Glycerol to Solketal for Fuel Additive: Recent Progress in Heterogeneous Catalysts

Is Fatimah [1,*] , **Imam Sahroni [1]** , **Ganjar Fadillah [1]** , **Muhammad Miqdam Musawwa [1]** ,
Teuku Meurah Indra Mahlia [2] and **Oki Muraza [3,*]**

[1] Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Islam Indonesia,
   Jl. Kaliurang Km 14, Sleman, Yogyakarta 55584, Indonesia
[2] School of Information, Systems and Modelling, Faculty of Engineering and Information Technology,
   University of Technology Sydney, Sydney, NSW 2007, Australia
[3] Center of Research Excellence in Nanotechnology and Chemical Engineering Department,
   King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
*   Correspondence: isfatimah@uii.ac.id (I.F.); omuraza@kfupm.edu.sa (O.M.)

Abstract: Biodiesel has been successfully commercialized in numerous countries. Glycerol, as a byproduct in biodiesel production plant, has been explored recently for fuel additive production. One of the most prospective fuel additives is solketal, which is produced from glycerol and acetone via an acetalization reaction. This manuscript reviewed recent progress on heterogeneous catalysts used in the exploratory stage of glycerol conversion to solketal. The effects of acidity strength, hydrophobicity, confinement effect, and others are discussed to find the most critical parameters to design better catalysts for solketal production. Among the heterogeneous catalysts, resins, hierarchical zeolites, mesoporous silica materials, and clays have been explored as effective catalysts for acetalization of glycerol. Challenges with each popular catalytic material are elaborated. Future works on glycerol to solketal will be improved by considering the stability of the catalysts in the presence of water as a byproduct. The presence of water and salt in the feed is certainly destructive to the activity and the stability of the catalysts.

Keywords: fuel additives; biodiesel; glycerol; solketal; solid acid catalysts.

1. Introduction

The exploration of renewable energy to supplement limited fossil fuels in the next few years is one the most concerned research topics. Among some renewable energy resources, biofuels are receiving intensive attention, especially for some countries with a large production of vegetable oils and bio-oils for biodiesel production [1–4]. Annual production and consumption of biodiesel is likely to increase significantly in the coming few years. Numerous sources of abundant edible and potential non-edible oils have been identified [5]. Regardless, this fact leads to increasing glycerol production as the byproduct of biodiesel conversion [2]. Due to the chemical process of the biodiesel production, the molar ratio of glycerol to the methyl ester is 3:1, or about 10% to 20% of the total volume of biodiesel produced is made up of glycerol. The rapid growth of biodiesel production has contributed much to the increasing glycerol production since it was reported that the worldwide production of glycerol increased from 7.8 billion liters in 2006 to 36 billion liters in 2018 [6,7]. This fact revealed that glycerol is an abundant renewable chemical feedstock in the world. The conversion of glycerol into more valuable chemicals is the best option to create a new market for glycerol and improve the sustainability of biodiesel production [7–14].

This mini review paper aims to emphasize the potential exploration of catalytic materials for the conversion of glycerol to solketal by analyzing recent papers, especially open literature from after 2010. Rahmat et al. (2010) [15] wrote an overview of glycerol conversion to fuel additives, with an emphasis on reaction parameters (catalyst, reactant, temperature, and reaction time). In the range of 2009 to 2018, Cornejo et al. [16] wrote a review in 2017 on glycerol valorization to fuel additives over different co-reactants. These included second feeds, such as formaldehyde, acetaldehyde, butanal, and acetone, and many others. Nanda et al. [17] published a review on solketal as a fuel additive, with an emphasis on the historical and future context. This paper also summarized the effect of acidity, reactor models, kinetics and reactor kinetics, and the daily procedure to use glycerol to solketal.

