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Review

Organic Carbonate Production Utilizing Crude Glycerol Derived as By-Product of Biodiesel Production: A Review

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Abstract: As a promising alternative renewable liquid fuel, biodiesel production has increased and eventually led to an increase in the production of its by-product, crude glycerol. The vast generation of glycerol has surpassed the market demand. Hence, the crude glycerol produced should be utilized effectively to increase the viability of biodiesel production. One of them is through crude glycerol upgrading, which is not economical. A good deal of attention has been dedicated to research for alternative material and chemicals derived from sustainable biomass resources. It will be more valuable if the crude glycerol is converted into glycerol derivatives, and so, increase the economic possibility of the biodiesel production. Studies showed that glycerol carbonate plays an important role, as a building block, in synthesizing the glycerol oligomers at milder conditions under microwave irradiation. This review presents a brief outline of the physio-chemical, thermodynamic, toxicological, production methods, reactivity, and application of organic carbonates derived from glycerol with a major focus on glycerol carbonate and dimethyl carbonate (DMC), as a green chemical, for application in the chemical and biotechnical field. Research gaps and further improvements have also been discussed.

Keywords: crude glycerol; glycerol carbonate; dimethyl carbonate; microwave irradiation; reaction kinetics

1. Introduction

Throughout history, the survival of human beings has been fully dependent on the resources found on the Earth. In recent times, the world has been threatened with increasing environmental problems, particularly global warming. Statistics show that the carbon dioxide (CO_2) levels in the atmosphere have been increasing every year and touched a record of 411.93 ppm in February

2020 [1]. Moreover, it is projected that conventional petroleum in Malaysia will run out by 2050 with the current consumption rate [2]. Hence, sustainable development by replacing conventional fossil fuels with alternative renewable and sustainable resources is a must to overcome the fossil fuel depletion issue and protect the global environment. Governments have also shown their initiatives by adopting new laws and regulations to ensure that the emission standards are being constricted for off-road, marine and stationary engines. Hence, alternative fuels have been explored and fostered, especially for transportation, construction, cultivation and electricity generation. Among the available renewable energy resources, biomass plays a significant role as feedstock in most biofuel production [3]. In the chemical industry, raw material origins are usually not the main issue. In contrast, cost and process effectiveness are the major driven of innovation. Nevertheless, the growth of sustainable consciousness, reinforced by both general society attitude and government initiatives, has pushed the researcher/chemist to take the naturally available raw material into consideration. As a result, the interest of researchers in exploring the alternative material and chemicals derived from sustainable biomass resources has been increased. The main aim of this article is to review the recent publications on the process of glycerol upgrading into glycerol carbonate. The catalytic activities, such as hydrotalcites, zeolites, heteropoly acids, and oxides, are emphasized. Further, the effect of different reaction conditions on the catalytic activities and selectivity of glycerol carbonate are also discussed in this article. Furthermore, issues that require further investigation have also been highlighted.

2. Biodiesel and Renewable Diesel

Petroleum diesel, i.e., conventional fossil fuel, is produced from petroleum-based crude oil. Crude oil is the combination of hydrocarbons, organic compounds, and small amounts of metal, which formation takes millions of hundreds of years. Crude oil is removed from the ground and transferred into a refinery. The crude oil is then passed through a heat-and-pressure based process within the refinery. To replace the conventional non-renewable petroleum diesel, biodiesel and renewable diesel are introduced (Figure 1). The major difference between biodiesel and renewable fuel will be explained shortly. As biodiesel and renewable diesel are in the form of liquid, unlike other renewable energy (i.e., hydro energy and solar energy), they can be directly used to operate current engines, especially transportation vehicles and industrial machines that are mostly operated by liquid fuel, without modification to their design.

Unlike petroleum diesel, biodiesel does not depend on fossil fuel. Biodiesel is usually produced from vegetable oils and/or animal fats through the transesterification process. In 2019, petrol stations in Malaysia switched from B7 to B10, to increase the sustainability of energy sources [4]. The next renewable alternative fuel is called renewable diesel. Renewable diesel, almost similar to biodiesel, is formed from waste agricultural products [5], mainly waste vegetable oils and animal fats. The main difference between renewable diesel and biodiesel is the production method. The production process of renewable diesel and petroleum diesel is the same, and hence, it is chemically similar to each other. However, the greenhouse gas emissions of renewable diesel (also known as hydro-treated vegetable oil or HVO) and traditional biodiesel are both smaller than those from fossil diesel. From an environmental perspective, the usage of biodiesel and renewable diesel fuel can significantly reduce the emissions of hydrocarbon, carbon monoxide, and particulate matter [6]. However, it is well-known that the combustion of biodiesel in diesel engine emits 10% more of NO_x in comparison to petroleum diesel. On the other hand, this increase in the NO_x emission issue can be solved by using renewable fuel combustion as it was reported that the use of renewable fuel leads to lower NO_x emission when compared to petroleum diesel [7,8]. Furthermore, as the chemical properties of renewable diesel and petroleum diesel are similar, that would mean a few things:

- The hydrogenation process makes the renewable diesel devoid of oxygen. Hence, the problem related to freezing temperature and storage, which are faced by biodiesel, will be avoided.
- Due to hydrogenation, the combustion of renewable diesel is cleaner than biodiesel.

- The engines that are designed for conventional diesel fuel are also compatible with renewable diesel, with no blending necessary since they are chemically the same.
- Along with the above, since the process is not a transesterification reaction, there will be no production of waste glycerol. Hence, the crude glycerol issue, which is the major concern of biodiesel production, will be eliminated.

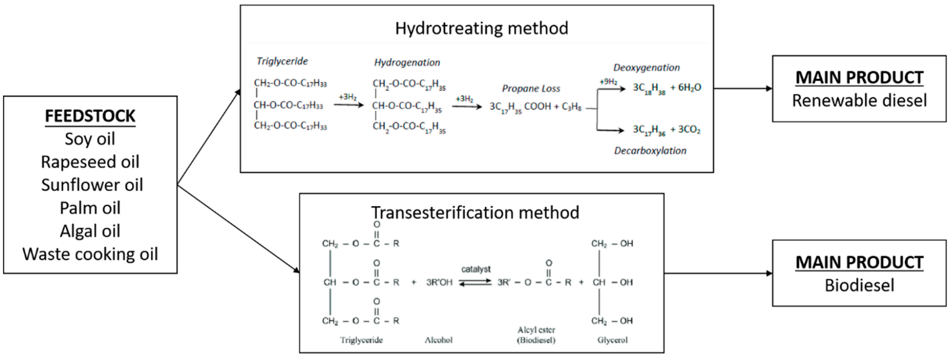

Figure 1. Processing for renewable diesel and biodiesel production.

