

Review

# Environmentally-Benign Dimethyl Carbonate-Mediated Production of Chemicals and Biofuels from Renewable Bio-Oil

Keon Hee Kim and Eun Yeol Lee \*

Department of Chemical Engineering, Kyung Hee University, Gyeonggi-do 17104, Korea; geoni@khu.ac.kr

\* Correspondence: eunylee@khu.ac.kr; Tel.: +82-31-201-3839

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**Abstract:** Due to the increasing emission of carbon dioxide ( $\text{CO}_2$ ), the development of fuels and chemicals based on renewable resources has attracted much attention. Bio-oil, as a carbon rich material, has been considered as a feedstock for biodiesel production. In conventional methanol-mediated transesterification of bio-oil for biodiesel production, significant amounts of glycerol are being generated as a byproduct. In order to overcome these issues, dimethyl carbonate (DMC) has been recently used as an alternative acyl acceptor to avoid the generation of glycerol. DMC is an environmentally-benign chemical reagent and reactive solvent due to safety, health, and environmental benefits. Moreover, DMC can be produced from  $\text{CO}_2$ . Co-production of biodiesel and chemicals such as glycerol carbonate is possible as the concept of zero-waste utilization of bio-oil. Value-added chemicals can be synthesized using DMC as a reagent. This paper provides a review on the physical and chemical properties of DMC as a solvent, as well as the production methods for DMC. DMC-mediated production of various chemicals and fuels in both chemical and enzymatic processes are discussed together with their pros and cons.

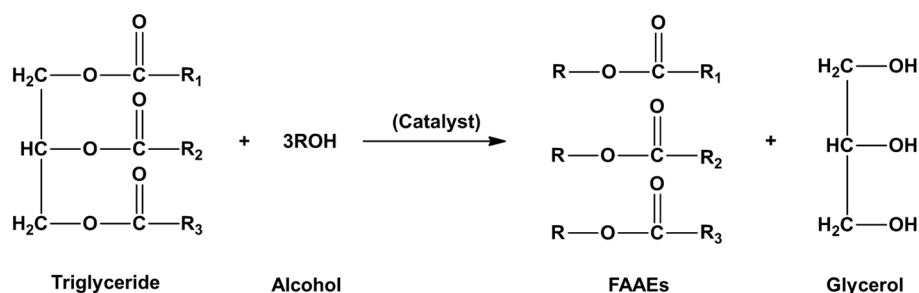
**Keywords:** biodiesel; bio-oil; dimethyl carbonate; glycerol carbonate

## 1. Introduction

The intensive consumption of petroleum-derived fuels and chemicals causes environmental and political concerns. In order to solve these issues, the development of renewable fuel and chemical production from biomass has increased. Bio-feedstocks are renewable, sustainable, biodegradable, environmentally friendly, and carbon neutral over the whole life cycle [1]. Bio-oils can be obtained from various biomasses, such as vegetable, animal, and microalgae, and are carbon-rich materials consisting of glycerol and three fatty acids with chain lengths between C8 and C20 [2]. Thus, they are considered as a practical alternative to petroleum resources for biofuel and chemical production.

The refined bio-oil (triglyceride) is mainly used as an alternative feedstock for biodiesel production. Biodiesel, defined as fatty acid alkyl esters (FAAEs), is produced by the transesterification of the refined bio-oil with alcohols in the presence of a catalyst. Various alcohols, including methanol, ethanol, propanol, butanol, and amyl alcohol are used as acyl acceptors in the transesterification reaction [3]. Among all of the alcohols, methanol and ethanol are most employed for conventional biodiesel production. Methanol is especially preferred on the industrial level because of its economic advantages [3,4]. However, methanol is a hazardous material that is handled carefully due to its toxicological and ecotoxicological properties [3,5]. The utilization of green solvents such as ethanol, iso-propanol, and n-butanol has been studied as an alternative to overcoming these issues of methanol [6–8]. However, alcohol-mediated transesterification processes generate approximately 10 wt % crude glycerol (Figure 1) [9]. With a growing biodiesel industry, a large surplus of glycerol has been produced [10,11]. For example, over 1400 kilo tons of glycerol were created from biodiesel production

in 2013 [12]. Glycerol, as a low-cost feedstock, can be used for chemical, pharmaceutical, and cosmetic industries, but the cost of separation and purification of crude glycerol is relatively high [10,13–15].



**Figure 1.** Reaction pathway of fatty acid alkyl ester (FAAE) synthesis from bio-oil and alcohol.

To overcome the issues of alcohol-mediated transesterification, an alternative novel acyl acceptor, dimethyl carbonate (DMC), has been employed for glycerol-free biodiesel synthesis. DMC is a green chemical reagent or reactive solvent due to its non-toxic impact on health and the environment [16]. Additionally, DMC is utilized as a versatile raw material for pharmaceuticals and as a solvent for various industrial applications [17,18]. Moreover, DMC synthesis from undesired CO<sub>2</sub> is a promising option for green-house gas mitigation [19].

