CHAPTER 2

Literature Review

2.1 Introduction

This chapter deals with the various literature on solketal synthesis from the glycerol derived from the trans-esterification process as a waste using heterogeneous acid catalysts. Various research literature has been focused on the characterization of catalysts and exploring the relationship between these catalysts and their catalytic activity in glycerol acetalization reactions.

2.2 Glycerol production and consumption

Glycerol is produced as a byproduct during the trans-esterification process using edible or non-edible oils. Approximately 10 wt. % of crude glycerol produced as a waste for every 100 wt.% of biodiesel production. The United States and Brazil are the fastest-growing countries, and they are currently increasing their production at a quicker rate than Europe. They are expected to achieve significant improvement in the near future. By the year 2025, experts suggested that biodiesel has the potential to replace 30 % of on-road diesel used in Brazil, Europe, India, and the U.S. [63]. Biodiesel, being cleaner, more environment friendly, and renewable in nature, serves as a valuable fuel for petro-diesel engines. According to the B2 policy of the United States, 2 % of petro diesel was replaced by biodiesel, and approximately 363 million kg of glycerol was added to the market by 2012. The world glycerol market size will be increased by USD 3.5 billion by 2027 by 4 % CAGR [64]. The large surplus in the current glycerol market represents a waste that must be eliminated or used to economize biodiesel production. With the growing countries and people's standard of living improved, the demand for high-quality glycerol increases. This glycerol, utilized in personal care products, cosmetics, and pharmaceuticals, is anticipated to drive the glycerol market throughout the forecast period. The Asia Pacific regions stand out both as significant consumers and exporters of glycerol, with Indonesia and Malaysia being the exporting nations. Several countries like

Russia, Germany, Netherlands, and Denmark are making a significant contribution to the largest glycerol imports within the region. According to the Department of Energy (DOE), glycerol serves as a significant building block for future biorefineries [65,66]. Enhancing the valorization of glycerol into various value-added products has the potential to reduce the net production cost of the B100 type of biodiesel from US$ 0.63 per liter to US$ 0.35 per liter, as illustrated by the Economic forecast [67].

2.3 Catalytic conversion of glycerol to value-added products

Glycerol is a significant byproduct that has three distinctive hydroxyl groups, which make it versatile and used as a substrate for various chemical reactions. Glycerol is non-toxic to humans as well as the environment, bio-degradable, and bio-sustainable in nature. Because of glycerol's multifunctional structure and properties, it can be valorized by different pathways. Moreover, the conversion of glycerol to various value-added products decreases not only the surplus of glycerol but also cleans the environment by synthesizing the energy sources. On the basis of these aspects, catalysts play a crucial role in achieving the green chemical technology for the activation and utilization of glycerol. Both homogeneous and heterogeneous catalysts have been utilized in glycerol conversion to various value-added products. Consequently, a series of innovative catalytic approaches have been employed over various reactions for glycerol conversion [68,69].