The demand for biodiesel, as a renewable liquid biofuel, has been increasing. Global biodiesel production is expected to reach 23.57 billion litres by 2025 [9]. Biodiesel is produced from vegetable oils or animal fats along with methanol via transesterification reaction [10,11]. The transesterification process is usually catalysed by sodium methoxide (CH_3NaO) for a single-feedstock biodiesel plant, and potassium hydroxide (KOH) or sodium hydroxide (NaOH) for a multiple-feedstock biodiesel plant. As an important source of sustainable energy fuel, the annual biodiesel production increased year by year. Worldwide, biodiesel production uses primarily vegetable oil as its raw feedstock. In the European Union, rapeseed oil is used as main feedstock, while in the United States it is soybean oil, and in Asia it is mainly palm oil. Moreover, algae has also been identified as a potential feedstock for biodiesel production [12]. Crude glycerol is the major by-product formed from biodiesel production via the transesterification reaction. The simplified biodiesel production process is shown in the flowchart (Figure 2).

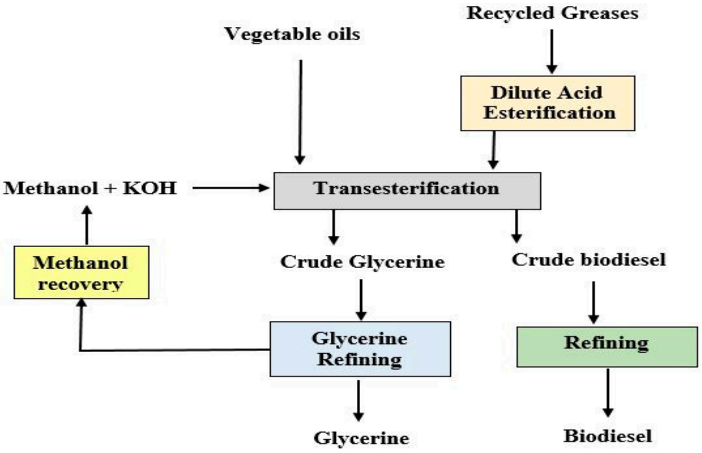

Figure 2. An overview of a standard biodiesel production process - Biodiesel and glycerol are the two main products.

3. Crude Glycerol – By-product of Biodiesel Production

Although the growth of the biodiesel industry has increased dramatically, especially between 2005 and 2015 (from 10% of total biofuel output to 25% in 2015), the biodiesel production still highly depend on the government policy and economic subsidies due to the high production costs of biodiesel [13].

Moreover, another major issue of biodiesel production is the generation of a by-product, crude glycerol. It is reported that 10 g of glycerol is generated for every 100 g of biodiesel produced [14–16]. Hence, the development of sustainable methods for exploiting this low cost organic raw material is imperative. Nevertheless, as there are impurities present in the crude glycerol, making the direct applications of crude glycerol restricted. The world markets for biodiesel are going into a period of precipitous, transitional growth, creating both uncertainty and opportunity [17]. Hence, an urgent solution is required to mitigate the problem of oversupply of this crude glycerol. Over the long term, biodiesel producers that are best able to evolve and adapt to advancement in technology, markets, feedstock, and government policies are most likely to succeed. One of the obvious ways to significantly improve the economic aspect of overall biodiesel production is the utilization and conversion of the glycerol by-product into value-added products [18]. With the estimate of the world market for biodiesel reaching 150 billion litres per year by 2016, this potentially means a stockpile of over 15 billion litres of crude glycerol available for refining and converting into value-added products per year [19]. The crude glycerol stream from the biodiesel process typically is about 50% glycerol or less and also contains an unused catalyst, alcohol, soap, water and salts. As mentioned previously, the presence of impurities lowers the value of the crude glycerol. Its value varies according to the level of impurities, which in turn is directly dependent on the type of feedstock used and the biodiesel synthesis method. The untreated crude glycerol can be used as animal feed, and for the co-digestion/co-gasification process but this can only be done on a short-term basis. The by-product crude glycerol will require a stringent purification process before it can be utilised in food, pharmaceutical or cosmetics fields. There are three main procedures in purifying crude glycerol. The first stage is the removal of free fatty acids, soap, and carried over catalyst via neutralization. The second step involves the evaporation of the excess methanol present in the crude. The third procedure, however, includes selective purification with the purpose to achieve the final product purity, through several methods, such as distillation (vacuum or azeotropic type), cation exchangers, which remove positively charged ions, or anion exchangers, which remove negatively charged ions, membrane separation with vaporization (pervaporation), and absorption [20]. In a recent review, a more detailed description of the purification of crude glycerol was reported [21]. The typical steps are summarised in Table 1 [22].

Table 1. Typical steps in crude glycerol purification [22].

Steps	Methods	Description
1	**Neutralization**	• Remove catalyst and soap by using acids. • If using sulphuric or hydrochloric acid, the final product of this stage will be in two phases. • If phosphorous acid is used, three phases of the final product will be obtained. √ Upper fraction: free fatty acids; middle fraction: glycerol and methanol; lower fraction: catalyst. √ Advantage: less harmful to the environment and tri-potassium phosphate, that is broadly used as fertilizer, is obtained as a by-product.
2	**Methanol removal**	• It is a must to remove methanol from glycerol fraction as it is toxic. • There is a huge amount of methanol in crude glycerol as a result of the excess addition of methanol during transesterification. • To remove the methanol, the evaporation process is conducted at 50–90 °C for at least 2 hours under vacuum.
3	**Vacuum distillation**	• Basically, glycerol can be polymerized into polyglycerol at a temperature above 200 °C. Hence, vacuum distillation is essential so that the purification process can be conducted without the polymerization of polyglycerol. • This method is optimal for small and medium-sized companies due to its high energy consumption as glycerol has high heat capacity.
	Ion exchange resins	• Removal of inorganic salts, free fatty acids, and free ions from crude glycerol.

One of the major drawbacks of the methods mentioned above is the high energy consumption. Therefore, it has triggered the researchers to find different ways for crude glycerol purification, such as membranes separation. The membrane separation process is driven by the concentration or electric potential difference between the two mediums [23,24]. As membrane separation is an eco-friendly technology, it has become more well-known recently in terms of biodiesel's waste glycerol purification. Despite all the processes mentioned, they are economically not viable for the smaller biodiesel producers. It is vital to develop a more eco-friendly, more efficient and economical process for crude glycerol purification, which could improve the cost-effectiveness of the overall biodiesel production [25,26].

Innovative methods for transforming glycerol into high value-added platform chemicals are being developed. Glycerol is one of the most versatile known chemicals with a wide variety of uses and applications such as in food, pharmaceutical, cosmetic, coating, and other industries. In the literature, several protocols for the synthesis of value-added products from glycerol have been reported and a significant number of platform molecules have been synthesized. Some of them have high potential in replacing petroleum-based products. As stated by Behr et al., all chemical products derived from glycerol are a result of one of many processes [27], as shown in Figure 3. These processes include the synthesis of glycerol esters, ethers, acetals and ketals, propanediols, epoxides, the oxidation and dehydration products of glycerol, and the production of synthesis gas. Several important chemicals can be obtained, among the more common ones are propane-diols, glycerol carbonate, epichlorohydrin, acrolein, esters of glycerol, fuel additives and glyceric acid [18,28–30]. Among these products, glycerol carbonate is one of the most attractive derivatives of glycerol reported in the last couple of years because of its high reactivity with amines, alcohols, carboxylic acids, ketones, and isocyanates. According to the market source, the cost for glycerol carbonate in 2017 ranged from US$2.4 to US$3 per kilogram, which means US$2400 to US$3000 per metric tonne [31].

