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Review

The Potential of Microwave Technology for Glycerol Transformation: A Comprehensive Review

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Abstract: Glycerol is a major by-product in biodiesel manufacturing, which accounts for around 10% of the biodiesel volume. A surplus of glycerol has led to the development of technologies for production of value-added products using glycerol as a raw material, following the "waste as a resource" strategy. Various techniques are available to carry out glycerol transformation, viz. carrying out processes under thermal heating, application of ultrasonic or hydrodynamic cavitation, microchannel technologies, etc. Microwave-assisted organic synthesis (MAOS) is a simple and innovative technology, which can be considered as a means of intensifying these processes. This review describes microwave irradiation as a valuable energy-efficient alternative to conventional heating for the production of value-added chemicals from glycerol via dehydration, hydrogenolysis, esterification, transesterification, etherification, and oxidation. In general, innovative and potential catalysts, approaches, and technologies are discussed and critically evaluated in terms of the possibilities and potential for further industrial implementation

Keywords: glycerol; organic synthesis; microwave irradiation; value-added product

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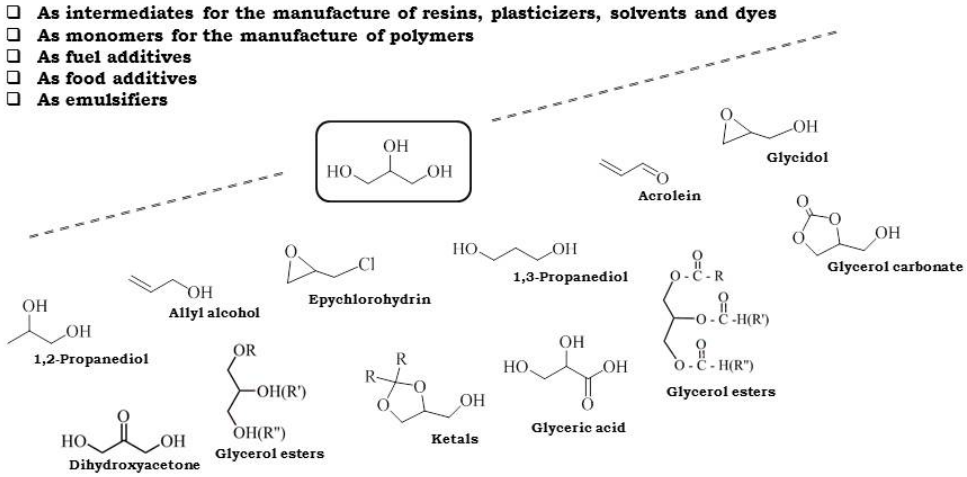
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1. Introduction

The availability of glycerol, a by-product in biodiesel fuel synthesis, has increased in recent years, making it a cost-effective option as a platform chemical for producing valuable derivatives. Thus, methods for the synthesis of acrolein, epichlorohydrin, 1,2- and 1,3-propylene glycols, glyceric and glycolic acids, dihydroxyacetone and glyceraldehyde, triacetin, and glycidol have already been developed on its basis (Scheme 1) [1–3]. To achieve a high yield of the desired product, the process often requires high temperatures and pressures. The use of microwave irradiation (MW) as a tool to perform a variety of catalytic transformations of glycerol has received much attention in recent years [4].

The use of MW energy instead of the thermal energy of heat carriers currently used in industrial installations allows users to reduce the energy costs, to significantly simplify technological schemes, to eliminate all processes and equipment associated with the preparation of a coolant, and also to reduce harmful emissions into the atmosphere. It should be noted that, until recently, the widespread use of microwave radiation in industrial production was hindered by the high cost of microwave field generators, but significant advances in engineering and technology have overcome this obstacle. In recent years, many papers have appeared in the literature on the conversion of glycerol into various chemical compounds using microwave irradiation. The data obtained in these works indicate the possibility of not only accelerating these processes but also controlling the rate and selectivity of the reaction. The purpose of this review is to analyze the literature published in

the last 10–15 years on the use of microwave irradiation for the catalytic transformation of glycerol.



Scheme 1. The main routes of the glycerol transformation to organics compounds.

2. General Aspects of Microwave Assistance as an Instrument for Organic Synthesis and Catalytic Processes

Nowadays, the energy of the electromagnetic field in the microwave range is increasingly being used to carry out chemical transformations of organic substances of various classes, including those of technological interest. The interest in such processes is due to the so-called "microwave effect", which is believed to be of key importance in increasing the efficiency and selectivity of chemical transformations. Microwave irradiation is non-ionizing electromagnetic radiation with a photon energy of ~10^{-5} eV (1 J/mol), the energy of a microwave quantum being insufficient to initiate chemical reactions by excitation and, moreover, by breaking chemical bonds. The use of microwave energy provides the following advantages: (a) homogeneous heating; (b) possibility of efficient heating of materials with low thermal conductivity; (c) high (more than 50%) coefficient of conversion of electrical energy consumed by the microwave generator into energy (heat) for heating reagents; (d) high degree of heating power density (up to 100 or more W/cm^3); (e) high final temperature of reagents (up to 1000 °C and higher); (f) high degree of controllability of the heating process [5].

The major advantage of microwave heating is the rapid transfer of energy by irradiation rather than by conduction or convection. This ensures rapid penetration of energy into the volume of materials transparent to microwave irradiation, i.e., instantaneous heating. The main effects related to the appearance of temperature gradients and non-equilibrium conditions are observed when a reaction medium or material consists of several phases with different microwave absorption coefficients. Microwave treatment allows reaction times to be reduced, yields and selectivities to be increased, and energy and reagent consumption to be reduced. The use of microwave energy pulses provides a further reduction in energy consumption.

Microwave heating is selective because different substances absorb microwave energy differently. This can lead to uneven heating of systems, such as only the catalyst or its active component. As a result, the reaction mixture may have a relatively low average temperature, while the chemical reaction itself occurs in areas with higher temperatures. In this case, due to the temperature gradient, non-equilibrium conditions arise when the resulting products enter the colder part of the reaction volume and are subjected to "quenching". This ensures that the product of the reaction, which may be more reactive than the starting compounds, does not undergo undesirable side reactions, thereby maintaining the overall selectivity to the target product. Microwave irradiation provides uniform heat supply through volume absorption, eliminating restrictions caused by low thermal conductivity of

dielectric media. Moreover, bulk heating results in no high temperature gradients within the sample. Efficient energy use is crucial in any technological process, including those in the chemical industry, to obtain target products. An increase in efficiency is a way to optimize such important economic indicators as material and energy intensity.

High-temperature endothermic reactions, such as pyrolysis, thermal and catalytic cracking of heavy hydrocarbons, dehydrogenation, and sintering of ceramics from various multicomponent oxides, are of significant interest to the chemical industry. These processes typically occur at temperatures ranging from 400–600 °C to 2000 °C and require the release of a large amount of energy in a small volume, making them energetic. The features described above of the microwave heating process, specifically the supply of heat to the reagents, enable the effective conduct of high-temperature endothermic chemical reactions.

Due to the rapid conversion of microwave energy into heat for reagent heating and the ability to turn the microwave power source on and off in a fraction of a microsecond, this process offers a high degree of controllability.

Efficient (i.e., with a high efficiency of converting irradiation energy into heat) microwave heating of samples is carried out in a reactor placed in a cavity resonator, which, as a rule, is a segment of a regular waveguide, limited at one end by a short connection diaphragm. Varying the dimensions of the resonator makes it possible to achieve a phase shift for electromagnetic waves propagating along the waveguide that is a multiple of 2π. Under this condition, a resonance phenomenon occurs, which is characterized by a high level of microwave energy accumulated in the resonator. Electromagnetic waves are reflected from the walls of the resonator and repeatedly pass through the sample. With each pass, the energy is partially absorbed in the sample, which is placed in the region of the maximum electric or magnetic component of the standing wave field in the resonator.

There are two types of reactor–resonators: with a high and low operating mode index (Figure 1).

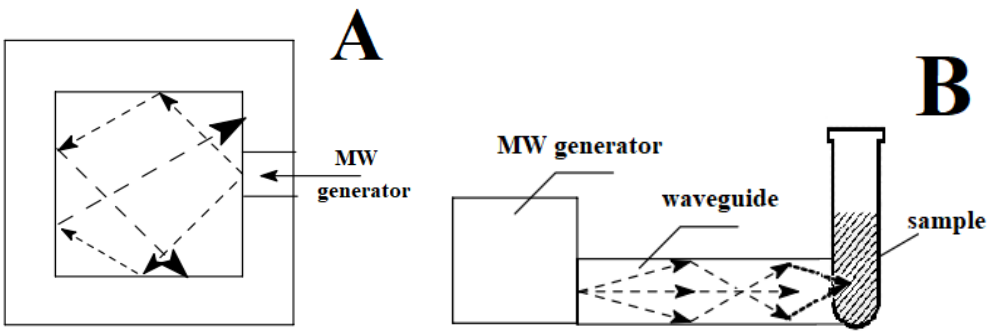


Figure 1. (**A**) Schematic drawing of the microwave field distribution in a common multimode parallel synthesis reactor. (**B**) Schematic drawing of the microwave field distribution in a monomode reactor.

Multimode resonators are metal chambers with dimensions much larger than the microwave wavelength (for example, a household microwave oven), which allows the existence of a large number of natural oscillations of the resonator and makes it possible to obtain an acceptable microwave field uniformity. This is important for processing large samples with dimensions of the order of the wavelength. However, achieving uniform heating of the sample in such devices can be challenging. In most home appliances, this problem is solved by using a rotating sample holder. However, this method of leveling the energy density across the resonator volume does not guarantee uniform heat treatment of the sample. The main disadvantage of multimode resonators is their low efficiency when heating substances with a low absorption coefficient of microwave energy. Therefore, it is advisable to use devices based on resonators with a low operating mode index in such cases. These systems are characterized by the high strength and known field geometry inside the resonator, allowing the sample to be positioned in a high field strength area.

However, the sample's dielectric properties and geometric dimensions can critically affect the resonant frequencies and field structure.

Currently manufactured commercial laboratory facilities, such as the systems "Mars" (based on a multimode resonator, power P = 400–1600 W) and "Discover" (based on a single mode resonator, power P = 300 W) from CEM Corporation (Matthews, NC < USA), are mainly used for microwave synthesis and sample preparation, where typical temperatures do not exceed 300 °C. Magnetrons, traveling wave lamps (TWTs), and klystrons are used as sources of microwave energy. When selecting a microwave generator, it is important to consider the unique characteristics of each source. Both sources can generate high levels of power for generating microwave energy. Klystrons, for instance, allow for precise control of amplitude, frequency, and phase of microwave waves. On the other hand, TWTs enable the adjustment and control of frequency and microwave power across a broad range. Currently, the magnetron is the primary source of microwave irradiation in research and technology installations due to its simple design and low cost.

Nowadays, solid-state microwave generators are widely used due to their high stability and the ability to tune frequency over a wide range, as well as regulate average power, resulting in improved heating uniformity. The leading manufacturers of transistors for microwave generators are currently the companies NXP (Ningbo, China) and Ampleon (Nijmegen, The Netherlands). Powerful solid-state microwave generators have an advantage over magnetrons in terms of the service life (up to 250,000 h), dimensions, and weight. Cellencor Inc. (Ankeny, IA, USA) [6] produces a family of industrial solid-state microwave generators with a power of up to 20 kW and 100 kW at frequencies of 2450 MHz and 915 MHz, respectively. However, due to the high cost of such devices, the question of their widespread use remains open. The list of companies and developers of microwave installations is significant and is presented, for example, in the paper [7].

At present, the area of microwave chemistry devoted to organic synthesis has been the most widely studied. The process of conducting organic synthesis with the assistance of microwaves is referred to as "microwave-assisted organic synthesis" (MAOS) [8]. Over the past 30 years, a huge number of chemical reactions have been studied; the results have been analyzed and systematized in numerous reviews and monographs. The most comprehensive analysis of these results can be found in the reviews [8,9]. These papers also discuss the nature of the thermal, associated with the phenomenon of local overheating, and "non-thermal" microwave effects.

Advantages of performing microwave-assisted reactions include: economy of energy, mild reaction conditions, reduction of time of synthesis, fast heating, fast change in regimes, fast cooling, non-equilibrium conditions of the process, selective heating, possibility to use pulse mode of operation, formation of hot spots/hot surfaces/superheated areas, reduced wall effects, no need to heat the walls, gases.