Many scenarios were conducted for the conversion of glycerol to different value-added chemicals, such as propane-acrolein, 1, 3-diol, propane-1,2-diol, acetal or ketal, polyols and polyurethane foams, glycerol carbonate, etc. [10,11,18]. Table 1 shows that among these glycerol conversions, the conversion of glycerol to solketal by acetalization is an interesting route. Solketal is one of the glycerol acetalization products together with glycerol acetal and glycerol formal (GlyF). Similar to other acetalization products, solketal can be used directly as a fuel additive for the reduction of soot and gum formation [19]. Solketal addition to a gasoline blend showed better fuel properties with a higher octane number [19]. Other applications of solketal are in solvents, inks, pharmaceuticals, and paints [20].

Table 1. Different conversion routes from glycerol to value-added products.

Conversion	Catalyst	Results	Ref
Etherification	Li/clay	Diglycerol isomer was also increased from 35% to 55% while the selectivity to aa isomer was decreased from 65% to 35%	[21]
Conversion glycerol to allyl Alcohol	K/Al_2O_3-ZrO_2-FeO_X Alkali metals supported to ZrO2-FeOx	Improvement in conversion With the increase of the K content in the catalyst, allyl alcohol yield increased up to 27%-C	[22]
Allyl alcohol	ZSM-5-supported iron catalysts	The prepared catalyst performed better for allyl alcohol production as compared to catalysts synthesized by other methods	[23]
Conversion alcohol to glycerol carbonate	$Mg_{3-x}Al_1Cu_x$	Transesterification of glycerol to glycerol carbonate (GC) increased to 96% of yields	[24]
Acetalization glycerol with acetone	MoPO supported to SBA-15	A 40% MoPO/SBA-15 showed a conversion of 100% and selectivity of 98%	[25]
Acetalization of glycerol with butanal	BEA zeolite with the ratio Si/Al of 40	Showed conversion of 88% and selectivity 80% of five member rings acetal (2-propyl-1,3-dioxolan-4-yl)methanol	[26]
Glycerol etherification with benzaldehyde	Cationic acidic resin	Achieving conversion of 93% and selectivity above 80% of 2-phenyl-1,3-di-oxan-5-ol	[27]
Acetalization of glycerol with mono-substitute benzaldehyde	MoO_x/TiO_2-ZrO_2	Glycerol conversion to 1,3-dioxolane (74%) within 30 min	[28]
Acetalization of glycerol with acetone	MoO_3 and WO_3 supported to SnO_2	A 71% glycerol conversion and a 96% solketal selectivity were achieved.	[29]

As shown in Table 2 and Figure 1, different types of catalyst materials were reported for the solketal production consisting of zeolites, clays, resins, heteropolyacids, and others. Each catalyst has both advantages and drawbacks. A homogeneous catalyst, such as H_2SO_4, offers high activity, however, these homogenous catalysts are corrosive, not recyclable, difficult to separate, and considerably more expensive. Similarly, chloride, such as tin chloride ($SnCl_2$), is also unwanted due to its corrosion tendency [30]. Reusability is also an important part of studies. Reusability is a factor which is studied as a typical sustainable principle. The basic mechanism of the metal salt catalysis is a nucleophilic attack by the hydroxyl group of glycerol to the carbocation obtained from the protonation step, resulting in the formation of the intermediate, followed by a water elimination step. The carbocation is produced from the Lewis or Brønsted acid sites, which activates the ketone carbonyl group through a protonation step (i.e., Brønsted acids) or polarization.