2.4 Catalytic approach towards solketal synthesis

Solketal is one of the versatile products among various value-added products that are synthesized from glycerol. Various literature has been reported for the acetalization of glycerol condensation with acetone in the presence of acidic heterogeneous catalysts to date. The solketal synthesis is catalyzed by both homogeneous and heterogeneous catalysts. The main advantage of the acetalization reaction of glycerol is that it requires a very simple reaction setup and a green process, and it is also applicable to both labs as well as industrial scales on the basis of the economic point of the scale. Ghosh et al., 2020b [70] synthesized the GS-SO_3H catalyst for acetalization of glycerol with acetone. This catalyst provided 91 % glycerol conversion at the optimized reaction condition of room temperature for 4 h of reaction duration. da Silva et al., 2020 [71] reported $Fe(NO_3)_3.9H_2O$ catalyst for solketal synthesis via acetalization of glycerol with acetone and obtained 90 % of glycerol conversion at the optimized reaction conditions of 25 ^oC for 1 h. A high molar ratio of acetone was required for the catalyst activity. The catalyst was efficient for glycerol conversion but reusable only for three consecutive cycles in the reaction process. Hidalgo-Carrillo et al., 2021[72] reported P-25 and Amberlyst-15 for the solketal synthesis. P-25 showed the glycerol conversion on optimizing reaction parameters like temperature, glycerol to acetone molar ratio, and time and observed that at 30 ^oC, 1:13 glycerol to acetone molar ratio, and 24 h, at 30 ^oC the glycerol conversion reached up to 97 %, while Amberlyst-15 showed 64 % of glycerol conversion at the same optimized reaction condition. However, these reactions take longer periods of time to achieve conversion. Vannucci et al., 2021 [48] **s**ynthesized the sulphonated zirconia and applied glycerol acetalization with acetone. The catalyst obtained 80 % of glycerol conversion at the optimized reaction condition of temperature 40 ^oC for 1h of reaction time. Although the catalyst was effective for glycerol conversion, the stability of the catalyst was low and reusable up to 4th run. The deactivation of the catalyst could be due to the leaching of sulfur from the catalyst's surface after a four-catalytic cycle in an acetalization reaction. Timofeeva et al., 2017 [73] prepared Montmorillonite clay that was modified with nitric acid to increase the acidity for the acetalization of glycerol. The synthesized catalyst showed 54 % glycerol conversion in the absence of any solvent at the optimized reaction condition of 50 ^oC temperature for 30 minutes of reaction time. However, the same reaction was applied in the presence of CH_3CN solvent, and the catalyst obtained 94 % of solketal. Although the catalyst has sufficient activity in the conversion of glycerol, the reusability of the catalyst was stable up to 3rd reaction cycle. The deactivation after the 3rd cycle was due to the leaching of the active Al^{3+} cation from the octahedral sheets when the concentration of HNO_3 acid was increased. Ana Cornejo et al. 2019 [74]employed solid acid commercial ion exchange resin for solketal synthesis in solventless conditions. They proposed a mathematical model for upscaling at bench size from a laboratory scale. Using this model, kinetic and thermodynamic parameters were obtained at suitable optimized reaction conditions. By applying this reactor model, the authors proposed several reaction mechanisms and explained each adsorption mechanism of the catalyst, and predicted the performance of glycerol acetalization reaction in varying the temperature range from 313 K to 333 K. They also compared the obtained glycerol conversion between the predicted value from model and the experimental value. Temperature also plays a vital role in this process; the chemical equilibrium constant can be influenced by increasing temperature and vice versa. Several homogeneous acid catalysts showed deactivation in solketal syntheses, like HCl, H_2SO_4, H_3PO_4, $SnCl_4$, and $Sn(OAc)_2$. When the catalyst was reused, the conversion of glycerol decreased dramatically after the first run in acetalization because of the conversion of all available acidic sites of the catalyst to their corresponding solketal [75]. Xuewen Li et al. 2019 [76] reported zirconyl chloride modified with H_3PO_4 solution was a very efficient catalyst for glycerol acetalization using glycerol and acetone. This catalyst provides 84.5 % solketal yield with 85.7 % conversion at an optimized reaction condition of 50 °C for a 3 h duration. They found that the catalyst used was easily recovered and recycled to the 5th cycle, and the catalytic activity was highly comparable to the homogeneous H_3PO_4. The authors also explained the effect of calcination temperature on catalytic activity. On increasing the calcination temperature of the modified catalyst from 200 °C to 600 °C, the conversion % of glycerol decreases could be attributed to the surface density of acid site id decreases. Similarly, another catalyst, SnO_2, promoted with W and Mo, was suggested by Mallesham et al., 2012 [61] for solketal synthesis. These catalysts were also found to be more efficient for solketal synthesis. The authors found that the conversion of glycerol with SnO_2 and promoted WO_3/SnO_2 and MoO_3/SnO_2 were 51, 67, and 75 %, respectively, at the same optimized reaction condition. It was observed that MoO_3/SnO_2 showed high catalytic activity in glycerol acetalization reaction as compared to others, which could be attributed to the availability of higher amounts of surface acidic sites and surface area. $SnCl_2$, being one of the homogeneous acid catalysts, was used in glycerol acetalization with acetone, as reported by Menezes et al., 2013 [77]. These catalysts provided 81 % glycerol conversion with 98 % selectivity towards solketal at the optimizing reaction parameters like acetone to glycerol molar reaction, reaction temperature, and time. These catalysts give a good conversion and show better recyclability up to the 4th catalytic cycle in comparison to other reported catalysts. They also suggested a reaction mechanism to explain the synthesized product yield by applying this homogeneous acid catalyst. Bronsted acid ionic liquids (BAILs) were also utilized for the solketal synthesis by Gui et al., 2016 [78]. Using this homogeneous acid catalyst, the desired product was isolated from the reaction matrix in quantitative yield and recyclable 4th catalytic cycle without significant loss in glycerol conversion and product selectivity. Similarly, Silva et al., 2015 [79] synthesized solketal using solvent-free medium hetero-poly acids and obtained 90 % of glycerol conversion. This homogeneous acid catalyst also showed good catalytic activity toward solketal synthesis and could be reused in at least three catalytic cycles. Metals (Ni, Co, or Pt) modified with vanadium oxide nanotubes (VOx-NTs) were tested for the synthesis of solketal by G. Luis et al., 2019 [52] using glycerol and acetone. The authors selected these suitable catalysts for glycerol acetalization; among them, NiVOx-

