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SYNTHESIS OF SUGAR CARBONATE: A BRIEF REVIEW

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ABSTRACT

Organic carbonate such as glycerol carbonate and propylene carbonate have been in an ever-increasing demand from researchers and industry sectors since it has high potential to be used in various applications either direct or indirect uses. For instance, it is used as the polar aprotic solvent due to their polarity, viscosity, low toxicity and high degradability. Another important organic carbonate is sugar carbonate. However, up to date, the main method to synthesis sugar carbonate is involved hazardous and toxic route through the phosgenation process and excess pyridine has to be neutralized. Besides, the yield of sugar carbonate was found to be low, approximately around 5%. Therefore, a safer and environmentally friendly route could be explored. Besides, the abundantly available renewable carbohydrate has a great potential to be utilized as feedstocks for the production of a sugar carbonate fine chemical. This review paper will briefly describe the properties and potentials of sugar carbonate for various applications followed by existing synthesis techniques. Apart from that, alternative synthesis approaches will be explored and proposed. At the end of the paper, the general perspective on the future of sugar carbonate chemical is briefly discussed.

Keywords: Sugar Carbonate, Organic Carbonate, Synthesis Technique, Green Chemistry

1. INTRODUCTION

Sugar carbonate is one of the organic carbonate compounds containing the carbonate functional group. In the realm of the preparation of sugar carbonate has practical difficulties which severely limit the usefulness of the compound. Organic carbonates receive a significant amount of attention from academician and industries throughout the history of chemistry. The conversion to organic carbonate or organic ester is being widely studied because of their reputed application as monomers for organic glasses, polymers, plasticizers, surfactants, curing agents, cross linking agents, and also solvents [1, 2].

Sugars are a class of carbohydrates that represent the largest fraction of biomass which is a major source of multiple hydroxyl groups. The carbohydrate such as glucose, fructose, sucrose, mannose, etc. can efficiently become as feedstock for the synthesis of sugar carbonates. Sugars are the source of food energy and people all around the world consumed sugar as part of a healthy, nutritious and balanced diet. It can be divided into three classes which are monosaccharides, disaccharides, and polyols. Those commonly found in food are glucose or mannose (fruits, table sugar, vegetables, honey, milk products, cereals), fructose (one of the main sugars found in fruit, vegetables, honey – the others are sucrose and glucose), and galactose (found in milk). In addition,



disaccharides consist of two monosaccharides that joined together. For example, sucrose exists due to glucose and fructose are linked together whereas lactose consists of glucose and galactose, and maltose consists of glucose and glucose altogether.

However, in the context of catalytic reaction in chemistry, an increasing effort has been devoted to finding the ways to utilize abundantly available sugars feedstock for the production of valuable organic chemical [3-6]. In recent years, sugars are slowly being used as alternative feedstock for the production of analog petrochemical based products [7-9]. An example of valuable chemical products can be produced from sugars are detailed in Figure 1. Therefore, any attempt in successfully utilized sugar as a feedstock for the production of valuable chemicals are crucial and important for future development especially in a chemical related industry [10-13].

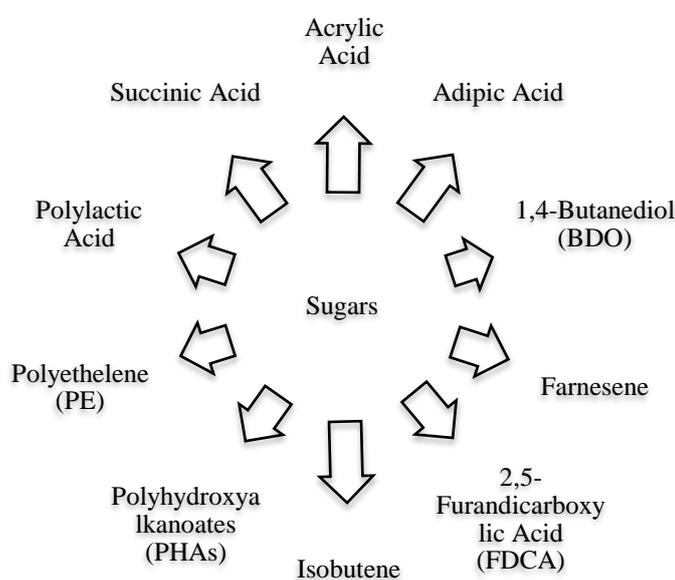


Figure 1: Efficient approaches the utilization of sugars as a platform chemical for the production of valuable compounds. [7-9]