However, homogeneous catalysts are not considered as environmental-friendly for the reaction system. Another challenge in the utilization of heterogeneous catalysts in solketal production is

the byproduct (water) formed during the reaction, which induces a reversible reaction. Heterogeneous catalysts are regenerated easily and are more easily handled. Many resin catalysts exhibited excellent conversion of glycerol to solketal and selectivity, where the best catalytic performance was obtained by amberlyst. However, it is not feasible for a higher scale of production due to the limitation of thermal stability, so it is not easy to regenerate. The higher thermal stability can be found in hierarchical zeolite. The highest conversion of glycerol to solketal of 72% and the selectivity of 72% are reached by using H-Beta (BEA framework) under the condition of 60 °C, stirring at 700 rpm, 5% of catalyst, and molar ratio of glycerol:acetone of 1:4 for H-BEA. Within the zeolite materials, MFI zeolite showed 80%, which is a lower catalytic activity in comparison with amberlyst, but with almost 100% selectivity. The lower conversion is due to the relatively narrow channel size that affects the transport of the reactant carried out and the shape selectivity.

Table 2. Classification of heterogeneous catalysts for solketal production.

Others	Heteropolyacid	Resin	Meso-SiO$_2$	Double Layer Hydroxide and Clay	Zeolites
Co/CNT	Si-W (tungstosilisic)	Amberlyst	KIT-6	ZrO$_2$ dolomite	Zeolite X
Na-lignosulfonate	HMQ-SJW	Cat. Ex.	Me-SBA-5J	Nb, AlOx	VnOx/FER MOR
SnF$_2$	H$_3$PW12040	Amberlyst-46	Hf-SBA-15	Nb oxy OH	BEA
Ionic liquid		Amberlyst-46	Mo-SBA-15	COK-S	Hierarchical
Carbon		KU-2-8	Sn TUD-1	MgLDH	BEA, MOR
		Lewatit GF101	Al-MCM-41	Montmorillonite	ZSM-5 (MFI)
		Sulfonic	Ga-MCM-4		DeAl BEA
		Amberlyst-35			Acidity BEA

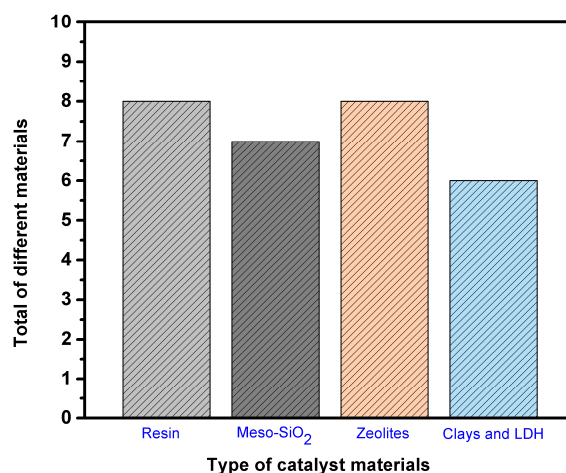**Figure 1.** Popularity of different types of catalytic materials for solketal production from 2014 to 2018. (Source: Web of Knowledge, https://www.webofknowledge.com, November 2018).

2. Glycerol-to-Solketal Over Resin Catalysts

Overall, the most important properties of solid acid catalysts for the conversion glycerol to solketal production was the Brønsted acidity of solid acids [31]. The conversion of glycerol to solketal with resin catalysts has been carried out [32–36]. Table 3 summarizes the conversion of glycerol to solketal over resin catalysts. A typical resin catalyst (i.e., amberlyst) catalyzed the reaction of glycerol with acetone to produce above 80% of the glycerol conversion. Guidi et al. [36] reported that a resin, amberlyst-36, which was applied at different reaction temperatures from 25 to 70 °C, was an excellent catalyst to convert glycerol with a conversion of 85% to 97% to solketal with a selectivity of 99%. The catalyst is also active at lower pressures with similar reaction parameters either in pure glycerol or in an equimolar reactant. According to some references, the high conversion was influenced not only by the surface acidity but also by the resin structure. Moreover, the surface acidity was an important parameter that played a crucial role in improving the selectivity and the conversion in the production of solketal.