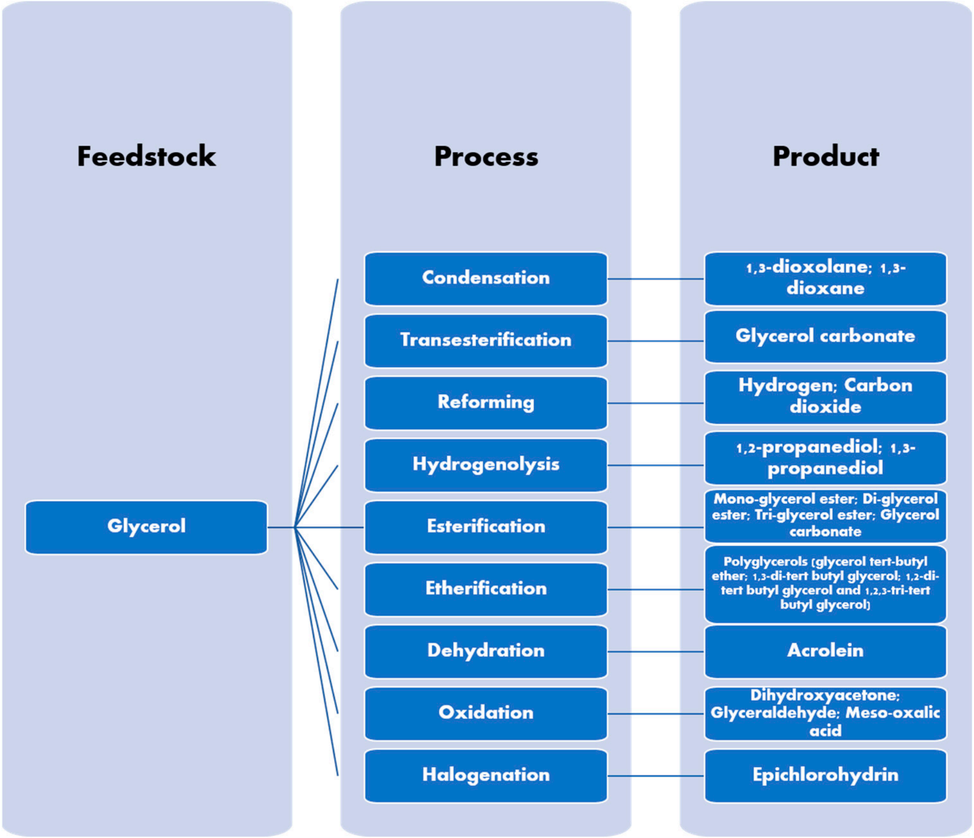

Figure 3. Different Chemical pathway for glycerol conversion to chemical derivatives (Adapted from [32]).

4. Glycerol Carbonate

Among the valuable raw chemicals derived from glycerol is glycerol carbonate (Gly-C) (i.e., 4-(hydroxymethyl)-1,3-dioxolan-2-one). Glycerol carbonate is a cyclic carbonate and its molecular structure presents a structural duality. It bears a hydroxyl group and 2-oxo-1,3-dioxolane group that gives Gly-C wide reactivity [33]. The Gly-C has excellent properties, such as good water-solubility, high boiling point, low toxicity, low flammability, good biodegradability, and a high flash point [34]. The glycerol carbonate is advocated as a useful and green building block in the field of organic chemistry as it is bio-based and has wide reactivity. Gly-C has a molar mass of 118.09 g/mol, and is widely used as a polar high boiling solvent, a surfactant component, a membrane component for gas separation and a component for industrial of coating, detergent, polymers, ink, paint, lubricant and electrolyte [28,35,36]. Furthermore, glycerol carbonate can also be used as chemical intermediates for the synthesis of other chemical compounds such as glycidol, which is employed in textile, plastics, pharmaceutical, and cosmetics industries [28,37].

Figure 4 shows the structural formula of glycerol carbonate. The hydroxyl group of glycerol carbonate consists of H-bonding and hence, glycerol carbonate has higher density properties. Besides, it has the potential to substitute petrochemically derived propylene carbonate. The general properties of glycerol carbonate and pure glycerol are shown in Table 2.

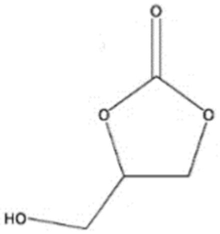

Figure 4. The glycerol carbonate molecular structure.

Table 2. The comparison of properties between glycerol carbonate and pure glycerol.

Properties	Unit	Glycerol Carbonate	Pure Glycerol
Molecular weight	g/mol	118.09	92.094
Density at 25 °C	g/ml	1.4	1.261
Boiling point	°C	354	290
Melting point	°C	−69	17.8
Vapour pressure at 177 °C	bar	0.008	0.003
Flash point	°C	190	177
Dielectric constant at 20 °C	ESU	111.5	42.5
Hansen solubility parameter delta D at 25 °C	$MPa^{1/2}$	17.9	17.4
Hansen solubility parameter delta P at 25 °C	$MPa^{1/2}$	25.5	12.1
Hansen solubility parameter delta H at 25 °C	$MPa^{1/2}$	17.4	29.3
Hildebrand solubility parameter at 25 °C	$MPa^{1/2}$	34.1	36.1
Viscosity at 25 °C	cP	85.4	1500

Glycerol carbonate (Gly-C) has several distinctive reactive locations: (a) the dioxolane ring with three carbon atoms, and (b) the suspended hydroxyl moiety. Hence, Gly-C has the ability to react not only as a nucleophile via its hydroxyl group, but also as an electrophile through its ring carbon atoms. These reactive sites provide potentials for utilizing glycerol carbonate as a precursor molecule for conversion to other intermediate chemicals, which ultimately are used in numerous direct and indirect applications. It has vast industrial applications and some of the potential industrial uses of Gly-C are presented in Table 3.

A sustainable route is to react urea with glycerol to produce glycerol carbonate, which has a vast perspective to be used as a replacement for fossil-fuel derived compounds. More studies were carried out to find environmentally friendly alternative paths in upgrading the waste glycerol into glycerol carbonate. Among the other promising routes for glycerol carbonate production, include reactions based on easily available raw materials, which are inexpensive and bio-based. Using enzymes as catalytic systems could generate more environmentally friendly alternatives. Based on an in-depth analysis of the recent publications on the subject, the present review will focus on glycerol carbonate syntheses routes, it's broad reactivity, and current applications.

Table 3. The potential application of glycerol carbonate in various industries.

