samuel Lalthazuala Rokhum

Department of Chemistry, National Institute of Technology Silchar, Silchar, Assam 788010, India

Correspondence should be addressed to Samuel Lalthazuala Rokhum; rokhum@che.nits.ac.in

Received 22 March 2022; Revised 6 May 2022; Accepted 7 May 2022; Published 31 May 2022

Copyright © 2022 Supongsenla Ao and Samuel Lalthazuala Rokhum. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The exponential rise of the biodiesel production has resulted in a considerable amount of glycerol as a by-product, which must be valorized to ensure the sector’s long-term viability. As a result, cost-effective glycerol conversions for significant value-added chemicals are essential for the biodiesel production in the long run. Solketal, a glycerol by-product, is obtained as a potential fuel additive in the biodiesel industry. Recently, several heterogeneous acid-catalysts stand out as a promising catalyst for solketal production where biomass-based catalyst gained attraction owing to their biodegradability, eco-friendly, and abundant availability. Furthermore, magnetic nanoparticles-derived catalysts along with sulfonated functionalized catalyzed, zeolites, resins, enzymatic, etc. have proved their efficiency in solketal production. In this review, a wider study on the recent advances of the catalysts has been discussed along with their preparation, various reaction parameters, its application, and efficiency for biodiesel industry. This study opens up incredible prospects for us to use renewable energy sources, which will benefit the industry, the environment, and the economy.

1. Introduction

Ever since the commencement of industrial revolution, fossil fuels have been the key source of energy and industrial chemicals. In the early twentieth century, petroleum exploration and its conversion to simple hydrocarbons were practiced by mankind. It has been estimated that by 2040, low cost supply of fossil fuels will no longer be available [1]. Hence, in the recent decades, efforts have been made to find an alternative fuel that can replace fossil fuels for sustainable environment and growing energy demand [2]. In this context, renewable energy sources such as solar, wind, geothermal, and biomass are all considered viable options [3].

Biodiesel, derived from biomass, has emerged as a replacement for fossil fuels in the transportation sector [4, 5]. It is eco-friendly, is biodegradable, and has the potential to minimize chemical emissions such as sulfur dioxide (100%), unburned hydrocarbon (68%), and polycyclic aromatic hydrocarbon (80–90%) [6]. It is estimated that by the year 2022, the demand of biodiesel will increase by 70% [7, 8]. As a result, it is important to improve the economic viability of biodiesel synthesis by changing three main features of the process: the raw materials used, the synthesis method, and the by-products [9]. For the purification of biodiesel, instead of following the complex method like wet washing and membrane extraction, dry washing method using silica as absorbent is highly appreciated owing to the simplicity in operation, reduced labor cost, and sustainability of biodiesel production [10]. Biodiesel is produced by nucleophilically trans-esterifying animal fat or vegetable oil with alcohol to yield fatty acid methyl ester (FAME) and by-product glycerol [11–13]. An outflow of glycerol, equal to around 10% of the biodiesel produced, is one of the results of this process [14, 15]. Hence, novel and economically viable approaches to convert glycerol to valuable chemical compounds are required.

Production of fuel additives such as ketals and cyclic acetals with aldehydes and ketones, respectively, is certainly one of the most advantageous glycerol applications [16].
Solketal, a product of glycerol and acetone, is a clean fuel additive that works wonders with enhancing the biodiesel product to a greater extent [17, 18]. It is synthesized by ketalizing glycerol and acetone in the vicinity of a catalyst, which results in the release of water as a by-product [19] (Scheme 1 and Scheme 2) showing the proposed mechanism of acetalization of glycerol and acetone.

Valorization of bioglycerol into solketal stands out to be a very successful process in the sustainability of biodiesel industry. It is an anti-knocking agent that helps biodiesel in gum formation [20], retains its octane number by enhancing stability [8], and also reduces viscosity [21, 22]. It also finds applications in industry, in the form of an adaptable solvent, as plasticizer in polymer trade, pharmaceutical, flavoring agent, and surfactant [20, 23, 24].

Generally, glycerol is condensed with acetone in the presence of substantial volumes of strong homogeneous acid catalysts [25, 26]. However, these approaches have limitations due to the use of nonrecyclable, high-cost chemicals in the product separation and purification processes. As a result, by replacing homogeneous catalysts with heterogeneous catalysts, the process’s long-term viability can be boosted. In the glycerol acetalization reaction, several heterogeneous solid acid catalysts such as biomass-derived catalysts [27], metal oxides [28], amberlys resins [29], transition metal as solid acid catalysts [30], niobia zirconia [31], magnetic nanoparticles [32], metal phosphates-supported heteropolyacids [33], and sulfonic acid mesostructured silica [34] have been tested in glycerol acetalization reaction.

Heterogeneous catalysts have a number of advantages over homogeneous catalysts, including ease of product separation from catalysts, high recyclability, thermal stability, product selectivity, solvent-free conditions, and, most importantly, ease of product separation from catalysts [35–37]. And therefore, by studying the current papers (2016 onwards), this brief review paper held to highlight the possible research of catalytic materials for the production of solketal through glycerol acetalization and some features, such as the result of different particular reaction parameters, product characterization, catalyst characterization, and reactor design, provided and investigated exclusively. Finally, its broad application and future potential are discussed.

2. Overview of Solketal Production

The synthesis of oxygen-containing fuel additives known as solketal, which can decrease the density and viscosity of fuels, stabilize the cetane number, and minimize the emissions of exhaust gases and carbon monoxide creation by the existence of oxygen, could be one of the possibilities [38–40]. Solketal has been in high demand as a gasoline additive on the global sustainable fuel markets as shown in Figure 1 [40]. The need for and enhancement of innovative ways leading to the conversion of crude glycerol into value-added chemical molecule solketal was represented in the form of analytical data in Figure 1.

Generally, glycerol and acetone are condensed in the occurrence of homogeneous/heterogeneous catalyst for the synthesis of solketal. However, the most common method is by acetalization reaction via heterogeneous catalysts [35, 41]. Although homogeneous catalysts have its advantages such as low cost and high activity [42], they have some significant drawbacks, such as the inability to regenerate catalysts, the amount of time it takes to boost the yield of glycerol ketals and acetals, and the requirement of solvents to eliminate water from the process [35, 43]. Owing to these drawbacks of homogeneous catalysts, switching to a heterogeneous catalyst promises to boost the process’s long-term viability. Nonetheless, in recent years, several heterogeneous catalysts were reported for the valorization of glycerol to solketal.

Silva et al. [44] analysed several catalysts like paratoluene sulfonic acid, Amberlyst-15, and zeolite beta for the conversion of glycerol in one of the first experiments on zeolites. As a result, the zeolite Beta (Si/Al = 16) conversion goes to 95% in 60 minutes. In fact, the high Si to Al ratio resulted in the hydrophobic property of zeolite, which avoids water from diffusing into the pores and retains the acid sites strength.

Nanda et al. [45] reported excellent second-generation catalyst research using ethanol as a solvent and Amberlyst-35 was used as a catalyst to achieve a yield of more than 74% under a reaction temperature of 25–45°C and a substrate ratio (mol) of glycerol to acetone at 2:1. In fact, by using ethanol as a solvent, they were able to drastically lower the reaction temperature. Furthermore, the third generation (Chen et al. [46]) carried out acetalization reaction of solvent-free glycerol under repetitive production techniques using heterogeneous catalysts. It is demonstrated here that innovative heterogeneous catalysts are capable of driving the catalytic procedure to harvest desirable products (solketal) with a high efficiency without the use of a solvent.

3. Characterization Techniques

3.1. Characterization Techniques of Solketal. The conversion to solketal from glycerol is usually monitored by thin layer chromatography (TLC) and confirmed by nuclear magnetic resonance (NMR) analysis and gas chromatography-high resolution mass spectroscopy (GC-HRMS).

The chemical environment of protons can be determined via ¹H-NMR. The ¹H-NMR resonance is the easiest to analyse in NMR, while the ¹³C resonance can be used to investigate organic adsorbates. Laskar et al. [37] investigated acetalization of glycerol to solketal and monitored the glycerol conversion to solketal. In the ¹H NMR spectrum of the product of glycerol acetalization, the two distinct singlets at δ 1.41 and 1.36 denote the six methyl hydrogen molecules of 1,3-dioxolane product while the broad singlet peak for hydroxyl appears at δ 2.05. Peaks in the region δ 4.20–4.06 and δ 3.77 have a total integration of five and represent the –CH and –CH₂ groups present in the product structure. ¹³C NMR spectra of the solketal product reveal that the methyl carbons are responsible for the most protected peaks, which occur at 24.80 and 26.22. The –CH carbon is responsible for the peak at 76.88, whereas the two –CH₂ carbons are responsible for the other two peaks at 66.46 and 62.90. The ketal carbon is responsible for the most deshielded peak,
Scheme 1: Synthesis of solketal from bioglycerol.

Scheme 2: Suggested mechanism for dioxolane synthesis in acetalization reaction.

Figure 1: Global industry trends and forecast to 2028 [40].
which occurs at 109.81. The two spectra clearly show that a 5-membered solketal product is formed selectively during glycerol acetalization.

The final product’s GC-HRMS chromatogram demonstrated the emergence of a single product peak at 13.29 min (Figure 2), which is more thermodynamically stable than the six-membered ring acetal. In addition, FT-IR spectroscopy was performed to investigate the product’s functional group [32, 47].

### 3.2. Characterization Techniques for the Catalyst

Although there are various techniques for examining solids, not all of them are ideal for studying real catalysts and some of them require specialised knowledge in order to understand the data. Heterogeneous catalysis deals with surfaces and is thus recommended in theory for surface-sensitive approaches. The sections that follow focus on methods in this area. Scanning electron microscopy (SEM) is a flexible technique for observing and analysing the morphology of catalyst microstructures. Laskar et al. [37] used SEM to examine their newly reported mesoporous polymer-catalysed catalyst in terms of dimensionality, size, forms, particle aggregation, aspect ratio, and porosity. EDS mapping is used to verify the sample’s compositional homogeneity, demonstrating all of the chemicals present that were emphasised in SEM pictures.

The use of transmission electron microscopy (TEM) to examine the morphology of different catalysts is proven to be a useful tool. Raikumari et al. [32] prepared a magnetic sulfonic acid-functionalized, silica-coated Fe₃O₄ magnetic nanoparticle (Fe₃O₄@SiO₂@SO₃H) catalyst for the conversion of glycerol to solketal and investigated it using TEM (Figure 3) and discovered that the nano-catalyst has a dimension of 10–20 nm and is spherical in nature. They confirmed the proper coating of Fe₃O₄ nanoparticles by SiO₂ layer (Figure 3(c) inset). In addition, the crystalline nature of the catalyst was observed from selected area electron diffraction (SAED) as shown in Figure 3(d).

In laboratories and industry, BET equipment is frequently used to measure the surface area, pore volume of materials, and pore size. Because the surface area has a direct influence on a catalyst’s activity, increasing the surface area usually increases the catalyst’s reactivity [48, 49]. Hence, high surface area is desirable in catalysis. Surface area of materials can be estimated by measuring the amount of adsorbed gas or by monitoring the concentration (or pressure) of adsorptive gases. According to da Silva et al. [44], ZSM-5 zeolite with tiny pores performed poorly in the acetalization reaction. Because these holes do not allow for reactant diffusion inside them, acetalization occurs either at the pore entrance or on the external surface decreasing the ketal yield. Amberlyst-15 contributed the finest performance owing to its mesoporous structure. Hence, not only the acid strength but also the porous structure influence the ketal yield.