In this paper, we review the physico-chemical properties (Section 2) and production methods (Section 3) of DMC, and chemical and biotechnical processes for DMC-based production of biodiesel and chemicals (Sub-Sections 4.1 and 4.2 in Section 4). The simultaneous production of biodiesel and value-added chemicals using renewable bio-oil in DMC is also discussed in terms of zero-waste utilization and CO<sub>2</sub>-sequestration (Sub-Section 4.3 in Section 4). This review paper deals with various research articles, review papers, and some patents.

## 2. Physico-Chemical Properties of DMC

DMC is a flammable (flash point 21.7 °C), colorless liquid with a melting point of 4.6 °C and boiling point of 90.3 °C, and a density of 1.069 g/cm<sup>3</sup> [18]. DMC, a nonpolar aprotic solvent, is slightly soluble in water (139 g/L) [20] and miscible with alcohol, ester, ether, and ketone [21]. The chemical reactivity of DMC is versatile. DMC has two carbon centers including carbonyl and methyl groups, with which a nucleophile may react. Thus, DMC is employed as a methylating or carboxylating agent [20,21].

The most important properties of DMC are low toxicity and high biodegradability (>90% within 28 days) [18,21]. The oral acute toxicity (LD<sub>50</sub>) of DMC for rats is 13.8 g/kg, which indicates that it is a non-toxic compound. In addition, DMC has a negligible toxic effect by inhalation [17,22]. Therefore, DMC can be safely handled compared to toxic methyl halides, dimethyl sulfate (DMS), and phosgene [18,20,22]. The toxicological and ecotoxicological properties of DMC, DMS, and phosgene are summarized in Table 1.

**Table 1.** Summary of toxicological and ecotoxicological properties of dimethyl carbonate (DMC), dimethyl sulfate (DMS), and phosgene (modified from [17,22]).

Properties	DMC	DMS	Phosgene
Oral acute toxicity (rats)	LD <sub>50</sub> 13.8 g/kg	LD <sub>50</sub> 0.44 g/kg	–
Acute toxicity per contact (cavy)	LD <sub>50</sub> > 2.5 g/kg	–	–
Acute toxicity per inhalation (rats)	LD <sub>50</sub> 140 mg/L; (4 h)	LD <sub>50</sub> 1.5 mg/L; (4 h)	LD <sub>50</sub> 0.016 mg/L; (75 min)
Mutagenic properties	None	Mutagenic	–
Irritating properties (rabbits, eyes, skin)	None	–	Corrosive
Biodegradability	>90% (28 days)	Rapid hydrolysis	Rapid hydrolysis

### 3. DMC Production Process

DMC has been produced by conventional methods or CO<sub>2</sub>-based methods (Figure 2). The conventional methods involve two methods: the non-phosgene route and the phosgene process [23]. The methods utilizing CO<sub>2</sub> include the direct DMC synthesis with methanol and indirect DMC synthesis with intermediates including CO<sub>2</sub>-derived urea, propylene carbonate, and ethylene carbonate.

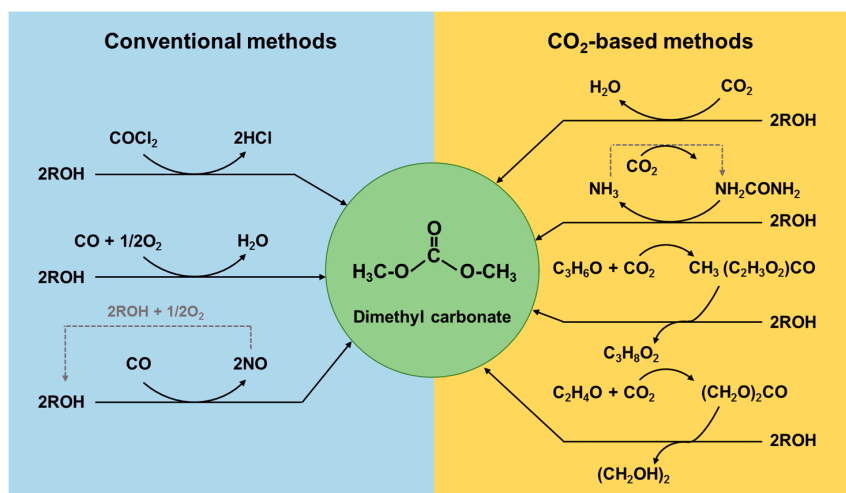


Figure 2. Synthesis routes of dimethyl carbonate modified from [17].

#### 3.1. Conventional Process of DMC Production

Until the 1980s, DMC was produced by the phosgene process. Despite a high yield, the phosgene process is no longer used due to high toxicity of phosgene and the equipment corrosion by the phosgene and HCl generated in the process [19,22]. Currently, DMC is produced by oxidative partial carbonylation, using methanol, carbon monoxide, and oxygen in the liquid or vapor phase [24,25]. Oxidative carbonylation of methanol is thermodynamically favorable and the process is operated at moderate conditions [17,26]. Chlorine-containing catalysts are usually employed in the processes, and chlorine is related to the activity of the catalyst [27]. The liquid phase method has a high space-time yield of DMC [17]. However, it has issues of a low production rate, equipment corrosion, difficult separation of products from catalysts, and rapid deactivation of catalysts by the accumulation of water [25,26]. In order to overcome the issues, the vapor phase method has been proposed. The vapor phase method can readily remove water that has a negative effect on catalysts. As an alternative phosgene-free route, carbonylation of methyl nitrites over Pd-based catalysts was also developed by Ube Industries, Ltd. [19]. In this method, alkyl nitrites were employed as an oxidizing agent, and water was not accumulated during the synthesis of DMC, which eliminated the negative effects of water on catalysts. Thus, anhydrous condition resulted in high catalytic activity and selectivity for a long reaction time [16]. However, phosgene-free routes still use toxic and corrosive compounds including nitrogen oxide, methyl nitrite, and carbon monoxide, and thus explosion might occur in methanol carbonylation method [17,19].