Chemical	Industry Application	References
Glycerol Carbonate	• Polymers and plastics • Polyesters • Polycarbonates • Polyamides • Polyurethane plastic coatings • Hyperbranched polyethers • Solvent for plastics and resins	[38]
	• Cosmetics and personal care • Emollient and solvent in nail polish remover, lipsticks, anti-perspirant sticks • Wetting agent for cosmetic clays	[33]
	• Chemicals • Chemical intermediate • Glycidol • Biolubricants • Biobased polar solvents • Liquid membrane in gas separation • Surfactants and detergents • Blowing agent	[39]
	• Pharmaceutical • Solvent for medicinally active species • Carrier in pharmaceutical preparations	[36]
	• Semiconductor • Electrolytes in lithium and lithium-ion batteries	[40]
	• Agricultural • Plant-activating agent	[41]
	• Building and Construction • Curing agent in cement and concrete	[42]

5. Existing Production Routes for Synthesis of Glycerol Carbonate

As mentioned previously, the conventional glycerol market is limited and any large increase in biodiesel production will cause a sharp decrease in its market price. In the last few years, there have been numerous reports in the literature concerning the synthesis of glycerol carbonate from glycerol. While some production methods are being applied at an industrial scale, several new promising synthesis methods were reported recently which are more sustainable. The greener pathway for synthesis of glycerol carbonate involves chemicals such as CO/H_2, organic carbonate (e.g., ethylene carbonate, dimethyl carbonate, and diethyl carbonate), and also carbon dioxide [36,37,43]. These pathways, overall, results in the chemical fixation of CO_2. Among these pathways, the transesterification between glycerol and dimethyl carbonate is one convenient method that could be performed under mild conditions (at 50–100 °C; under atmospheric pressure) in the presence of a catalyst, as shown in Figure 5 [37,43,44]. The catalysts used to convert glycerol to glycerol carbonate can be homogeneous catalysts such as K_2CO_3, NaOH, and H_2SO_4 [44,45], enzymatic catalysts [44], or heterogeneous catalysts such as CaO, NaOH/γ-Al_2O_3, and Mg/Al/Zr mixed oxide [28,35,45]. Table 4 summarizes the reaction conditions for various types of synthesis pathway for glycerol carbonate production. Meanwhile, Table 5 presents the advantages and limitations of the different routes for the synthesis of glycerol carbonate.

Table 4. Different routes for the synthesis of glycerol carbonate (Gly-C) and their experimental conditions.

Reference	Reactants Mole Ratio	Solvent	Temperature (°C)	Pressure (MPa)	Reaction Time (h)	GC Yield (%)	Catalyst
Glycerol + CO							
[46]	5 : 1 : 5 (K_2CO_3 toSe to glycerol)	Dimethylformamide	20	0.1	6	83	None
[46]	5 : 1.5 : 3 : 1 (Et_3N to CuBr to S to glycerol)	Dimethylformamide or Dimethyl sulfoxide	80	1	21	92	None
[41]	Excess CO and O_2	Dimethylformamide	140	3	2	85	0.25 mol% $PdCl_2$(phen) + 2.5 mol% KI
Glycerol + CO_2							
[47]	1.5 : 1 : 1 ($N(CH_2CH_3)_3$ to HCl to glycerol)	Free	100	2.5	1	90	-
[48]	1 : 3 : 3 (K_2CO_3 to HCl to glycerol)	Free	80	0.1	30	80	KOH then HCl
[49]	Excess CO_2	Methanol	140	5.0	59	0.24	$RhCl_3$ + PPh_3 + KI
Glycerol + EC							
[50]	2 : 1 (EC to glycerol)	Free	80	0.1	1.5	92	RNX-MCM41
[51]	2 : 1 (EC to glycerol)	Free	50	0.1	5	82	7 wt% Al/MgO hydrotalcite
[51]	2 : 1 (EC to glycerol)	Free	50	0.1	5	78	7 wt% MgO
[51]	2 : 1 (EC to glycerol)	Free	50	0.1	5	68	7 wt% Al/Mg hydrotalcite
Glycerol + DMC							
[52]	39 : 1 (DMC to corn oil)	Supercritical DMC	380	15-25	0.5	By-product	None
[53,54]	42 : 1 (DMC to rapeseed Oil)	Supercritical DMC	350	20	0.2	By-product	None
[55]	6 : 1 (DMC to soybean oil)	tert-Butanol	60	0.1	48	92	10 wt% lipase (Novozyme 435)
[56]	10 : 1 (DMC to corn oil)	Free	60	0.1	15	62	10 wt% lipase (Novozyme 435)
[34]	10 :1 (DMC to glycerol)	Free	60	0.1	4	59	12 wt% lipase (Aspergillus niger)
[57]	10 : 1 (DMC to glycerol)	Free	70	0.1	48	90	Lipase (Novozyme 435)
[58]	5 : 1 (DMC to glycerol)	Dimethylformamide	100	0.1	0.5	79	Calcined hydrotalcite-hydromagnesite
[28]	5 : 1 (DMC to glycerol)	Free	75	0.1	1.5	95	Mg/Al/Zr
[59]	2 : 1 (DMC to glycerol)	Free	78	0.1	1	99	3 wt% KF/hydroxyapatite
[60]	5 : 1 (DMC to glycerol)	Dimethylformamide	100	0.1	1	75	Uncalcined Mg–Al hydrotalcite
[61]	2.5 : 1 (DMC to glycerol)	Benzene	60	0.1	2	95	4 mol% CaO

Table 4. *Cont.*

Reference	Reactants Mole Ratio	Solvent	Temperature (°C)	Pressure (MPa)	Reaction Time (h)	GC Yield (%)	Catalyst
			Glycerol + DEC				
[62]	3 : 1 (DEC to camellia oil)	Free	50	0.1	24	95	Lipases (Lipozyme TL IM and Novozym 435)
[63]	21 : 1 (DEC to glycerol)	Dimethyl sulfoxide	-	0.1	8	84	Hydrotalcites supported on Al_2O_3
[64]	17 : 1 (DEC to glycerol)	Free	130	0.1	60	97	Mg/Al hydrotalcite-like
			Glycerol + Urea				
[65]	1 : 1 (urea to glycerol)	Free	140	1.4×10^{-2}	6	46	Ionic liquids immobilized onto a structurally modified Merrifield peptide resin
[66]	1 : 3 (urea to glycerol)	Free	140	3.0×10^{-3}	1	91	0.5 wt% calcined La_2O_3
[67]	1.5 : 1 (urea to glycerol)	Free	150	0.1	4	55	Gold, gallium, and zinc supported on oxides and zeolite ZSM-5
[68]	1 : 1 (urea to glycerol)	Free	145	0.1	4	69	Co_3O_4/ZnO nanodispersion
[51]	1 : 1 (urea to glycerol)	Free	145	3.9×10^{-3}	5	72	Calcined Zn hydrotalcite

Table 5. Advantages and disadvantages of different routes of glycerol carbonate production.