Although amberlyst-46 and amberlyst-36 is a similar material, both types of resins have a different acid capacity and structure morphology. Furthermore, all resins showed good selectivity to solketal (>80%), and the important catalytic parameter of the resin to conversion glycerol is the acid capacity (oversulfonated resin). With the highest acid capacity (sulfonic acid), these catalyst materials can improve not only the selectivity to solketal production but also the conversion of raw glycerol to above 90%. Another important thing to be highlighted as a limitation of the catalyst activity is the presence of NaCl as a poison for the surface acidity, which is possibly due to the impurities in glycerol.

Table 3. Glycerol-to-solketal over resin catalysts.

Source	Catalyst	Condition	Conversion	Selectivity to Solketal	Remark	Ref
Glycerol and Acetone	Amberlyst-15	50 °C	92%	96%	Glycerol:acetone = 1:2, 7.0 g of amberlyst-15 in 96 min	[32]
Glycerol and Acetone	Amberlyst-46	60 °C	84%	97%	%1 (w/w) catalyst, 30 min	[33]
Glycerol and Acetone	Amberlyst DPT-1	70 °C	97%	98%	Glycerol:acetone = 1:2 at ambient pressure	[34]
Glycerol and Acetone	DT-851 sulfonic acid resin	58 °C	95%	99%	Glycerol:acetone = 1:20, catalyst DT-851 sulfonic acid resin dosage is 5% (wt., calculated by glycerol), reaction time is 2 h.	[35]
Glycerol and acetone	Amberlyst-36	25 °C	85%–97%	99%	At 10 barr and 25 °C, A36 was a highly active catalyst allowing good-to-excellent conversion (85%–97%) and selectivity (99%) when either pure or wet glycerol was used as a reagent.	[36]

Note: glycerol to the second reactant ratio was presented as molar ratio.

3. Glycerol-to-Solketal over Mesoporous Silica

Koranyi et al. [37] reported the superiority of hafnium and zirconium modified TUD-1 as superior catalysts for the conversion of glycerol to solketal. These two catalysts (Hf-TUD-1 and Zr-TUD-1) were more active than Sn-MCM-41 and Al-TUD-1. The Zr and Hf-TUD-1 are examples of active metal-modified mesoporous silica in which Hf and Zr are in the framework. Their activity was higher than FAU(USY) and Al(TUD-1). The highest conversion of glycerol to solketal was more than 50%. The catalytic activity was a function of (i) the number of acid sites, (ii) the presence of mesopores, (iii) the existence of a large surface area, and (iv) the hydrophobicity of the catalyst [38]. The later, the hydrophobicity of the catalyst, was crucial to prevent the hydrolysis of solketal [37–41]. According to Table 4, Cs 2.5/KIT-6 catalyst was one of the best catalysts for the conversion of glycero-to-solketal [42]. KIT-6 was selected because of its large surface area (600–1000 m^2/g), active sites, and accessible pores [42].

Numerous references reported that mesoporous silica catalysts have the advantage of high stability in the conversion of glycerol to solketal, resulting in products with a relatively large percentage of conversion (95%) and selectivity to solketal (98%) [37,42–46]. The mesoporous structure with an activated surface by sulfonic acid might be applied efficiently for the conversion of glycerol to fuel additive [37,43,47]. A sulfonic acid-functionalized mesoporous polymer (MP-SO$_3$H) contains a high acidity surface (1.88 mmol/g). The surface acidity of catalytic materials can accelerate the formation products of solketal via ketalization reactions as shown in Figure 2.

Table 4. Glycerol-to-solketal over mesoporous silica.