#### 3.2. DMC Production from Carbon Dioxide

CO<sub>2</sub> from fossil fuels is the most abundant waste gas leading to the greenhouse effect. The method of converting CO<sub>2</sub> into value-added chemicals has recently attracted much interest [28]. The production of DMC using CO<sub>2</sub> as C1 feedstock has been considered as a green chemistry route compared to the conventional process. Processes for DMC production from CO<sub>2</sub> possess several routes such as the direct reaction with methanol and indirect reaction with intermediate compounds (urea, ethylene carbonate, propylene carbonate) [18,19].

The direct synthesis of DMC from CO<sub>2</sub> and methanol is an environmentally-benign method for CO<sub>2</sub> utilization, free from the risk of explosion in oxidative carbonylation. In general, organometallic complexes and inorganic bases have been used in the direct synthesis of DMC from CO<sub>2</sub> and methanol at near supercritical conditions [29–31]. Jiang et al. [31] analyzed the effect of H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> as a catalyst in the direct synthesis of DMC from CO<sub>2</sub> and methanol. H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> possessed a high catalytic activity for DMC production when compared to a pure zirconia catalyst because H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> has not only Lewis acid sites, but also Brønsted acid sites. Brønsted acid sites in the H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>/ZrO<sub>2</sub> were more effective for methanol activation than Lewis acid sites. However, this method still remains at the laboratory-scale because the DMC conversion was very low due to the reaction equilibrium limitation and kinetic inertness of CO<sub>2</sub> [16].

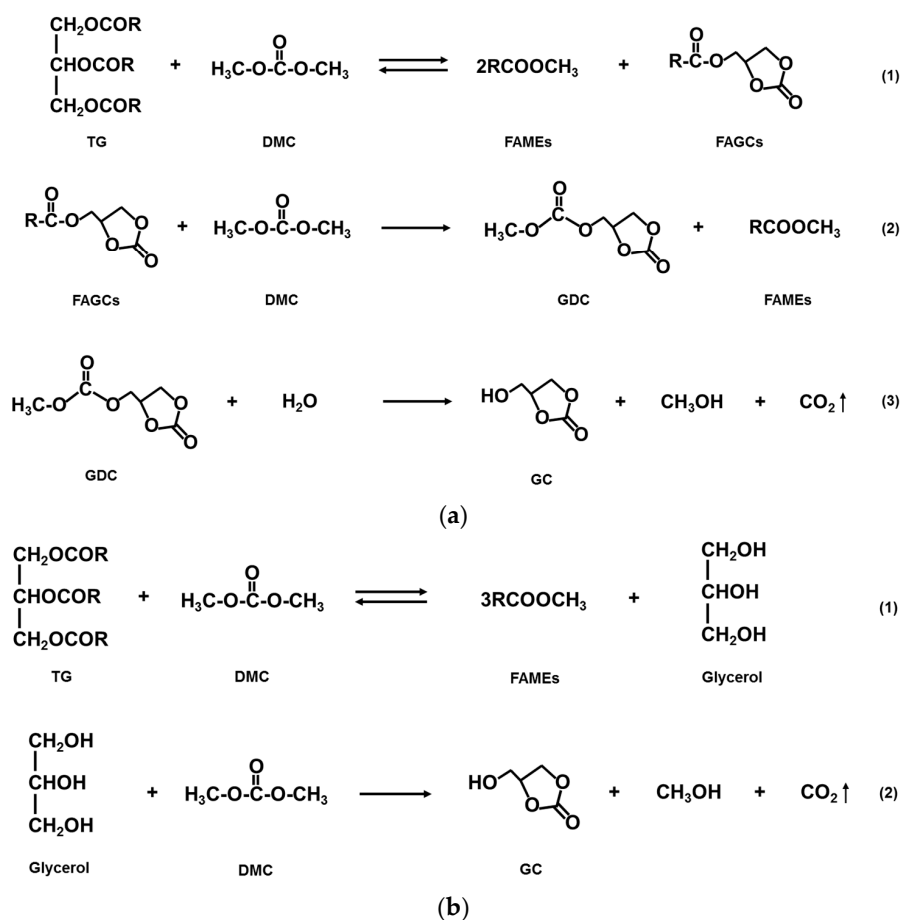
In indirect routes, urea, ethylene carbonate, and propylene carbonate are synthesized from CO<sub>2</sub> with ammonia, ethylene oxide, and propylene oxide, respectively. DMC was produced through subsequent transesterification of these compounds with methanol [19]. The production of DMC by alcoholysis of urea was performed using organic tin, polyphosphoric acid (PPA), metal oxide, and zinc compounds [32]. In propylene carbonate and ethylene carbonate routes for DMC production, valuable chemicals such as propylene glycol and ethylene glycol were obtained as byproducts [19]. Alkali metal compounds, silica-supported ionic liquids, and alkali-treated zeolite were effective in transesterification [32]. Kongpanna et al. [19] reported the techno-economic analysis of three processes for DMC synthesis. The CO<sub>2</sub> direct synthesis and propylene carbonate route were less competitive than the other CO<sub>2</sub> utilizing routes because of high positive value of Gibbs free energy and low DMC yield [19]. The ethylene carbonate route is a promising method for DMC preparation in terms of atom efficiency, total energy consumption (11.4% improvement), and net CO<sub>2</sub> emission (13.4% improvement) [19].