For the characterization of solid catalysts, Fourier Transform Infrared Spectroscopy (FTIR) is a common approach, not least because it permits an extensive range of setups and configurations that may be fitted to the nature of the sample under research. Konwar et al. [50] investigated their mesoporous catalysed for solketal synthesis through FTIR spectroscopy, and the samples exhibited the typical bands of -SO₃H functionalized semicarbonised materials: 1700 cm⁻¹ (C-O, C=O), 1033 cm⁻¹ and 1008 cm⁻¹ (S=O symmetric stretching), 3500 cm⁻¹ (S-OH stretching), and 1175 cm⁻¹ and 1240 cm⁻¹ (asymmetric SO₂ stretching) peaks appeared at 997 cm⁻¹/1039 cm⁻¹ and 1140 cm⁻¹/1215 cm⁻¹, respectively. With varying absorbance, the carbonised samples also displayed typical bands of carbonyl groups (C=O, C-O, near 1700 cm⁻¹), characteristic peaks of incompletely carbonised materials (attributable to C=C aromatic ring modes), symmetric CH stretching (near 2900 cm⁻¹), and peaks near 1580 cm⁻¹ (attributable to C=C aromatic ring modes).

Thermogravimetric analysis (TGA) is mainly utilised for understanding certain thermal events such as absorption, adsorption, desorption, vaporization, decomposition, sublimation, oxidation, and reduction [51]. Rodrigues et al. [52] used TGA to investigate the thermal stability of the functional groups of carbon present in the catalyst, discovering untreated activated carbon thermograms profiles showing an early weight loss at temperatures below 383 K attributed to moisture vaporization and another thermal decomposition at 923 K which was accredited to the evolution of CO₂, owing to the decomposition of carboxyl, anhydride, and lactone groups.

In catalyst research, X-ray photoelectron spectroscopy (XPS) has been widely utilised to do broad qualitative assessments, explore the depth profile distribution of active species, and estimate dispersion, clustering, and other morphological changes. XPS can offer information on the composition and chemical state of surfaces and interfaces that have a significant impact on the material’s properties [49]. The surface conformation and valence states of surface Zr and Mo species of the ZrMo-KIT-6(5) catalyst were clarified using XPS by Li et al. [53]. The signals of Zr 3d, Mo 3d, Si 2p, and O 1s can be seen in the spectra, indicating that Zr and Mo species have been effectively introduced. Two distinct peaks are found for the Zr 3d signal with binding energies of 184.7 and 182.4 eV, which are assigned to the Zr⁴⁺. In addition, the Mo 3d spectrum shows two contributions, which are attributed to the Mo⁶⁺ and are positioned at 235.5 and 232.6 eV, respectively [53]. The peak of the Si 2p
signal is 103.5 eV, indicating the presence of Si$^{4+}$ species. A large peak is seen for the O 1s signal at 533.2 eV, which is attributable to the Si-O bond in the material. All of these findings point to the presence of ZrO$_2$, MoO$_3$, and SiO$_2$ species in the ZrMo-KIT skeleton.

One of the most essential techniques for assessing the crystallinity or amorphous nature of a catalyst is X-ray diffraction (XRD, also known as WAXS: wide-angle X-ray scattering). XRD is restricted to powder-pattern identification of crystalline phases for most catalysts. Extended range order exists in zeolites and catalysts with good crystallinity, and XRD can provide a detailed explanation of their structure. Using powder XRD, Hussein et al. [54] investigated the textural morphology and structure of materials. Ga-silicate powder XRD patterns showed an intense first-order $d_{100}$ diffraction peak centred at $2\theta = 1.0^\circ$, which is accounted for the solid’s mesostructure. The lack of a strong peak in wide-angle XRD patterns indicates the amorphous nature of the silica framework and the absence of large clusters of gallium oxide. A comprehensive XRD investigation as a function of Fe loading was done to see if doped Fe affects the crystal structure of PKU-1 [55]. Furthermore, Lebail Refinement enlargements of crystal data, such as the cell volume axis and the c-axis, support the fact that Fe atoms have a greater radius (0.645, CN = 6) than Al atoms (0.535, CN = 6). Techie-Menson et al. [56] found a broad distinctive peak around $2\theta = 20^\circ$ for both homopolymers and copolymers, as well as some acute but fewer intense peaks in the range of $2\theta = 25$–60. This shows that the polymers have a high proportion of amorphous regions and a small amount of crystalline regions. As a result, they are semicrystalline and susceptible to hydrolytic or photolytic degradation.

4. Catalyst Study

4.1. Recent Catalyst Developments. The majority of recent research on solketal production has focused on the development of recoverable heterogeneous or homogeneous catalysts. Numerous technologies for the synthesis of solketal have been presented throughout the years, most notably the utilisation of heterogeneous catalysts and continuous processes. The most current studies on catalyst performance (from 2016 to the present) are examined and summarised in this review.

4.2. Metal-Based Catalysts. Metal-based catalyst are the most widely synthesized catalyst due to their high thermal stability especially calcination, cheap price, high availability, strong acidity, and high recyclability [57, 58]. Recently, metal-organic frameworks (MOFs) have emerged as the most promising materials because of their enormous surface area, changeable pore size, structural stability, and tailorable functions [59, 60]. It is made up of inorganic and organic components that are linked together by strong bonds. In the acetalization of acetone and glycerol, the isostructural MOFs of the families MIL-100(M) and MIL-53(M) with varied M = V, Al, Fe, and Cr were explored [61]. At 25°C, MIL-
100(V) has a high activity and selectivity. Glycerol conversion is shown to decrease in the following order: V<sup>3+</sup> > Al<sup>3+</sup> > Fe<sup>3+</sup> > Cr<sup>3+</sup>. Catalytic parameters are said to be dependent on the length of the M-O bond and the sort of metal ion. Bakur et al. [59] also investigated the Bronsted acidity of the MOFs UiO-66 (Zr, Ce, and Hf) for the effective solketal synthesis. The exceptional catalytic activity was presented by UiO-66(Hf) for solketal production leading to solketal synthesis. The excellent performance was attributed to the Bronsted acidity of the MOFs UiO-66 (Zr, Ce, and Hf) for the effective metal ion. Bakur et al. [59] also investigated the Bronsted acidity dependent on the length of the M-O bond and the sort of reaction cycle by washing with acetone and drying at 550°C, Reena et al. [22]. The catalyst was revived after the initial drop in activity was attributed to the loss of Co<sup>II</sup> (Co<sup>III</sup>xAl<sub>2x</sub>)O<sub>4</sub> and that the conversion of glycerol increased as the number of strong acid sites varied. For instance, using a sulfated zirconia catalyst resulted in an 85.7% glycerol conversion in 180 minutes at 40°C. At 40°C, the Zr-S-400 catalyst had an initial reaction rate of 0.0497 mol·min<sup>-1</sup>·g<sup>-1</sup> and attained an 80% glycerol conversion in 1 hour. After four catalytic cycles, the Zr-S-400 material remained stable, confirming the stability of the surface sulfate species (S/Zr 0.2). A series of zirconium and molybdenum species incorporated into ordered mesoporous silicate KIT-6 (ZrMo-KIT6) materials were designed and synthesized from a one-pot hydrothermal method [53]. The ZrMo-KIT-6(0) material without adding Zr and Mo species shows poor activity; however, with the introduction of Zr and Mo species, the catalytic performance is gradually improved. The TOF values of catalysts containing less than 5% Zr and Mo are similar (163 h<sup>-1</sup> for 1%, 159 h<sup>-1</sup> for 3%, and 147 h<sup>-1</sup> for 5%). This demonstrates that the widely distributed Zr and Mo species are the active sites for the acetalization of glycerol with acetone. The acetalization reaction is catalysed by the interaction between Zr and Mo species, which creates acid sites. Furthermore, even after five cycles, there was no discernible loss of catalytic performance.

An exciting result was spotted over ZrPP-20 by Li et al. [66]. Both ample acidity (1.30 mmol·g<sup>-1</sup>) and an appropriate hydrophilicity/hydrophobicity balance were attributed with the highest activity of ZrPP-20. A suitable hydrophobic surface could avoid deactivation from deposited condensation water, resulting in a subtle decrease in substrate adsorption. As a result, tweaking the ZrPP-x catalyst's hydrophilicity/hydrophobicity balance possibly will make these acid sites more active in the acetalization reaction of glycerol with acetone. In addition, ZrP-200 (layered zirconium phosphate) [70] is a very active and selective reusable compound. The excellent performance of ZrP-200 is mainly attributed to its high surface density (43.6 m<sup>2</sup>·g<sup>-1</sup>) and acid sites (1.3 mmol·g<sup>-1</sup>). This reaction was also active...
with H₃PW₁₂O₄₀, H-ZSM-5, H zeolite, and Amberlyst-15; however the selectivity of solketal was lower than that of ZrP-200. Because of its high activity, high selectivity, ease of separation, and cheaper price, layered ZrP-200 offers the potential for industrial application. SiO₂-Al₂O₃ was not as useful because it had lower acidity when compared to Keggin-type {H₃}-355, {H₄}-355, and Dawson-type {H₆}-355 catalysts. H₃O⁺-355 showed the superacidity (H₀ = −12.95). It is also showing the maximum catalytic activity among the HPA catalysts employed in this study with no significant leaching being observed. Leaching of metals also play a vital role and may subsidise more than 80% of the degradation. To further confirm the effect of the metal ions leached from the solid catalyst, ICP-OES was conducted [22]. Besson and Gallozet in their work [44] confirmed the leaching through ICP-AES measurement, which revealed that there was a cost of platinum and bismuth after oxidation of L-sorbose on Pt-Bi/Al₂O₃ catalyst; this might be mainly due to the unprecise controllability of alumina in the reaction medium. Rajkumari et al. [32], in their leaching test, reported that very limited leaching of sulfonic group was reflected and hence heterogeneity of the catalyst was maintained. Table 1 lists a number of metal-based catalysts that have been employed to convert glycerol to solketal.

In 2021, Rajkumari et al. [72] reported an efficient ultrasound-assisted room temperature synthesis of solketal by acetalization of glycerol with acetone using an easily recoverable sulfonic acid-functionalized, silica-coated Fe₃O₄ magnetic nanoparticle catalyst. For ultrasonically aided acetalization, the catalyst has an outstanding TOF of 0.842 (mol·g⁻¹·h⁻¹). The FSS catalyst was magnetically recycled for up to five catalytic experiments while maintaining a 95% glycerol conversion and maintaining its selectivity. Similarly, da Silva et al. [67] evaluated a number of commercial transition metal salts, finding that Fe(NO₃)₃·9H₂O had the best catalytic activity, nearly transforming all of the glycerol to solketal with 95% selectivity within a time duration of just 30 minutes. Additional Lewis and Bronsted acid catalysts were compared to Fe(NO₃)₃·9H₂O performance. The Fe(NO₃)₃ catalyst outperformed the Bronsted acid catalysts in terms of efficiency (H₂SO₄ and PTSA). Esposito et al. [26] investigated various types of iron (III) catalysts in an instrumentation where water was removed by molecular sieves to transfer the reaction equilibrium more toward product formation and observed that FeCl₃(1-NO₂) performed best, attaining nearly total glycerol conversion and 100% selectivity to solketal.