Synthesis Methods	Merit	Demerit	References
Direct Carbonation • Carbon monoxide+ Crude glycerol	• High selectivity enhancing the chances of commercialisation.	• Large amount of by-products produced. • Carbon monoxide is toxic so it needs to be handled extra safely in the laboratory and industrial stages. Hence, this has restricted its usage. • Catalyst poisoning due to the use of carbon monoxide.	[46,69,70]
• Carbon dioxide+ crude glycerol	• Direct sequestration of CO_2.	• This reaction is thermodynamically restricted. • Carbon dioxide is too stable and leads to a very low conversion rate. So, this method is currently not feasible. • Require highly reactive catalysts and high energy consumption for the conversion of CO_2.	[69,71,72]

Table 5. *Cont.*

Synthesis Methods	Merit	Demerit	References
Transcarbonation • Phosgene + crude glycerol	• Simple and effective oldest method for the production of organic carbonates. • Glycerol carbonate can be obtained by this method with a good yield.	• Require highly toxic and corrosive gas and hence, need extra precaution during handling it. Therefore, it makes this route very restricted. • Process is characterized by a low atom economy and is recognized as unsafe and highly polluting.	[33,51]
• Urea + crude glycerol	• Urea is a cheap and readily available raw material and no azeotrope formation is required.	• High quantity of ammonia produced as a by-product, which leads to poor selectivity, so limiting its industrial implementation. • The relatively high reaction temperatures and the utilization of homogenous and/or uneasily recoverable catalysts- have negative economical impacts on this method.	[29,67,73,74]
• Ethylene carbonate + crude glycerol	• Production of desired higher valued carbonates. • Reaction temperature used for this method is relatively low.	• Ethylene carbonate is expensive • Facing difficulty during the purification process of glycerol carbonate as ethylene carbonate used in this process have a high boiling point (261°C).	[33,75]
• Dimethyl carbonate (DMC) + crude glycerol, or diethyl carbonate (DEC) + crude glycerol	• DMC/DEC is a versatile chemical and eco-friendly. DMC/DEC has high chemical reactivity and superior physical properties. It can be used in a one-step-one-pot reaction system. • With DMC/DEC, rigorous separation and high energy consumption are not required. Besides, this method is less time-consuming in comparison with the reaction involve phosgene and alkylene carbonates. • DMC has low boiling point (90°C) and so, easier the distillation separation process.	• Industrial grade DMC is approximately three times more expensive than methanol (MeOH).	[76–78]

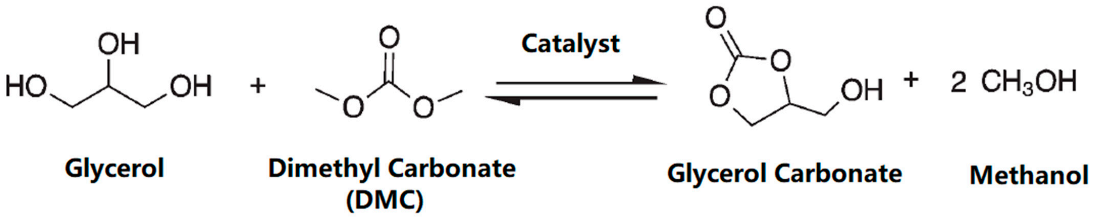

Figure 5. Reaction mechanism between glycerol and dimethyl carbonate for glycerol carbonate production [37].

6. Microwave Assisted Conversion of Glycerol/Glycerol Derivatives to Organic Carbonates

Organic carbonates are very important compounds having a simple structure, high polarity, low viscosity, low toxicity and degradability [79]. These compounds are able to replace hazardous reagents in some organic processes. Two main classes of organic carbonates are cyclic and linear carbonates. The total market production of both cyclic and linear organic carbonates is about 18 million tons per year and mainly produced from phosgene [80]. Figure 6 shows some of the more commercially important organic carbonates (dimethyl carbonate (DMC), diethyl carbonate (DEC), cyclic carbonates (CC), diphenyl carbonate (DPC)) and their properties.

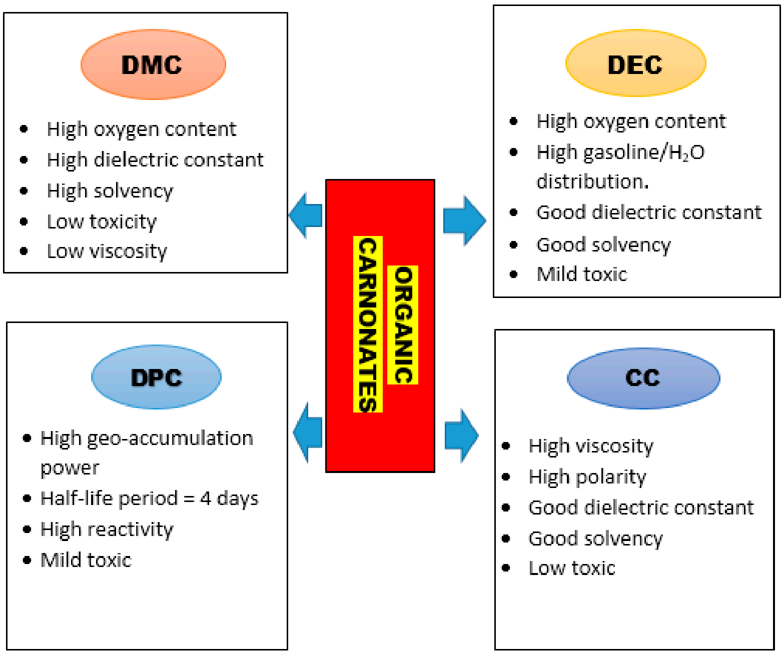

Figure 6. The properties of various organic carbonates (Adapted from [80]).

Different methods have been deployed for the typical synthesis of glycerol carbonate from glycerol as depicted in Table 4 (such as the reaction of glycerol with urea, direct carbonation of glycerol with phosgene, or carbon monoxide and oxygen reaction). However, there are technical and environmental drawbacks accompanying the reaction of glycerol with urea, such as high reaction temperature (150 °C) required. The carbonation reaction is known as an environmentally hazardous process due to the toxicity of phosgene and CO [70]. Given the toxicity of phosgene, alternative routes for the synthesis from carbon dioxide are becoming more and more relevant. A greener method for the production of glycerol carbonate is the carbonation of glycerol with carbon dioxide (catalysed by Sn). This method, however, has low yield (below 35%) due to the thermodynamic limitation [81]. Most of the other methods also have disadvantages such as low Gly-C yield, vacuum operation condition to separate ammonia continuously, or difficulty in the separation of products [82,83]. Several new non-phosgene methods including alcoholysis of urea, carbonylation of alcohols using CO_2, oxy-carbonylation of alcohols, and transesterification of alcohols and carbonates have been developed for synthesizing organic carbonates. If applied, some of these new routes would lower the emission of CO_2 into the atmosphere about seven times (0.92 tons per ton of product, compared to 6.62 tons at present) [28,35,36]. Carbon dioxide (the most significant and long-lived greenhouse gas) is produced by most significantly by combustion of organic materials and fossil fuels. Instituting chemical processes and industries based on carbon as a building block would be paramount to reduce CO_2 levels in the atmosphere. As stated earlier, a specific problem in this context is the issue of CO_2 reactivity (the carbon atom in CO_2 is in its most oxidized state, - hence, makes the molecule highly stabile with low reactivity). The suitable catalyst system can overcome the high reaction barrier, but in general, these reactions still require rather harsh conditions. Researchers are discovering new, environmentally benign, green processes for the synthesis of value-added chemicals and platform molecules.