NT could play a key role in solketal production, which is attributed to its high thermal stability and water-tolerant properties. The CoVOx-NT and PtVOx-NT were not selected as a good candidate for glycerol acetalization could be ascribed to the deactivation during the reaction due to the lack of thermal stability. They also performed the reaction in three different carbonyl compounds, namely, furfuraldehyde, benzaldehyde, and butyraldehyde, in order to examine the influence of these substrates on glycerol acetalization. The results confirmed that acetone gives the highest glycerol conversion compared to other substances. Li et al., 2018 [80] synthesized a layered double hydroxide (LDH) with a different ratio of Co/Al via the coprecipitation method. They synthesized $Co[II](Co[III]_xAl_{2-x})O_4$ catalysts by varying the molar ratio of Co and Al and applied them in the solketal synthesis under mild conditions. They also investigated the correlation between the catalyst's acidic surface density and catalytic activity and found that the activity of LDH was directly influenced by the acidic density. Authors found that the 69.2 % glycerol conversion with 98.6% selectivity at optimized reaction conditions of 130 ^oC for 3 h over $Co[II](Co[III]_{1.25}Al_{0.75})O_4$. Recently, some acid-modified catalyst was reported for efficient glycerol conversion. Sulfonated modified catalysts like SO_4^{-2}/CeO_2-ZrO_2 as an efficient heterogeneous acid catalyst applied in glycerol acetalization were reported by Kulkarni et al., 2021 [50]. They got a good conversion of glycerol at 100 ^oC with 9 h of reaction time. Laskar et al., 2018 [57] synthesized a mesoporous p-phenol sulfonic acid formaldehyde resin by the condensation polymerization of p-phenol sulfonic acid with formaldehyde and using it for solketal synthesis. They obtained 97 % of glycerol conversion with 100 % selectivity by using this catalyst. Some waste-based modified acid catalysts were also used in solketal synthesis. Goncalves et al., 2016 [81] synthesized an acidic carbon-based catalyst for glycerol acetalization derived from biodiesel waste. This catalyst was synthesized by varying the different mass ratios of glycerin: sulfuric acid at