Peng et al. [69] prepared heteropoly acids (HPA) [H₃O⁺]-355 by calcination of tetrameric Ta/W mixed addenda. The acidic strength (H₀) was vastly dependent on the crystal water content. The catalyst with lower crystal water content had stronger acidity when compared to Keggin-type H₃O⁺-355, [H₄O⁺]-355, and Dawson-type [H₆O⁺]-355 catalysts. [H₃O⁺]-355 catalyst showed the superacidity (H₀ = −12.95). It is also showing the maximum catalytic activity among the HPA catalysts employed in this work with no significance in leaching. Leaching of metals also play a vital role and may subsidise more than 80% of the degradation. To further confirm the effect of the metal ions leached from the solid catalyst, ICP-OES was conducted [22]. Besson and Gallozet in their work [44] confirmed the leaching through ICP-AES measurement, which revealed that there was a cost of platinum and bismuth after oxidation of L-sorbose on Pt-Bi/Al₂O₃ catalyst; this might be mainly due to the unpredictable controllability of alumina in the reaction medium. Rajkumari et al. [32], in their leaching test, reported that very limited leaching of sulfonic group was reflected and hence heterogeneity of the catalyst was maintained. Table 1 lists a number of metal-based catalysts that have been employed to convert glycerol to solketal.

### Table 1: Metal-based catalyst for solketal synthesis.

| Sl no. | Catalyst                       | Reaction condition | Conversion (%) | Selectivity (%) | Catalyst cycle | Ref.   |
|--------|--------------------------------|--------------------|---------------|----------------|---------------|--------|
| 1      | MIL-100 (M)                    | 1:4.5, 35, 20, 25  | 85.4          | 98             | 3 (85/—)      | [61]   |
| 2      | Uio-66 (Hf)                    | 1:4, 60, 10, RT    | 94.5          | 97.2           | 5 (>80/>85)   | [59]   |
| 3      | Basolite F300                  | 1:4, 60, 1, 50     | 84.3          | —              | —             | [62]   |
| 4      | Mo(VI)/ZrO₂                    | 1:6, 8, 1,08, 60   | 98            | 98             | 6 (98/98)     | [22]   |
| 5      | Zr-S-400                       | 1:6, 60, 0.6, 40   | 80            | 86             | 4 (60/72)     | [47]   |
| 6      | Zirconium organophosphonate    | 1:10, 180, 5, 40   | 90.2          | 98.5           | 5 (87.5/—)    | [66]   |
| 7      | Zr-MO-KIT-6                    | 1:8, 480, 5, 50    | 85.8          | 97.8           | 5 (85/97)     | [53]   |
| 8      | Cu-mor                         | 1:3, 15, 43.47, 100 | 95          | 98             | 5 (94/97)     | [30]   |
| 9      | α-Zirconium phosphates         | 1:10, 180, 5, 50   | 85.7          | 98.6           | 5 (80/98)     | [55]   |
| 10     | Silica-coated-Fe₃O₄ magnetic NPs| 1:5, 15, 5, 28     | 97            | 100            | 5 (95/100)    | [32]   |
| 11     | PKU-1                          | 1:5, 360, 18, 45   | 92.8          | 98.3           | 4 (77/—)      | [55]   |
| 12     | FeCl₃ (1-NO₂)                  | 1:4, 90, 1,09, 50  | 94            | 98             | —             | [26]   |
| 13     | Sn₂SiW₁₂O₄₀                    | 1:4, 60, 3, RT     | 97            | 99             | 3 (>90/>90)   | [67]   |
| 14     | Co[II][Co[III]₃Al₁₋₅]O₄        | 1:10, 360, 5, 130  | 69.2          | 98.6           | 5 (51/—)      | [28]   |
| 15     | CoOₓ/SnO₂                      | 1:5, 180, 19.2, 60 | 92            | 100            | 6 (65/—)      | [65]   |
| 16     | HC-SZ                          | 1:3, 80, 1,08, 60  | 96            | 94             | 6 (82/79)     | [68]   |
| 17     | HPA ([H₂O]-0.355)              | 1:2, 40, 1,8, 25   | 100           | 98             | 5 (>90/98)    | [69]   |

*aGlycerol: acetone molar ratio, reaction time (min), catalyst loading (wt.%) temperature (°C), RT (room temperature); bCatalyst cycle with % conversion/ selectivity;
with enlarged pores, higher amount of strong acidic sites, and small crystallite size (low diffusion path length) achieved the highest conversion (86%). Dealumination lowered glycerol conversion by lowering the number of strong acidic sites. Rossa et al. [76], who also used H-Beta, found that the lowering in activity and number of reusability was due to the blocking of acidic sites by water molecules formed within the pores, rather than the deactivation of surface acidic sites, once the zeolite’s hydrophobicity prevented water from reaching the catalyst’s surface. This contradicts what Da Silva et al. [77] conveyed in a similar work using the same catalyst, where it was confirmed that the hydrophobic zeolite environment expels water formed from the pores, preserving the acid sites while also avoiding water diffusion from the medium to the interior of the pores. Under diverse settings, the performance of numerous zeolites demonstrated that beta zeolites may attain the highest conversion rates [75]. Jamil et al. [78] obtained bio-glycerol from the esterification of waste “date seed” oil. Because of the existence of a great mesopore volume, which permits more interaction of reactants with acidic sites inside the channels and which therefore leads to the more production of solketal, the AB-3 type had low silica to alumina ratio of 18, compared to 19.1 for the AB-1 type, but it gave high bio-glycerol conversion and selectivity to solketal. As a result, it can be inferred that the pore volume is the most efficient parameter for bio-glycerol conversion. The large drop in yield after the third run can be attributable to the deposition of some reactants or a decrease in catalyst active sites [75].

HR/Y-W20 zeolite [79] achieved conversions up to 100%, after 90 minutes. Leaching test was done which shows no significant loss in activity and selectivity, whereas the decrease in the activity of [5V] Si-ITQ-6 [80] after third cycle was accredited to the presence of water which led to leaching of the catalyst. Other zeolites tested, such as beta zeolite [81] and Nb₂₅-HUSY [82], had poor catalytic activity due to the first’s hydrophilic identity, which retains the water formed as a by-product inside the pores and deactivates the acid sites, and the second’s small pore diameter, which restrains the reaction from taking place within the pores and restricts the reaction from occurring inside the pores. The water molecules generated as a co-product remained adsorbed on the catalyst’s surface, and the increased quantity of water molecules formed by consecutive adsorption in the same site led to vanadium leaching, thus according recycling of [10V] Si-ITQ-6 [79]. As a result, acetone was utilised for the washing process, with no evidence of leaching.

Kowalska-Kus et al. [83] developed heterogeneous catalysts like zeolites (BEA, MFI) for the production of solketal from crude glycerol and acetone. It was found that beta and hierarchical ZSM-5 (HCl) improved catalytic performance; also, water does not disturb the acetalization over beta and hierarchical ZSM-5 zeolites but instead MONG (inorganic salts-matter organic nonglycerol, MONG) and ash are accountable for catalyst deactivation in the acetalization of crude glycerol. MFI zeolite [77] had a catalytic activity of 80%, which is lower than ambersil, but with nearly full selectivity. The reduced conversion is owing to the comparatively small channel size, which impacts the reactant transport as well as shape selectivity. Venkatesha et al. [19] described another situation in which BEA zeolite was treated with phenoldisulfonic acid (PDSDA) to create dealuminated zeolites and used as a catalyst for acetalization of glycerol to solketal. Dealumination zeolite steadily increases in surface area and porosity but decreases in acid levels resulting from increasing the PDSA concentration during treatment. The reaction between glycerol and acetone is catalysed by untreated BEA zeolite, which produces six-membered dioxane and five-membered dioxolane, with the latter having the highest selectivity of 83%. The decreased pore volume and decreased acid quantity are responsible for the enhanced selectivity for the five species. MCM-22 [85], a hierarchical zeolite with a narrow mesopore size range, has a lot of potential for converting biomass-derived platform molecules.

Vanadium oxides have a low acidity and specific area, although dispersion over appropriate carriers such as alumina, silica, titania, and zirconia can improve both of these properties [86–88]. Abreu et al. [89] investigated the acetalization of glycerol using V-MCM-41 catalyst where they concluded that the catalytic activity was reliant on the amount of acid sites produced due to the attachment of vanadium in the silica framework. Vanadium oxides are leached by water molecules formed during the reaction, which is the main cause of poor recyclability. Based on the study, the crystallite size and acidity are the most determining factors in the activity of the zeolite as a catalyst [90, 91]. The simpler it is for reactants and products to diffuse through the zeolite pores, the smaller the crystal size of zeolite. Dealumination and desilication procedures can alter the pore structure of zeolite. Not only may the process modify the materials in the mesopores, but it can also boost catalytic activity [92, 93]. Several zeolite catalysts for valorization of glycerol to solketal are given in Table 2 (entries 1–11).

Clay’s low cost is one of the key benefits that make them a viable option for industrial use. The most recent research focuses on altering its textural and acid properties to increase conversion and selectivity. Timofeeva et al. [94] examined the transformation of montmorillonite with nitric acid (HNO₃), while Amri et al. [95] investigated the alteration of natural clay with hydrochloric acid (HCl) to improve the acidity of raw clay. In the reaction medium, both systems utilised solvents (acetonitrile and isopropanol, respectively) and mild conditions (273 K and ambient pressure) due to their higher density of strong acidic sites; the first study has better conversion values, 94%, with a lower catalyst loading. In a batch reactor using a 0.5 M nitric acid-activated catalyst, Timofeeva et al. found that the clay catalyst produced the best outcomes in relation to glycerol conversion and selectivity to solketal.

Gutiérrez-Acebo et al. [96] used microwave irradiation to manufacture MK-10 catalysts for the manufacturing of solketals, which resulted in higher conversion but somewhat poorer selectivity to the desired products than those prepared using conventional heating. The highest conversion (62–68%) and selectivity values to the target products were found in sulfonated montmorillonite (72–86%). This has
been attributed to the catalyst’s greater surface density of Brønsted acid sites (0.77 meq H⁺ g⁻¹). However, amongst all acid-treated catalysts, the metakaolin K3 catalyst [97] was made known as best catalytic properties, high surface area, and pore size after acid activation with 3.0 mol·dm⁻³ at 98°C for 3 h, which could be due to the dealumination process, which causes surface breakdown during the activation of acid. Besides, after acid activation, leaching and destruction in the kaolin clay structure resulted in the formation of finely scattered Si oxides or the removal of various cations blocking surface pores or interlaminar spaces, as well as the formation of surface pores/cracks, all of which made a significant contribution to an advancement in the physical properties of kaolin clay. Raw kaolin clay was activated using a simple acid activation procedure, and it is low cost, widely available, and environmentally acceptable, making it an attractive green chemical manufacturing method as well as one of the most advantageous uses for solketal production.

In another work, the synthesis of solketal by the acetalization of glycerol with acetone effectively applied out by means of using various Algerian acid-activated clays (Maghnia-H⁺) under autogenous pressure in the absence of solvents [98]. The results reveal a strong catalytic activity, with solketal production interest reaching 95% at 40°C for a reaction duration of 48 hours, with complete selectivity and glycerol conversion of nearly 89%. The chemoselective nature of solketal synthesis has been hypothesised as a mechanism. These findings suggest that acid-activated clays from Algeria can be employed to use as a catalyst for the environmentally friendly acetalization of glycerol. Table 2 (entries 12–16) displays several clay catalysts used for solketal synthesis.

### 4.4. Biomass-Derived Heterogeneous Catalysts

Biomass is a sustainable organic resource derived from plants and animals that is used to generate energy, heat, and fuel. The current trend shows that the application of natural biological source of calcium source proved to be a potential heterogeneous catalyst for acetalization and transesterification. Mainly, because it is highly efficient, nontoxic, environment friendly, and noncorrosive, it eliminates the product of waste water [99]. On top of that, it is abundantly available [100] and there is no imminent disposable problem since it is biodegradable [4]. Carbon-based materials were functionalized and activated with acid groups for solketal production, in view of the ample source of biomass as a precursor.