2. SUGAR CARBONATE PROPERTIES AND APPLICATIONS

Organic carbonates own some of the important properties as presented in Table 1[4, 14, 15]. Due to the low toxicity, low volatility, high boiling point, high flash point, and biodegradability, an organic carbonate having fundamental criteria which make it suitable for many applications as shown in Figure 2[15-17]. Therefore, it is clear that organic carbonates play an important role in modern life and now becoming more readily available on a worldwide basis.



Table 1: Physical properties of non-cyclic and cyclic organic carbonates

Organic Carbonate	Boiling Point/ K	Density ^(293 K) / g.cm ⁻³	Viscosity ^(298 K) / Pa.s	biodegradability / day	Oxygen content
Dimethyl carbonate (DMC)	363	1.07	5.90x10 ⁻⁴	88%	53.3%
Diethyl carbonate (DEC)	399	0.98	7.53x10 ⁻⁴	75%	40.7%
Ethylene carbonate (EC)	521	1.34	2.56x10 ⁻³	Readily	54.5%
Propylene carbonate (PC)	515	1.20	2.50 x10 ⁻³	94%	47.1%
Glycerol carbonate (GC)	138	1.40	6.10x10 ⁻²	Readily	54.2%

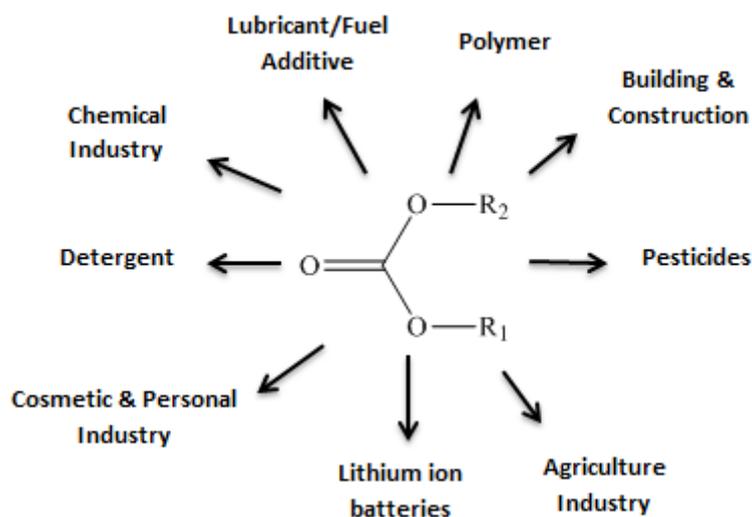


Figure 2: Organic carbonate potential applications



From that point of view, sugar carbonate such as D-mannose carbonate (2,3-O-Carbonyl- α -D-mannopyranose) also demonstrates comparable characteristics as commercially available and largely produced organic carbonates counterpart. The main characteristics of D-mannose carbonate are given in Table 2[18]. Based on Table 2, this compound has the molecular weight of 206 g mol⁻¹ with low toxicity, high boiling point (876 K), high flash point (527 K) and biodegradable. The basic properties of D-mannose carbonate allow it to possess similar application as proved by other commercially available organic carbonates.