184 ^{o}C. The acid functionalized group and acidity of the catalyst were enhanced by increasing of glycerol: sulfuric acid ratio. They got 80 % of glycerol conversion with 95 % solketal selectivity at optimized reaction condition of a 1:4 molar ratio of glycerol to acetone, at room temperature for 120 min. The synthesized catalyst was found to be stable up to the 5th catalytic cycle, providing 76 % of solketal yield. Similarly, other waste-derived catalysts like C-SO_3H catalyst were synthesized by Saikia et al., 2022 [82]. A sulfonated cellulose-based heterogeneous acid catalyst was synthesized by cellulose modified with concentrated sulfuric acid in hydrothermal conditions. Authors applied this catalyst in microwave-assisted conditions for the acetalization of glycerol and got 97.1 % of glycerol conversion at 70 ^{o}C for 10 min. The catalytic activity of the catalysts was retained even after the 5th catalytic cycle, which makes the catalyst more efficient for solketal synthesis. Ao et al., 2023 [83] also synthesized a sulfonic acid-functionalized aromatic carbonaceous catalyst for solketal synthesis. This carbonaceous heterogeneous acid catalyst was synthesized by using glucose modified with sulfuric acid applied for glycerol acetalization under microwave irradiation conditions. They got 98.1 % of glycerol conversion with 100 % selectivity of five-membered solketal at 70 ^{o}C for 10 minutes of reaction time and a 1:5 glycerol to acetone molar ratio. The recovery of the catalyst was surveyed over the 6th catalytic cycle with 98.1% of solketal yield.

Here are a number of the reports published regarding the application of transition metal-based heterogeneous acid catalyst modified with sulfonation to enhance the surface acidity of the catalyst in the acetalization reaction of glycerol with acetone, despite its remarkable fundamental properties. Transition metals are extensively studied for catalytic application due to the presence of their exceptional thermal stability, relatively high surface area, biological and chemical activity, efficient thermal conductivity, and distinctive redox properties. They have the tendency to catalyze various reactions, including acylation, cracking, alkylation, isomerization of alkane, esterification, transesterification, and dehydration of alcohol. In this study, we examined the catalytic performance of synthesized heterogeneous acid catalysts based on transition metals in the solketal synthesis, and we also elucidated the several characterization techniques for the catalyst that contribute to its effective activity in glycerol acetalization. The primary objective of our research work was to synthesize a catalyst based on transition metals and apply them for solketal synthesis by acetalization reaction of glycerol with acetone. Furthermore, we also investigated the effect of active metal sites on transition metal support in glycerol acetalization, as well as the impact of catalytic activity after modification on solketal synthesis.

2.5 Reaction mechanism involved in glycerol acetalization reaction

A plausible reaction mechanism for glycerol acetalization was proposed by using glycerol and acetone in the presence of a heterogeneous acid catalyst. This reaction mechanism follows the Langmuir-Hinshelwood (LH) mechanism on the basis of previously reported literature. This reaction mechanism has been proposed in various steps, as shown in Figure 2.1. Firstly, the molecule of glycerol and acetone diffused onto the catalyst's surface, which adsorb by the catalyst pore. In 1st step, the acetone carbonyl group is protonated by the acidic sites of the catalyst, which increases the electrophilicity of carbonyl's carbon. 2nd step involves the attack of a lone pair of -OH group of glycerol, which acts as a nucleophile on the most electrophilic carbon center. 3rd step is accompanied by the deprotonation with the formation of the hemiacetal intermediate. This hemiacetal is unstable and further attacks by the -OH group of glycerol via SN_2 nucleophilic substitution reaction with the elimination of water molecules. If the adjacent -OH group attacks on the tertiary intermediate carbon, the five-membered cyclic ketal (solketal) is produced. Whereas if the terminal -OH group attacks on this intermediate, then the six-membered cyclic ketal is produced by the cyclization process. The synthesized five-membered solketal is kinetically more stable than the six-membered acetal. Thus, this reaction normally favors solketal production [60,84,85]