A new remarkable environment-free catalyst was developed by Gonçalves et al. [101], where a carbon-based solid catalyst from biodiesel surplus acidified by sulfuric acid (H₂SO₄) was produced which indicated a glycerol conversion of 80% and a selectivity up to 95%. The acidity was attributed to the presence of sulfur group (0.9 mmol·g⁻¹) out of the total acidity of 3.8 mmol·g⁻¹. Furthermore, no appreciable leaching was detected which confirmed the heterogeneity of the catalyst. Another sulfonic acid-functionalized activated carbon from corncob was investigated for solketal synthesis by Kaur et al. [102]. The corncob is activated using NaOH and further functionalized with sulfuric acid to obtain a catalysed carrying a high surface area of 779.831 m²·g⁻¹ with a pore volume of 0.428 cc·g⁻¹ and acidic sites of 0.187 mmol·g⁻¹ catalysing the reaction at a conversion rate of 80%. Omes et al. in their findings noted that when sulfur-containing surface groups are added and the removal of the pollutant is boosted due to a stronger affinity amongst the reactants and the catalyst surface, favouring the production of highly reactive hydroxyl radicals in the pollutant’s proximity [103]. By reacting bio-oil with sulfuric acid, Carvalho Ballotin et al. [104] produced an effective amphiphilic carbon catalyst. The catalyst helped in the production of a blend from two immiscible phases, glycerol and 2-propanone, which had a considerable impact on the reaction interface and solketal yield. The sulfonic groups, with an acidity of 0.30 mmol·g⁻¹, are the acid sites

### Table 2: Zeolite and clay catalyst for solketal synthesis.

| Sl no. | Catalyst                  | Reaction conditiona | Conversion (%) | Selectivity (%) | Catalyst cyclec | Ref.  |
|--------|---------------------------|---------------------|---------------|-----------------|-----------------|-------|
| 1      | H-BEA                     | 1:4, 60, 5, 60      | 70            | 98.3            | 5 (51.7/98)     | [75]  |
| 2      | Beta -zeolite             | 1:6, 240, 10, 60    | 94.26         | 94.21           | 5 (>80/80)      | [62]  |
| 3      | Dealumination of BEA zeolites | 1:1, 30, 5, 4, 30  | 80            | 100             | 4 (77/100)      | [19]  |
| 4      | Germanosilicate           | 1:6, 240, 10, 60    | 56            | 98              | 6 (>40/70)      | [81]  |
| 5      | MFI                       | 1:1, 120, 1, 70     | 80            | 99              | —               | [83]  |
| 6      | H-ZSM-5                   | 1:3, 60, 9, 36, 50  | 85            | 98              | —               | [84]  |
| 7      | Nb₂-OH⁻/HUSY              | 1:2, 180, 4, 40     | 66            | 98              | 2 (58/98)       | [82]  |
| 8      | [5V] Si–ITQ-6             | 1:3, 120, 5, 60     | 100           | 99              | 3 (>80—)        | [80]  |
| 9      | HR/Y–W20                  | 1:10, 90, 10, 40    | 100           | 97.9            | 4 (97/95)       | [79]  |
| 10     | V–MCM-41                  | 1:6.5, 60, 10, 60   | 92            | 97              | 3 (33.5—)       | [89]  |
| 11     | MCM-22                    | 1:6, 120, 5, 40     | 91            | 97              | 4 (82/96)       | [85]  |
| 12     | HNO₃-modified montmorillonite clay | 1:2.5, 15, 5, 20 | 94            | 95.4            | 3 (—/73)        | [94]  |
| 13     | HCl-activated clay        | 1:6, 60, 5, 20      | —             | 69.3            | 5 (—)           | [95]  |
| 14     | Montmorillonite MK-10     | 1:1, 120, 5, 40     | 68            | 86              | 3 (61/60)       | [96]  |
| 15     | Metakaolin K3             | 1:6, 90, 1.5, 50    | 77            | 84              | —               | [97]  |
| 16     | Algerian acid-activated clays | 1:4, 2880, 4, 3, 40 | 89            | 95              | —               | [98]  |

aGlycerol: acetone molar ratio, reaction time (mins.), catalyst loading (wt. %), temperature (°C). bGlycerol: furfural. cCatalyst cycle with % conversion/selectivity. 
accountable for material activity in this substance. With no considerable leaching, the catalyst was regenerated four times (Table 3, SI no. 4).

Another set of acetalization of glycerol has been carried out by Domínguez-Barroso et al. [105], using sulfonic acid-functionalized carbon catalyst, where the acidic sites was 1.5 mmol·g⁻¹ before activation by NaOH and the latter 2.9 mmol·g⁻¹ which was supported by the surface carboxylic group associated with carbon support. Fernández et al. [106] presented the catalytic production of solketal which was catalysed by sulfonated hydrothermal carbons (SHTC), which has sulfur content of 0.60–0.77 mmol·g⁻¹. They were made from glucose and cellulose, and depending on the hydrothermal treatment settings, they had variable textural qualities. At room temperature, the sulfonated carbons showed good catalytic activity for the production of solketal; up to 86%. SHTC’s catalytic activity was compared to that of several commercially available acid catalysts, including Dowex 50Wx2, Nafion silica SAC-13, and Amberlyst-A15 with perfluoroalkylsulfonic sites Deloxan, and it was observed that SHTC is more reactive.

A one-pot carbonization and activation of yeast biomass [52] using H₃PO₄ has successfully increased the surface area of the produced activated carbonaceous material with surface area reaching from 983 to 1208 m²·g⁻¹. The surface area was reliable on the activating agent concentration. Tuning with nitric acid altered the surface of the activated carbons, causing a series of reformed activated carbons that retained oxygen-containing groups, like carboxylic groups, leading to solketal production. The activated carbonaceous material was further oxidised to afford a highly acidic activated carbon. The high acidity of the acidic activated carbon is attributed to the presence of carboxyl groups, carboxylic anhydrides, quinone carbonyl groups, lactones, and phenolic hydroxyl groups as detected using Boehm titration. The total acidity of the acidic carbon material was found to be as high as 5.3 mmol·g⁻¹ and used as a solid catalyst for valorization of glycerol to solketal in 91% conversion with 97% selectivity. The undesirable creation of carboxylate esters by reactivity of the glycerol with the stronger acid sites can be linked to the slight drop in conversion observed (-COOH) [89].

A new sustainable acid catalyst was developed by Mota et al. [107], upon the hydrothermal carbonization of carrageenan, a natural sulfated polysaccharide obtained from red macro algae, which when compared to commercialised Amberlyst-15 resin, showed better conversion up to 98%. SEM images show the disintegration of the original carrageenan structure during HTC processing, with microbeads (1.5–8m) shaped and sized similarly to glucose, sucrose hydrochars, and starch made under identical conditions (Figure 4). The HTC catalyst also exhibited minor loss of catalyst activity upon 5 repeated runs.

Sankaranarayanan et al. [108] studied the manufacture of solketal from a variety of natural sources containing calcium, dolomite, seashells, chicken eggshells, and cuttlebone. The maximum production (84%) of solketal was produced from magnesium and calcium mixed oxides obtained from dolomite. The highest surface area and pore volume at 15 m²·g⁻¹ and 0.018 cm³·g⁻¹ respectively, were revealed by dolomite oxide catalyst along with a basic strength of 0.92 mmol·g⁻¹. Acidic carbons from biodiesel residues (5-HMF) at room temperature also give conversions as high as 78% for the glycerol acetalization which was reported by Mantovani et al. [109]. Table 3 contains different biomass-derived catalysts for solketal production. The existence of acid groups, primarily sulfonic groups, was discovered to be a critical component for greater catalytic performance in the acid-modified carbon catalyst; another aspect is the increased acid density and the wide mesopores of the carbon structure. Kaur et al. [110] used risk husk to derive acidic catalyst for ketolization of glycerol and acetone for solketal production, which give a conversion of 55% and selectivity of 100% with a catalyst of 5 wt.%. The use of this biomass as a catalyst is a good initiative and recommended as India being the second largest producer and exporter of rice in the world.

### Table 3: Biomass-derived catalyst for solketal synthesis.

| Sl no. | Catalyst | Reaction condition | Conversion (%) | Selectivity (%) | Catalyst cycle | Ref. |
|-------|----------|-------------------|---------------|----------------|---------------|-----|
| 1.    | Yeast-activated carbons | 1:4, 300, 3, RT | 91            | 97             | 4 (81/96)     | [52] |
| 2.    | Acidic carbon | 1:2, 60, 3, 100 | 82            | 95             | 5 (74—)       | [101] |
| 3.    | AAC-CC    | 1:8.8, 60, 3, 100 | 80.3          | —              | 3 (76—)       | [102] |
| 4.    | BS₃₂       | 1:10, 120, 0.6, 25 | 90            | 98             | 4 (95—)       | [104] |
| 5.    | SO₃H-C     | 1:8, 300, 10, 57  | 80            | 100            | —             | [105] |
| 6.    | SHTC       | 1:7, 240, 1, 25   | 80            | 100            | 2 (—)         | [106] |
| 7.    | HTC-carrageenan | 1:20, 360, 0.14¹, 70 | 87          | 97             | 5 (—)         | [107] |
| 8.    | Dolomiteoxide | 1:2, 360, 7, 150  | —             | 84             | 5 (—/61)      | [108] |
| 9.    | Gly-SO₃H   | 1:3, 120, 10, 100 | 85            | 69             | 3 (—/36)      | [109] |
| 10.   | ACrice_husk | 1:4, 120, 5, 100  | 55            | 100            | —             | [110] |

¹Glycerol: acetone molar ratio, reaction time (mins.), catalyst loading (wt. %), temperature (°C). ²Glycerol:propanone, mmol of strong acidic site (SO₃H); ³catalyst cycle with % conversion/selectivity, AAC-CC = acid activated carbon catalyst, SO₃H-C = acid carbon-based structured catalyst, and gly-SO₃H = glycerol sulfonated.

4.5. Glycerol Acetalization Using Resins. Resin is a solid or highly viscous substance of plants or synthetic origin that is typically convertible into polymers. Resins have catalytic activity similar to sulfuric acid, but with the advantages of quicker product separation, less by-product reactions, less equipment corrosion, less pollution, energy savings, and
continuous production. It also provides for a more environmentally friendly procedure because no trash is generated and resins may be reused multiple times without modification [111, 112]. Amberlite IR-120, Dowex 50, X-8 100, and Tulsion T-42 were utilised as catalysts since they are reusable polymeric SO$_3$H-functionalized cation exchange resins. Resins can substitute liquid acid catalyst in many catalysis applications because they provide strong acid sites on H$^+$ form (solid acid catalyst) and are very much stable to water and cheap [113].

In recent years, several resins/polymers were reported for the glycerol conversion to solketal as shown in Table 4. A certain kind of resin catalyst (amberlyst) prompted the reaction of glycerol with acetone, resulting in a glycerol conversion of over 80%. An experimental research using ethanol as the solvent was done in a batch reactor to obtain a kinetic model appropriately representing the process. The effect of numerous variables such as catalyst particle size, agitation speed, temperature, acetone to glycerol molar ratio, and catalyst amount were examined, and the activation energy was found to be $39.78 \pm 0.34 \times 10^3$ J·mol$^{-1}$ with essentially full selectivity [114].

Wet impregnation was utilised to make gallium silicates, which were then used to acetalize glycerol with acetone to make solketal. Glycerol conversion was only 34%, while selectivity was 94%, which can be attributed to the active sites being fully accessible as a consequence of the impregnation technique [54]. For solketal synthesis, NKC-9 resin catalyst [121] and Indion 225 Na [111] were also utilised, resulting in good selectivity. NCK-9 resin was

Figure 4: SEM thermograms of the K-carrageenan catalyst.
reported to have an activation energy of 44.312 kJ·mol⁻¹. There was no evidence of leaching, indicating that the catalyst is heterogeneous.