Microwave technologies can be utilized both to prepare catalysts and carry out catalytic reactions [10–12]. The chemical industry may find MW-assisted catalytic reactions an interesting technology due to the selective effect of microwaves on catalysts and individual components of reaction mixtures [10]. The method relies on the fact that substances possess different abilities to absorb microwave energy because of their dielectric properties, such as dielectric constant (ε') and dielectric loss factor (ε''). To evaluate the absorption capacity, the parameter used is the tangent of the dielectric loss angle (tan δ). It is widely accepted that materials with tan $\delta > 0.1$ absorb microwave energy effectively, while weakly absorbing materials have a tan δ in the range of 0.1–0.01. Table 1 demonstrates the dielectric properties of substances involved in the chemical transformations of glycerol. Glycerol has a high absorption coefficient and effectively interacts with microwave radiation, which can accelerate chemical reactions.

Table 1. Dielectric properties of organic compounds and catalysts [8,9,13,14].

Reagent	The Dielectric Constant (ε′)	Dielectric Loss Factor (ε″)	Loss Tangent (tan δ)
Organic compounds			
Glycerol	6.47	3.31	0.512
Acetone	20.3	1.14	0.056
Dimethylcarbonate	3.15	0.09	0.030
Formic acid	58.5	42.24	0.722
Acetic acid	6.2	1.08	0.174
Solvents			
Water	80.1	9.93	0.124
Methanol	32.3	21.16	0.655
DMSO	45.0	37.13	0.825
Acetonitrile	37.5	2.33	0.062
Hexane	1.9	0.04	0.020
Catalysts			
0.25 M HCl/MM	2.06	0.09	0.042
H_2SO_4	29.10	112.20	3.856

Applying this approach in a heterogeneous "reagent + catalyst" system can selectively heat the catalyst or its active component, creating non-equilibrium conditions for endothermic catalytic reactions to occur. Moreover, it is feasible to quickly "quench" the primary products of thermal or catalytic transformations that occur on the surface of a heated catalyst when they diffuse into the volume of a colder reaction mixture surrounding the catalyst without absorbing microwave energy. In this case, the formation and stabilization of transformation products are possible, the composition of which is atypical for the conditions of traditional ("uniform") heating of the catalytic system. In the case of a homogeneous system, when the catalyst has a low absorption coefficient compared to the components of the reaction mixture, selective heating can promote efficient desorption of intermediates and reaction products from the catalyst surface, including by-products, thereby preventing the deactivation of active centers. For example, in the synthesis of solketal from glycerol and acetone, microwave irradiation contributes to the removal of water formed during the reaction from the catalyst's pores [14]. Whereas the conventional reflux unit is relatively slow and inefficient for transferring energy to the reaction mixture because it depends on convection currents and thermal conductivity of the medium (reaction vessel, reactants and solvent phase, etc.), microwave irradiation provides volumetric heating "in the core" (direct interaction of microwave energy with the reaction mixture), which leads to a rapid and uniform temperature rise. Microwave heating is an efficient and fast way to carry out chemical transformations. It has become a widespread and important tool not only in synthetic organic chemistry but also in the synthesis of catalysts, including nanomaterials and nanostructures. The use of microwave irradiation in organic synthesis can significantly reduce the reaction time and increase the yield of the product by reducing the formation of undesirable by-products. Note that, in general, microwave irradiation does not affect the reaction mechanism.

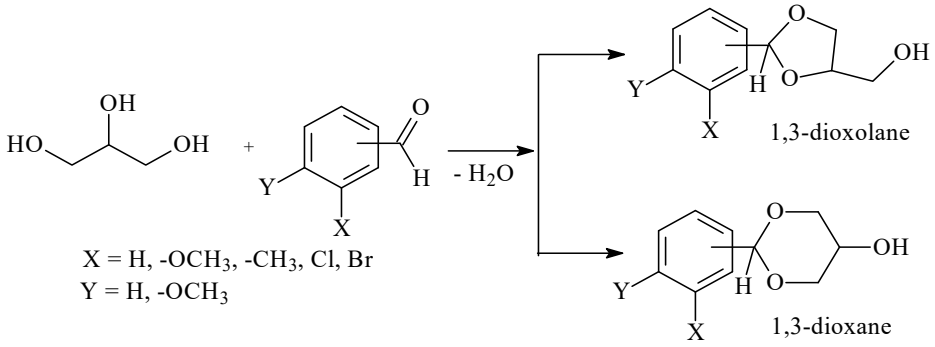
3. Catalytic Transformation of Glycerol Under Microwave Irradiation

3.1. The Acetalization of Glycerol with an Aldehyde

3.1.1. Synthesis of Acetals and Ketals from Glycerol

The products of the condensation reaction of glycerol with aldehydes and ketones are considered as the most promising fuel additives, "green" solvents for the paint industry and fine organic synthesis processes [15–17]. The reaction of a carbonyl compound (aldehyde or ketone) with glycerol in the presence of most often acidic catalysts, for example, H_2SO_4,

p-toluenesulfonic acid (p-TSA), aluminosilicates, zeolites, etc., is the conventional chemical route to obtain acetals and ketals (Scheme 2) [17–19].



Scheme 2. Acetalization of glycerol with aldehydes.

A high yield of products is one of the advantages of this method. However, this method has its drawbacks, such as a long reaction time, complex processing protocols required to isolate the product, as well as the high sensitivity of heterogeneous catalysts to moisture. Pawar et al. [20] were able to solve these problems by carrying out the acetalization process of aldehydes/ketones with glycerol without a catalyst or solvent, using microwave irradiation (Table 2). Glycerol acts as both a reagent and a solvent in this case. As a result, benzaldehyde conversion was only 66% when the benzaldehyde/glycerol mole ratio was 1:1. However, increasing the glycerol content in the reaction mixture (benzaldehyde/glycerol mole ratio of 1:2) resulted in a 95% conversion of benzaldehyde. The optimal reaction conditions are as follows: use a molar ratio of glycerol to aldehyde/ketone of 2, heat to 140 °C, apply microwave power of 600 W, and expose to microwaves for 15 min.

The electronic effects of substituents in the benzene ring impact the conversion of carbonyl compounds (aldehydes or ketones) and the selectivity of the reaction for either acetal with a five-membered ring (5-M) or ketal with a six-membered ring (6-M) (Table 2). In the case of para-substituted benzaldehydes, an increase in the electron-donating properties of the substituent results in a decrease in their conversion in the following order [21]:

$$-H\ (95\%) > -CH_3\ (70\%) > -OCH_3\ (59\%),$$

The selectivity towards 5-M increases in the following order:

$$-H\ (56\%) \sim -CH_3\ (55\%) < -OCH_3\ (65\%).$$

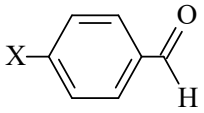
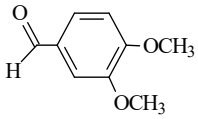
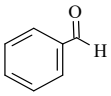
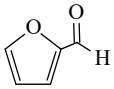
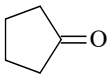
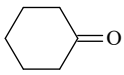
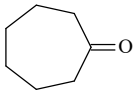
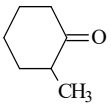
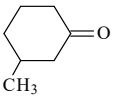
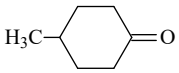
The conversion of aldehydes is not affected by the electron-withdrawing substituents, nor is the selectivity of the reaction.

The conversion of aliphatic aldehydes through reaction with glycerol at their boiling points depends on the chain length of the alkyl group. The conversion decreases in the following order [20]:

butanal (80 °C, 90%) > pentanal (100 °C, 81%) > hexanal (120 °C, 77%) > > heptanal (140 °C, 60%) > decanal (140 °C, 17%).

A similar correlation was observed in the presence of Amberlyst-15 ion-exchange resin [22].

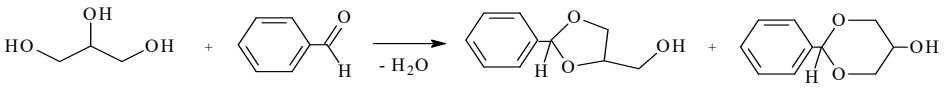
Table 2. Reaction of glycerol with ketones and acetals under MW irradiation [20] *.

№	Aldehyde/Ketone	Conversion of Gly, (%)	Selectivity, (%)	
			5-M	6-M
	X			
1	H	95	56	44
2	$-OCH_3$	59	65	35
3	$-CH_3$	70	55	45
4	−Cl	84	54	46
5	−Br	83	53	47
	Other aldehydes and ketones			
6		96	53	47
7		98	60	40
8		75	45	55
9		68	96	4
10		90	98	2
11		77	99	1
12		60	22	78
13		65	48	52
14		79	46	54

*—Experimental conditions: 60 mmol of glycerol, 30 mmol of aldehyde/ketone, 600 W, 140 °C, 15 min.

Table 2 shows that the reaction between glycerol and cyclic ketones has a selectivity towards 5-M of 96–99%. The conversion of a cyclic ketone is influenced by the ring's spatial structure, and steric factors have a noticeable effect on both conversion and selectivity, as observed for methylcyclohexanones. The conversions for 2-methylcyclohexanone, 3-methylcyclohexanone, and 4-methylcyclohexanone were 60%, 65%, and 79%, respectively, with selectivities of 22%, 48%, and 46%, respectively. In the case of 2-methylcyclohexanone, the selectivity change can be explained by steric repulsion between the methyl and ketone groups, which are in close proximity. Table 3 demonstrates that adding a catalyst to the reaction mixture has no significant impact on the distribution of reaction products. However, in all cases, a slight decrease in benzaldehyde conversion is observed. This is likely due to active site blockage by formed water molecules.

Table 3. Reaction of glycerol with benzaldehyde under MW irradiation [20] *.



5-M 6-M

№	Catalyst	Conversion of Gly (%)	Selectivity (%)	
			5-M	6-M
1	Without catalyst	95	56	44
2	p-TSA	67	47	53
3	Nafion SAC-13	81	56	44
4	Amberlyst-15	80	55	45
5	Montmorillonite K10	84	56	44
6	H-beta	85	55	45
7	ZSM-5	62	53	47
8	SBA-15	85	53	47
9	MCM-41	78	57	43

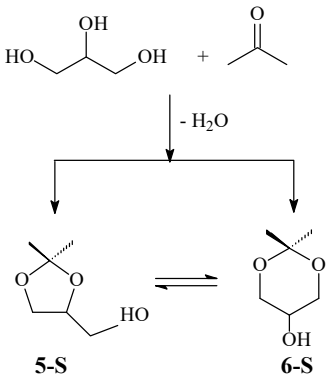
* Experimental conditions: 60 mmol of glycerol, 30 mmol of aldehyde/ketone, 100 mg of catalyst, 600 W, 140 °C, 15 min.

Castro et al. [23] reported on the synthesis of acetals as fuel additives produced from glycerol under microwave treatment using p-sulfonic acid of calix[4]arene supported on silica as a catalyst. They investigated the effect of reaction temperature, reaction time, and the amount of the heterogeneous catalyst on the yield of acetal in the reaction of benzaldehyde and glycerol without any solvent. The optimal conditions were found to be 5 wt.% of the catalyst, 110 °C, and 20 min. The study identified twelve products by ^{1}H NMR with yields varying from 6 to 99%.

3.1.2. Synthesis of Solketal from Glycerol and Acetone

The production of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (solketal) is of particular interest. Its use can increase the octane number, reduce tar formation in gasoline [24,25], and improve phase stability and ignition ability of gasoline fuel [26]. According to Data Bridge Market Research [27], the global market for high-purity solketal (>96%) is expected to grow at a rate of 3.5% and reach USD 108.4 billion by 2028.

Currently, solketal is produced through the reaction of glycerol and acetone in the presence of acid catalysts (Scheme 3). This reaction yields a five-membered ring acetal (5-S), a six-membered ring ketal (6-S), and water. Both homogeneous and heterogeneous catalysts can catalyze this process. However, the challenges of separating homogeneous catalysts from the reaction mixture and their subsequent use have led to an increased focus on the development of heterogeneous catalysts [16,28–30].



Scheme 3. Cyclocondansation of glycerol with acetone.

Zeolites, cation exchange resins, mixed oxides, silicate materials containing $-SO_3H$ groups, and montmorillonite clay modified with mineral acids can be used as heterogeneous catalysts [15–17]. However, activity of all catalysts decreases during the reaction, caused by the adsorption of water molecules on the active center. Furthermore, to achieve a high yield of 5-S (82–99%) regardless of the catalyst type, the crucial factor is the extended reaction time, ranging from 30 min to 12 h, when conducting the reaction under conventional TH conditions. In 1994, Cablewski et al. were the first to synthesis 5-S using a continuous microwave reactor with p-TSA as the catalyst [31]. The highest yield of 5-S, at 84%, was achieved with a high acetone/glycerol molar ratio of 13.5, under MW irradiation at 140 °C for 15 min. Since then, both homogeneous (H_2SO_4 and $FeCl_3$) and heterogeneous catalytic materials (silicate materials and carbon materials containing $-SO_3H$ groups, MOR zeolite modified with copper ions, and amorphous aluminophosphate (AlPO) modified with iron ions) have been used (Table 4) [32–37].