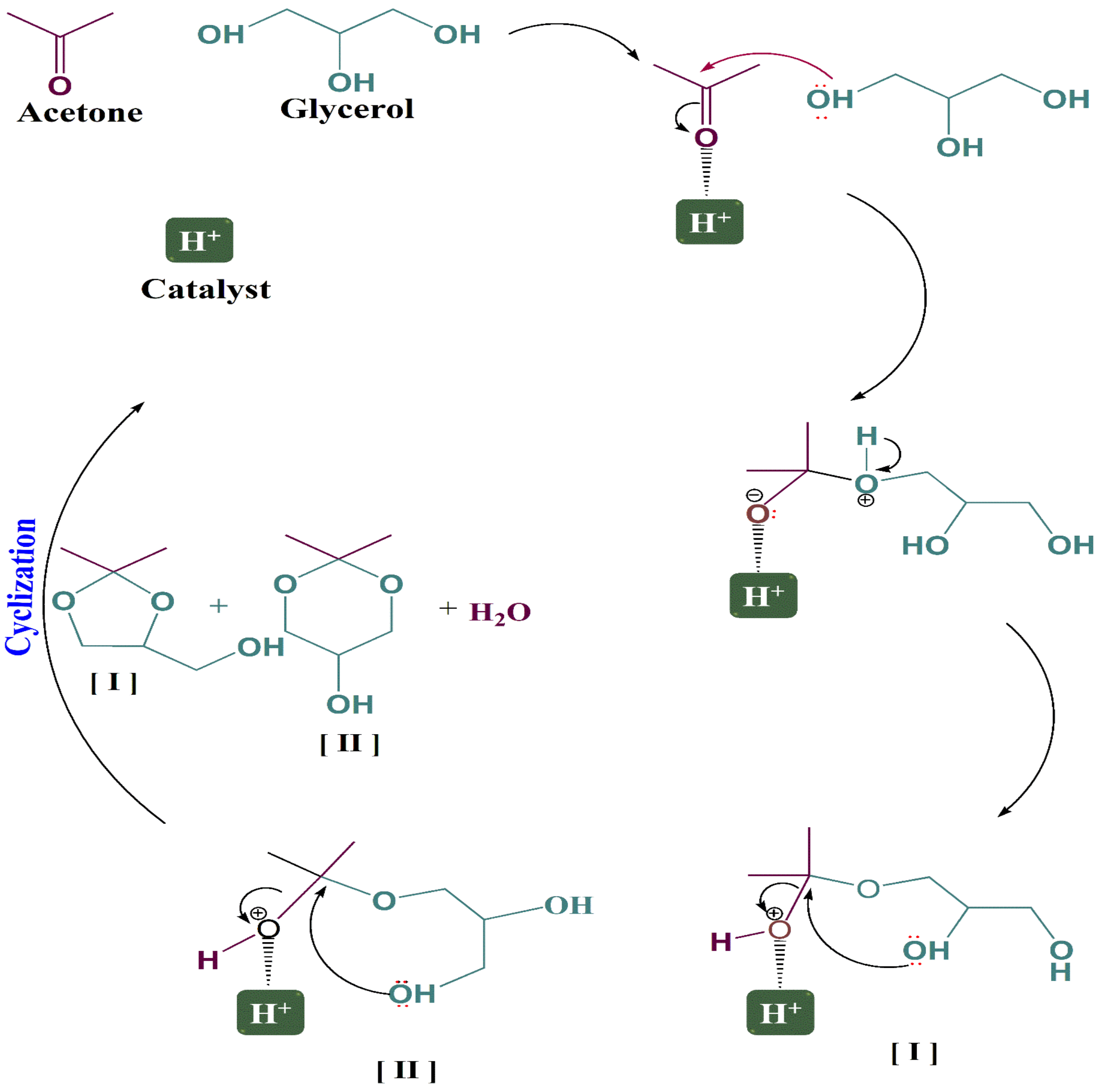

Figure 2.1 Plausible reaction mechanism for solketal synthesis using acid catalyst