Konwar et al. [50] established a unique and environmentally acceptable approach for synthesising a strong solid acidic mesoporous or macroporous carbon catalyst from Na-lignosulfonate (LS), a side product of sulfite pulping. Interestingly, the best LS catalyst has a large specific surface area (122 m²·g⁻¹) and stable -SO₃H sites (1.21 mmol·g⁻¹), indicating that it has a lot of promise for continuous solketal synthesis. Furthermore, all resins demonstrated strong solketal selectivity (>80%), and the acid capacity of the resin is an important catalytic parameter for converting glycerol.

Solketal synthesis from glycerol by means of an acid-functionalized resin catalyst was examined by Laskar et al. [37] in 2018. The resin was prepared by reacting p-phenolsulfonic acid with formaldehyde in a reflux condenser for 6 h. The catalytic activity test was performed which gives 97% of glycerol conversion with a full selectivity (100%) The catalyst showed worthy stability and can be recycled up to 4th cycle, giving a selectivity of 100% in all the cycles. Churipard et al. [121] prepared sulfonic acid-functionalized mesoporous polymer catalyst (MP-SO₃H) by postsynthetic modification of mesoporous poly-di-vinylbenzene by incorporating sulfonic acid. MP-SO₃H performed better than the other conventional acid catalysts with 94% conversion and 98.5% selectivity for solketal. Higher activity of the catalyst is mainly accredited due to an greater accessibility of acidic sites (2.3 mmol H⁺·g⁻¹) in higher mesoporous surface area and easy flow of product due to larger pore size [1, 76]. Leaching of the catalyst was observed after three reaction cycles which was attributed to the adsorption of reactants/product moieties on the surface that stick on even after washing with solvent.

Sulfonic ion exchange resins Lewatit GF101 was used for the synthesis of solketal by Esteban et al. [118]. A glycerol conversion of 96% and selectivity of 80% was obtained with a very low catalyst loading (0.5 wt. %). In another work, strongly acidic solid meso/macroporous carbon catalyst was prepared using Na-lignosulfonate, by-product from sulfite pulping via mild pyrolysis (350–450°C). Due to its highly porous nature and stability of -SO₃H with acidity of 2.99–5.0 mmol·g⁻¹, sites showed brilliant activity with glycerol conversion up to 92%. TGA profile revealed that the most significant weight loss was observed around 180–615°C, which corresponded to the elimination of surface functional groups and carbonization stages. This demonstrates the utility of pyrolysis and carbonization as a strategy for raising the degree of crosslinking in LS, refining its heterogeneity, and decreasing its solubility [50]. Nafion NR50 prepared by Ricciardi et al. [120] promotes the quantitative and selective acetalization of glycidol with acetonitrile giving 88% selectivity to solketal with TOF of 20 h⁻¹. Also, sulfonated silica was prepared from the treatment of a silica gel with sulfuric acid and used for acetalization of glycerol to solketal giving a selectivity of 99%. Solketal produced was further used for the production of solketal ester [119].

Among all the catalysts reported in Table 4, the catalyst Cs/KIT-6 was one of the best for solketal production using glycerol and acetone, with 95% glycerol conversion and a selectivity of 98%. For of its wide surface area (600–1000 m²·g⁻¹), active sites, and accessible pores, KIT-6 was chosen. Cs 2.5 seemed to have a lower reaction rate than KIT-6 in bulk due to the high viscosity of the solvent-free reaction media, which hindered the reagent contacts with the catalyst surface [46].

UA-20 [122] proved to be an effective solid acid catalysts using glycerol and acetone for the synthesis of solketal, in the absence of a solvent. The catalyst was prepared by the reaction of nitrile (trimethylphosphonic acid) and La₃⁺. One positive factor about this catalyst is that, although it gives low conversion in the first cycle, the catalyst is stable upon reuse after washing and drying, exhibiting a similar conversion even after three cycles. Furthermore, almost all resins listed revealed high selectivity for solketal (>80%), and the acid capacity of the resin is an important catalytic parameter for converting glycerol [123]. By possessing the maximum acid

---

**Table 4: Ion-exchange resins for solketal synthesis.**

| Sl no | Catalyst | Reaction condition | Conversion (%) | Selectivity (%) | Catalyst cycle | Ref. |
|------|----------|-------------------|---------------|----------------|---------------|-----|
| 1    | Purolite CT275 | 1:12, 300, 5, 50 | 91 | 99.5 | — | [114] |
| 2    | NKC-9 | 1:1, 20, 2, 50 | 67 | NAᵇ | — | [115] |
| 3    | Indion 225 Na | 1:5, 180, 5, 55 | 31.9 | NAᵇ | — | [111] |
| 4    | PSF -polymer | 1:5, 240, 8, 60 | 97 | 100 | 4 (84/100) | [37] |
| 5    | Cs/KIT-6 | 1:1, 5, 15, 5, 25 | 95 | 98 | — | [46] |
| 6    | Cs₂.5 | 1:6, 60, 5, 25 | 94 | 98 | — | [46] |
| 7    | Ga-silicates | 1:4, 180, 1, 80 | 34 | 95 | 4 (22/) | [54] |
| 8    | Lignosulfonate-based protonic acids | 1:8, 25, 0.5 g, 40 | 94 | 99.5 | 3 (90/—) | [50] |
| 9    | Amberlyst-46 | 1:2, 30, 1, 60 | 84 | 97 | 9 (/62) | [116] |
| 10   | Amberlyst-15 | 1:3, 140, 3, 60 | 87.41 | 90 | — | [117] |
| 11   | Amberlyst-35 | 1:2, 480, 0.5, 30 | 70 | NAᵇ | — | [64] |
| 12   | Lewatit GF101 | 1:12, 240, 0.5, 40 | 96 | 80 | — | [118] |
| 13   | SiO₂-SO₃H | 1:20, 480, 20, 50 | NA | 99 | — | [119] |
| 14   | Nafion NR50 | 1:43, 1080, 20, RT | 90 | 88 | 4 (>90/80) | [120] |
| 15   | MP-SO₃H | 1:1, 30, 0.1, 30 | 94 | 98.5 | 3 (89/—) | [121] |
| 16   | UAV-20 | 1:10, 360, 5, 55 | 56 | 90 | 3 (56/80) | [122] |

ᵃGlycerol: acetone molar ratio, reaction time (mins.), catalyst loading (wt. %), temperature (°C).ᵇCatalyst cycle with % conversion/selectivity.
capacity (sulfonic acid), these catalyst materials may improve not only the selectivity of solketal synthesis but also the conversion of raw glycerol to over 90%. The existence of NaCl as a surface acidity toxin, which is likely owing to the impurities present in glycerol, is another important issue to consider as a catalytic activity restriction [103]. Nanda et al. [29] and Moreira et al. [64] presented an approach for synthesis of solketal using a fixed-bed reactor, both at 313 K and a molar ratio of 2:1, acetone/glycerol, the first, with the ion-exchange resin Amberlyst-36, achieving a conversion of 74%, and the latter, with Amberlyst-35 achieving conversion of 81%. Ilgen et al. [116] developed a similar technique that used Amberlyst-15 and obtained great conversion with a difficulty of excess methanol removal. Amberlyst-15 performed well as a solid catalyst, yielding the greatest glycerol conversion of 87.41%. All resins showed high selectivity due to the presence of surface acidity (oversulfonated resin). In the synthesis of solketal, surface acidity was a critical element in increasing selectivity and conversion.

4.6. Ionic Liquids. Ionic liquids are currently of great importance, frequently employed for various catalytic applications because of their customizable physicochemical properties and structures [27, 63]; they are also ecologically acceptable as they can be used as catalysts and solvents even at room temperature [124]. The acetalization process has also made use of such liquids [125, 126].

Ji et al. [63] conducted ketalization of glycerol with acetone in a batch reactor over an ionic liquid [P(C$_2$H$_5$)$_3$C$_1$H$_2$] [TsO] (TTPT). The TTPT catalyst was recycled and reused 10 times without evident losses in quantity or activity, yielding a maximum solketal yield of 86%. Meanwhile, Arun et al. [126] employed sulfuric acid as a catalyst to convert glycerol to solketal with an 81.36% yield. Zhou et al. [125] reported a stable solid acid catalyst synthesized by polycondensation of p-phenolsulfonic acid on KH$_2$PO$_4$-modified SiO$_2$ (PSF/K-SiO$_2$) for the glycerol acetalization at room temperature. The characterization results of PSF/K-SiO$_2$ confirmed greater surface area and surface acidity than that of PSF resin (copolymer of para-phenolsulfonic acid and formaldehyde) and nonmodified SiO$_2$ supported with PSF resin (PSF/SiO$_2$). PSF/K-SiO$_2$ thus was highly active and stable in glycerol acetalization.

Gui et al. [124] synthesized and used Bronsted acid ionic liquids (BAILs) for the first time as efficient catalysts in the acetalization of glycerol/acetone to generate solketal under relatively moderate reaction conditions (room temperature) and short reaction periods. In terms of conversion and selectivity, Bronsted acid ionic liquids performed the best as compared to other catalytic systems. Catalyst reusability was confirmed using one of the BAILs (BAIL-1), which was recovered and reused in four reaction cycles without losing catalytic activity or selectivity using a simple approach. As a result, the BAILs contribute to the benefits of homogeneous/heterogeneous catalysis in terms of high selectivity, as well as conversion and recyclability.

5. Conclusion and Future Scopes

This study outlines the numerous methodologies and strategies for converting glycerol to solketal, as well as recent work in improving conversion and selectivity of the desired products. The valorization of glycerol to solketal can be done via both homogeneous as well as heterogeneous acid catalysts. The vast mainstream of studies are carried out on heterogeneous catalysts, which can be effortlessly isolated from the reaction mixture using simple filtration techniques.

Various reaction parameters (such as temperature, reactants, duration, and catalyst nature) have a substantial impact on the reaction’s development. Recent breakthroughs in catalyst synthesis and characterization have yielded ground-breaking findings in this field. Notwithstanding the advancements, enhancing selectivity and yield remains a difficult task. The low equilibrium constant is the fundamental constraint to acetalization. As a result, shifting the equilibrium to the product side by eliminating water from the reaction mixture interrupts the reaction. Adding surplus of acetone would be the way to solve this issue. There are a few scientific studies in the literature that address this problem, and they use water-tolerant catalysts such as zeolites, metals, mesoporous silica, heteropoly acid, or polymer-based catalysts to address the problem. In the future years, more development on low-aluminium mesoporous silica and ionic liquids materials is expected. In addition, solketal production would be a milestone with the development and applications of the nano and MOF catalyst, enhancing the possibility of becoming the coming generation catalysts, which will aid in the growth of the long-term environmentally friendly, highly effective, and economically feasible biodiesel technology.

Ultimately, some advanced techniques for solketal synthesis are worth noting—when it comes to heating methods, microwave irradiation is always preferred because heat is shifted directly to the reaction molecules and is more efficient; in addition, the process is safer because it responds faster than ultrasonication and conventional heating:

(i) Magnetic nanomaterials synthesize highly active catalyst containing high surface area and highly recoverable [32]. Metals are deactivated by over-oxidation [57].

(ii) Zeolite catalyst are highly studied due to their equal pore distribution and stability to heat. The acidity of zeolite catalysts for converting glycerol to solketal is widely acknowledged [79, 127]. Clays have a number of features that make them a viable industrial material [95].

(iii) Metal-organic framework (MOF) catalyst gives efficient reaction owing to their exceptionally large surface area and porosity in comparison with the rest [59].