Microwave irradiation has been used for the synthesis of many organic compounds. The uptake of this technique was sluggish for about 12–14 years after the original publications on the benefits of conducting organic reactions in a microwave in the mid-1980s. However, since the year 2000, there has been an upsurge in publications describing the utilization of microwave synthesis. This trend is most probably correlated to the availability of instruments designed specifically for organic synthesis, hence, allowing microwave reactions to be conducted in a safe and reproducible manner. Among the obvious advantages of microwave heating include more uniform and rapid heating resulting in reduced reaction time for the synthesis of chemicals. Since glycerol is a very good absorber of microwave radiations, microwaves could play a greater role in the synthesis of Gly-C. In microwave irradiation, efficient internal heating is produced by the direct coupling of microwave energy with the solvent, reagents or catalysts in the reaction mixture. The radiation passes through the walls of the vessel directly into the whole reaction mixture, since the reaction vessels are made out of microwave-transparent materials. In typical microwave reactors, the magnetrons (microwave generators) produce microwave radiation of wavelength 12.25 cm, which corresponds to a frequency of 2.45 GHz. Two mechanisms are responsible for the microwave heating, dipolar polarisation and ionic conduction. By using closed vessels, higher pressures can be attained and the superheating effects are greatly magnified, hence, it is possible to maintain solutions at temperatures above their conventional reflux temperature. The higher purity of products often observed in microwave-assisted reactions is largely attributed to the homogeneous and smooth in situ heating. The heating process is also easily controllable because the energy input stops immediately when the power is turned off. It is important to point out that microwave energy cannot break chemical bonds. Compared to classical heating, microwave irradiation provides the advantage of allowing high-temperature reaction. Another advantage of microwave heating is the non-thermal effects due to specific heating of polar intermediates produced during the reaction. These polar intermediates will lead to modified selectivity, enabling polymerization which otherwise could not be performed with thermal heating. For a more detailed account of microwave-assisted reactions, some excellent reviews can be referred [84–87].

Despite all the studies on the synthesis of Gly-C, only a few studies mentioned the microwave-assisted synthesis of Gly-C. In a microwave-assisted reaction, the rate of a reaction involving glycerol as a reactant can be greatly improved due to the high dielectric properties of glycerol [88]. Along with similar scope, polyglycerols has been evaluated over several years as a way of utilizing excess crude glycerol. Polyglycerol have received a lot of attention as a hydrophilic component for neutral surfactants and emulsifiers for food, cosmetic and pharmaceutical. They comprise mainly of glycerol oligomers of low molecular mass. The conventional synthesis of polyglycerols is from glycerol. It involves drastic conditions (high temperature and alkaline conditions), resulting in a complex mixture of oligomers with no well-defined chemical composition [89]. Recently, the production of polyglycerols derivatives and glycerol carbonate using microwave irradiations has been demonstrated [88]. By using microwave irradiation, the synthesis of glycerol oligomers, can be performed under relatively mild conditions using glycerol carbonate as a valuable starting material. In this case, the reaction did not require any solvent or reactant and was completed in a relatively short time. Hence, microwave-assisted polymerization of glycerol carbonate presents the advantages of using less-hazardous conditions and better energy efficiency. On top of that, the experimental conditions allow no usage of any solvent, reactant, or purification steps [90].

In a recent report the transesterification of crude glycerol (GLY) at 70% and 86% purity with dimethyl carbonate (DMC) using calcium oxide (CaO) as catalyst was performed with both the conventional heating and microwave-assisted process [91]. In both the processes, it was found that 70% purity of crude GLY gave a higher yield of Gly-C, with the microwave technique showing better energy efficiency. In their work the highest yield of Gly-C (93.4%) was obtained under the microwave system (crude GLY purity of 70%, 1 wt% of CaO as catalyst, 2:1 M ratio of DMC: GLY at 65 °C, 5 minutes reaction). While the impurities and leftover catalyst residue in the crude GLY are generally undesirable for the conventional transesterification process, it is interesting to note that some impurities (methanol, soap, salt, and fatty acids) in the crude glycerol had demonstrated positive effect [92]. According to the authors, crude GLY performs better than pure GLY in microwave heating because of greater energy efficiency. Thus, direct utilization of crude GLY from the biodiesel plant to produce GLY-C via microwave irradiation transesterification is a viable and economical option [91].

More microwave efficiency in synthesis was demonstrated in a reaction for the production of 2,3-dihydroxypropyldecanoate using glycerol derivatives. In this process the microwave-assisted synthesis (solvent-free) was performed by esterification of decanoic acid in the presence of two distinct glycerol derivatives, glycidol, and glycerol carbonate. The process uses microwave irradiation with an output power of 200–400 W, involving decanoic acid and glycerol derivatives (stoichiometric proportions), with an organo-catalyst. The microwave-assisted synthesis notably enhances the selectivity in 2,3-dihydroxypropyl decanoate (at 300 W, 91%), reinforcing the efficiency and selectivity of the microwave-assisted method [93].

7. Dimethyl Carbonate

Dimethyl carbonate (DMC) is a valuable and green platform chemical and /or solvent which continues to attract a lot of attention. Dimethyl carbonate (DMC) is an environmentally benign chemical and is widely used as a carbonylation agent. DMC has been classified as one of the greenest solvents in terms of safety, health and environmental criteria [94,95]. It is a nonpolar aprotic solvent having good miscibility with water. It is non-toxic and biodegrades readily in the atmosphere. In terms of its usage, DMC can be a potential replacement for methyl ethyl ketone, ethyl acetate, methyl isobutyl ketone, and most other ketones. Moreover, DMC is a green substitute for highly toxic and hazardous compounds such as (i) dimethyl sulfate and halohydrocarbons in methylation reactions and (ii) phosgene ($COCl_2$) in carboxymethylation (methoxycarbonylation) reactions [96]. Among the reaction routes for the production of DMC, the transesterification route and direct synthesis from methanol and CO_2 is the most attractive one due to the inexpensive raw material and the avoidance of corrosive reagents, such as phosgene and dimethyl sulphate [97]. Various catalysts have been studied extensively. Different dehydrating agents and additives have been used to minimize the effect of water produced during the reaction and improving the catalytic performance of the catalyst. Currently, the most established commercial pathway for the production of DMC is through oxidative carbonylation of methanol using O_2. In addition, new alternative processes for DMC from CO_2 are being developed. Direct synthesis of dimethyl carbonate (DMC) from CO_2 and methanol is a very attractive reaction. This is because CO_2 as a greenhouse compound can be consumed in this process [96]. Patents have already been registered for use of DMC and DEC as a fuel additive in gasoline due to their excellent blending properties, high octane number, and oxygen content. Diesel engines are much more efficient than gasoline engines, however, they suffer from NOx and particulate emissions. Many studies have already been reported on the reduction of hydrocarbons, CO, NOx, and particulate emission from diesel engines because of the use of organic carbonates as oxygenate in the fuel [98–100].