#### 4. DMC-Mediated Production of Fuels and Chemicals

DMC has been widely used in various chemical industry as an attractive green chemical [32]. The DMC-mediated processes for the production of fuel and chemical production were reviewed according to the chemical and enzymatic catalysts.

##### 4.1. DMC-Mediated Process for Biodiesel Production

In biodiesel production using transesterification with bio-oil, methanol is commonly used as an acyl acceptor. However, there are some problems such as lower miscibility with oil, denaturation of enzymes, and the overproduction of glycerol [10,33]. In particular, the glycerol byproduct needs to be separated because it cannot be directly added to fuels due to its higher viscosity, instability at high temperature, and lower solubility in hydrocarbons [5]. The separation process would increase the biodiesel production cost. Therefore, using DMC as a novel acyl acceptor has been recently proposed for glycerol-free biodiesel production. DMC is known to be a green reagent and prevents co-production of glycerol [15]. In addition, glycerol derivatives, such as glycerol carbonate and glycerol dicarbonate, are obtained as value-added byproducts through DMC-mediated transesterification [15]. Glycerol carbonate and glycerol dicarbonate can be used as additives or chemical intermediates, thus can mitigate the glycerol surplus from conventional biodiesel process [15]. Two possible reaction pathways in DMC-mediated transesterification have been proposed (Figure 3). Zhang et al. [34] suggested a plausible reaction route in which fatty acid glycerol carbonate esters (FAGCs) as intermediates react with DMC to produce glycerol dicarbonate and fatty acid methyl esters (FAME). Then, glycerol dicarbonate is converted into glycerol carbonate via hydrolysis. Another possible reaction route is that glycerol carbonate is synthesized from the glycerol backbone [35]. Additionally, the remaining non-reacted DMC can be employed as a fuel additive for diesel engines [36]. The DMC-mediated process for biodiesel synthesis is an irreversible reaction because it produces CO<sub>2</sub> in the final step, thus the yields of DMC are high [37]. The CO<sub>2</sub> generated via DMC-based transesterification can be utilized again for DMC synthesis.



**Figure 3.** Two possible reaction pathways for DMC-mediated transesterification: (a) one was suggested by Zhang et al. [34], (b) while the other was suggested by Min et al. [35]. TG, triglyceride; DMC, dimethyl carbonate; FAMES, fatty acid methyl esters; FAGCs, fatty acid glycerol carbonate esters; GDC, glycerol dicarbonate; GC, glycerol carbonate.

#### 4.1.1. Chemical Process for DMC-Based Biodiesel Production

The transesterification reaction between bio-oils and DMC produces FAMES and value-added glycerol derivatives such as glycerol carbonate and glycerol dicarbonate. Basic catalysts like KOH, sodium methoxide, sodium hydride, and some amines are most widely used for DMC-based transesterification [15,38–43]. Table 2 shows the use of alkaline catalysts for DMC-based biodiesel production. Panchal et al. [41] investigated the effect of different acid and base catalysts (HCl, H<sub>2</sub>SO<sub>4</sub>, KOH, and NaOH) for DMC-based biodiesel production. The maximum yield of FAMES was achieved with the KOH catalyst. In an alkaline condition, a methoxide anion generated from DMC has a high catalytic activity in the transesterification reaction, as it is strongly basic [34,43]. The nucleophilic attack of the methoxide anion at the carbonyl carbon in triglyceride generates a tetrahedral intermediate, and then results in formation of one mole of FAME. The use of sodium methoxide as an alkali catalyst allows for a high yield of FAMES under mild conditions in the transesterification reaction. Kai et al. [42] achieved a maximum conversion of 96% at 65 °C for 2 h with 2.0 wt % sodium methoxide catalyst and a 3:1 molar ratio of DMC and oil. Triazabicyclodecene (TBD), as a nitrogen-containing catalyst, is a non-ionic organic base catalyst and has higher catalytic activity than other nitrogen based catalysts in the transesterification reaction [38,40]. Moreover, unrefined acidic oil (free fatty acid; FFA) can be used in the presence of TBD since the complex of TBD and FFA is soluble in the reaction solution, and thus there is no formation of soap or emulsions [44]. However, these processes generate alkaline waste water in their production plant [45].