(iv) Ionic liquids combine the benefits of homogeneous and heterogeneous catalysts, but their main disadvantage is typically their high cost [124].
(v) Biomass-derived catalyst has abundant availability of feedstocks, easy synthesis, and is biodegradable. As a result, in the future, the key goal for catalyst manufacture will be to use more ecologically friendly techniques and materials [17, 52].

Data Availability

No data were used to support this study.

Conflicts of Interest

The authors declare no conflicts of interest.

References

[1] G. P. da Silva, M. Mack, and J. Contiero, "Glycerol: a promising and abundant carbon source for industrial microbiology," Biotechnology Advancements, vol. 27, no. 1, pp. 30–39, 2009.

[2] M. Ramos, A. P. S. Dias, J. F. Puna, J. Gomes, and J. C. Bordado, "Biodiesel production processes and sustainable raw materials," Energies, vol. 12, no. 23, p. 4408, 2019.

[3] M. Akia, F. Yazdani, E. Motae, D. Han, and H. Arandiyan, "A review on conversion of biomass to biofuel by nanocatalysts," Biofuel Research Journal, vol. 1, no. 1, pp. 16–25, 2014.

[4] B. Changmai, C. Vanalveni, A. P. Ingle, R. Bhagat, and S. L. Rokhum, "Widely used catalysts in biodiesel production: a review," RSC Advances, vol. 10, no. 68, pp. 41625–41679, 2020.

[5] U. I. Nda-Umar, I. Ramli, Y. H. Taufiq-Yap, and E. N. Muhamad, "An overview of recent research in the conversion of glycerol into biofuels, fuel additives and other bio-based chemicals," Catalysts, vol. 9, no. 1, 2019.

[6] M. A. Fazal, A. S. M. A. Haseeb, and H. H. Masjuki, "Biodiesel feasibility study: an evaluation of material compatibility; performance; emission and engine durability," Renewable and Sustainable Energy Reviews, vol. 15, no. 2, pp. 1314–1324, 2011.

[7] D. Gielen, F. Boshell, D. Saygin, M. D. Bazillian, N. Wagner, and R. Gorini, "The role of renewable energy in the global energy transformation," Energy Strategy Reviews, vol. 24, pp. 38–50, 2019.

[8] C. J. A. Mota, C. X. A. Da Silva, N. Rosenbach, J. Costa, and F. Da Silva, "Glycerin derivatives as fuel additives: the addition of glycerol/acetone ketal (solketal) in gasoline," Energy and Fuels, vol. 24, no. 4, pp. 2733–2736, 2010.

[9] M. De Torres, G. Jiménez-Osés, J. A. Mayoral, and E. Pires, "Fatty acid derivatives and their use as CFPP additives in biodiesel," Bioresource Technology, vol. 102, no. 3, pp. 2590–2594, 2011.

[10] M. Catarino, E. Ferreira, A. P. Soares Dias, and J. Gomes, "Dry washing biodiesel purification using fumed silica sorbent," Chemical Engineering Journal, vol. 386, Article ID 123930, 2020.

[11] F. Ma and M. A. Hanna, "Biodiesel production: a review" journal series, agricultural research division, institute of agriculture and natural resources, university of nebraska-lincoln," Bioresource Technology, vol. 70, no. 1, pp. 1–15, 1999.

[12] R. N. Menchavez, M. J. Morra, and B. B. He, "Co-production of ethanol and 1,2-propanediol via glycerol hydrogenolysis using Ni/Ce-Mg catalysts: effects of catalyst preparation and reaction conditions," Catalysts, vol. 7, no. 10, pp. 290–314, 2017.

[13] X. Yin, X. Duan, Q. You, C. Dai, Z. Tan, and X. Zhu, "Biodiesel production from soybean oil deodorizer distillate using calcined duck eggshell as catalyst," Energy Conversion and Management, vol. 112, pp. 199–207, 2016.

[14] P. F. F. Amaral, T. F. Ferreira, G. C. Fontes, and M. A. Z. Coelho, "Glycerol valorization: new biotechnological routes," Food and Bioproducts Processing, vol. 87, no. 3, pp. 179–186, 2009.

[15] B. Delfort, I. Durand, A. Jæcker, T. Lacome, X. Montagne, and F. Paille, "Diesel fuel compounds containing glycerol acetals," United States Patent, vol. 2, pp. 1–4, 2005.

[16] J. Deutsch, A. Martin, and H. Lieske, "Investigations on heterogeneously catalysed condensations of glycerol to cyclic acetals," Journal of Catalysis, vol. 245, no. 2, pp. 428–435, 2007.

[17] L. S. Al-Saadi, V. C. Eze, and A. P. Harvey, "A reactive coupling process for co-production of solketal and biodiesel," Green Processing and Synthesis, vol. 8, no. 1, pp. 516–524, 2019.

[18] A. R. Trifoi, P. S. Agachi, and T. Pap, "Glycerol acetals and ketals as possible diesel additives. A review of their synthesis protocols," Renewable and Sustainable Energy Reviews, vol. 62, pp. 804–814, 2016.

[19] N. I. Venkatesha, Y. S. Bhat, and B. S. Jai Prakash, "De-alkuminated BEA zeolite for selective synthesis of five-membered cyclic acetal from glycerol under ambient conditions," RSC Advances, vol. 6, no. 23, pp. 18824–18833, 2016.

[20] S. Pariente, N. Tanchoux, and F. Fajula, "Etherification of glycerol with ethanol over solid acid catalysts," Green Chemistry, vol. 11, no. 8, pp. 1256–1261, 2009.

[21] S. Gadamsetti, N. P. Rajan, G. S. Rao, and K. V. R. Chary, "Acetalization of glycerol with acetone to bio fuel additives over supported molybdenum phosphate catalysts," Journal of Molecular Catalysis A: Chemical, vol. 410, pp. 49–57, 2015.

[22] S. Reena, S. Shamshuddin, V. Vasantha, and J. D’Souza, "Synthesis of solketal over zirconia based acid catalysts," Bangladesh Journal of Scientific & Industrial Research, vol. 54, no. 1, pp. 31–38, 2019.

[23] A. L. Maksimov, A. I. Nekhaev, D. N. Ramazanov, Y. A. Arinicheva, A. A. Dryubenko, and S. N. Khadzhiev, "Preparation of high-octane oxygenate fuel components from plant-derived polyols," Petroleum Chemistry, vol. 51, no. 1, pp. 61–69, 2011.

[24] C. J. A. Mota, "Valorization of the glycerol by-product of biodiesel production," Advances in Biodiesel Production, R. Luque, J. A. Melero, eds, Woodhead, Cambridge, UK, pp. 232–253, 2012.

[25] E. García, M. Laca, E. Perez, A. Garrido, and P. Julian, "Newclass Of acetal derived from glycerin as a biodiesel fuel component," Energy and Fuels, vol. 22, pp. 4274–4280, 2008.

[26] R. Esposito, M. E. Cucciolito, A. D’Amora, R. Di Guida, F. Montagnaro, and F. Ruffo, "Highly efficient iron (III) molecular catalysts for solketal production," Fuel Processing Technology, vol. 167, pp. 670–673, 2017.

[27] J. Corrêa, R. P. V. Faria, and A. E. Rodrigues, "Continuous valorization of glycerol into solketal: recent advances on catalysts, processes, and industrial perspectives," Sustainable Chemistry, vol. 2, no. 2, pp. 286–324, 2021.
[28] X. Li, L. Zheng, and Z. Hou, “Acetalization of glycerol with acetone over Co[II]/Co[III] A12− O4 derived from layered double hydroxide,” Fuel, vol. 233, pp. 565–571, 2018.

[29] M. R. Nanda, Z. Yuan, W. Qin, H. S. Ghaziasrak, M. A. Poirier, and C. Xu, “Catalytic conversion of glycerol to oxygenated fuel additive in a continuous flow reactor: process optimization,” Fuel, vol. 128, pp. 113–119, 2014.

[30] S. S. Priya, P. R. Selvakannan, K. V. R. Chary, M. L. Kantam, and S. K. Bhargava, “Solvent-free microwave-assisted synthesis of solketal from glycerol using transition metal ions promoted mordenite solid acid catalysts,” Molecular Catalysis, vol. 434, pp. 184–193, 2017.

[31] P. S. Reddy, P. Sudarsanam, B. Mallesham, G. Raju, and B. M. Reddy, “Acetalisation of glycerol with acetone over zirconia and promoted zirconia catalysts under mild reaction conditions,” Journal of Industrial and Engineering Chemistry, vol. 17, no. 3, pp. 377–381, 2011.

[32] K. Rajkumari, B. Changmai, A. K. Meher et al., “A reusable magnetic nanocatalyst for bio-fuel additives: the ultrasound-assisted synthesis of solketal,” Sustainable Energy Fuels, vol. 5, no. 8, pp. 2362–2372, 2021.

[33] B. Mallesham, B. Govinda Rao, and B. M. Reddy, “Production of biofuel additives by esterification and acetalization of bioglycerol,” Comptes Rendus Chimie, vol. 19, no. 10, pp. 1194–1202, 2016.

[34] G. Morales, M. Paniagua, J. A. Melero, G. Vicente, and C. Ochoa, “Sulfonic acid-functionalized catalysts for the valorization of glycerol via transesterification with methyl acetate,” Industrial & Engineering Chemistry Research, vol. 50, no. 10, pp. 5898–5906, 2011.

[35] I. Fatimah, I. Sahroni, G. Fadillah, M. M. Musawwa, T. M. I. Mahlia, and O. Muraza, “Glycerol to solketal for fuel additive: recent progress in heterogeneous catalysts,” Energy, vol. 12, no. 15, p. 2872, 2019.

[36] D. Y. C. Leung, X. Wu, and M. K. H. Leung, “A review on biodiesel production using catalyzed transesterification,” Applied Energy, vol. 87, no. 4, pp. 1083–1095, 2010.

[37] I. B. Laskar, K. Rajkumari, R. Gupta, and L. Rokhum, “Acid-functionalized mesoporous polymer-catalyzed acetalization of glycerol to solketal, a potential fuel additive under solvent-free conditions,” Energy & Fuels, vol. 32, no. 12, pp. 12567–12576, 2018.

[38] J. F. Izquierdo, M. Montiel, I. Palés et al., “Fuel additives from glycerol etherification with light olefins: state of the art,” Renewable and Sustainable Energy Reviews, vol. 16, no. 9, pp. 6717–6724, 2012.

[39] D. Hernández, J. J. Fernández, F. Mondragón, and D. López, “Production and utilization performance of a glycerol derived additive for diesel engines,” Fuel, vol. 92, no. 1, pp. 130–136, 2012.

[40] “Global Solketal Market – Industry Trends and Forecast to 2028. Data Bridge Market Research,” 2020, https://www.databridgemarketresearch.com/reports/global-solketal-market.

[41] I. Zahid, M. Ayoub, B. B. Abdullah et al., “Production of fuel additive solketal via catalytic conversion of biodiesel-derived glycerol,” Industrial & Engineering Chemistry Research, vol. 59, no. 48, Article ID 20961, 2020.

[42] T. M. Mahreni and M. M. A. Nur, “Production of solketal (2,2-Dimethyl-1,3-dioxolane-4-methanol) from glycerol and acetone by using homogenous acidic catalyst at the boiling temperature (preliminary study),” Journal of Physics: Conference Series, vol. 1295, no. 1, Article ID 012004, 2019.

[43] M. Checa, S. Nogales-Delgado, V. Montes, and J. M. Encinar, “Recent advances in glycerol catalytic valorization: a review,” Catalysts, vol. 10, no. 11, pp. 1279–1341, 2020.