Filho et al. [35] investigated the catalytic properties of conventional homogeneous catalysts, such as H_2SO_4 and $FeCl_3$, under MW irradiation. Glycerol conversion was found to be 99.9% with an acetone/glycerol molar ratio of 6 and 0.22 wt.% of $FeCl_3{\cdot}6H_2O$ and H_2SO_4 in the reaction mixture, respectively, within 15 and 20 min (Table 4). To explain the high activity of the studied materials, the dielectric spectra of the reaction media were measured during the reaction. According to the studies performed, the reaction media exhibited a high loss tangent ($0.2 < \tan\delta < 0.4$ at 2.45 GHz) during the reaction, indicating a high absorption of microwave energy. Microwave irradiation was found to alter the vapor–liquid equilibrium, resulting in an increased concentration of acetone/water in the vapor phase. This shift in equilibrium favors the formation of 5-S and 6-S.

Aguado-Deblas et al. demonstrated synthesis of 5-S from glycerol and acetone under microwave irradiation in the presence of amorphous and mesoporous SiO_2 containing $-SO_3H$ groups (Table 4) [33]. Three series of SiO_2-SO_3H samples were prepared:

Series 1. KIT-SO_3H, SBA-SO_3H, and Am-SO_3H materials were obtained by interaction of KIT-6, SBA-15, and amorphous SiO_2 with $ClSO_3H$ in CH_2Cl_2 solution at 0 °C.

Series 2. KIT-PrSO_3H, SBA-PrSO_3H, and Am-PrSO_3H were obtained by refluxing the corresponding SiO_2 with (3-mercaptopropyl)trimethoxysilane in an ethanol solution.

Series 3. KIT-PrSO_3H TH, SBA-PrSO_3H TH, and Am-PrSO_3H TH were prepared by hydrothermal synthesis at 180 °C by reacting the corresponding SiO_2 with (3-mercaptopropyl) trimethoxysilane in a methanol solution.

The study showed that when using SiO_2-SO_3H materials, the selectivity of the reaction to 5-S was over 90% at a molar ratio of acetone to glycerol of 12:1, 5 wt.% of catalyst, a temperature of 40 °C, microwave power below 100 W, and a reaction time of 2 min (Table 4). The activity of SiO_2-SO_3H materials was found to be directly proportional to the surface density of $-SO_3H$ groups (Figure 2). The study results demonstrate the superior effectiveness of microwaves over conventional heating. This is confirmed by comparing the catalytic properties of SBA-SO_3H under identical conditions. The conversion of glycerol and selectivity of the reaction to 5-S were lower under TH conditions (59% and 66%, respectively) compared to microwave-assisted synthesis conditions (90% and 97%, respectively) at a molar ratio of acetone/glycerol of 1:2, 12.5 wt.% catalyst, and 40 °C for 2 min.

Table 4. Synthesis of solketal from glycerol and acetone under MW irradiation.

№	Catalyst	Experimental Conditions				Catalytic Properties		EF ** (g/g)	Ref.
		Catalyst * (wt.%)	Acetone/Gly (mol/mol)			Conversion of Gly (%)	Selectivity of 5-S (%)		
1	H_2SO_4	0.22	6/1	-	20	99.9	>90	-	[35]
2	$FeCl_3$	0.22	6/1	-	1 (15)	81.2 (99.9)	>90	-	[35]
3	Am-SO_3H	5	12/1	40	2	74	92	13.6	[33]
4	KIT-SO_3H	5	12/1	40	2	55	87	9.6	[33]
5	SBA-SO_3H	5	12/1	40	2	90	97	17.5	[33]
6	Am-$PrSO_3H$	5	12/1	40	2	78	94	14.7	[33]
7	KIT-$PrSO_3H$	5	12/1	40	2	74	93	13.8	[33]
8	SBA-$PrSO_3H$	5	12/1	40	2	72	98	14.1	[33]
9	Am-$PrSO_3H$ TH	5	12/1	40	2	89 (82)	96 (93)		[33]
10	KIT-$PrSO_3H$ TH	5	12/1	40	2	91 (90)	98 (92)	17.8	[33]
11	SBA-$PrSO_3H$ TH	5	12/1	40	2	90 (85)	98 (96)	17.6	[33]
12	22%H_2SO_4/SiO_2 (commercial)	5	12/1	40	2	90 (0)	98 (0)	17.8	[33]
13	SAFACAM (C-SO_3H)	8	5/1	70	10	98.1	100	12.3	[36]
14	1%Cu-MOR	4	1/1	100	15	81	79	16.0	[34]
15	1%Cu-MOR	4	2/1	100	15	86	88	18.9	[34]
16	1%Cu-MOR	4	3/1	100	15	95	98	23.3	[34]
17	1%Cu-MOR	5	3/1	25	120	75	80	12.0	[34]
18	Fe-AlPO	6	2.5/1	60	30	94	96	15.0	[37]
19	0.25 M HCl/montmorillonite	1.8	2.0/1	50	15	87.3	96.7	46.7	[14]
20	0.25 M HCl/montmorillonite ***	2.8	2.4/1	50	15	79.1	99.2	28.0	[14]
21	0.25 M HCl/montmorillonite ***	2.28	6.24/1	56	15	93.0	98.1	40.0	[14]

* Catalyst content based on weight of glycerol. ** EF—Weight ratio of solketal/catalyst. *** Reaction was carried out in a MeOH solution.

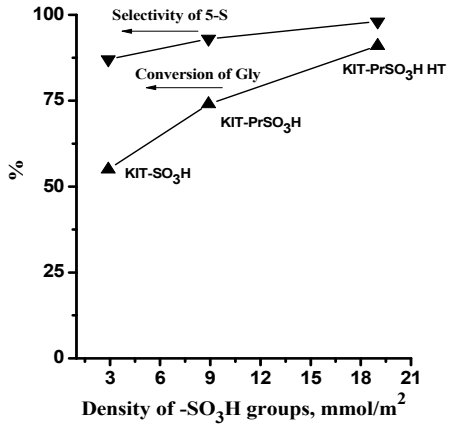


Figure 2. Correlation between the density of acid sites in SiO_2-SO_3H samples and conversion of glycerol and selectivity towards 5-S.

According to Ao et al. [36], aromatic carbonaceous material functionalized with sulfonic acid (sulfonic-acid-functionalized carbonaceous material, SAFACAM) allowed the authors to obtain 5-S from glycerol and acetone with a 100% selectivity and 98.1 ± 0.4% glycerol conversion at 6:1 molar ratio of acetone/glycerol, 8 wt.% of the catalyst, MW power 50 W, 70 °C, and 10 min under MW irradiation (Table 4). SAFACAM was obtained by the action of glucose with H_2SO_4 for 18 h at 80 °C. SAFACAM was used for six cycles with a moderate loss of activity (conversion 82.3 ± 0.2% in the sixth cycle).

Mordenite (H-MOR, Si/Al—20 mol/mol) modified with $M(NO_3)_2$ (M = Fe(II), Co(II), Ni(II), Cu(II), Zn(II), 1 wt.% metal) can also be used as a catalyst for the synthesis of 5-S [34]. The optimal conditions for obtaining 5-S with high yield were a 3:1 molar ratio of acetone to glycerol, 4 wt.% of the catalyst, microwave power of 500 W, a temperature of 100 °C, and 15 min of microwave heating. Under these conditions, in the absence of a catalyst, the conversion of glycerol did not exceed 8%. However, in the presence of H-MOR, the conversion of glycerol increased significantly to 66%, with selectivities towards 5-S and 6-S of 64% and 36%, respectively. After modifying H-MOR with $M(NO_3)_2$, the selectivity towards 5-S increased significantly, while the selectivity towards 6-S decreased. Depending on the type of metal, the conversion of glycerol decreased from 95% to 86% in the following series:

$$1\%Cu\text{-}MOR > 1\%Ni\text{-}MOR > 1\%Fe\text{-}MOR > 1\%Co\text{-}MOR \sim 1\%Zn\text{-}MOR,$$

while the selectivity towards 5-S decreased from 98% to 81% in the following order:

$$1\%Cu\text{-}MOR > 1\%Ni\text{-}MOR > 1\%Fe\text{-}MOR > 1\%Zn\text{-}MOR \geq 1\%\ Co\text{-}MOR.$$

The highest conversion of glycerol of 95% with a 98% selectivity towards 5-S was observed in the presence of Cu-MOR (Table 4). This result correlates with the order of the change in the electronegativity of ions, which can indirectly characterize the order of the change in the acidity of 1%M-MOR materials.

Prasad et al. [37] discovered that Fe-AlPO (4.2 wt.% Fe(III)) was the most effective catalyst among the samples obtained by modifying amorphous aluminophosphate with metal nitrates (Zr(IV), Cr(III), Fe(IIII)). The conversion of glycerol and selectivity towards 5-S were 94% and 96%, respectively, in the presence of the Fe/SAPO material at the acetone/glycerol molar ratio of 2.5, 6 wt.% of Fe-AlPO, 60 °C for 30 min (Table 4). The authors stated that this catalyst could potentially replace the homogeneous catalyst, p-TSA.

The synthesis of 5-S from glycerol and acetone was demonstrated under MW irradiation in the presence of montmorillonite modified with 0.25 mol/L HCl [14]. The reaction was studied in a methanol solution, with a ratio of 1 mL of MeOH per 1 g of glycerol. Previously, it was observed that the addition of methanol to the reaction solution did not

significantly affect the reaction rate and yield of solketal during the process of obtaining solketal from glycerol and acetone under thermal heating conditions. In contrast, the addition of water, ethanol, dimethyl sulfoxide, and sodium chloride significantly slowed down the process [38,39].

This approach made it possible to plot the kinetic curves of glycerol consumption and 5-S and 6-S accumulation for reactions carried out under MW and TH conditions at the acetone/glycerol molar ratio of 2.4, 1.8 wt.% of the catalyst, and 50 °C. As can be seen from Figure 3, the use of microwave irradiation resulted in a significant increase in the conversion of glycerol and the yield of 5-S. The reaction under TH conditions achieved a maximum yield of 5-S at 44.5% in 30 min. Meanwhile, the maximum yield of 5-S of 72.1% was observed after 10 min under MW irradiation. The conversion of glycerol and the selectivity towards 5-S were 87.3% and 96.7%, respectively, when the reaction was carried out without adding MeOH at the acetone/glycerol molar ratio of 2, a catalyst loading of 1.8 wt.% (calculated per the amount of loaded glycerol), 50 °C, and 15 min microwave treatment.

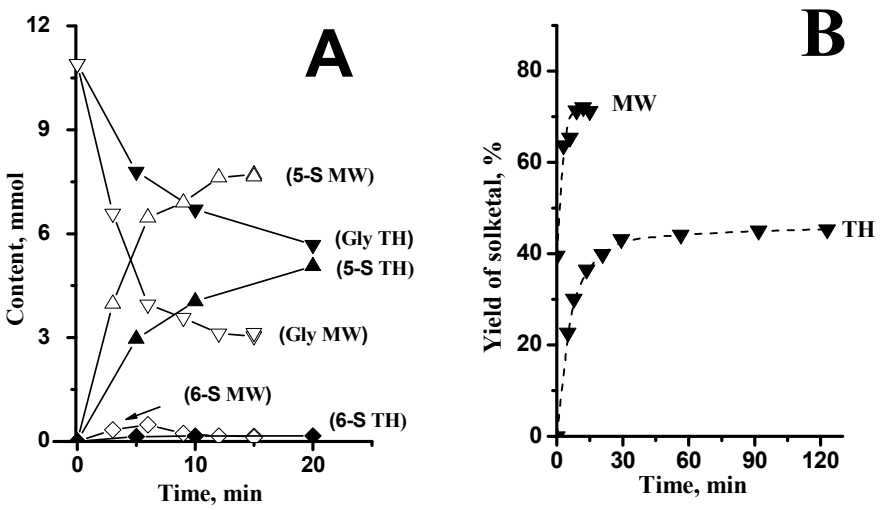


Figure 3. (**A**) Kinetic curves of glycerol consumption (Gly) and 5-S and 6-S formation from glycerol and acetone in the presence of 0.25 M HCl/MM under TH and MW irradiation. (**B**) Kinetic curve of the solketal yield in the reaction of glycerol and acetone in the presence of 0.25 M HCl/MM under TH and MW irradiation (Experimental conditions: 21.7 mmol of glycerol, 53.2 mmol of acetone, 2 mL of methanol, 1.8 wt.% of the catalyst, 50 °C) (Reprinted with permission from Ref. [14]. Copyright 2024 Copyright Springer Nature).