**Table 2.** Summary of studies using chemical catalysts during DMC-mediated transesterification.

Feedstock	Catalyst	Catalyst Amount (%)	Molar Ratio (Oil:DMC)	Reaction Conditions	Yield (%)	Reference
Soybean oil	KOCH <sub>3</sub>	6.5	1:9	200 °C, 10 bar, 1 h	95.8	[5]
Canola oil	NaOCH <sub>3</sub>	2	1:3	65 °C, 2 h	>96.0	[42]
Palm oil	KOH	8.5	1:9	65–75 °C, 8 h	96.2	[34]
<i>Pongamia pinnata</i> seed oil	KOH	4	1:3 ( <i>w/w</i> )	90 °C, 6 h	96.0	[41]
Karanja oil	KOH	9	1:10	80 °C, 8 h	>96.0	[43]
Soybean oil	TBD <sup>a</sup>	5	1:3	90 °C, 5 h	>99.5	[38]
Canola oil	TBD <sup>a</sup>	1.5	1:6	60 °C, 2 h	98.0	[39]
Canola oil	TBD <sup>a</sup>	2.5	1:3	60 °C, 1.013 bar, 6 h	99.45	[40]

<sup>a</sup> Triazabicyclodecene.

#### 4.1.2. Enzymatic Process for DMC-Based Biodiesel Production

In order to overcome the drawbacks of chemical catalysis, enzymatic transesterification has been recently studied [46–52]. The enzymatic transesterification reactions using DMC as an acyl acceptor for biodiesel production are compared in Table 3. The enzymatic process has relatively easy separation, which could lower downstream separation cost [53]. Furthermore, the enzymatic process has the advantages of being environmental friendly and consuming less energy than a chemical process because it is performed under mild conditions [52,54]. Immobilization of enzymes on a suitable support allows reuse. One of the drawbacks of immobilized enzymes in the transesterification reaction is deactivation by short-chain alcohols and glycerol [52]. Enzyme deactivation can be prevented by employing DMC as an acyl acceptor [54]. In general, Novozyme 435 prepared from *Candida antarctica* lipase has been widely used as a biocatalyst for DMC-based biodiesel production. Go et al. [55] found that Novozyme 435 is more suitable for DMC-based biodiesel production than other reported lipases due to its non-specific nature.

Most of the studies on enzymatic transesterification using DMC utilize edible vegetable oils as renewable feedstock [35,48,55]. Edible oils, such as soybean oil, corn oil, and sunflower oil, cause the moral issue of using food resources for fuel production [56]. Recently, non-edible bio-oils, such as waste cooking oil and microalgae oil, have been explored as attractive options. Waste cooking oil was converted to biodiesel through DMC-mediated transesterification using Novozyme 435 in a solvent-free system [49]. Waste cooking oil can reduce feedstock cost for biodiesel production. With respect to microalgae, they have higher CO<sub>2</sub> fixation rates and growth rates than terrestrial plants. Additional advantage is that some microalgae can accumulate abundant amounts of oil (50–80% of dry biomass) [52,57]. Lee et al. [50] and Jo et al. [51] reported that lipase-catalyzed transesterification for DMC-based biodiesel production was performed using microalgae, *Chlorella* sp. KR-1, and the maximum yields were 75.5% and 90.5%, respectively. The optimum temperature was in the range of 40 and 70 °C because the maximum allowable temperature for lipase was 70 °C. In biodiesel production using microalgae, DMC was utilized not only as a transesterification reagent, but also as a solvent for bio-oil extraction from biomass, which makes production process simple and cost effective [50–52].

**Table 3.** Summary of studies using bio-catalysts during DMC-mediated transesterification.

Feedstock	Catalyst	Catalyst Amount (%)	Molar Ratio (Oil:DMC)	Reaction Conditions	Yield (%)	Reference
Corn oil	Novozyme 435	10	1:10	60 °C, 24 h	94.0	[35]
Cottonseed oil	Novozyme 435	10	1:4.5	50 °C, 24 h	96.4	[45]
Palm oil	Novozyme 435	20	1:10	55 °C, 24 h	90.5	[47]
Soybean oil	Novozyme 435	100 g/L in t-butanol	1:6	60 °C, 48 h	84.9	[48]
Soybean oil	Novozyme 435		1:10	60 °C, 48 h	96.4	[55]
Waste cooking oil	Novozyme 435		1:6	60 °C, 4 h	86.6	[49]
<i>Chlorella</i> sp. KR-1	Novozyme 435	20	1:10 ( <i>w/v</i> )	70 °C, 24 h	90.5	[51]
<i>Aurantiochyrium</i> sp. KRS101	Novozyme 435	30	1:5 ( <i>w/v</i> )	50 °C, 12 h	89.5	[52]



#### 4.1.3. Fuel Properties of DMC-Based Biodiesel

The main difference of DMC-based transesterification with the conventional method using methanol is the formation of FAGCs in the methyl ester phase. Fabbri et al. [38] examined the chemical features and physical properties of DMC-based biodiesel as a fuel. Based on fuel property, the presence of FAGCs in DMC-based biodiesel has a negative effect on flow properties compared to conventional biodiesel (pure FAMES). DMC-based biodiesel has a higher pour point and viscosity than pure FAMES because FAGCs are 86 Da larger than FAMES [38,58]. Nevertheless, DMC-based biodiesel can be used as an additive, and the addition of 20% DMC-based biodiesel to diesel was adequate for normal fuel performance. When compared to pure FAMES, the emission levels of PAHs during combustion of FAGCs were not significantly different, although more oxygen atoms are present in FAGCs. Despite the presence of FAGCs in the FAMES phase, the cetane number was similar to pure FAMES. The fuel properties of DMC-based biodiesel are summarized in Table 4.