Source	Catalyst	Condition	Conversion	Selectivity to Solketal	Remark	Ref
Glycerol and Acetone	Cs 2.5/KIT-6	25 °C	95% in 15 min	98%	Glycerol:acetone = 1:6, catalyst loading was 5 wt.%.	[42]
Glycerol and formaldehyde	Propylsulfonic Acid Functionalized SBA-15 Mesoporous Silica	90 °C	91.5 in 8 h	98%	Glycerol:formaldehyde = 1:1.5 with 4 wt.% catalyst loading	[43]
Glycerol and Acetone	arenesulfonic acid-functionalized silica	70 °C	84% in 30 min	81%	Glycerol:acetone = 1:6	[44]
methyl acetate to glycerol	Sulfonic acid-functionalized mesostructured SBA-15 silicas	170 °C	99.5% in 4 h	74.2%	Glycerol:methyl acetate = 1:50 and catalyst loading (7.5 wt.% based on glycerol)	[45]
Glycerol and acetone	A sulfonic acid-functionalized mesoporous polymer (MP-SO$_3$H)	30 °C	94%	98.5%	The MP-SO$_3$H catalyst performed better than other conventional solid acid catalysts	[46]
Glycerol and acetone	Zr-TUD-1	80 °C	64%		Glycerol:acetone = 1:2, 25 mg of catalyst, at room temperature, for 6 h.	[37]
Glycerol and acetone	Hf-TUD-1	80 °C	65%		Glycerol:acetone = 1:2, 25 mg of catalyst, at room temperature, for 6 h.	[37]

Note: glycerol to the second reactant ratio was presented as molar ratio.
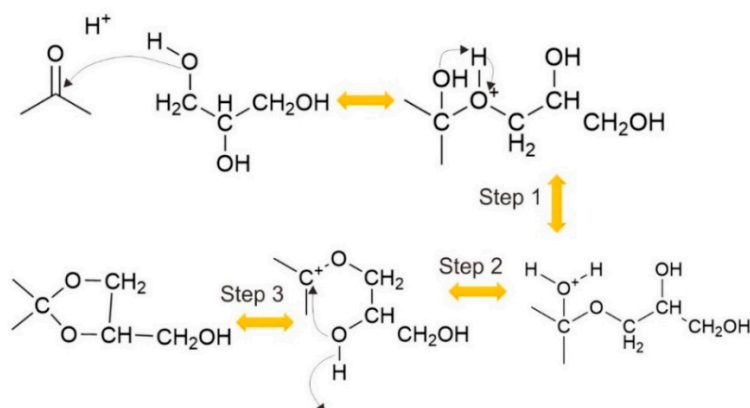
Figure 2. Scheme of mechanism for the ketalization reaction of glycerol and acetone.

4. Ketalization of Glycerol over Clay Minerals

Malaya et al. [17,48] studied different clay-based catalysts with different acid strengths ranging from 0.12 to 5.7 meq/g [17]. The results show that a stronger acidity improved the conversion of glycerol up to ca. 80%. As shown in Table 5, solketal production from glycerol used two different sources, namely acetone or formaldehyde over solid acid catalysts [49–52]. Based on the conversion of glycerol and selectivity to solketal, the clay catalyst which showed the optimum results was reported by Timofeeva et al. in a batch reactor with activated catalyst by nitric acid of 0.5 M [53]. In the activated K10 montmorillonite by acid solution, this impact causes an increasing rate of reaction with the acid site of the material. It is well-known that the acid activation of natural montmorillonite with nitric acid can change the structure of montmorillonite (leaching of Al^{3+} cations from the octahedral to increase the surface area and microporosity of catalyst materials) [54–56]. The reaction of solketal production is shown in Figure 3. The use of formaldehyde as the major source of solketal production has a lower conversion value (only 83% glycerol conversion), with the K10 montmorillonite used as a catalyst. It may be due to the formation of the hemiacetal or hemicetal via two different pathways. The reaction between glycerol and acetone is preferred as it produces a more stable intermediate,

hemicetal compound, with a tertiary carbenium ion [37]. While, in the reaction between glycerol with formaldehyde, the produced hemiacetal formation is not a stable carbenium ion. Thus, the conversion value for the glycerol-formaldehyde system is relatively small as compared to the reaction where acetone is used as a co-reactant [57–59].

Table 5. Glycerol-to-solketal over clay minerals.