Efficiencies of catalysts were compared based on the parameter EF calculated using Equation (1):

$$EF = \frac{M_{5-S}}{M_{cat}} \quad (1)$$

where $M_{5\text{-}S}$—amount of 5-S formed (g), M_{cat}—weight of the catalyst in the reaction mixture (g). Table 4 shows that 0.25 M HCl/MM has the highest efficiency (46.7) compared to other catalytic systems, with EF values ranging from 9.6 to 23.3. Interestingly, the EF value for 0.25 M HCl/MM decreases with the addition of methanol. Despite increasing the acetone/glycerol ratio to 6.24, the EF value remains lower (40.0) than when the reaction is carried out without the addition of methanol. This suggests that the use of a solvent affects the thermodynamic equilibrium and reaction kinetics of the system. Moreover, the solvation of reagents affects the interaction between particles of catalyst, which in turn affects their reactivity. The results of a study [14] show that the efficiency of the reaction is greater under microwave (MW) assistance compared to the process carried out under conventional heating. The reason for this is that the heterogeneous catalyst absorbs MW radiation efficiently, which results in its heating and water removal from the surface.

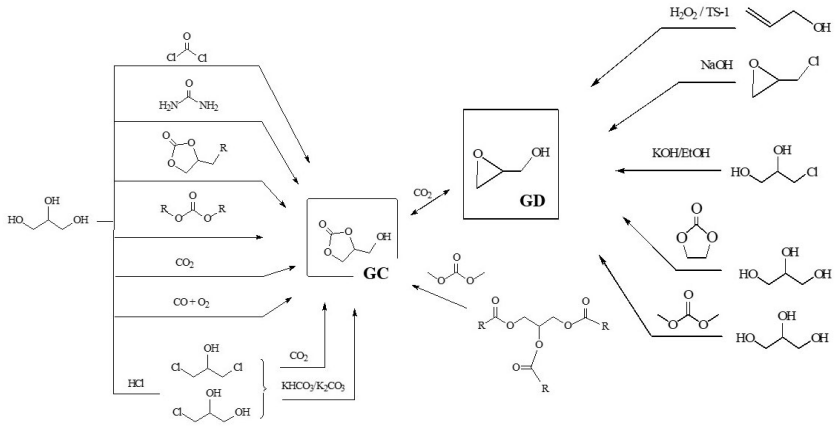
Simultaneously, high values of the absorption coefficient (tan δ) for the initial reagents, solvent, and reaction products ensure uniform heating of the entire reaction volume. This leads to a shift in the liquid → gas equilibrium, causing the acetone/water mixture to partially pass into the gas phase and reduce the concentration of water in the reaction volume [35].

3.2. Synthesis of Glycerol Carbonate

3.2.1. The Main Methods for the Synthesis of Glycerol Carbonate

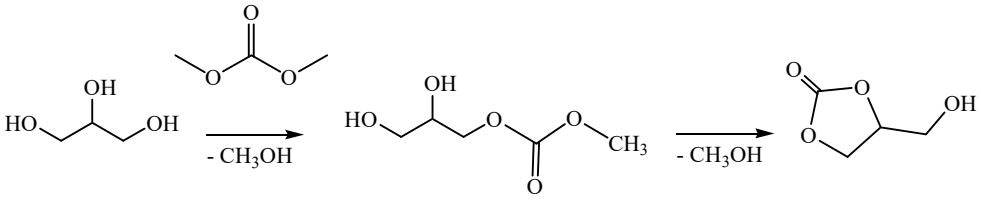
Glycerol carbonate is a molecule with a unique structure that contains a functional -OH group acting as a nucleophile and an oxygen-containing cycle acting as an electrophile through a carbon atom in the ring. Because of its specificity, GC can be used as a solvent and as a raw material for synthesizing various chemical compounds and polymers. Despite its many applications, the commercial use of GC is still being developed. According to Maximize market research, in 2021 the global GC market was estimated at USD 1.25 billion [40]. It is expected to grow at a rate of 7.43% and reach USD 2.23 billion by 2029. The main GC producers are Huntsman International LLC (Woodlands, TX, USA), Eurisotop (Cambridge Isotope Laboratories, (CIL), Tewksbury, MA, USA/Saint-Laurent, QC, Canada), UBE Industries India Private Ltd. (Gurgaon, India), Inkemia Green Chemicals Inc. (Houston, TX, USA), TCI Chemicals Pvt. Ltd. (Chennai, India), Carbon Scientific Co., Ltd. (Daventry, UK), Acros Organics (Geel, Belgium), Griffin Co., Ltd. (Seoul, Republic of Korea), Dow-DuPont Chemical (Philadelphia, PA, USA), BASF (Ludwigshafen, Germany), Kao (Tokyo, Japan), Kasei (Kundani, Japan), Korea SK (Seoul, Republic of Korea), France INRA (Paris, France), etc. The annual production is about $(3 \div 5) \times 10^4$ tons. At the same time, half of the world production of GC is provided by Huntsman International LLC and is about 1.5×10^4 tons. In 2009, Huntsman International LLC became the leader in commercializing the JEFFSOL® Glycerine Carbonate series of GCs using glycerol, a by-product of biodiesel, as a feedstock.

Currently, there are four methods (Scheme 4) for synthesizing GC from glycerol: carboxylation (including oxidative), transesterification with alkylene and alkyl carbonates, urea glycerolysis, and reaction with phosgene. Note that the first three methods are the most environmentally friendly approaches as they lead to the chemical fixation of CO_2.



Scheme 4. The main routes of glycerol carbonate and glycidol synthesis.

The phosgene method. This was the first method developed to obtain GC (Scheme 5). This method was first mentioned in 1883 [41]. In 1948 Franklin et al. reported that GC can be synthesized with a 90% yield in the presence of alkali or alkaline earth metal salts at 30 °C for 6 h [42]. Despite its high GC yield and low operating temperature, the method has significant drawbacks due to the high toxicity of phosgene and the need for additional precautions when handling it [43,44].



Scheme 5. Synthesis of glycerol carbonate from glycerol and dimethyl carbonate.

The use of urea. The urea alcoholysis method can be considered as an interesterification reaction between glycerol and urea (Scheme 4). Since this reaction is thermodynamically hindered, in order to shift the equilibrium of the system towards the formation of GC, the process must be carried out at a low pressure, or NH_3 formed as a result of the reaction must be removed. Note that ammonia can be easily converted to urea by reacting with CO_2, creating a closed technological process [45,46].

CO_2 conversion method. From a sustainable development perspective, the most ideal method for synthesizing GC on an industrial scale is to use readily available reagents such as glycerol and CO_2 (Scheme 4). This approach could contribute to the reduction of several million tons of CO_2 emissions per year. Currently, the CO_2 conversion method is considered the most environmentally friendly reaction route for GC synthesis, despite its thermodynamic challenges. Carbon dioxide is a stable compound, which results in low reactivity. However, CO_2 can be activated by using catalysts at high temperatures and pressures [47–50].

Oxidative carbonylation with CO. This method has been developed in recent years. It is a one-pot process using a bifunctional catalyst. The process combines the oxidation of CO with molecular oxygen to form CO_2 and the reaction of CO_2 with glycerol (Scheme 4). Commonly used catalysts are transition metal compounds of Groups IB and VIIIB, with typical metal salts such as Cu and Pd. The reaction conditions for oxidative carbonylation with CO are relatively mild, and GC yield can reach 70–90%. However, due to the toxicity and explosiveness of CO, there are potential safety and environmental risks, limiting its industrial use [45].

Organic carbonate application. The interesterification method involves reacting glycerol with aliphatic or cyclic organic carbonates, such as dimethyl carbonate (DMC), diethyl carbonate, ethylene carbonate, or propylene carbonate, to form GC and alcohol (Scheme 4). The interesterification method is the most widely used and studied approach for synthesizing GC. Although organic carbonates are more expensive than CO_2, CO, or urea, they are still widely researched due to their ease of implementation [45]. DMC is the most commonly used organic carbonate due to its availability and reactivity.

The reaction typically occurs at low pressures and temperatures, usually not exceeding 70–120 °C, to prevent the formation of by-products such as ethylene glycol, propylene glycol, methanol, or ethanol, depending on the type of carbonate used. This helps to shift the chemical equilibrium towards the formation of GC [43]. It is important to note that the reaction temperature is also dependent on the type of carbonate used. The temperature required for the transesterification reaction of glycerol with ethylene carbonate (35–80 °C) is lower compared to that of DMC (75–120 °C). However, DMC is preferred in the industry due to the lower energy required for the process of GC isolation. Additionally, DMC has a lower boiling point (90 °C) compared to ethylene carbonate (261 °C) and ethylene glycol (197 °C) as well as methanol (65 °C). Furthermore, reactions involving DMC are typically conducted at atmospheric or elevated pressures, whereas reactions involving ethylene carbonate are commonly performed under reduced pressure (0.005 MPa) [51].

3.2.2. Synthesis of Glycerol Carbonate from Glycerol and Dimethyl Carbonate

Currently, the reaction between glycerol and DMC is widely used to synthesize GC (Scheme 5). The reaction can occur with or without a catalyst. To prevent the decomposition of GC to glycidol (GD) in the non-catalytic method, supercritical conditions (300 °C,

20–40 MPa) and a DMC/glycerol molar ratio of 10:1 are necessary. With these conditions, the yield of GC reaches 98% in just 15 min [52]. Using basic type catalysts provides milder conditions for the process. The reaction occurs in two steps. During the first stage, glycerol interacts with alcoholate anion (nucleophile) molecules, resulting in a nucleophilic reaction of the carbonyl atom of DMC and the formation of 2,3-dihydroxypropyl methyl carbonate. Subsequently, intramolecular nucleophilic substitution leads to the formation of GC [53,54].

Organic carbonates used in excess can serve as solvents, making the use of solvents optional. The molar ratio of organic carbonates to glycerol typically ranges from 2:1 to 5:1, which shifts the reaction equilibrium towards the desired product. This approach is considered more efficient than removing by-products by adding molecular sieves [43,51]. Table 5 shows the main catalytic materials used for this process, as well as their main advantages and disadvantages. Note that selecting the appropriate catalyst is crucial for enhancing the yield and selectivity to GC. Homogeneous catalysts, such as NaOH and K_2CO_3, can offer superior catalytic activity, but their separation and reuse pose significant challenges. As a result, there has been a significant focus on the advancement of heterogeneous catalysts in recent years. Below we demonstrate how MW irradiation can be used to produce GC from glycerol.

Among heterogeneous catalysts, calcium-based oxide catalytic systems are the most extensively studied. Numerous studies have shown that their activity increases with the atomic number of the metallic element due to the increased strength of the basic sites. Calcium oxide exhibits stronger basicity compared to other metal oxides. Generally, the catalytic activity of calcium-based systems decreases in the following series:

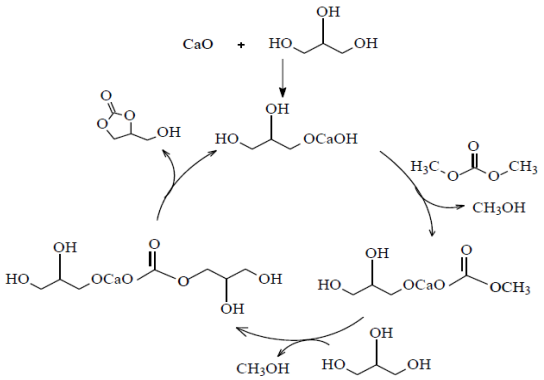
$$CaO > Ca(OH)_2 > MgO > CaCO_3.$$

The catalytic activity of CaO is dependent on its purity, specifically the levels of $Ca(OH)_2$ and basic calcium carbonate $Ca_x(OH)_y(CO_3)_z$. As the concentration of $Ca(OH)_2$ increases, which can occur due to water adsorption from the environment and its reaction with CaO, the activity of CaO decreases.

A comparable effect is also observed in the instance of $Ca_x(OH)_y(CO_3)_z$, which may accumulate during the reaction because of the interaction of CaO or $Ca(OH)_2$ with CO_2 from the environment. The catalytic activity can be restored by calcining CaO at 900 °C for 12 h. For instance, when the molar ratio of DMC to glycerol is 5, and the catalyst is present at 10 wt.% (calculated based on the weight of loaded glycerol), and the reaction is carried out at 75 °C for 1.5 h in the presence of uncalcined CaO, the conversion of glycerol and the yield of GC are 74.5% and 64.0%, respectively. However, in the presence of calcined CaO at 900 °C, the conversion of glycerol and the yield of GC are 94.1% and 91.1%, respectively [55].

According to the reaction mechanism analyzed using various physicochemical methods, it was suggested that the active intermediate of the composition $Ca(C_3H_7O_3)(OCO_2CH_3)$ is formed through the interaction of CaO with glycerol and DMC (Scheme 6). This intermediate then reacts with a second glycerol molecule, forming GC through intermolecular nucleophilic substitution [56].