**Table 4.** Properties of biodiesel synthesized via DMC-mediated transesterification.

	Unit	ASTM <sup>a</sup>	DMC-Based Biodiesel		
			Reference [38]	Reference [41]	Reference [43]
Cetane number		47	50.1		
Kinetic viscosity (40 °C)	mm <sup>2</sup> /s	1.9–6.0	4.1	5.2	5.6
Density (25 °C)	kg/m <sup>3</sup>	-	0.88	0.89	0.885
Flash point	°C	130	160	122	144
Pour point	°C	−15 to 10	−3.8	3	
Acid number	mg KOH/g	0.0–0.50	<0.5	0.28	0.42
Phosphorus content	mg/kg	0–10			5

<sup>a</sup> ASTM (D6571-2007).

#### 4.1.4. Techno-Economic and Life Cycle Analysis of Enzymatic Biodiesel Production

Techno-economic analysis (TEA) is a key indicator for successful industrial scale implementation [59]. Although there is no TEA on enzyme-catalyzed biodiesel production in DMC, its TEA can be deduced from the case study on conventional biodiesel production. Jegannathan et al. [60] evaluated TEA of biodiesel production by using alkali catalyst and biological catalysts (soluble and immobilized enzyme). The ton-based production cost of immobilized lipase process was expected to be 206.96% higher than alkali catalyst process, while 323.9% lesser than free enzyme process due to expensive enzyme reuse. The lipase cost is expected to be 49.7% of total production cost. Therefore, reuse of immobilized lipase had a significant effect on biodiesel production. For example, when lipase price are 1500, 1000, 750, 200, and 100 \$/kg, respectively, the immobilized lipase needs to be reused for more than 320, 210, 160, 50, and 20 batch reactions without significant loss of catalytic activity [61]. Sotoft et al. [62] also investigated TEA of enzymatic biodiesel production. The estimated biodiesel price was 0.73–1.79 €/kg based on enzyme price of 762.71 €/kg and 0.05–0.75 €/kg with enzyme price of 7.63 €/kg. In the case of DMC-based biodiesel production, not only production of biodiesel but also co-production of value-added glycerol carbonate derivatives needs to be considered due to high cost of DMC.

Life cycle analysis (LCA) is a valuable tool for assessment of product's net environmental impact. Harding et al. [63] conducted a LCA of both inorganic and enzyme catalysis for biodiesel production. The LCA result showed that the enzymatic catalysis showed less environmental impact when compared to inorganic catalysis. All of the LCA impacts (fresh water aquatic toxicity, human toxicity, terrestrial ecotoxicity, ozone layer depletion, global warming, acidification, and photochemical oxidation) were expected to be low in the enzyme catalysis. Jegannathan et al. [64] studied the LCA of biodiesel production using alkali and enzyme (soluble and immobilized) catalysts. When biodiesel production capacity is 1 Mg, the immobilized lipase process has higher environmental impact than sodium hydroxide and soluble enzyme, because multi-step unit operations of lipase immobilization lead to the increase of raw materials and energy. However, as the production capacity increases, the immobilized

lipase process shows lower environmental impacts compared to other two processes due to benefit of enzyme reuse. Based on the LCA, enzymatic production of biodiesel with DMC would be better than that with methanol in other conventional organic solvent because DMC is considered less toxic to human and the environment.

#### 4.2. DMC-Mediated Process for Chemicals Production

DMC has many applications, such as fuel additives and chemical synthesis reagent [17]. In organic synthesis, DMC is used as a chemical intermediate (carbonylating or methylating reagent) and it can replace conventional reagents such as halohydrocarbon ( $\text{CH}_3\text{X}$ ,  $\text{X} = \text{I}, \text{Br}, \text{Cl}$ ), dimethyl sulfate, and phosgene [16,65].

##### 4.2.1. Chemical Process for DMC-Based Chemicals Production

Brønsted and Lewis acids were used in DMC-mediated carboxymethylation and methylation with various alcohols and phenols [66]. Deshmukh et al. [67] reported that the use of Brønsted and Lewis acidic ionic liquids enhanced the yield of diphenyl carbonate (DPC) synthesis. DPC, one of the most important intermediates for producing various organic and polymeric materials, was produced by a two-step process involving transesterification and the disproportionation reactions [17,66]. The synthesis of five- and six-membered heterocycles from 1,4-, 1,5-diols or 1,4-aminoalcohols with DMC has been developed with a nitrogen bicyclic base. N- and O-based heterocycles are used as antimicrobial, antioxidant, antimitotic, antiangiogenic, and neurotogenic agents, due to their biological activity [68]. Five- and six-membered carbonates were produced using carbonate phosphonium salts as a catalyst for the transesterification of DMC with diols [69]. Pyo et al. [70] developed the synthetic methods of five- and six-membered cyclic carbonates from various mono-alcohols in the presence of DMC and molecular sieves without any additional solvent or catalyst. These methods could provide an alternative route for the phosgene-free synthesis of polyurethane and polycarbonates [67,70]. Aliphatic polycarbonates were synthesized by DMC and aliphatic diols-based condensation polymerization. Various catalysts, such as Sn compounds, calcined MgAl hydrotalcites, Ca, a  $\text{TiO}_2/\text{SiO}_2$  complex system, and sodium alkoxide, have been used in the condensation polymerization of various diols with DMC to produce aliphatic polycarbonates [71–75]. Aliphatic polycarbonates are attractive materials due to their favorable biodegradability, biocompatibility, and non-toxic characteristics [74,75]. López-Garzón et al. [76] developed a green upgrading process for dimethyl succinate production by using DMC as a solvent and an alkylating agent catalyzed by a strong anion exchange resin.