Source	Catalyst	Condition	Conversion	Selectivity to Solketal	Remark	Ref
Glycerol and acetone	Montmorilonite modified by HNO$_3$	T = 25 °C	94%	95.4%	Glycerol:acetone = 1:4, 10 mg of catalyst, time at 10 min	[53]
Glycerol and benzaldehyde	K10 Montmorillonite	T = 40 °C	83%	99%	Glycerol:benzaldehyde dimethyl acetal = 1:1.1 at 6 h.	[17]
Glycerol and acetone	K10 clays	T = 30 °C	87%	85%	Glycerol:acetone = 1:6, catalyst loading was 3 wt.% of total reactant weight, time at 120 min	[60]
Glycerol and formaldehyde	K10 Montmorillonite	T = 70 °C	80%	-	Glycerol: formaldehyde = 1:1.2	[61]
Glycerol and acetone	K10 Montmorillonite	T = 40 °C	69%	68%	Glycerol:acetone = 2:6, P=600 psi, The amount of catalyst in each run was determined by the selected weight hourly space velocity (WHSV) at 4 h^{-1}	[48]

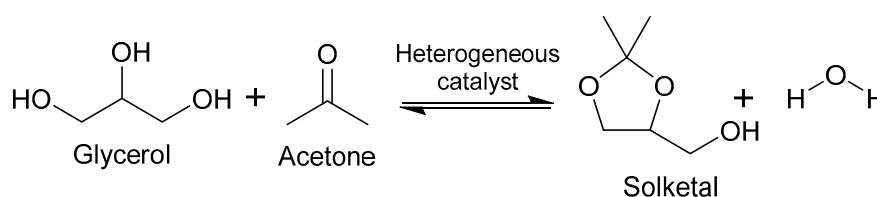Note: glycerol to the second reactant ratio was presented as a molar ratio.

Figure 3. Synthesis scheme of glycerol to solketal.

Koranyi et al. (2012) [37] reported the effect of water as an impurity in the acetalization of glycerol. The presence of water reduced the activity ca. 50% lower than the one with the model compound (pure glycerol). A high number of Brønsted and Lewis sites does not correspond directly to a high activity. Dealumination FAU and Al-TUD-1 with a high Brønsted and Lewis acidity were poor in the acetalization of glycerol [37]. Hydrophobic catalysts, such as hafnium and TUD-1 zirconium on TUD-1, are very prospective for glycerol to solketal. Ammaji et al. (2017) [62] also reported a similar observation, as the Zr-SBA-15 was the most active and selective catalyst.

5. Perspective on Ketalization of Glycerol over Hierarchical Zeolites

Dmitriev et al. (2016) [63] reported that zeolite beta was the most active solid acid catalyst as compared to amberlist-35 and cation-exchange resin (KU-2-8) [62]. The zeolite beta applied was a commercial one from zeolyst with SiO$_2$/Al$_2$O$_3$ of 25 and a zeolite beta made by Angarsk. Kowalska et al. [64,65] studied the effect of (i) different zeolite topologies (MFI, BEA, and MOR), (ii) Si/Al ratio from 9.2 to 25.8, and (iii) mesoporosity. Two parent MFI zeolites with different Si/Al were applied (Si/Al = 12 and Si/Al = 27) [64]. The hierarchical zeolites were obtained by desilication using 0.2 M NaOH and dealumination using citric acid (0.5 M) and nitric acid (0.5 M). The diffusion limitation of the parent zeolites was considered as the highest activity of the parent MFI was significantly lower than the one from the hierarchical MFI. A high selectivity (up to 100%) to solketal was obtained with an acetone:glycerol ratio of 1. A higher acetone to glycerol ratio was obtained over a higher acetone to glycerol ratio. Both desilication and dealumination are very effective in improving the catalyst stability of zeolite based catalyst [66–68].