Various catalyst systems have been proposed in the literature, including mixed oxides, anion exchange resins, ionic liquids, and zeolite-like imidazolate frameworks. However, to achieve a high yield of GC, a high DMA/glycerol molar ratio or a high reaction temperature is required. In the last 10 years, several works have appeared in the literature in which the process of GC production from glycerol and DMC is carried out under the action of MW irradiation. These studies demonstrate that this approach can significantly increase the reaction rate and selectivity towards glycerol carbonate compared to the process carried out under TH conditions.



Scheme 6. Reaction mechanism of interaction of glycerol with dimethyl carbonate in the presence of CaO.

Compounds based on Ca(II) and Al(III) having a hydrocalumite structure. Granados-Reyes et al. [57] demonstrated the possibility of obtaining GC from glycerol and DMC using microwave irradiation. The process was carried out in the presence of Ca(II)- and Al(III)-based compounds having a hydrocalumite structure as catalysts. The materials were obtained by coprecipitation by adding an aqueous solution of 2 M NaOH (pH 11.5 ± 0.1) to the corresponding salts of calcium and aluminum chlorides (HC1) or calcium and aluminum nitrates (HC2) in a Ca(II)/Al(III) molar ratio of 2, while stirring during precipitation with magnetic stirring or ultrasound (US). Then the samples were aged by refluxing under normal heating at 60 °C for 24 h (HC1R24, HC2R24, HC1USR24, HC2USR24) or under microwave conditions (Mw) at 60 °C for 6 h (HC1RMw6, HC2RMw6, HC1USRMw6, HC2USRMw6) (Tables 6 and 7).

The catalytic properties of the materials were studied in a N_2 atmosphere for 3 h at a DMC/glycerol molar ratio of 3.5, 0.15 g of the catalyst, and 90 °C. As can be seen from the data collected in Tables 6 and 7, for all catalysts, the use of microwave irradiation leads to a high conversion of glycerol and a particularly high selectivity for GC compared to under conventional thermal heating (TH). Thus, in the presence of HC1R24, the conversion of glycerol under microwave and high-temperature conditions was 88% and 71%, respectively, and in the presence of HC2R24, 88% and 70%, respectively. Selectivity for GC in the presence of HC1R24 and HC2R24 under microwave conditions is significantly higher (84% and 73%, respectively) compared to TH (61% and 55%, respectively).

Teng et al. [58] investigated the interesterification reaction of glycerol with DMC in the presence of CaO under MW irradiation to produce GC. The study used glycerol of different grades. As can be seen from Table 7, high yields of GC can be obtained using both TH and MW irradiation. Microwave synthesis has been shown to be an energy-efficient method for preparing GC. In just 5 min at 65 °C and a DMC/glycerol molar ratio of 2 with 1 wt.% CaO, a 94.2% yield was achieved. It is worth noting that bioglycerol from biodiesel production can be used directly without the need for purification. This method is more economical and less energy-intensive for the synthesis of glycerol carbonate.

Changmai et al. [59] have developed a catalyst based on biowaste, Musa acuminata peel ash (MAPA), for the synthesis of GC under MW irradiation. The catalyst's high basicity, large surface area, and mesoporous nature effectively contributed to the conversion of glycerol to GC. When the reaction was carried out under MW irradiation (DMA/glycerol mole ratio of 2, 6 wt.% of the catalyst, 75 °C, and 15 min), glycerol conversion and GC selectivity were 99% and 99.5%, respectively, which was higher than those under conventional heating (18% conversion and 98.5% selectivity).

Table 5. Advantages and disadvantages of catalysts for the reaction of glycerol with DMC.

№	Catalyst		Advantages	Disadvantages
1	Catalysts based on metal oxides	CaO, MgO, CaO-Al_2O_3, MgO/ZrO_2, etc.	- High activity - Low cost of catalyst preparation - High reaction efficiency	- The need for activation - Leaching of the active component is possible - Fast decontamination
2	Catalysts based on salts	$NaAlO_2$, Na_3PO_4, K_2CO_3, etc.	- High activity and process efficiency - Low cost of catalyst preparation	- Dissolution in the reaction mass - Problems with separation from the reaction mass - Problems with reuse
3	Catalysts based on hydrotalcite	Hydrotalcite HTC-Ni modified with Ni, etc.	- Easy separation from the reaction mass - It is possible to regulate the physicochemical properties - High stability	- Average activity
4	Ionic liquids	[TMG][TFE], [Bmin]Im, etc.	- High stability - Reusable	- High material cost - The complexity of the process
5	Enzymatic catalysts	Lipase of *Aspergillus niger*, enzyme Novozym 435, etc.	- Mild reaction conditions - No toxic residues	- Complex cooking - High material cost - Fast decontamination

Table 6. Catalytic properties of Ca/Al-formed systems in the reaction of glycerol with dimethyl carbonate [57].

№	Catalyst	Properties		Catalytic Method	Catalytic Properties *		
		Ca/Al (mol/mol)	S_{BET} (m^2/g)		Conversion of Gly (%)	Selectivity (%)	
						GC	GD
$Ca_2Al(OH)_6Cl{\cdot}2H_2O$ (10.0 < H- < 13.4) **							
1	HC1R24	1.98	13	MW	88	84	8
				TH	71	61	10
2	HC1RMw6	1.87	10	MW	82	86	13
				TH	78	63	11
3	HC1USR24	1.97	6	MW	86	78	8
				TH	84	65	10
4	HC1USRMw6	1.88	7	MW	85	74	13
				TH	78	59	11
$Ca_2Al(OH)_6NO_3{\cdot}2H_2O$ (10.0 < H- < 13.4) **							
5	HC2R24	1.79	9	MW	88	73	19
				TH	70	52	14
6	HC2RMw6	1.63	9	MW	86	92	8
				TH	81	65	7
7	HC2USR24	1.78	16	MW	86	85	13
				TH	79	60	12
8	HC2USRMw6	1.85	25	MW	86	87	8
				TH	82	59	10
Amorphous phase $Ca(Al)O_x$ (6.8 < H- < 8.2) **							
9	cHC1R24-450	1.98	11	MW	64	78	15
				TH	61	58	14
Amorphous phase $Ca(Al)O_x$ + $CaCO_3$ (6.8 < H- < 8.2) **							
10	cHC1RMw6-450	1.87	12	MW	78	75	10
				TH	76	65	14
11	cHC2R24-450	1.79	9	MW	63	77	8
				TH	60	58	14
12	cHC2RMw6-450	1.63	10	MW	87	53	2
				TH	84	30	14
Mayenite + CaO (13.4 < H- < 15.0) **							
13	cHC1R24-750	1.98	4	MW	95	87	12
				TH	91	80	12
14	cHC1RMw6-750	1.87	5	MW	87	88	12
				TH	85	70	13

* Experimental conditions: DMC/glycerol = 3.5:1 mol/mol, N_2 atmosphere, 0.15 g of the catalyst, 90 °C, 3 h; ** The basicity of the catalysts was determined using Hammett indicators: phenolphthalein (pK_a = 8.2), Nile blue A (pK_a = 10.1), tropaolin O (pK_a = 11), thiazole yellow G (pK_a = 13.4), and 2,4-dinitroaniline (pK_a = 13.4). = 15).

Table 7. Comparison of methods for obtaining GC from glycerol and dimethyl carbonate.

№		DMC/Gly (mol/mol)	CaO (wt.%)	T (°C)	P (MPa)	Time (min)	Yield of GC (%)	Ref.
1	MW/bio-Gly	2	1	65	0.1	5	94.2	[58]
2	Water bath/Gly	2	2	75	0.1	30	90.2	[60]
3	Water bath/Gly	5	6	75	0.1	90	64.1	[61]
4	Authoclave/Gly	3.5	3.6	95	0.6	90	95.3	[60]

Das et al. studied glycerol transesterification with dimethyl carbonate in the presence of a solid base catalyst from Mangifera indica peel ash under MW irradiation [62]. The catalyst's basic properties, combined with its developed surface area and mesoporous

pore structure, make it beneficial for this reaction. At a DMC:glycerol ratio of 3:1 and a temperature of 80 °C, the glycerol conversion rate reached 98%, with 100% selectivity to the target product. The catalyst was able to withstand five cycles.

Luo et al. [63] investigated the catalytic properties of sodium silicate (Na_2SiO_3) in the synthesis of GC under MW heating. The study found that the catalytic activity of $Na_2SiO_3 \cdot 9H_2O$ increased after calcination at 200 °C (Table 8). However, the activity of anhydrous Na_2SiO_3 was somewhat lower than that of homogeneous NaOH. Anhydrous Na_2SiO_3 is an efficient, environmentally friendly, cheap, and readily available heterogeneous catalyst. It can be obtained by simply calcining commercial $Na_2SiO_3 \cdot 9H_2O$ at a relatively low temperature (200 °C). This reaction can be accelerated by MW irradiation. Under optimal reaction conditions, GC yields reach over 90% in less than 10 min using as little as 1% Na_2SiO_3 as the catalyst.

Table 8. Catalytic properties of Na_2SiO_3 [63] *.

№		Conversion of Gly (%)	Selectivity of GC (%)
1	Without catalyst	-	-
2	Na_2SiO_3-200	93	98
3	Na_2SiO_3-300	93	98
4	Na_2SiO_3-400	92	98
5	$Na_2SiO_3 \cdot 9H_2O$	73	97
6	NaOH	98	99

* Experimental conditions: 50 mmol of glycerol, 150 mmol of DMC, 1.6 wt.% of the catalyst, 90 °C, 0.5 h, MW mode.

Wang et al. [64] also studied catalytic properties of Na_2SiO_3 under MW irradiation. The maximum glycerol conversion and glycerol carbonate yield achieved 96.7% and 94.3%, respectively, at 95 °C for 15 min. Note that the glycerol conversion and glycerol carbonate yield remained constant at 175 W of MW power and a reaction time of 50 s. These results showed that the constant power mode is more efficient than the constant temperature mode. Additionally, the results showed that Na_2SiO_3 was more effective than CaO when using the constant power mode, resulting in reduced energy consumption with increased microwave power.

Prakruthi et al. [65] compared the catalytic properties of four layered double hydroxides (LDHs), namely Mg,Al-LDH, Cu,Al-LDH, Ni,Al-LDH, and Zn,Al-LDH, under MW and TH conditions. The transesterification of glycerol with DMC was studied at 120 °C, a DMC/glycerol molar ratio of 3, and 0.5 g of the catalyst (0.92 g of glycerol). The data obtained showed that the conversion of glycerol decreased in the following order:

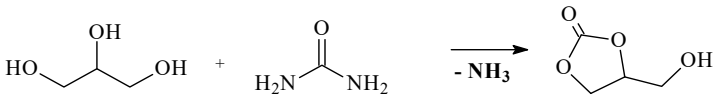
$$\text{Zn,Al-LDH} > \text{Mg,Al-LDH} > \text{Ni,Al-LDH} > \text{Cu,Al-LDH}.$$

regardless of the method of carrying out the reaction. Microwave irradiation enables the reaction to be completed in 60 min with an 80–92% conversion of glycerol and 100% selectivity for GC. In contrast, under TH conditions, the reaction takes 8 h.

Under solvent-free conditions, glycerol carbonate can be selectively synthesized using DMC and different polymorphs of MnO_2 as catalysts [66]. The highest activity and selectivity were demonstrated by δ-MnO_2. A comparison between microwave (80 °C) and conventional (120 °C) modes of operation revealed the advantages of the former.

3.2.3. Synthesis of Glycerol Carbonate from Glycerol and Urea

Glycerolysis of urea to glycerol carbonate is an important pathway for the conversion of glycerol (Scheme 7). The literature contains limited information on this reaction when subjected to MW irradiation.



Scheme 7. Synthesis of glycerol carbonate from glycerol and urea.

Zhang et al. [67] produced GC from glycerol and urea without a solvent using microwave heating. Catalysts such as $ZnSO_4$, $ZnCl_2$, $CuSO_4$, and $MgSO_4$ were used (Table 9). The study demonstrated that MW technology greatly increased the reaction rate, resulting in a 93.7% yield of GC. The authors compared the reaction under MW and TH conditions and found that after 40 min and after 100 min the yields of GC were 80.6%/39.8% and 90.0%/61.0%, respectively. They attributed the acceleration of the reaction to intense local heating resulting from the transfer of energy from microwaves to the reagents.

Table 9. Glycerolysis of urea to glycerol carbonate in the presence of different oxides and salts.