Most starting materials that react with DMC for chemical intermediate production have been petroleum-derived chemicals. Recently, green chemicals derived from biomass have drawn increasing interest. In particular, glycerol carbonate as an environmentally-benign chemical, is an important value-added product due to its versatile applications, such as ingredients for cosmetics and pharmaceuticals, electrolyte for Li-ion batteries, and monomer of plastics [17,77]. The transesterification of glycerol in DMC is a preferred method because it is conducted at mild conditions [17]. As previously mentioned, glycerol is a byproduct in the biodiesel industry. However, biodiesel-derived glycerol (bio-glycerol) cannot satisfy purity and cost requirement [13]. For efficient and economical utilization of bio-glycerol, it needs to be converted to value-added chemicals, such as glycerol carbonate [78–81]. Transesterification of glycerol with DMC is thermodynamically favorable based on the equilibrium constant [80]. The effect of various acid and basic homogeneous and heterogeneous catalysts on the synthesis of glycerol carbonate via transesterification has been studied by Ochoa-Gómez et al. [78], and high yield (>95%) of glycerol carbonate was obtained by using CaO as a catalyst. The activity of the CaO catalyst dramatically increased by the calcination of CaO due to calcium hydroxide removal from its surface. Among the heterogeneous catalysts, alkali metal oxide, or mixed oxide catalysts have been widely used for glycerol carbonate formation [81].



#### 4.2.2. Enzymatic Process for DMC-Based Chemicals Production

Recently, biotechnological processes using immobilized lipase for DMC-based chemical production have been accomplished. Enzymatic-catalyzed reactions can proceed with high selectivity under mild conditions [82]. Six-membered cyclic carbonates, as environmentally benign monomers for polyurethanes and polycarbonates, can be synthesized from DMC with trimethylopropane (TMP) or diols using immobilized *Candida antarctica* lipase (Novozyme 435) [83–86]. Six-membered cyclic trimethylene carbonate was synthesized from 1,3-diols and DMC with a low yield (53%) in a solvent system of acetonitrile and toluene (4:1, *v/v*) using lipase [83]. Recently, Bornadel et al. [86] developed a solvent-free synthesis of six-membered carbonate using lipase in a flow reactor. A high conversion (81.6%) was obtained in the solvent-free system.

For ecofriendly synthesis of glycerol carbonate, lipases from *C. antarctica* and *Aspergillus niger* have been employed as a biocatalyst [87–90]. Lipase-catalyzed production of glycerol carbonate had a high yield (~99%) from glycerol and DMC using Novozyme 435 in the presence of tetrahydrofuran (THF) solvent [87]. However, THF is toxic, thus a solvent-free system was proposed to solve the toxicity problem. Lee et al. [88] used glycerol-coated silica gel as the substrate instead of free glycerol due to poor solubility of glycerol in hydrophobic DMC, and achieved a high yield (90%) of glycerol carbonate without solvent. Glycerol carbonate synthesis using *A. niger* lipase exhibited only 25–60% yield [89,90]. From these results, *C. antarctica* lipase has higher catalytic activity than *A. niger* lipase for glycerol carbonate synthesis from glycerol and DMC. In addition, glycerol carbonate can be obtained as a value-added byproduct by enzymatic transesterification (biodiesel production process) between renewable bio-oil and DMC. Glycerol carbonate and biodiesel were obtained with a conversion of 92% and 84.9%, respectively, by transesterification using Novozyme 435 with *tert*-butanol as a solvent [48]. Min et al. [35] reported that the co-production of glycerol carbonate and biodiesel were produced with conversions of 62.5% and 94%, respectively, from corn oil and DMC via the Novozyme 435-catalyzed transesterification without any solvent. For in-situ lipase-catalyzed transesterification in one-pot batch reaction, Jo et al. [51] obtained 16.73 mg of glycerol carbonate/g biomass from microalgae, *Chlorella* sp. KR-1, containing 40.9% (*w/w*) lipid under the optimal condition. Table 5 summarizes DMC-mediated production of various chemicals.