Rossa et al. [69] conducted the kinetics study of acetalization of glycerol with acetone to produce solketal with optimization of the kinetics parameters. Zeolite beta with an Si/Al of 19 was applied to find the best parameters: (i) External mass transfer (stirring rate), (ii) temperature, (iii) catalyst amount, and (iv) glycerol to acetone ratio. The targeted goals were glycerol conversion and solketal selectivity. The experimental design for beta zeolite showed that the suggested reaction parameters are: Temperature at 60 °C, stirring rate of 700 rpm, catalyst loading of 5%, and glycerol to acetone ratio of 1:3. A higher acetone content will increase the conversion of glycerol [24,70]. However, an increase of the acetone to glycerol ratio will increase the exergy destruction rate due to a reduction in the rate of formation toward the product and a higher consumption of electrical exergy to the acetalization reactor [20,71–80].

Hierarchical zeolite shows excellent glycerol conversion and selectivity to solketal through acetalization reactions. The catalytic materials show a higher glycerol conversion (until more than an 80% glycerol conversion) as compared to other porous and non-porous catalysts due to a large pore size and easy molecular diffusivity. The enhancement of the catalytic activity of zeolites in glycerol acetalization, through the generation of a hierarchical porosity, has been applied by different authors as shown in Table 6. Based on the literature, the crystallite size was one of the most determining factors in the activity of hierarchical zeolite as a catalyst [64,81–85]. The smaller the crystal size of zeolite, the easier the diffusion of the reactant and products though the zeolite pores [73,86,87]. The pore structure of the zeolite can be changed through the dealumination and desilication processes. The process not only can change the mesopore materials but also can increase the catalytic activity (improving the accessibility and mass transfer on the surface) [88]. Hierarchical zeolites with different topologies, such as ZSM-5 (MFI) [67,89,90], beta (BEA) [81,91,92], and Y (FAU) [64], have also been used in the acetalization of glycerol, and the results show that smaller pores can produce high glycerol conversion and selectivity to selectivity (almost 100% selective for solketal formation). However, overall, all materials displayed very good catalytic performance when reacting equimolar mixtures of glycerol and acetone [37,39]. From the experiments on H-beta zeolite, it was found that dealumination resulted in a decrease of strong acid sites, thus decreasing the catalytic activity.

Table 6. Glycerol-to-solketal over hierarchical zeolite catalysts.

Source	Catalyst	Condition	Conversion	Selectivity to Solketal	Remark	Ref
Glycerol and acetone	hierarchical (micro-mesoporous) MFI zeolites (pore diameter 0.51–0.55 nm)	T = 70 °C	80%	100%	Glycerol:acetone = 1:1, catalyst in the amount of 1% related to glycerol.	[64]
Glycerol and acetone	H-B-1 zeolites	T = 28 °C (room temperature)	86%	98.5%	Glycerol:acetone = 1:2, catalyst amount = 5 wt.% referred to glycerol in 1 h.	[73]
Glycerol and acetone	Dealumination of BEA Zeolites	T = 30 °C	80%	100%	Glycerol:acetone = 1:1, t = 30 min, catalyst loading was 0.5 g	[72]
Glycerol and acetone	H-Zeolite (pore size 4.10 nm)	T = 70 °C	75%	92%	Glycerol:acetone = 1:3 were used with 0.05 g of catalyst for 2 h	[65]
Glycerol and acetone	H-BEA Zeolite	T = 60 °C	70%	97.9%	Glycerol:acetone = 1:4, catalyst amount was loading at 5 wt.% for 1 h.	[69]

6. Solketal Synthesis over Carbon/Activated Carbon-Based Catalyst

Considering the abundant source of biomass as carbon and activated-carbon precursor, activated carbons were functionalized with acid groups for solketal synthesis [93,94]. Some papers showed the excellent performance of activated carbon for catalyzing the conversion of glycerol to solketal (Table 7) and some of these exhibited a high activity and selectivity under green conditions (solvent-free conditions at a mild temperature). The high surface area of activated carbon preserves the higher surface acid sites by some modification, including acid, metal, and composite modifications [24,95–97]. Therefore, they are promising candidates as heterogeneous catalysts for the acetalization of acetone with

glycerol. From the utilization of acid functionalized activated carbon, the superior catalytic activity of the four acid-treated carbons was underlined as compared to the untreated activated carbon, confirming the importance of the higher number and strength of acid sites generated by the acid treatments. The catalysts were prepared by HNO_3 and H_2SO_4 treatment to activated carbon. The catalytic activity of the catalyst showed excellent performance due to the high conversion and selectivity at room temperature.