[44] C. X. A. da Silva, V. L. C. Gonçalves, and C. J. A. Mota, “Water-tolerant zeolite catalyst for the acetalisation of glycerol,” Green Chemistry, vol. 11, no. 1, pp. 38–41, 2009.

[45] M. R. Nanda, Z. Yuan, W. Qin, H. S. Ghaziasrak, M. A. Poirier, and C. C. Xu, “Thermodynamic and kinetic studies of a catalytic process to convert glycerol into solketal as an oxygenated fuel additive,” Fuel, vol. 117, pp. 470–477, 2014.

[46] L. Chen, B. Nohair, D. Zhao, and S. Kaliaguine, “Highly efficient glycerol acetalization over supported heteropoly acid catalysts,” ChemCatChem, vol. 10, no. 8, p. 1918, 2018.

[47] J. A. Vannucci, N. N. Nichio, and F. Pompeo, “Solketal synthesis from ketalisation of glycerol with acetone: a kinetic study over a sulfated zirconia catalyst,” Catalysis Today, vol. 372, pp. 238–245, 2021.

[48] U. V. A. Vis, S. Yurdakal, C. Garlisi, O. Levent, M. Bellardita, and G. Palmisano, “(Photo) catalyst characterization techniques: adsorption isotherms and BET, SEM, FTIR, UV-vis, photoluminescence, and electrochemical characterizations,” Heterogeneous Photocatalysis, vol. 4, pp. 87–152, 2019.

[49] B. Delmon, J. Haber, and J. H. Block, “Manual of methods and procedures for catalyst characterization (technical report),” Pure and Applied Chemistry, vol. 67, pp. 1257–1306, 1995.

[50] L. J. Konwar, A. Samikannu, P. Mäki-Arvela, D. Boström, and J. P. Mikkola, “Lignosulfonate-based macro/mesoporous solid protonic acids for acetalization of glycerol to bio-additives,” Applied Catalysis B: Environmental, vol. 220, pp. 314–323, 2018.

[51] S. Loganathan, R. B. Valapa, R. K. Mishra, G. Puzahenthri, and S. Thomas, “Thermogravimetric analysis for characterization of nanomaterials,” Thermal and Rheological Measurement Techniques for Nanomaterials Characterization, vol. 3, pp. 67–108, 2017.

[52] R. Rodrigues, M. S. Santos, R. S. Nunes, W. A. Carvalho, and G. Labuto, “Solvent-free solketal production from glycerol promoted by yeast activated carbons,” Fuel, vol. 299, Article ID 120923, 2021.

[53] Z. Li, Z. Miao, X. Wang et al., “One-pot synthesis of ZrMo-KIT-6 solid acid catalyst for solvent-free conversion of glycerol to solketal,” Fuel, vol. 233, pp. 377–387, 2018.

[54] H. Hussein, A. Vivian, L. Fusaro, M. Devillers, and C. Aprile, “Synthesis of highly accessible gallosilicates via impregnation procedure: enhanced catalytic performances in the conversion of glycerol into solketal,” ChemCatChem, vol. 12, no. 23, pp. 5966–5976, 2020.

[55] W. Wang, X. Zeng, Y. Deng et al., “Fe doped aluminoborate PKU-1 catalysts for the ketalization of glycerol to solketal: unveiling the effects of iron composition and boron,” Chinese Chemical Letters, vol. 33, 2021.

[56] R. Teich-Menson, C. K. Rono, A. Etale, G. Mehmana, J. Darkwa, and B. C. E. Makhubela, “New bio-based sustainable polymers and polymer composites based on methacrlylate derivatives of furfural, solketal and lactic acid,” Materials Today Communications, vol. 28, Article ID 102721, 2021.

[57] M. Besson and P. Gallezot, “Selective oxidation of alcohols and aldehydes on metal catalysts,” Catalysis Today, vol. 57, pp. 127–141, 2000.
A. A. Refaat, "Biodiesel production using solid metal oxide catalysts," *International Journal of Environmental Science and Technology*, vol. 8, no. 1, pp. 203–221, 2011.

V. R. Bakuru, S. R. Chiripard, S. P. Maradur, and S. B. Kalindiri, "Exploring the Brønsted acidity of UiO-66 (Zr, Ce, Hf) metal-organic frameworks for efficient solketal synthesis from glycerol acetalization," *Dalton Transactions*, vol. 48, no. 3, pp. 843–847, 2019.

Y. T. Liao, B. M. Matsagor, and K. C. W. Wu, "Metal-organic framework (MOF)-derived effective solid catalysts for valorization of lignocellulosic biomass," *ACS Sustainable Chemistry & Engineering*, vol. 6, no. 11, pp. 13628–13643, 2018.

M. N. Timofeeva, V. N. Panchenko, N. A. Khan et al., "Isotransitional metal-carboxylates MIL-100(M) and MIL-53(M) (M= V, Al, Fe and Cr) as catalysts for condensation of glycerol with acetone," *Applied Catalysis A: General*, vol. 529, pp. 167–174, 2017.

H. Sulisisto, I. Perdana, F. T. Pratiwi, and I. Hartati, "Kinetics and thermodynamics studies of ketalization of glycerol and acetone in the presence of baseilite F300 as catalyst," *IOP Conference Series: Materials Science and Engineering*, vol. 742, no. 1, Article ID 012007, 2020.

Y. Ji, T. Zhang, X. Gui, H. J. Shi, and Z. Yun, "Solvantless ketalization of glycerol to solketal with acetone over the ionic liquid [PC4H9]3C4H12[TsO]," *Chinese Journal of Chemical Engineering*, vol. 28, no. 1, pp. 158–164, 2020.

M. N. Moreira, R. P. V. Faria, A. M. Ribeiro, and A. E. Rodrigues, "Solketal production from glycerol ketalization with acetone: catalyst selection and thermodynamic and kinetic reaction study," *Industrial & Engineering Chemistry Research*, vol. 58, no. 38, pp. 17746–17759, 2019.

S. Bewana, M. Joe Ndolomingo, R. Meijboom, and N. Bingwa, "Cobalt oxide promoted tin oxide catalysts for highly selective glycerol acetalization reaction," *Inorganic Chemistry Communications*, vol. 128, Article ID 108578, 2021.

X. Li, Y. Jiang, R. Zhou, and Z. Hou, "Acetalization of glycerol with acetone over appropriately-hydrophobic zirconium organophosphonates," *Applied Clay Science*, vol. 189, Article ID 105555, 2020.

M. J. da Silva, A. A. Rodrigues, and P. F. Pinheiro, "Solketal synthesis from glycerol and acetone in the presence of metal sals: a lewis or brønsted acid catalyzed reaction," *Fuel*, vol. 276, Article ID 118164, 2020.

V. T. Vasantha, N. J. Venkatesha, S. Z. M. Shamshuddin, J. Q. D’Souza, and B. G. V. Reddy, "Sulphated zirconia supported on cordierite honeycomb monolith for effective synthesis of solketal from acetalisation of glycerol with acetone," *ChemistrySelect*, vol. 5, no. 2, pp. 602–608, 2018.

Q. Peng, X. Zhao, D. Li et al., "Synthesis of bio-additive fuels from glycerol acetalization over a heterogeneous Ta/W mixed addenda heteropolyacid catalyst," *Fuel Processing Technology*, vol. 214, Article ID 106705, 2021.

X. Li, Y. Jiang, R. Zhou, and Z. Hou, "Layered α-zirconium phosphate: an efficient catalyst for the synthesis of solketal from glycerol," *Applied Clay Science*, vol. 174, pp. 120–126, 2019.

M. J. da Silva, M. G. Teixeira, D. M. Chaves, and L. Siqueira, "An efficient process to synthesize solketal from glycerol over tin (II) silicotungstate catalyst," *Fuel*, vol. 281, Article ID 118724, 2020.

K. Rajkumari, D. Das, G. Pathak, and S. L. Rokhum, "Waste-to-useful: a biowaste-derived heterogeneous catalyst for a green and sustainable Henry reaction," *New Journal of Chemistry*, vol. 43, no. 5, pp. 2134–2140, 2019.

B. Rongxian, T. Yisheng, and H. Yizhuo, "Study on the carbon dioxide hydrogenation to iso-alkanes over Fe–Zn–M/M zeolite composite catalysts," *Fuel Processing Technology*, vol. 86, no. 3, pp. 293–301, 2004.

D. W. Lee, Y. M. Park, and K. Y. Lee, "Heterogeneous base catalysts for transesterification in biodiesel synthesis," *Catalysis Surveys from Asia*, vol. 13, no. 2, pp. 63–77, 2009.

P. Manjunathan, S. P. Maradur, A. B. Halgeri, and G. V. Shanbhag, "Room temperature synthesis of solketal from acetalization of glycerol with acetone: effect of crystalsllite size and the role of acidity of beta zeolite," *Journal of Molecular Catalysis A: Chemical*, vol. 396, pp. 47–54, 2015.

V. Rossa, Y. D. S. P. Pessanha, G. C. C. Díaz, L. D. T. Câmara, S. B. C. Pergher, and D. A. G. Aranda, "Reaction kinetic study of solketal production from glycerol ketalization with acetone," *Industrial & Engineering Chemistry Research*, vol. 56, no. 2, pp. 479–488, 2017.

M. J. Da Silva, A. A. Julio, and F. C. S. Dorigeto, "Solvant-free heteropolyacid-catalyzed glycerol ketalization at room temperature," *RSC Advances*, vol. 5, no. 55, pp. 44499–44506, 2015.

F. Jamil, S. K. Saxena, A. H. Al-Muhtaseb et al., "Valorization of waste “date seeds” bio-glycerol for synthesizing oxidative green fuel additive," *Journal of Cleaner Production*, vol. 165, pp. 1090–1096, 2017.

A. Talebian-Kikalahieh and S. Tarighi, "Hierarchical faujasite zeolite-supported heteropoly acid catalyst for acetalization of crude-glycerol to fuel additives," *Journal of Industrial and Engineering Chemistry*, vol. 79, pp. 452–464, 2019.

L. H. Vieira, L. G. Possato, T. F. Chaves, S. H. Pulcinielli, C. V. Santilli, and L. Martins, "Studies on dispersion and reactivity of vanadium oxides deposited on lamellar ferrierite zeolites for condensation of glycerol into bulky products," *Molecular Catalysis*, vol. 458, pp. 161–170, 2018.

I. Podolean, J. Zhang, M. Shamzhy, V. I. Pârvulescu, and J. Ćeja, "Solvant-free ketalization of polyols over germanosilicate zeolites: the role of the nature and strength of acid sites," *Catalysis Science and Technology*, vol. 10, no. 24, pp. 8254–8264, 2020.

C. Ferreira, A. Araujo, V. Calvino-Casilda et al., "Y zeolite-supported niobium pentoxide catalysts for the glycerol acetalization reaction," *Microporous and Mesoporous Materials*, vol. 271, pp. 243–251, 2018.

I. Kowalska-Kus, A. Held, and K. Nowinska, "Solketal formation from glycerol and acetone over hierarchical zeolites of different structure as catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 426, pp. 205–212, 2017.

I. Kowalska-Kus, A. Held, and K. Nowinska, "A continuous-flow process for the acetalization of crude glycerol with acetone on zeolite catalysts," *Chemical Engineering Journal*, vol. 401, Article ID 126143, 2020.

M. V. Rodrigues, C. Okolie, C. Sievers, and L. Martins, "Organosilane-assisted synthesis of hierarchical MCM-22 zeolites for condensation of glycerol into bulky products," *Crystal Growth & Design*, vol. 19, no. 1, pp. 231–241, 2019.