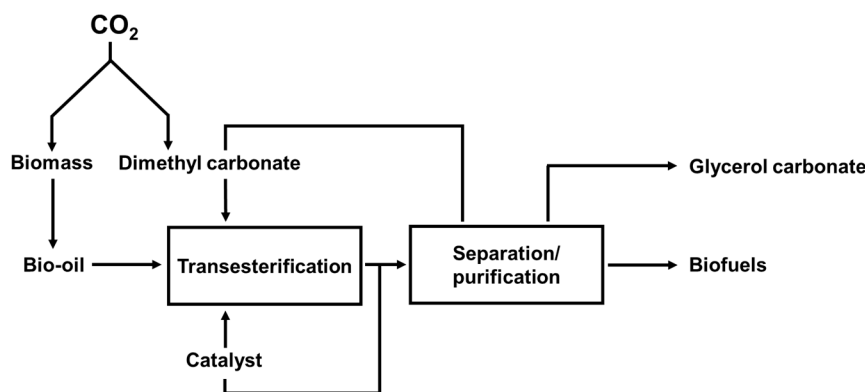
**Table 5.** Various applications of DMC-based chemicals.

Product	Reaction (with Reference)	Usage
Diphenyl carbonate	DMC with phenol [17] DMC with alcohols [66]	Use as a solvent, plasticizer, and chemical intermediate for various organic and polymeric compounds
Five- and six-membered carbonates	DMC with diols [70] DMC with trimethylopropane [85]	Use for pharmaceuticals such as antimicrobial, antioxidant, antimitotic antiangiogenic
Five- and six-membered heterocycles	DMC with aminoalcohols [68]	Use as a chemical intermediate for engineering thermoplastics, as well as pharmaceutical applications
Glycerol carbonate	DMC with glycerol [78] DMC with bio-oil (triglycerides) [54]	Prominent role as the monomer during plastic synthesis Use as ingredients for cosmetics and pharmaceuticals Use as an electrolyte for Li-ion batteries
Dimethyl succinate	DMC with succinate by O-alkylation reaction [76]	Use as solvent and polymer additives, as well as in coating and painting applications

#### 4.3. Assessment of DMC-Mediated Co-Production of Biofuels and Chemicals from Renewable Bio-Oil

Bio-oil (biomass-derived oil) and DMC can both be produced via the capturing of CO<sub>2</sub> (CO<sub>2</sub> sequestration), thus the simultaneous production of biofuels and chemicals using bio-oil and DMC can effectively reduce the CO<sub>2</sub> (Figure 4). The DMC-mediated process for integrated production of biofuels and chemicals provides zero-waste utilization of renewable bio-oil and is expected to have commercial potential due to easy separation and purification of product and byproduct, simple downstream treatment, and the formation of a high-value byproduct instead of low-value glycerol [43]. Rathore et al. [43] evaluated the economic potential of the DMC-mediated process of biofuel and

chemical production from renewable oil. The gross profit margin was expected to be 22.81% higher in the DMC-based co-production of biofuels and chemicals due to the high revenue of glycerol carbonate [43,45,91]. Recently, the development of transformer insulating oil from bio-oil has been investigated [92]. Transformer insulating oil has a higher price than biodiesel. Thus, the co-production of high value-added transformer insulating oil and glycerol carbonate derivatives using DMC would be potentially applicable for industrial implementation.



**Figure 4.** Sustainable and green production of biofuels and glycerol carbonate derivatives.

## 5. Concluding Remarks

DMC is a green chemical and reagent based on its environmentally-benign properties and broad applications. In the DMC-mediated processes for biofuels and chemicals production, there are two types of catalysts used: chemical (acid and base) and enzyme. The chemical catalysis is faster than the enzymatic process. Among the different kinds of chemical catalysis, alkaline catalysis has been widely employed in DMC-mediated biofuels and chemicals production [34,41,66,69,78]. The cost of alkaline catalysts, such as metal hydroxides, alkoxides and metal oxides, is comparatively cheaper than enzyme, and high yields have been obtained with chemical catalysis [59]. In contrast, chemical catalysis processes have several drawbacks, such as a high energy requirement, additional downstream process for removing inorganic salts, and large amounts of water for product purification.

Enzyme catalysis is considered an environmentally-benign technology. Lipase has been used as a catalyst in the transesterification for biofuel and chemical production [46–48,83,88]. The enzymatic process is conducted at milder conditions compared to the chemical catalysis process, thus requiring less energy consumption. During enzyme catalysis, product separation and purification processes are simple due to high product purity and generation of less wastewater. A disadvantage is that the enzyme-catalyzed product is expensive due to high enzyme cost. Reuse of immobilized lipase can reduce the production cost [52].

DMC-based biodiesel offers some advantages over methanol-based biodiesel with respect to a better lubricating fuel property and oxidation stability [38,43]. In addition, glycerol carbonate as a value-added co-product can lead to a higher gross profit margin of DMC-based biodiesel when compared to conventional biodiesel production. From an economic perspective, the DMC-mediated process for co-production of biofuels and chemicals had shown its potential for its implementation in industry [45]. Additionally, this process may be zero-waste utilization of renewable bio-oil.

At present, the production cost of the DMC-mediated process is 34.7% greater than the methanol-based process due to the high market price of DMC [43]. Thus, a DMC-mediated process is burdensome for industrial applications in terms of price competitiveness. Commercial production of DMC from carbon dioxide with more competitive price will be one of the key success factors for industrial implementation of DMC-mediated production of biofuels and chemicals in the near future.

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