Table 2: Main properties of D-mannose Carbonate

Organic Carbonate	Molecular Weight/ Kg/mol	Boiling Point/ K	Density ^(293 K) / g.cm ⁻³	Enthalpy of Vaporization/ KJ/mol	Flash Point/ K
D-mannose Carbonate (C ₇ H ₁₀ O)	206	876	1.7	102.9	526

3. CURRENT SYNTHESIS METHOD

Previously, the phosgenation technique was initially used for the synthesis of sugar carbonate[11-13]and other organic carbonates [19]. The hazard presented by hazardous phosgene (COCl₂) materials which pose a threat to the environment and excess pyridine that had been used as an organic base in the reactions intended for the process has to be neutralized [17]. Besides, the yield of carbonate compounds produced using this route is significantly low, which is less than 5%. Other alternative synthesis techniques also have been tested using chloroformate ester that had been diluted in an organic base [20] and in aqueous alkali [6]. However, the use of chloroform ester is highly flammable and inhalation of the vapour may cause lung oedema. The reaction of the chloroformic ester in the presence of the pyridine as the organic base would produce carbonyl derivative compounds [20]. Table 3 listed detail available general methods for the synthesis of sugar carbonate and its derivatives.

Table 3: Listing detail available method for the synthesis of sugar carbonate and its derivatives

Starting material	Method	Product	Reference
Glucose, fructose, mannose, galactose, and arabinose	Phosgene in an organic base	Sugar dicarbonate	[11]
Glucose, cellobiose, fructose, galactose, mannitol, and sucrose	Chloroformic ester in an organic base and aqueous alkaline	Sugar carbonate derivatives	[6, 20]

4. POTENTIAL SYNTHESIS APPROACHES

In 19's, a review of the nature and general behaviour of the sugars has led researchers [21] to inquire into the prospect of preparing sugar carbonates and to consider the possibility of the occurrence of such compounds. These substances should conform to two types of carbonates represented by the cyclic and noncyclic as shown in Figure 3.



Cyclic

Noncyclic

Figure 3: Two types of carbonate (cyclic and acid noncyclic)

The cyclic carbonate is indicated by ethylene carbonate from the reaction of ethylene glycol and phosgene for noncyclic, indicated by condensing the sodium derivative of ethylene glycol with methyl chloroformate. Thus, these reactions suggested a possible method for the synthesis of sugar carbonate through carbonylation of multi-hydroxyl containing compound[6]. Therefore, existing approaches in converting polyol to respective organic carbonates (glycerol carbonate, ethylene carbonate, propylene carbonate, etc.) could be adapted.

Direct carbonylation through carbon dioxide (CO_2) as carbonyl source has been introduced as an alternative and environmentally friendly route; however, CO_2 has some thermodynamic limitations resulting in poor yield[22]. In most cases, the relatively high temperature is required with a pressurized system in order to assist CO_2 solubility. Another example is through carbonylation in the presence of CO followed by an oxidation reaction. However, the toxicity associated with CO hindered further development of this catalytic process. For that reason, existing and current commercial process for the production of organic carbonates proceed through trans carbonation method. For example, in the case of glycerol carbonate as target compound which commercially produced by Huntsman Petrochemical Corporation, trans carbonation of ethylene carbonate and glycerol was used, and the glycerol could be originated from crude glycerol originated from Biodiesel industry. The main drawbacks of this approach are due to the expensive source of carbonate as well as the use of synthetically derived catalyst [15, 23].

Alternatively, favored route of synthesis opted for the organic carbonate could be involved the use of urea as a carbonyl source under solvent-free reaction condition [24-26]. The reaction is considered near green technology approach and relatively low operational cost due to abundant and readily available of urea. A study by Sonnati and co-researchers reviewed that the existence of catalyst bearing Lewis acidic site will produce better yield of target product [15]. The reaction parameters especially the reaction temperature and time, as well as urea to polyol molar ratio, is found to have a significant effect on yield of organic carbonate as targeted product, whereas the method to remove the released ammonia, either through flowing gas or vacuum system seems to provide indifferent outcome[25]. High temperature or prolong the reaction time may lead to producing another by-products, thus reduce the yield of organic carbonate [27] whereas molar ratio of polyol to urea may affect the yield of target carbonate product. In term of reaction pathways, several groups reported that carbamate compound was generated first and then it was converted into carbonate through the intramolecular interaction between the hydroxyl group and the carbonyl group in the reaction of urea with polyol compound[26, 28]. The carbonate step would be more difficult compared to the carbamate step because of the reduced nucleophilicity of the hydroxyl group in carbamate. Thus, the synthesis of carbonate from carbamate molecule required higher temperature with the presence of an active catalyst.