I. Rossetti, G. F. Mancini, P. Ghigna et al., "Spectroscopic enlightening of the local structure of VO X active sites in crystalite (II) silicotungstate catalysts, for the study of glycerol hydride hydrocarbon synthesis from glycerol ketals," *Dalton Transactions*, vol. 43, no. 5, pp. 2134–2140, 2019.
the selective oxidation of light alkanes,” *Catalysis Today*, vol. 298, pp. 145–157, 2017.

[88] R. Bulánek, A. Kalužová, M. Setnička, A. Zukal, and P. Cičmanec, “Study of vanadium based mesoporous silicas for oxidative dehydrogenation of propane and n-butane,” *Catalysis Today*, vol. 179, no. 1, pp. 149–158, 2012.

[89] T. H. Abreu, C. I. Meyer, C. Padró, and I. Martins, “Acidic V-MCM-41 catalysts for the liquid-phase ketalization of glycerol with acetone,” *Microporous and Mesoporous Materials*, vol. 273, pp. 219–215, 2019.

[90] A. B. Halgéri and J. Das, “Novel catalytic aspects of beta zeolite for alkyl aromatics transformation,” *Applied Catalysis A: General*, vol. 181, no. 2, pp. 347–354, 1999.

[91] A. Galadima and O. Muraza, “Hydrocracking catalysts based on hierarchical zeolites: a recent progress,” *Journal of Industrial and Engineering Chemistry*, vol. 61, pp. 265–280, 2018.

[92] Q. Yu, C. Cui, Q. Zhang et al., “Hierarchical ZSM-11 with intergrowth structures: synthesis, characterization and catalytic properties,” *Journal of Energy Chemistry*, vol. 22, no. 5, pp. 761–768, 2013.

[93] L. G. Possato, T. F. Chaves, W. H. Cassinelli, S. H. Pulcinelli, E. Gutiérrez-Acebo, F. Guerrero-Ruiz, M. Centenero, I. Zahid, M. Ayoub, B. B. Abdullah, M. H. Nazir, “Continuous-flow process for glycerol conversion to solketal using a brønsted acid functionalized carbon-based catalyst,” *Catalysts*, vol. 9, no. 7, p. 609, 2019.

[94] P. Fernández, J. M. Fraile, E. García-Bordejé, and E. Pires, “Sulfonated hydrothermal carbons from cellulose and glucose as catalysts for glycerol ketalization,” *Catalysts*, vol. 9, no. 10, p. 804, 2019.

[95] C. J. A. Mota, J. R. Dodson, B. P. Pinto, and D. R. Fernandes, “Sustainable acid catalyst from the hydrothermal carbonization of carrageenan: use in glycerol conversion to solketal,” *Biomass Conversion and Biorefinery*, vol. 1, pp. 1–11, 2021.

[96] S. Sankaranarayanan, W. Jindapon, and C. Ngamcharussrivichai, “Valorization of biodiesel plant-derived products via preparation of solketal fatty esters over calcium-rich natural materials derived oxides,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 81, pp. 57–64, 2017.

[97] M. Mantovani, D. Mandelli, M. Gonçalves, and W. A. Carvalho, “Fructose dehydration promoted by acidic catalysts obtained from biodiesel waste,” *Chemical Engineering Journal*, vol. 348, pp. 599–606, 2018.

[98] J. Kaur, P. Gera, M. K. Jha, and A. K. Sarma, “A study on conversion of glycerol into solketal using rice husk-derived catalyst,” *Advances in Energy Research*, vol. 2, pp. 599–606, 2020.

[99] H. Sulistyo, D. P. Priadana, Y. W. Fitriandini, T. Ariyanto, H. Sulistyo, D. P. Priadana, Y. W. Fitriandini, T. Ariyanto, “Utilization of glycerol by ketalization reactions with acetone to produce solketal using indion 225 Na as catalyst,” *International Journal of Technology*, vol. 11, no. 1, pp. 190–199, 2020.

[100] E. Gutiérrez-Acebo, F. Guerrero-Ruiz, M. Centenero, J. S. Martínez, P. Salagre, and Y. Cesteros, “Effect of using microwaves for catalysts preparation on the catalytic acetalysis of glycerol with furfural to obtain fuel additives,” *Open Chemistry*, vol. 16, no. 1, pp. 386–392, 2018.

[101] K. Alali, F. Lebsir, S. Amri, A. Rahmouni, E. Srasra, and N. Beshes, “ Algerian acid activated clays as efficient catalysts for a green synthesis of solketal by chemoselective acetalization of glycerol with acetone,” *BULLETIN OF CHEMICAL REACTION ENGINEERING AND CATALYSIS*, vol. 14, no. 1, pp. 130–141, 2019.

[102] J. Kaur, A. K. Sarma, P. Gera, and M. K. Jha, “Process optimization with acid functionalised activated carbon derived from corn cob for production of 4-hydroxymethyl-2,2-dimethyl-1,3-dioxolane and 5-hydroxy-2,2-dimethyl-1,3-dioxane,” *Scientific Reports*, vol. 11, pp. 1–12, 2021.

[103] P. Fernández, J. M. Fraile, E. García-Bordejé, and E. Pires, “Sulfonated hydrothermal carbons from cellulose and glucose as catalysts for glycerol ketalization,” *Catalysts*, vol. 9, no. 10, p. 804, 2019.

[104] C. J. A. Mota, J. R. Dodson, B. P. Pinto, and D. R. Fernandes, “Sustainable acid catalyst from the hydrothermal carbonization of carrageenan: use in glycerol conversion to solketal,” *Biomass Conversion and Biorefinery*, vol. 1, pp. 1–11, 2021.

[105] S. Sankaranarayanan, W. Jindapon, and C. Ngamcharussrivichai, “Valorization of biodiesel plant-derived products via preparation of solketal fatty esters over calcium-rich natural materials derived oxides,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 81, pp. 57–64, 2017.

[106] M. Mantovani, D. Mandelli, M. Gonçalves, and W. A. Carvalho, “Fructose dehydration promoted by acidic catalysts obtained from biodiesel waste,” *Chemical Engineering Journal*, vol. 348, pp. 599–606, 2018.

[107] J. Kaur, P. Gera, M. K. Jha, and A. K. Sarma, “A study on conversion of glycerol into solketal using rice husk-derived catalyst,” *Advances in Energy Research*, vol. 2, pp. 599–606, 2020.

[108] H. Sulistyo, D. P. Priadana, Y. W. Fitriandini, T. Ariyanto, H. Sulistyo, D. P. Priadana, Y. W. Fitriandini, T. Ariyanto, “Utilization of glycerol by ketalization reactions with acetone to produce solketal using indion 225 Na as catalyst,” *International Journal of Technology*, vol. 11, no. 1, pp. 190–199, 2020.

[109] E. Gutiérrez-Acebo, F. Guerrero-Ruiz, M. Centenero, J. S. Martínez, P. Salagre, and Y. Cesteros, “Effect of using microwaves for catalysts preparation on the catalytic acetalysis of glycerol with furfural to obtain fuel additives,” *Open Chemistry*, vol. 16, no. 1, pp. 386–392, 2018.

[110] K. Alali, F. Lebsir, S. Amri, A. Rahmouni, E. Srasra, and N. Beshes, “ Algerian acid activated clays as efficient catalysts for a green synthesis of solketal by chemoselective acetalization of glycerol with acetone,” *BULLETIN OF CHEMICAL REACTION ENGINEERING AND CATALYSIS*, vol. 14, no. 1, pp. 130–141, 2019.

[111] M. K. Lam, K. T. Lee, and A. R. Mohamed, “Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: a review,” *Biotechnology Advances*, vol. 28, no. 4, pp. 500–518, 2010.

[112] G. Pathak, D. Das, K. Rajkumari, and S. L. Rokhm, “Exploiting waste: towards a sustainable production of biodiesel using musa acuminate peel ash as a heterogeneous catalyst,” *Green Chemistry*, vol. 20, no. 10, pp. 2365–2373, 2018.

[113] M. Gonçalves, R. Rodrigues, T. S. Galhardo, and W. A. Carvalho, “Highly selective acetalization of glycerol with acetone to solketal over acidic carbon-based catalysts from biodiesel waste,” *Fuel*, vol. 181, pp. 46–54, 2016.
[116] O. Ilgen, S. Yerlikaya, and F. O. Akyurek, “Synthesis of solketal from glycerol and acetone over amberlyst-46 to produce an oxygenated fuel additive,” *Periodica Polytechnica Chemical Engineering*, vol. 61, no. 2, pp. 144–148, 2017.

[117] H. Sulistyo, I. Hapsari, Budhijanto, W. B. Sediawan, S. S. Rahaya, and M. M. Azis, “Heterogeneous catalytic reaction of glycerol with acetone for solketal production,” *MATEC Web of Conferences*, vol. 268, Article ID 07004, 2019.

[118] J. Esteban, M. Ladero, and F. García-Ochoa, “Kinetic modelling of the solventless synthesis of solketal with a sulphonic ion exchange resin,” *Chemical Engineering Journal*, vol. 269, pp. 194–202, 2015.

[119] S. L. Barbosa, P. C. Lima, W. T. P. dos Santos, S. I. Klein, G. C. Clososki, and F. J. Caires, “Oxygenated biofuels: synthesis of fatty acid solketal esters with a mixture of sulfonated silica and (Bu4N) (BF4) catalyst,” *Catalysis Communications*, vol. 120, pp. 76–79, 2019.

[120] M. Ricciardi, L. Falivene, T. Tabanelli, A. Proto, R. Cucinelli, and F. Cavani, “Bio-glycidol conversion to solketal over acid heterogeneous catalysts: synthesis and theoretical approach,” *Catalysts*, vol. 8, no. 9, p. 391, 2018.

[121] S. R. Churipard, P. Manjunathan, P. Chandra et al., “Remarkable catalytic activity of a sulfonated mesoporous polymer (MP-SO3H) for the synthesis of solketal at room temperature,” *New Journal of Chemistry*, vol. 41, no. 13, pp. 5745–5751, 2017.

[122] I. C. M. S. Santos-Vieira, R. F. Mendes, F. A. Almeida Paz, J. Rocha, and M. M. Q. Simões, “Solketal production via solvent-free acetalization of glycerol over triphosphonic-lanthanide coordination polymers,” *Catalysts*, vol. 11, no. 5, p. 598, 2021.

[123] A. Perosa, A. Moraschini, M. Selva, and M. Noè, “Synthesis of the fatty esters of solketal and glycerol-formal: biobased specialty chemicals,” *Molecules*, vol. 21, no. 2, p. 170, 2016.

[124] Z. Gui, N. Zahrtmann, S. Saravanamurugan et al., “Bronsted acid ionic liquids (BAILs) as efficient and recyclable catalysts in the conversion of glycerol to solketal at room temperature,” *ChemistrySelect*, vol. 1, no. 18, pp. 5869–5873, 2016.

[125] R. Zhou, Y. Jiang, H. Zhao, B. Ye, L. Wang, and Z. Hou, “Synthesis of solketal from glycerol over modified SiO2 supported p-phenolsulfonic acid catalyst,” *Fuel*, vol. 291, pp. 120207–120209, 2021.

[126] G. Arun, M. Ayoub, U. Deshannavar et al., “Valorization of solketal synthesis from sustainable biodiesel derived glycerol using response surface methodology,” *Catalysts*, vol. 11, no. 12, pp. 1537–1623, 2021.

[127] H. Serafim, I. M. Fonseca, A. M. Ramos, J. Vital, and J. E. Castanheiro, “Valorization of glycerol into fuel additives over zeolites as catalysts,” *Chemical Engineering Journal*, vol. 178, pp. 291–296, 2011.