The conventional way for the direct synthesis of DMC requires the use of an autoclave along with solid base K_2CO_3 and CH_3I additive, high pressure and long reaction time of over 2 h. In this reaction, the dimethyl ether (DME) appeared as a by-product and its proportion reached 7%–31% of the total products [101]. More studies, including the mechanism of reaction are directed towards the conversion of CO_2 and methanol to DMC. The synthesis of dimethyl carbonate (DMC) from CO_2 and methanol under milder reaction conditions using reduced cerium oxide catalysts and reduced copper-promoted Ce oxide catalysts were reported recently [102]. The report stated that the conversion of methanol was low (0.005%–0.11%) when the milder condition was used. The mild reaction conditions for DMC synthesized were as follows: the reaction time was 2 h, low temperature of 353 K, and low total pressure of 1.3 MPa using reduced Cu–CeO_2 as catalyst (0.5 wt% of Cu). New development in organic synthesis is the increasing interest in applying microwave irradiation. With high heat efficiency, microwave irradiation can accelerate the reaction and decrease the run time resulting in fewer by-products than by conventional heating, but there was very few literatures on the synthesis of DMC concerning microwave energy. Conventional heating methods are not an effective method to transfer energy to the reactants of a reaction mixture because the thermal conductivity of the various materials affects the energy transfer process. On the other hand, during microwave irradiation, molecules are efficiently heated internally by the direct coupling of energy from microwaves. Furthermore, current microwave instruments can precisely control the temperature, even allowing reaction mixtures to be superheated in a closed vessel. A study reported that the synthesis of dimethyl carbonate (DMC) from CO_2 and methanol required about 2 min for maximum yield of DMC when a power of 800 W was used. In the case of decreasing microwave power to 450 W, this reaction could be completed in 10 min and the yield of DMC was at least the same as in non-microwave reaction using conventional heating (autoclave) [101]. The reaction temperature under microwave irradiation was obviously lower than that with conventional heating, but the corresponding DMC yield was higher. It is very likely that microwave energy could be efficiently absorbed by the reactants, especially by methanol leading to a rate acceleration effect. The authors also claimed that in the reaction conditions used, about 2.5% of DME formed as a by-product in the conventional heating (autoclave). In contrast, only 0.4% of DME (by-product) was produced when the reaction was irradiated by microwave [101]. In the microwave irradiation, due to the interaction of the microwave energy with the molecules at a very fast rate, the real reaction temperature is higher than the average temperature of the medium. Hence, both energy consumption and reaction time are reduced by means of microwave irradiation. On the down-side, the microwave-assisted reaction has some disadvantages such as difficulty in the scale-up from laboratory to industrial scale due to the penetration depth of microwave radiation into the material is only a few centimeters. There are safety issues concerning the industrial vessel that need to be addressed, especially for uncontrolled heating.

Recently, there were reports on the usage of dimethyl carbonate instead of using alcohol as an alternative method to produce biodiesel. In this reaction, the product of triglyceride and dimethyl carbonate reaction is fatty acid methyl ester (FAME) and fatty acid glycerol carbonate (FAGC). Subsequently, FAGC then reacts with another molecule of dimethyl carbonate to generate another FAME molecule and glycerol dicarbonate. Accordingly, the overall reaction involves one molecule of triglyceride and two molecules of dimethyl carbonate to generate three molecules of FAME and one molecule of glycerol dicarbonate. This would enable biodiesel production without the production of waste glycerol as a by-product. Ilham and Saka firstly investigated biodiesel production from rapeseed oil in supercritical dimethyl carbonate using a batch-type reactor [103]. The reaction steps for biodiesel production under supercritical dimethyl carbonate conditions are shown in Figure 7.

A study about biodiesel production under supercritical dimethyl carbonate conditions is still limited. A complete conversion to biodiesel about 94% (w/w) was made at 350 °C, 20 MPa, oil-to-dimethyl carbonate molar ratio of 1:42 after 12 min [103]. In addition, there is no previous report about reaction kinetics of oil conversion to biodiesel in supercritical dimethyl carbonate. Optimization studies on biodiesel production using supercritical dimethyl carbonate method have also been carried out in recent years. Recently, Kwon et al. performed non-catalytic biodiesel production from coconut oil using dimethyl carbonate under ambient pressure [76]. They conducted an experiment via a continuous flow mode using a tubular reactor. They reported that a complete conversion to biodiesel was achieved in a short reaction time of 1–2 min at 365-450 °C under ambient pressure, obtaining 98%. By using DMC to produce biodiesel, it is envisaged that the glut of crude glycerol in the market will be reduced. The glycerol carbonate obtained from the reaction is a much valuable product. It has higher economic value and it is used in many reactions as green chemical or solvent. The properties and benefits of glycerol carbonate have been mentioned earlier.

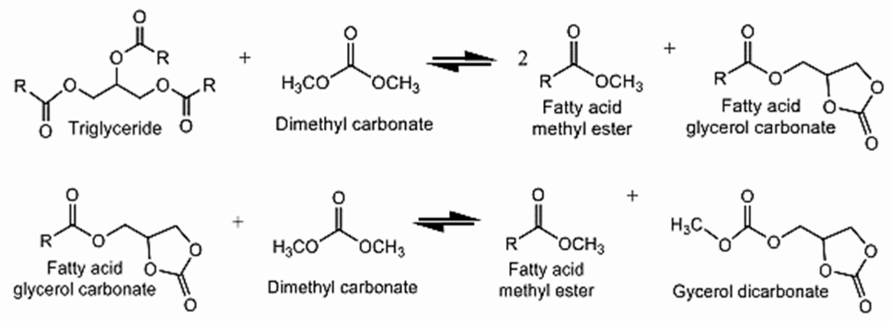

Figure 7. Reaction scheme for biodiesel production under supercritical dimethyl carbonate condition.

8. Kinetic Model of Transesterification of Glycerol with Dimethyl Carbonate

Transesterification of glycerol is also known as transcarbonation. As its name implies, it involves the carbonate exchange reaction between the alcohols and carbonate sources [33]. One of the carbonate sources is dimethyl carbonate, DMC. DMC is an environmentally friendly chemical and has been widely studied in producing the value-added glycerol carbonate with different catalysts such as, potassium methoxide (CH_3OK) [104], trisodium phosphate [78], calcium oxide (CaO) [91], Mg-Al hydrotalcite [105], guanidine ionic liquids [106], lipase [107], K-zeolite [108], and others. Notice that the transcarbonation of glycerol with DMC is a reversible reaction as shown in Figure 5. Thus, an excess amount of DMC should be used in order to shift the chemical equilibrium towards the formation of glycerol carbonate. Moreover, Jiabo Li and Tao Wang concluded that the chemical equilibrium constant of the reaction of glycerol and DMC increased as the reaction temperature increased. In order words, the formation of glycerol carbonate is more favourable by increasing the reaction temperature [61].

To gain more understanding about the transesterification of glycerol, its kinetic study has been conducted and reported by several researchers [104,109,110]. The kinetic study is usually performed to obtain the kinetic parameters (reaction rate) for the ease of comparison with other works. Typically, the kinetic analysis includes the investigation of the effect of different factors on reaction speed, which is essential for the system design, and the optimization of chemical reaction [111]. In addition, more information regarding the characteristics of a reaction mechanism can be obtained [112]. Moreover, it allows the construction of a mathematical model that can represent a specific chemical reaction. In determining the unknown parameters for a mathematical model, a series of experiments with high accuracy should be conducted. However, recent times different types of modelling technique has been introduced and eventually reduce the number of experiments [113].