№	Catalyst	Experimental Conditions	Conversion of Gly (%)	Yield of GC (%)	Ref.
1	$ZnCl_2$	2.8 wt.% of the catalyst (based on weight of glycerol), 150 °C, 40 min, 600 W, 15 kPa, urea/glycerol—1:1 mol/mol	60.7	60.3	[67]
2	$MgSO_4$		58.1	57.2	[67]
3	$CuSO_4$		55.8	53.1	[67]
4	$ZnSO_4$		81.8	80.6	[67]
5	ZnO	2 wt.% of the catalyst (based on weight of glycerol), 120 °C, 60 min, N_2 atmosphere, MW irradiation, urea/glycerol—43.5:43.51 mol/mol	63.0	35.8	[68]
6	MgO		61.5	33.3	[68]
7	Al_2O_3		58.1	30.0	[68]
8	HT-2C		40.1	63.8	[68]
9	HT-1C		63.2	85.5	[68]

Gupta et al. [68] synthesized GC using MW irradiation in the presence of metal oxides, such as Al_2O_3, MgO, and ZnO (Table 9). The reaction was carried out in a nitrogen atmosphere at a molar ratio of urea to glycerol equal to 1, with 2 wt.% of the catalyst (based on the weight of loaded glycerol), at 120 °C for 60 min of microwave heating of the reaction mass. In the absence of a catalyst, the conversion of glycerol and the selectivity for GC were 40.2% and 38.4%, respectively. The addition of a catalyst to the reaction mixture resulted in an increase in glycerol conversion to 58.1–63.0% and GC selectivity to 46.8–56.7%. These values are higher than those obtained under TH conditions (where glycerol conversion was 59% and GC selectivity was 36% in 4 h). Layered double hydroxides based on Zn/Mg/Al, HT-1C (Zn/Mg/Al—9.6:1.2:1 mol/mol/mol), and HT-2C (Zn/Mg/Al—4.9:1.6:1 mol/mol/mol) exhibited the highest activity. In the presence of HT-2C, glycerol conversion and selectivity to GC were 65.1% and 63.8%, respectively. In contrast, in the presence of HT-1C, glycerol conversion and selectivity to GC were 73.8% and 85.5%, respectively. The higher basicity of the HT-1C sample explains its higher activity compared to HT-2C, as supported by the data of temperature-programmed desorption of CO_2.

3.3. One-Pot Synthesis of Glycidol from Glycerol and Dimethyl Carbonate

Glycidol (GD) is a crucial raw material for producing polyglycerol, glycerol ester, dihydroxypropylamine, UV-curing agents for perfumes and cosmetics, detergents, drugs, coatings, and semiconductors. Several methods for synthesizing GD currently exist (Scheme 4). The industrial method for obtaining GD is based on the direct oxidation of allyl alcohol with an aqueous solution of hydrogen peroxide. This is a heterogeneous catalytic process carried out in the presence of nanostructured titanium silicalite TS-1 in methanol [69,70]. The process is performed in an excess of allyl alcohol at a temperature of 35–50 °C and a molar ratio of allyl alcohol to hydrogen peroxide equal to (10–30):1. The maximum yield of GD is 90.1% achieved at 50 °C and a molar ratio of 20:1.

Another method for obtaining GD involves the interaction of glycerol monochlorohydrin with an alkaline agent in an organic solvent medium, specifically dichloroethane with azeotropic distillate formed during water synthesis (Scheme 4) [71]. Despite its high yield of 85–90%, this method is not environmentally friendly. One disadvantage of this method is the generation of a significant amount of wastewater that is contaminated with mineral and organic impurities. The purification process is laborious and has high energy costs.

Scheme 4 also shows another method of obtaining GD by decarboxylation of GC [72–75]. Despite a high yield of 85–90%, this method is not environmentally friendly due to the production of wastewater contaminated with mineral and organic impurities, which requires costly purification. Thermal decarboxylation without the use of a catalyst can be used to isolate GC, preventing its polymerization [73]. This method is advantageous compared to other preparation methods for GD, as it results in pure GD in a single stage by combining decarboxylation of GC with vacuum evaporation. However, a temperature above 175 °C is required to achieve a yield of 60% or more.

The possibility of catalytic decarboxylation of GC using various catalysts such as phosphates, pyrophosphates, chlorides, bromides, acetates, carbonates, and bicarbonates of alkali and alkaline earth metals was demonstrated [76]. In the presence of these catalytic systems, GD is obtained with a yield above 70%, but the process must be carried out in a vacuum and at temperatures above 195 °C. Therefore, this method is also very expensive in terms of energy costs.

Lee et al. demonstrated the possibility of using ionic liquids as catalysts for the synthesis of GD from GC [77]. Despite the high yield of GD, their use has its drawbacks, mainly associated with the high boiling point of ionic liquids (above 165 °C), which makes it difficult to isolate GD.

One-pot synthesis of glycidol from glycerol and dimethyl carbonate (Scheme 4). This approach makes it possible to obtain GD both by a one-pot [78–85] and two-step method with the formation of GC and its subsequent decarboxylation to GD [75,78,85,86] (Table 10). Undoubtedly, the one-pot process is cost-effective and more promising than the two-step procedure.

One-pot synthesis of GD from glycerol and DMC can be carried out under homogeneous conditions in the presence of tetraethylammonium amino acid ionic liquids as catalysts (Table 10) [83]. In their presence, the process proceeds at 130 °C with a high conversion of glycerol (94–96%) and a 68–82% selectivity towards GD (depending on the basicity of the anion).

One-pot synthesis of GD from glycerol and DMC can also be carried out in the presence of heterogeneous catalytic systems. Thus, Kondavar et al. [79] developed a one-pot method for the synthesis of GD in the presence of mixed metal oxides Ba-M (1:1) (M–Ce, La, Nd) in a DMF solution at 120 °C (Table 10). The maximum conversion of glycerol (98%) and selectivity towards GD (80%) were obtained in the presence of Ba-Ce (1:1) at 120 °C.

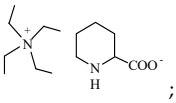
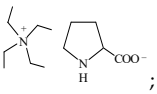
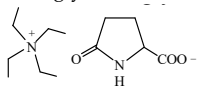
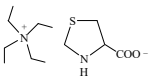
Devi et al. [81] synthesized a catalyst based on rice husk doped with potassium ions. In the presence of this catalyst, the glycerol conversion and GD selectivity were 60.8% and 62.9%, respectively (Table 10).

GD can be obtained in the presence of Amberlite-IRA400 anion exchange resin (Table 10) [83]. GD was formed with a 52% selectivity and 87% glycerol conversion at 130 °C in 2 h of the reaction.

One-pot synthesis of GD under solvent-free conditions has been demonstrated. As a catalyst, it was proposed to use KNO_3 supported on Al_2O_3 in an amount of 15–80 wt.% and calcined at 500–900 °C (30% KNO_3/Al_2O_3) (Table 10) [82]. However, this protocol has low selectivity towards GD.

Table 10. Synthesis of glycidol by one-pot and two-step methods.

№	Catalyst	Experimental Conditions (°C, h, Solvent)	Conversion of Gly (%)	Selectivity (%)		Ref.
				GC	GD	
		One-pot process				
1	$[N_{2222}]$[Pipe]	130, 2.0, DMF	96	18	82	[83]
2	$[N_{2222}]$[H-pyr]	130, 2.0, DMF	12	75	25	[83]
3	$[N_{2222}]$[Thio]	130, 2.0, DMF	11	90	10	[83]
4	$[N_{2222}]$[Pro]	130, 2.0, DMF	94	32	68	[83]
5	Ba:Ce (1:1)	120, 1.5, DMF	98	18	80	[79]
6	Ba:La (1:1)	120, 1.5, DMF	97	45	52	[79]
7	Ba:Ce (1:1)	120, 1.5, DMF	98	34	63	[79]
8	BaO	120, 1.5, DMF	98	70	29	[79]
9	K-RHA	90, 1.0, DMF	60.8	-	62.9	[79]
10	Amberlite-IRA400	130, 2.0, DMF	87	48	52	[83]
11	30%KNO_3/Al_2O_3 (800 °C)	70, 2.0, -	95.1	33.2	66.8	[82]
12	15%KNO_3/Al_2O_3 (800 °C)	70, 2.0, -	94.0	53.5	43.1	[82]
13	40%KNO_3/Al_2O_3 (800 °C)	70, 2.0, -	93.5	51.5	44.9	[82]
14	30%KNO_3/Al_2O_3 (700 °C)	70, 2/0, -	91.6	41.4	58.6	[82]
15	30%KNO_3/Al_2O_3 (900 °C)	70, 2.0, -	90.3	50.6	44.0	[82]
16	0.5%ZIF-8/AM-4	100, 8, -	94.2	21.6	78.4	[84]
		Two-step method *				
17	$Zn(NO_3)_2$	130, 90, -	95	-	85.6	[70]
18	$ZnCl_2$	130, 90, -	95	–	84.9	[70]
19	ZnO	180, -, DMF	86.5	–	53.6	[85]
20	Zn:La (1:9)	180, -, DMF	97.9	–	77.9	[85]
21	[BMIM]$NO_3/Zn(NO)_2$ 1/1	175, 45, -	98	–	78.0	[70]

* Decarboxylation of glycerol carbonate to glycidol: $[N_{2222}]$[Pipe]  ; $[N_{2222}]$[Pro]  ; $[N_{2222}]$[H-pyr]  ; $[N_{2222}]$[Thio]  .

Recently [84], GD has been prepared in the presence of composite materials based on layered titanosilicate material (AM-4, Aveiro-Manchester 4) and zeolitic imidazolate framework-8 (ZIF-8) (ZIF-8/AM-4). ZIF-8/AM-4 materials with varying ZIF-8 content were synthesized using a two-step procedure. In the first step, zinc cations replaced interlayer sodium cations in the AM-4 framework. During the solvothermal procedure of the second step, ZIF-8 particles were formed by modifying the Zn/AM-4 samples with 2-methylimidazole. The catalytic properties of the resulting ZIF-8/AM-4 materials were investigated in the reaction of glycerol with DMC at a molar ratio of DMC/glycerol equal to 2, with 7.9 wt.% of the catalyst (based on the weight of loaded glycerol), at 90 °C for 24 h. The study revealed that the content of ZIF-8 in the composite affects the conversion of glycerol and the distribution of products. The presence of 0.5% ZIF-8/AM-4 resulted in a maximum GD yield of 73.8% with a selectivity of 78.4% (Figure 4). The next increase in ZIF-8 content in the ZIF-8/AM-4 composition resulted in a decrease in glycerol conversion and selectivity towards GD. In the presence of ZIF-8, the glycerol conversion and GD selectivity were 71.3% and 0.4%, respectively. The decrease in activity was explained by the size of the ZIF-8 microcrystals, a reduction in the strength of the basic sites, and an increase in the microporosity of the materials.

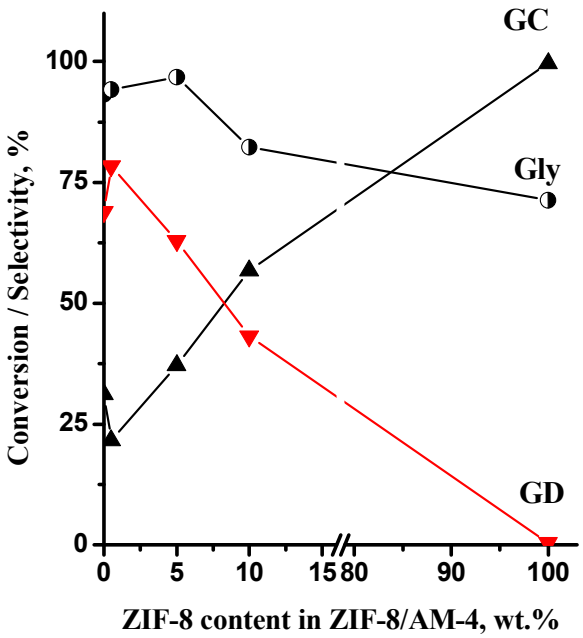
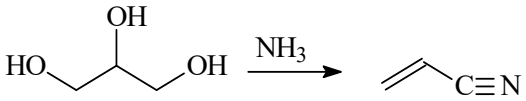


Figure 4. Effect of the ZIF-8 content in the ZIF-8/AM-4 composite on the conversion of glycerol and selectivity towards GC and GD (Experimental conditions: 13.7 mmol of glycerol, 27.4 mmol of DMC, 7.9 wt.% of the catalyst, 90 °C, 24 h).

There is a lack of literature on the one-pot synthesis of GD under MW irradiation. Chinese authors [86] demonstrated the possibility of synthesizing GD from glycerol and DMC under solvent-free conditions in the presence of sodium, potassium, and lithium alkali metal silicates. Table 11 shows that the reactions can proceed effectively in static, microwave, and flow-circulation reactors at a molar ratio of glycerol/DMC of (1–10), with a catalyst loading of 0.5–15.0 wt.% (based on the weight of glycerol) and a temperature range of 50–250 °C. It is worth noting that MW irradiation is more advantageous than other methods, as the reaction under MW assistance takes only 5 min with 89–99% conversion of glycerol and 62–69% selectivity for GD.

3.4. Preparation of Other Products from Glycerol (Acrylonitrile, Acrolein, Ethers, Esters of Glycerol)

Acrolein and acrylonitrile are the most important products that can be produced from glycerol (Scheme 8).