Table 7. Glycerol-to-solketal over carbon/activated carbon-based catalyst.

Source	Catalyst	Condition	Conversion	Selectivity to Solketal	Remark	Ref
acetone and glycerol	acid functionalized activated carbon	Room temperature, glycerol to acetone molar ratio of 1:4	97%	96%	The highest number and strength of acid sites generated by the acid treatments onto activated carbon gave better yield and selectivity	[39]
glycerol with benzaldehyde at	Graphene	100 °C and 120 °C	97%		Graphene catalyst produced 76% yield at 100 °C and 85% yield at 120 °C, selectivity 100%	[98]
acetone and glycerol	sulfonated carbon-silica-meso composite materials	acetone and glycerol molar ratio of 1:6, re- fluxed at 70 °C	82%	99%		[99]
acetone and glycerol	acidic carbon-based catalysts		80%	95%		[93]
acetone and glycerol	Ni-Zr supported on mesoporous activated carbon	Room Temperature glycerol/acetone ratio of 1:10	75%	100%	Conversion and selectivity are affected by glycerol/acetone ratio and temperature	[100]

From the acid-modified carbon catalyst, it was found that the presence of acid groups, mainly sulfonic groups, was the key factor for the improved catalytic performance. A similar pattern also appeared from the Ni-Zr support on the activated carbon [100], in which the active metal contributes by enhancing the catalyst acidity. Another factor affecting the catalytic activity was the higher total acid density, the large mesopore of the carbon structure, and the activity of the metals.

7. Perspective and Conclusions

This mini review highlighted the recent development on solid catalysts for the conversion of glycerol-to-solketal. The product is an additive for fuels, which are very useful to reduce GHGs and to improve the economic viability of biodiesel business [6,8,16,20,34,101–105]. Tailor-made heterogeneous catalyst for an optimal conversion of glycerol is developed and required. Five major heterogeneous catalysts were emphasized in this study: Resins, mesoporous silica, zeolites, clays, and activated carbons. The stability of catalysts is one of the main hurdles for the commercialization of glycerol to solketal. Even though the reaction temperature was considered as mild, the stability of most of the solid catalysts decayed in the presence of water as a byproduct and other impurities (NaCl, methanol) from the glycerol source. The deactivation rate is even higher when the raw glycerol (contaminated with water) was fed to the reactor [106–109]. Therefore, the viability of the commercial plant depends on (i) the source of feeds [110], (ii) availability of glycerol and other feeds, and (iii) cost of glycerol as the feed. In general, at least three main challenges were identified:

a.   The presence of water and impurities in the feed.
b.   The shift from the batch reactor to the fixed bed reactor.
c.   The presence of equilibrium offers other difficulties as higher acetone demand is expected. However, higher acetone to glycerol will lead to destructive instruments.

Acidity is agreed as an important properties of zeolite catalysts for glycerol to solketal. Strong acidity and medium hydrophobicity were expected in the design of the reactor. Based on some limitations of the catalyst performance, the utilization of raw glycerol directly will reduce

the stability of the catalyst. This review described how a better material should be designed for the optimum conversion of glycerol (and generally polyol) to solketal. Hydrophobic catalysts, such as hafnium/TUD-1 and zirconium/TUD-1, are very prospective for glycerol to solketal. Extended works on low aluminum mesoporous silica materials are expected in the coming years.

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