5. SUMMARY AND PERSPECTIVE

The utilization of abundantly available bio-based materials as a feedstock in placed of depleted non-renewable hydrocarbon source for the production of fine and specialty chemicals are essentially important for the sustainable future. Therefore, successfully synthesized sugar carbonate via carbohydrate or sugar feedstock will significantly contribute to the aforementioned effort. However, proper choice of synthesis approach is essential, and this shall consider the safety aspects as well as high yield of target carbonate compound produced. It is clear that the previous synthesis method did not fulfill those requirements, even the possible new adapted approaches suffered from several setbacks. In our view, the possible technique, for now, is through urea as carbonyl source. Nevertheless, a few considerations shall be deliberate and closely planned. For example, a simple sugar such as glucose will easily degrade and caramelized at high-temperature reaction conditions, thus conflicted with the optimum temperature require activating urea. Those situations might hinder the catalytic reaction and subsequently suppress the overall yield of the target product. With the



bright potential ahead, those problems and challenged is worth to explore by both academicians and industry sector. Indeed, it will pave the way to unlock the huge potential lying in sugars as a chemical feedstock in chemical industry.

6. REFERENCES

- [1] J. P. Parrish, R. N. Salvatore, and K. W. Jung, "Perspectives on alkyl carbonates in organic synthesis," *Tetrahedron*, vol. 56, pp. 8207-8237, 2000.
- [2] T. Sakakura and K. Kohno, "The synthesis of organic carbonates from carbon dioxide," *Chemical Communications*, pp. 1312-1330, 2009.
- [3] B. Schöffner, F. Schöffner, S. P. Verevkin, and A. Börner, "Organic carbonates as solvents in synthesis and catalysis," *Chemical reviews*, vol. 110, pp. 4554-4581, 2010.
- [4] M. A. Pacheco and C. L. Marshall, "Review of dimethyl carbonate (DMC) manufacture and its characteristics as a fuel additive," *Energy & Fuels*, vol. 11, pp. 2-29, 1997.
- [5] J. Nemirowsky, "Ueber die Einwirkung von Chlorkohlenoxyd auf Aethylenglycol; vorläufige Mittheilung," *Journal für Praktische Chemie*, vol. 28, pp. 439-440, 1883.
- [6] C. F. Allpress and W. N. Haworth, "CL.—Sugar carbonates and their derivatives. Part I," *Journal of the Chemical Society, Transactions*, vol. 125, pp. 1223-1233, 1924.
- [7] C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning, and K. Egeblad, "The renewable chemicals industry," *ChemSusChem*, vol. 1, pp. 283-289, 2008.
- [8] A. Corma, S. Iborra, and A. Velty, "Chemical routes for the transformation of biomass into chemicals," *Chemical reviews*, vol. 107, pp. 2411-2502, 2007.
- [9] H. Danner and R. Braun, "Biotechnology for the production of commodity chemicals from biomass," *Chemical Society Reviews*, vol. 28, pp. 395-405, 1999.
- [10] L. Hough and J. Priddle, "CYCLIC CARBONATE DERIVATIVES OF CARBOHYDRATES," ed: SOC CHEMICAL INDUSTRY 14 BELGRAVE SQUARE, LONDON SW1X 8PS, ENGLAND, 1959, pp. 1600-1601.
- [11] W. N. Haworth and C. R. Porter, "LXXXVI.—Crystalline α -methylmannofuranoside (γ -methylmannoside). Part I," *Journal of the Chemical Society (Resumed)*, pp. 649-651, 1930.
- [12] L. Hough, J. Priddle, and R. Theobald, "The carbonates and thiocarbonates of carbohydrates," *Advances in carbohydrate chemistry*, vol. 15, pp. 91-158, 1961.
- [13] L. Hough, J. Priddle, and R. Theobald, "363. Carbohydrate carbonates. Part II. Their preparation by ester-exchange methods," *Journal of the Chemical Society (Resumed)*, pp. 1934-1938, 1962.
- [14] A. Arteconi, A. Mazzarini, and G. Di Nicola, "Emissions from ethers and organic carbonate fuel additives: a review," *Water, Air, & Soil Pollution*, vol. 221, pp. 405-423, 2011.
- [15] M. O. Sonnati, S. Amigoni, E. P. T. de Givenchy, T. Darmanin, O. Choulet, and F. Guittard, "Glycerol carbonate as a versatile building block for tomorrow: synthesis, reactivity, properties and applications," *Green Chemistry*, vol. 15, pp. 283-306, 2013.
- [16] A. B. McEwen, H. L. Ngo, K. LeCompte, and J. L. Goldman, "Electrochemical properties of imidazolium salt electrolytes for electrochemical capacitor applications," *Journal of the Electrochemical Society*, vol. 146, pp. 1687-1695, 1999.
- [17] A.-A. G. Shaikh and S. Sivaram, "Organic carbonates," *Chemical reviews*, vol. 96, pp. 951-976, 1996.
- [18] (19-Jan-2017). *2,3-O-(Oxomethylene)hexopyranose*. Available: http://www.chemspider.com/Chemical-Structure.3291868.html?rid=9c6b96f8-b7c8-44ee-a50f-a740033a6988&page_num=0
- [19] O. Dermer, J. McKelta, and G. Weismantel, "Encyclopedia of Chemical Processing and Design," ed: Marcel Dekker, New York, 1999.