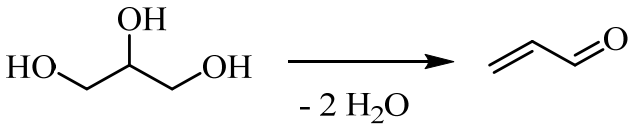


Scheme 8. Synthesis of acrylonitrile from glycerol.

Table 11. One-pot synthesis of glycidol from glycerol and dimethyl carbonate in the presence of sodium silicate [86].

№	Catalyst (wt.%)	Experimental Conditions					Method of Synthesis	Catalytic Properties			Yield of GD (%)
		DMC (mmol)	Gly (mmol)	DMC/Gly (mol/mol)	T (°C)	Time (min)		Conversion of Gly (%)	Selectivity (%)		
									GC	GD	
1	4.35	0.15	0.05	3/1	90	5	MW	85	38	62	52.7
2	8	0.1	0.05	2/1	90	5	MW	90	35	65	58.5
3	4.35	0.15	0.05	3/1	90	3	MW	90	31	69	62,.1
4	4.35	0.15	0.05	3/1	50	30	MW	>99	32	68	67.3
5	4.35	0.15	0.05	3/1	250	30	Autoclave	56	35	65	36.4
6	0.5	0.15	0.05	3/1	90	90	Autoclave	60	45	55	33.0
7	4.35	0.15	0.05	3/1	90	90	Flow-circulation reactor	>99	28	72	71.3
8	15	0.25	0.05	5/1	100	180	Flow-circulation reactor	>99	22	78	77.2
9	2	0.4	0.05	8/1	120	10	Flow-circulation reactor	>99	33	67	66.3

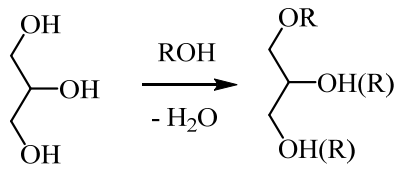
The conversion of glycerol into acrolein (Scheme 9) via dehydration can be considered a benign method of glycerol processing. This reaction occurs on diverse catalysts such as zeolites, metal oxides, heteropoly acids, phosphates, and pyrophosphates. Recent studies on acrolein production from glycerol were analyzed by Abdullah et al. [87]. The use of MW irradiation in this process reduces catalyst deactivation due to coke formation and enhances catalyst stability and reusability. The highest acrolein selectivity of 92% was achieved using modified zeolite ZSM-5. The catalyst Zr6 (MOF-808), based on a metal–organic framework, demonstrated an acrolein selectivity of 91%.



Scheme 9. Synthesis of acrolein from glycerol.

Xie et al. proposed suppressing coke formation during the reaction of glycerol dehydration by using MW heating [88,89]. This approach achieved a uniform temperature profile within the catalyst particles. The study focused on a WO_3/ZrO_2@SiC catalyst that absorbs MW energy. The researchers examined the impact of reaction temperature, ZrO_2/SiC ratio, and space velocity on glycerol conversion and selectivity to acrolein. The use of the MW mode of operation resulted in a lower process temperature. At 250 °C, glycerol was converted 100% with a 70% selectivity for acrolein. The selectivity of acrolein was found to be dependent on the acidity of the catalyst. Additionally, the MW treatment proved to be effective in the in situ regeneration of the spent catalyst.

Under MW conditions, the synthesis of ethers from glycerol and alcohols (Scheme 10) was extensively studied [90–93]. Zeolites (dealuminated HY and HZSM-5), aluminophosphates with different Al/P ratios, silica, titania, as well as carbon materials functionalized by sulfonic acids were used as catalysts. Most studies were performed with tert-butyl alcohol.



Scheme 10. Synthesis of ethers from glycerol and alcohols.

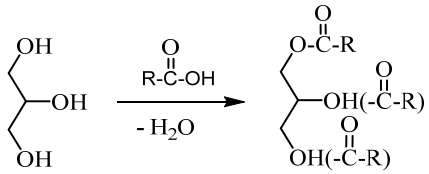
The zeolites and aluminophosphates were initially treated with 3-mercaptopropyltri methoxysilane, followed by oxidation of the thiol group with H_2O_2, and subsequently with 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane to introduce sulfonic acid groups. The yields of glyceryl-tert-butyl ether ranged from 13% to 21% at 75–85 °C with a 15 min MW treatment time. The modified HY zeolites exhibited higher activity than the HZSM-5 zeolites, likely due to their larger pore size and hydrophilic properties, which were beneficial for catalyst performance. In the case of the carbon-based catalysts, $-SO_3H$ groups were introduced by treatment with sulfuric acid. A conventional heating procedure provided a similar conversion (about 20%) but with increased reaction time (6 h).

The kinetics of glycerol etherification with tert-butyl ether on aluminophosphates was studied under MW irradiation [94]. A CuAlPO catalyst demonstrated the highest activity in a short period of time with 95% glycerol conversion and 68% selectivity to higher ethers (di- and tri-substituted ethers).

Esters produced from glycerol, like triacetin (1,2,3-triacetylpropane), can be used as octane boosters, additives to diesel fuel, as well as food additives. Luque et al. reported on glycerol transformations (both etherification and esterification) on polysaccharide-derived mesoporous materials with acidic properties [95]. In the case of etherification using a series of alcohols, high selectivities to both 1- and 2-positions were found.

Ionic liquids are known to be very good MW-absorbing substances, the tan δ value for some of them reaches 3, and the higher the temperature, the larger the loss tangent. Therefore, the paper by Khan et al. on elective esterification of glycerol over ionic liquid-functionalized (imidazolium hydrogen sulfate) cellulose under MW conditions is of interest [96]. The glycerol conversion and the selectivity with respect to triacetin were close to 100% with the time of MW treatment of 8 min. The catalyst demonstrated very good recyclability in five consecutive runs.

Clays modified with H_3PO_4 can also act as efficient catalysts for esterification of glycerol with acetic acid in the MW-assisted process (Scheme 11) [97]. The yield of acetins reached 26.4% at the glycerol:acetic acid molar ratio of 1:3, 90 °C, 1 h. Under conventional heating, the yield of acetins was 22.5%. Under the MW conditions, the monoacetin content in acetins was 67%.



Scheme 11. Esterification of glycerol with carboxylic acids.

Natural zeolite with a Si/Al ratio of 6 was tested in the production of triacetin under MW irradiation [98]. The glycerol conversion was over 95%, whereas the selectivities to monoacetin, diacetin, and triacetin were 43.0, 48.6, and 8.3%, respectively, at 90 min.

Di- and triacetins were produced under microwave heating with hydroxylated magnesium fluorides as catalytically active materials [99]. The catalyst activity is governed by the density and nature of acid sites (Lewis acid sites and Brønsted acid sites) at the external surface. Glycerol conversion over 90% and selectivities to di- and triacetins higher than 85% were observed.

Umrigar et al. reported on esterification and ketalization of levulinic acid with glycerol on desilicated zeolite β (Scheme 11) [100]. Both conventional and microwave-assisted modes were compared. The reaction temperature was 170–180 °C, reaction time—20–80 min, and microwave input power—300–500 W. Conversion of 99–100% was obtained with product selectivity to esters of 69% and keto-ester of 22% in the MW process.

There were further studies aimed at increasing the chain length in the glycerides that have wide application in food and pharmaceutical industries. So, glycerides of C8–C10 fatty acids were synthesized under ultrasound and MW conditions [101]. The consecutive microwave and ultrasound treatments demonstrated the highest glycerol conversion of 99.7% in 20 min. The conversion under conventional heating was just 40% in 180 min.

Monoglycerides are also demanded on the industrial scale. Qadariyah et al. prepared glycerol monostearate in MW conditions [102]. The influence of the input MW power (40–80 min) and reaction temperature (120–160 °C) and time (up to 80 min) on the product yield was investigated with HCl as a catalyst. At 160 °C, the yield of glycerol monostearate reached 88.4%. The same team explored the microwave (300 W) synthesis of glycerol monooleate [103] with H-ZSM-5 zeolite catalyst. With the reaction time of 50 min at 160 °C, the product yield was as high as 92%.

Another example of MW-assisted synthesis of glycerol trioleate (a lubricant) is presented by Kong et al. [104]. Methane sulfonic acid catalyst without any solvent provided the conversion of 90% (191 °C, 104 min). Under conventional heating conditions, the conversion was only 39.5%.

Glycerolysis can be used for removal of free fatty acids in any feedstock [105]. This process's efficiency has been enhanced by using MW irradiation in comparison with conventional heating. A significant decrease in the reaction time from 240 to 25 min and temperature from 200 °C to 105 °C was observed under MW conditions vs. the conventional approach. The rate constant for microwave glycerolysis was six times higher than that found

in the conventional mode. Energy consumption was slashed from 203.6 kJ/g (conventional operation) to 35.3 kJ/g (MW synthesis).

The use of MW irradiation turned out to be more efficient than conventional heating even in the case of biosynthesis of glycerol monolaurate using an enzyme [106]. The MW biosynthesis was performed with Novozym 435 in a reverse microemulsion system dispersed by Aerosol-OT. Under MW conditions, 125.9 mol/l (36 wt.%) of glycerol monolaurate was produced in 30 min, which is 150% compared to conventional heating. It was also found that a larger interface of the reaction system was formed under microwave irradiation and microwave irradiation favored a less compact state of enzyme, facilitating the transition of conformational states, thereby accelerating the reaction.

3.5. Synthesis of Fuel Components and Synthesis Gas from Glycerol Under Microwave Conditions

Glycerol is a potential feedstock for producing H_2, as 1 mol of glycerol can theoretically produce up to 4 mol of hydrogen. Additionally, when glycerol is gasified at high temperatures to produce hydrogen, CO can be obtained as one of the gaseous products. Alternatively, the syngas (H_2 + CO) obtained from glycerol could be used as a feedstock in Fischer–Tropsch synthesis to produce methanol or hydrocarbons [107]. Pyrolysis of glycerol into synthesis gas and oil was described in [108,109]. The highest yield of syngas, but the lowest H_2/CO ratio, was found in the case of glycerol reforming as compared to other biomass-derived waste resources. MW heating was characterized by enhanced syngas yields compared to thermal pyrolysis. The microwave process was shown to be less time and energy consuming in comparison to the thermal mode of operation.

The reaction of water–glycerol solution conversion into hydrogen under MW heating conditions (600 W) was studied on a NiO/zeolite catalyst [110,111]. The influence of the MW power, NiO content, and space velocity on the glycerol conversion and selectivity to H_2 was carefully investigated. The conversion reaches 96.67% at 73.5% selectivity towards hydrogen. Additives of CaO were beneficial for the enhancement of the glycerol conversion and increasing the H_2 yield. The maximum glycerol conversion for the NiO/zeolite-CaO catalysts was 98.8% with the hydrogen purity reaching 96.6% at NiO and CaO contents of 20 wt.% and 50 wt.%, respectively.

MW-assisted pyrolysis of glycerol into a mixture of hydrogen, methane, and CO_2 on a carbon-based catalyst was studied in a plug-flow reactor in an oxygen-deficient environment [112]. The inert carrier gas space velocity and pyrolysis temperature dramatically affect the product yield. The maximum hydrogen yield was equal to 35.2% at 600 °C. Silicon carbide can be used as microwave-energy-absorbing material and a support for nickel catalysts [113,114]. The microwave power ranged from 110 to 880 W, the reaction temperature from 500 °C to 1400 °C, which can be achieved within a few minutes, i.e., much faster than in the case of conventional heating. For the non-catalytic reaction at 220 W (700 °C), the conversions were 19–23% with syngas of the composition H_2/CO = 1.27. In the catalytic run, the highest syngas yield was obtained for the 1%Ni/SiC catalyst, the highest H_2/CO being 2.72 for 0.5%Ni/SiC.

Except for synthesis gas, pyrolysis oil and other fuel components can be produced from glycerol under microwave heating using appropriate catalysts. The recent review by Okoye et al. [115] presents examples of the reduction in the energy consumption and improvement of the operational safety while using significantly milder reaction conditions in an MW reactor compared to the TH system.

Glycerol was pyrolyzed under MW heating in an oxygen-deficient environment with activated carbon as a catalyst [116]. The pyrolysis temperature varied from 300 °C to 800 °C. Both liquid and gaseous products were obtained with the yields of 15–42% and 55–82%.

MW-assisted pyrolysis at 300–800 °C on a carbon-based catalyst was applied to convert glycerol [117]. Analysis of the energy content showed that overall energy profit increases with decreasing temperature and increasing residence time.