Based on previous work there are four suitable kinetic models in describing the reaction of transesterification of glycerol with DMC, as summarized in Table 6 [104]. Each model involves two equations for the reaction before and after a certain conversion value, the critical conversion, X_{crit} to account for the effect of different phase regime on the catalytic behaviour. The first equation describes the reaction under the biphasic regime in which the catalysts are soluble only in the glycerol-rich stage with certain concentration, C_{cat}'. Moreover, the first order was assumed with respect to the concentration of glycerol, C_{gly}. The DMC, however, reacts at a constant concentration, C_{DMCsol}. The second equation of the proposed models describes the reaction under the single-phase stage (at X larger than X_{crit}) where the catalysts are assumed to be dissolved in the entire reaction medium at C_{cat}. In addition, unlike the previous equation, the first-order effect was estimated for both concentrations of glycerol, C_{gly} and DMC, C_{DMC}. As mentioned previously, the transesterification of glycerol with DMC is a reversible reaction. With the use of excess DMC, the reaction tends to shift to the production of glycerol carbonate. Nevertheless, the effect of reversible should be taken into consideration in proposing the kinetic model, and thus, kinetic models 2 and 4 are suggested.

In addition, more complex kinetic models (kinetic models 3 and 4) were contemplated by accounting for the nature of the catalyst and its potential deactivation. This is because it had already been investigated that some of the catalysts suffered from deactivation in the transesterification process of glycerol with DMC [104,108,114,115]. Catalyst deactivation is defined as the loss of catalytic activity over time. It is a continuing concern in the catalytic reaction, especially in the practice of industrial catalytic process. Generally, the causes of catalyst deactivation can be divided into three groups, which are chemical, mechanical and thermal. More specifically, the catalyst deactivation process can be explained by six basic mechanisms, including poisoning, fouling, thermal degradation and sintering, vapor formation, vapor-solid and solid-solid reactions, and crushing. Despite the best effort to avoid catalyst deactivation, it is inevitable that all catalyst will decay. To restore the catalytic activity, regeneration of the catalyst is usually the first choice, and disposal of the catalyst is the last resort. However, the ability to regenerate the catalyst highly relies on the reversibility of the deactivation process mentioned previously. As an example, sintering is basically irreversible. On the other hand, some poisons can be removed through chemical washing, oxidation and/or mechanical and heat treatment. Further details can be obtained from [116].

Li and Wang investigated the deactivation effect of the alkali solid catalyst (calcium oxide, calcium hydroxide and calcium methoxide) in the transesterification process of glycerol with DMC [114]. They found that the alkali solid catalysts reacted with glycerol and glycerol carbonate, transformed into basic calcium carbonate and eventually, deactivated the catalysts as the basic calcium carbonate consists of less catalytic strength. In the transesterification of glycerol with DMC that utilized K-zeolite as the catalysts, the deactivation phenomenon observed might be attributed to the reduction of the available active spaces for the conversion of glycerol to glycerol carbonate [108]. Moreover, it is reported that the use of crude glycerol led to rapid catalyst deactivation, which was not observed for runs with pure glycerol [117]. This is because the impurities present in the crude glycerol has limited the catalytic activity, resulting in significant deactivation of the catalyst. However, pure glycerol is far more expensive than crude glycerol. Hence, understanding the effect of impurities in crude glycerol on catalyst performance is crucial to optimize the overall production cost of glycerol carbonate.

Table 6. Kinetic models for the transesterification of glycerol with dimethyl carbonate.

Model Number	**Reaction Type**	**Potential Catalyst Deactivation**	**If $X \leq X_{crit}$**	**If $X > X_{crit}$**
1	Irreversible	Excluded	$r_1 = k_1 \cdot C_{cat'} \cdot C_{Gly} \cdot C_{DMCsol}$	$r_1 = k_1 \cdot C_{cat} \cdot C_{Gly} \cdot C_{DMC}$
2	Reversible			$r_1 = k_1 \cdot C_{cat} \cdot C_{Gly} \cdot C_{DMC}$ $r_2 = k_2 \cdot C_{cat} \cdot C_{GC} \cdot C_{MeOH}$
3	Irreversible	Included	$r_1 = k_1 \cdot C_{cat'} \cdot \left[(1-\beta) \cdot e^{-k_d \cdot t} + \beta \right] \cdot C_{Gly} \cdot C_{DMCsol}$	$r_1 = k_1 \cdot C_{cat} \cdot \beta \cdot C_{Gly} \cdot C_{DMC}$
4	Reversible			$r_1 = k_1 \cdot C_{cat} \cdot \beta \cdot C_{Gly} \cdot C_{DMC}$ $r_2 = k_2 \cdot C_{cat} \cdot \beta \cdot C_{GC} \cdot C_{MeOH}$

In conjunction with the kinetic models stated in Table 6, the Arrhenius equation is applied to consider the temperature effect, T as in equation (1):

$$\ln k = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \tag{1}$$

where k indicates the kinetic constants of the reaction, A is the pre-exponential factor, E_a symbolizes the activation energy (kJ/mol), and lastly, R is the ideal gas constant (8.314 J/mol.K).

9. Summary and Future Perspectives

The worldwide inclination to embrace a sustainable and bio-compatible process has led to the development of systems focused on the use of CO_2 and CO_2-based compounds as feedstocks, promoters, and reaction media. In the present article, the synthesis of various carbonates has been reviewed with the main emphasis on the usage of crude glycerol as the raw material. Production of surplus glycerol in the biodiesel industry is a pressing issue and the industry is looking for ways to utilize and transform crude glycerol into valuable products, such as glycerol carbonate, with green solvent, the dimethyl carbonate (DMC) especially. DMC is one of the simplest carbonates and is termed as the green compound of the 21st century due to its low toxicity, high biodegradability and peculiar reactivity. Although studies on organic carbonates have been done extensively, there remain some shortcomings that must be resolved. In this regard, different ways to improve the thermodynamically limited equilibrium conversion to shift towards DMC formation is crucial (DMC yield is only around 1%, even at thermodynamically favourable, high-pressure conditions). Therefore, the development of high activity and high stability catalysts are crucial. Determining the mechanistic kinetics in the synthesis of organic carbonates has the potential to inspire improved catalyst design, which will result in mitigating the problems of long reaction times and high reaction temperatures. Furthermore, microwave-assisted organic synthesis is well known due to its shorter reaction time, lower operating temperature, volumetric heating mechanism, specific microwave effect, and rapid heating. The specific microwave effect is the non-thermal effect of microwave irradiation which causes the specific heating of polar intermediates and leads to a modified selective reaction, that normally cannot be performed using conventional heating. However, non-thermal microwave effects should be further investigated as their presence is still a controversial issue, especially in the chemical synthesis area. Moreover, mechanisms and process improvements using microwave irradiation are very limited and further work is needed in order to develop an understanding of these synthesis routes.

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