- [20] G. Zemplén and E. Desiderius László, "Einige neue Derivate der Glucose und der Cellobiose," *Berichte der deutschen chemischen Gesellschaft*, vol. 48, pp. 915-926, 1915.
- [21] S. W. Challinor, W. N. Haworth, and E. L. Hirst, "XXXIV.—The compound uronic acids. Structure of the aldobionic acid from gum arabic," *Journal of the Chemical Society (Resumed)*, pp. 258-265, 1931.
- [22] J. Li and T. Wang, "Chemical equilibrium of glycerol carbonate synthesis from glycerol," *The Journal of Chemical Thermodynamics*, vol. 43, pp. 731-736, 2011.
- [23] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, and F. Lindner, "Improved utilisation of renewable resources: new important derivatives of glycerol," *Green Chemistry*, vol. 10, pp. 13-30, 2008.
- [24] M. H. Ab Rahim, Q. He, J. A. Lopez-Sanchez, C. Hammond, N. Dimitratos, M. Sankar, *et al.*, "Gold, palladium and gold-palladium supported nanoparticles for the synthesis of glycerol carbonate from glycerol and urea," *Catalysis Science & Technology*, vol. 2, pp. 1914-1924, 2012.
- [25] N. A. S. Zuhaimi, V. P. Indran, M. A. Deraman, N. F. Mudrikah, G. P. Maniam, Y. H. Taufiq-Yap, *et al.*, "Reusable gypsum based catalyst for synthesis of glycerol carbonate from glycerol and urea," *Applied Catalysis A: General*, vol. 502, pp. 312-319, 2015.
- [26] V. P. Indran, M. Hasbi, A. Rahim, M. Gaanty Pragas, M. Mashitah, and Y. Y. H. Taufiq, "Boiler Ash-Catalysed Synthesis of Glycerol Carbonate from Glycerol," 2013.
- [27] T. W. Turney, A. Patti, W. Gates, U. Shaheen, and S. Kulasegaram, "Formation of glycerol carbonate from glycerol and urea catalysed by metal monoglycerolates," *Green Chemistry*, vol. 15, pp. 1925-1931, 2013.
- [28] L. Wang, Y. Ma, Y. Wang, S. Liu, and Y. Deng, "Efficient synthesis of glycerol carbonate from glycerol and urea with lanthanum oxide as a solid base catalyst," *Catalysis Communications*, vol. 12, pp. 1458-1462, 2011.