Another way to include glycerol in the value chain is its use in the reaction of glycerolysis of different natural oil grades, such as neem oil [118]. Neem oil is a low-cost feedstock

oil that may be used but after a pre-treatment process (glycerolysis) to reduce the free fatty acids content to less than 1%. Since the conventional (thermally induced) glycerolysis process requires long reaction times, the authors studied MW irradiation to increase the rate of this process. The influence of the reaction time (5 or 9 min), temperature (100 °C or 120 °C), oil to glycerol molar ratio (1:1 or 1:2), and sulfuric acid (a catalyst) concentration (2% or 4.5%) was investigated. The reaction temperature was found to affect the reduction in the free fatty acids content the most. The highest efficiency was achieved at the oil to glycerol ratio of 1:1, catalyst loading of 2%, time of 6 min, and reaction temperature of 120 °C. Under these conditions the reduction in the free fatty acids content reached 91.8%.

Glycosylation of diverse monosaccharides with different alcohols, including glycerol, under MW heating was shown to be extremely efficient [119]. Montmorillonite K-10 clay catalyzed Fischer type glycosylation and the catalyst was reused three times without any decrease in the activity and anomeric selectivity. With glycerol, the products glycosylated at primary alcohol groups formed only.

3.6. Other Valuable Products of Microwave Glycerol Conversion

Luque et al. reported on oxidative glycerol transformations on mesoporous materials [95]. The Starbon® material as a support for palladium-catalyzed selective oxidation of glycerol to both glycolic and oxalic acids. The catalyst can be recycled without any significant loss of the activity.

Hydrogen peroxide was used as an efficient oxidant of glycerol under MW conditions. Crotti et al. oxidized primary and secondary alcohols, including glycerol, with H_2O_2 with iron(II) complexes $[FeL_3](OTf)_2$ (L = 2,2′-bipyridine, 2,2′-bipyrimidine, 1,10-phenanthroline and substituted analogs) and $[FeL_2](OTf)_2$ (L = bis(2-pyridinylmethyl)amine, 2,6-di(2-pyridyl)pyridine) [120,121]. Introduction of nitrogen atoms in the composition of the ligands, i.e., the addition of heterocyclic amino acids, namely the use of $[Fe(bpydeg)_3](OTf)_2$ (bpydeg = N4,N4-bis(2-(2-methoxyethoxy)ethyl)[2,2′-bipyridine]-4,4′-dicarboxamide) complexes, allowed the authors to increase the efficiency of the catalysts. The major product was formic acid, and in some cases dihydroxyacetone was found in the products.

Lactic acid is an extremely important product of industry, especially for the synthesis of polylactates, biodegradable polymers. There are many publications on the thermal conversion of glycerol to lactic acid, but the number of papers focused on microwave processes is very limited. Glycerol was converted to lactic acid under MW conditions by Finn et al. [122]. Ir(I), Ir(III), and Ru(II) N-heterocyclic carbene (NHC) complexes with sulfonate-functionalized groups in the presence of an aqueous base were used in this process as catalysts and comparison of TH and MW heating was performed. The most active catalyst reaches a TOF of 45,592 h^{-1} (MW) and 3477 h^{-1} (TH) with 1 equiv of KOH, and the reaction proceeds at a constant rate for at least 8 h. Although higher activity is observed with KOH, the catalysts are also highly active with the weaker base, K_2CO_3 (13,000 h^{-1} and concurrent formation of formate). The protocol can be modified to achieve quantitative conversion of glycerol in only 3 h. The high activity of these catalysts compared to non-sulfonated analogs is attributed to the stabilization the lactate product in aqueous media. The most active catalyst retains equal activity for crude glycerol. A mechanism is proposed for the most active catalyst precursor involving O-H oxidative addition of glycerol.

A mixture of liquid products, such as monohydric (10–62 wt.%) and polyhydric (0–46 wt.%) alcohols, carboxylic acids (0–9 wt.%), and C3-ketones (0–80 wt.%), was derived from a 30 wt.% glycerol aqueous solution under hydrothermal MW-assisted conditions [123]. The process occurred in the presence of a Ni-Co/Al-Mg oxide catalyst (5–15 wt.%) at 150–250 °C and pressures of 5–12 MPa for 1–2 h. The glycerol conversion reached 54%. Monohydric alcohols and C3-ketones preferentially formed with short reaction times and/or low catalyst amounts. An increase in the reaction time and catalyst loading favored an increase in the content of polyhydric alcohols and a decrease in the content of C3-ketones. The production of C3-ketones (72 wt.%) is highest at 210 °C, 5 MPa, and

synthesis time of 2 h. Additionally, 40% of glycerol can be transformed into monohydric (79 wt.%) and polyhydric (21 wt.%) alcohols at 250 °C, 8.2 MPa, and 2 h.

A quite unexpected product, 3-picoline, was produced from glycerol under MW conditions [124]. The liquid-phase reaction proceeds under mild conditions in the presence of acetic acid, and the heating source dramatically affected the yield of 3-picoline. The yield of 3-picoline was enhanced by MW heating, while very low yields of 3-picoline were found under conventional heating. The effect of the nature and composition of a series of heterogeneous catalysts was identified. A 71% yield of 3-picoline was observed on TiO_2 at 100 °C with 20 min of microwave heating, and this was the best catalyst found so far for this reaction.

Another fascinating example was reported by Ainembabazi et al. [125], who demonstrated efficient transfer hydrogenation of CO_2 and carbonates from glycerol to yield formic acid and lactic acid. Thermally stable and water-soluble Ir(I) and Ir(III) N-heterocyclic carbene complexes bearing sulfonate groups are the best performers for this process. The most efficient catalyst was [Ir(NHC-Ph-$SO_3-)_2CO_2$]Na that demonstrates a very high activity at an extremely low catalyst loading (10 ppm) at 150 °C under either MW or TH conditions. The cation of the carbonate salt affects the catalyst activity, with Cs_2CO_3 being most efficient (TON = 27,850 and 13,350 for lactate and formate formation in 6 h, compared to TON = 15,400 and 8120 for K_2CO_3). Additives of Cs(I) ions significantly increase the activity of the catalyst even when K_2CO_3 is used. The catalyst solubility in aqueous media and the presence of π-acceptor carbonyl ligands were supposed to be the key factors affecting the activity. A mechanism of the reaction is proposed, which includes several stages: O-H oxidative addition of glycerol, β-hydride elimination, bicarbonate dehydroxylation, insertion, and reductive elimination.

3.7. Synthesis of Polymers Based on Glycerol

One new avenue of research is leading to polymer products produced directly from glycerol. Application of polyglycerol in food, polymer, cosmetic, and pharmaceutical industries is steadily growing. The first mention of this type of glycerol conversion goes back to 2015 [126]. Optimization of the etherification of glycerol to polyglycerols in the presence of Na_2CO_3 as a catalyst under MW heating without any solvent was reported. The reaction parameters were as follows: 220 °C and 270 °C, catalyst concentration 1 wt.% and 3 wt.%, reaction duration 0.5–3 h. Diglycerols, triglycerols, and tetraglycerols with smaller amounts of pentaglycerols and cyclic diglycerols were identified in the reaction products. Cyclic diglycerols are undesirable products and the formation is favored by high temperatures and increased reaction times. A higher catalyst loading has a positive impact on the production of target products. The glycerol conversion was 93%, with 70% of the overall yield of diglycerols + triglycerols + tetraglycerols at 270 °C with a catalyst loading of 3 wt.% and reaction duration 1 h. Note that the yield of cyclic diglycerols was about 7%.

Also, one of the first publications on MW-assisted synthesis of copolymers of glycerol, i.e., poly(glycerol-sebacate) elastomers (a material for soft tissue repair), was issued in 2013 [127]. The reported state-of-the-art approaches to the preparation of these copolymers include a two-stage process with pre-polymerization and curing, and the reaction may take several days. The rapid synthesis of these elastomers was performed by MW-assisted pre-polymerization taking a few minutes with the following curing step at 150 °C (4–24 h).

Upscaling of the glycerol polymerization was carried out by Nguyen et al. [128] with a yield of the product of 100 g at a 100% glycerol conversion under MW treatment for 30 min in the presence of K_2CO_3. The molecular weights of the products were up to 1000 g/mol with a narrow dispersity ($D < 1.5$). The same authors [129] developed a continuous oligomerization process of glycerol conversion to polyglycerol under MW conditions with K_2CO_3 as a catalyst. Linear and branched-chain diglycerol and triglycerol regioisomers were produced, in particular, a mixture of diglycerol (50.2 wt.%), triglycerol (22.1 wt.%), tetraglycerol (9.5 wt.%), and pentaglycerol (4.3 wt.%).

Comparison of glycerol conversion to polyglycerol under conventional and MW heating modes of operation has been performed by Sajid et al. [130]. The investigation revealed that the optimal regime for the MW process (3 h, Li/MK-10 clay-based catalyst) is capable of achieving a 90% conversion of glycerol into polyglycerol, whereas the most optimal conventional heating regime allows one to reach only 80% conversion in 8 h with Na_2CO_3 as a catalyst. The same group studied cerium nitrate and lithium nitrate supported on montmorillonite K-10 clay (MK-10) as catalysts [131]. The highest glycerol conversion was 94% with a yield of target products of 70% at 260 °C and 5 h of MW-assisted reaction time. The selectivity towards undesired polyglycerols was 24%. The authors also tried to use aluminum pillared clay as a support for the catalyst, which was LiOH [132]. The Li loading varied from 10 to 30 wt.%, the catalyst loadings from 2 to 4 wt.%, and the reaction temperature from 200 to 240 °C with reaction time ranging from 1 to 4 h. The best catalyst was found to be 20 wt.% Li/AlPC, which had a large surface area of 95 m^2/g, basicity of 34.5 mmol/g, and average pore diameter of 19.2 nm. The highest glycerol conversion was 98.9% with a polyglycerol yield of 90.5% (at catalyst loading of 3 wt.%, 220 °C, and 3 h). Another type of catalyst was Li-intercalated montmorillonite clay [133]. The highest glycerol conversion of 98% was achievable in 4 h with the highest diglycerol yield of 45%.

4. Summary and Outlook

Currently, glycerol is widely used both as a solvent and a building block in various industries. MW technology has many advantages over conventional thermal processes, as evidenced by numerous data. Among the advantages are the possibility of efficient heating of materials with low thermal conductivity and the high degree of controllability of the heating process. Furthermore, MW irradiation allows the process to be carried out in a shorter time and produce products with the highest yield.

1. The MW mode was demonstrated to be effective in synthesizing ketals and acetals from glycerol and ketones. Application of MW technology results in increasing reaction rates and product yields compared to the conventional TH mode. For instance, in the synthesis of solketal from glycerol and acetone, using MW mode resolves the issue of blocking of active sites of the catalyst by water molecules and produces solketal with a yield of over 95%.

2. MW irradiation can be used as a useful tool in regulating the reaction rate of glycerol with dimethyl carbonate. In addition, MW irradiation can activate glycerol carbonate produced during the reaction and promote its decomposition into glycidol. Combining these two reactions enables one-pot synthesis of glycidol. It is important to note that the choice of catalyst is crucial for this process, as it must have both acidic sites for the reaction of glycerol with dimethyl carbonate and basic sites for the subsequent decomposition of the resulting glycerol carbonate. Currently, this is an area of active research, with scientists searching for bifunctional catalysts for one-pot processes.

3. MW energy can also improve the catalytic process of obtaining other products, such as acrylonitrile, acrolein, ethers, and esters of glycerol, polymers based on glycerol, fuel components, and synthesis gas. Currently, there is still a lack of knowledge regarding the kinetics and mechanisms of glycerol reactions under microwave irradiation.

4. Many studies have shown that MW technology is advantageous for treating glycerol formed from biomass to obtain various chemicals on the laboratory scale. Currently, there are several limitations to the application of these results in industry. One of the problems of MW technology's application in industry is significant investment for the replacement of current conventional systems by MW equipment.

Therefore, this area of study could be an attractive prospect for future exploration. It is important to note that this area is in the early stages of research, and we should expect rapid development in the future, thanks to the modernization of MW equipment.

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Abbreviations

MW	Microwave irradiation
TH	Thermal heating
HT	Hydrothermal synthesis
Gly	Glycerol
DMC	Dimethyl carbonate
GC	Glycerol carbonate
GD	Glycidol
5-M	Acetal obtained from glycerol and aldehyde/ketone
6-M	Ketal obtained from glycerol and aldehyde/ketone
5-S	Solketal, acetal obtained from glycerol and acetone
6-S	Ketal obtained from glycerol and acetone
AlPO	Aluminophosphate
p-TSA	p-Toluenesulfonic acid, tosylic acid
DMSO	Dimethyl sulfoxide
DMF	Dimethylformamide
TWT	Traveling wave lamp
MAOS	Microwave-assisted organic synthesis
SAFACAM	Sulfonic-acid-functionalized carbonaceous material
MAPA	Musa acuminata peel ash
LDH	Layered double hydroxide
NHC complexes	N-heterocyclic carbene complexes

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