CHEMICAL ENGINEERING RESEARCH AND DESIGN XXX (2014) XXX–XXX

Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: www.elsevier.com/locate/cherd

Techno-economic evaluation of different CO_2-based processes for dimethyl carbonate production

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A B S T R A C T

In this work, several chemical processes for production of dimethyl carbonate (DMC) based on CO_2 utilization are evaluated. Four CO_2-based processes for production of DMC are considered: (1) direct synthesis from CO_2 and methanol; (2) synthesis from urea; (3) synthesis from propylene carbonate; and (4) synthesis from ethylene carbonate. The processes avoid the use of toxic chemicals such as phosgene, CO and NO that are required in conventional DMC production processes. From preliminary thermodynamic analysis, the yields of DMC are found to have the following order (higher to lower): ethylene carbonate route > urea route > propylene carbonate route > direct synthesis from CO_2. Therefore, only the urea and ethylene carbonate routes are further investigated by comparing their performances with the commercial BAYER process on the basis of kg of DMC produced at a specific purity. The ethylene carbonate route is found to give the best performance in terms of energy consumption (11.4% improvement), net CO_2 emission (13.4% improvement), in global warming potential (58.6% improvement) and in human toxicity-carcinogenic (99.9% improvement) compared to the BAYER process. Also, the ethylene carbonate option produces ethylene glycol as a valuable by-product. Based on the above and other performance criteria, the ethylene carbonate route is found to be a highly promising green process for DMC production.

Keywords: Dimethyl carbonate; CO_2-based synthesis; Process evaluation; Energy consumption; Net CO_2 emission; Sustainability analysis

1. Introduction

Carbon dioxide accumulation in the atmosphere is a major cause of concern with respect to the increasing global temperature of the earth and severe climate changes. The CO_2 is primarily released from long-term storage via combustion of fossil-fuel. It has been estimated that the worldwide energy-related CO_2 emissions are increasing at a rate of about 2.1% per year (Xu et al., 2010). It is therefore necessary to decrease the emission of CO_2 to the atmosphere on a global scale. The CO_2 emissions from the petrochemical sector, for example, oil refineries, LNG sweetening, ammonia, ethane and other petrochemical process and ethylene oxide to atmosphere are estimated around 1460 $MtCO_2$/year, while, CO_2 utilization in chemical process such as urea, methanol, dimethyl ether, tert-butyl methyl ether (TBME) and organic carbonate is estimated around 178 $MtCO_2$/year (Aresta et al., 2013). Although, no single solution will be sufficient in reducing this large net CO_2 emission, a potential strategy could be to more utilize CO_2 as a chemical feedstock for conversion to more valuable chemicals (Centi and Perathoner, 2009). However, the utilization of CO_2 for the production of fine chemicals is severely limited by the

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http://dx.doi.org/10.1016/j.cherd.2014.07.013

reaction equilibrium in most cases and they have been widely reported (Omae, 2012). The high stability of carbon dioxide leads to a very low driving force, which has to be compensated if higher value chemical products are to be produced what is necessary is to first create a full reaction tree of higher value chemicals that can be produced directly or indirectly with CO_2 as a reactant. This requires each synthesis route to be investigated for thermodynamic feasibility and availability of catalysts, when necessary. Having the reaction tree, different synthesis routes can be investigated to find the best set of value-added products by CO_2 utilization and thereby reduction of net CO_2 emission as a first step, the synthesis routes for a selected set of higher value products could be investigated based on known reaction data.

This work focuses on the evaluation of the production of dimethyl carbonate (DMC) by several reaction routes. DMC is an important carbonylating and methylating reagent used in various fields such as medicine, pesticides, composite materials, flavoring agent and electronic chemicals (Omae, 2012; Pacheco and Marshall, 1997). Although processes for the production of DMC are well-established, for example, BAYER (Kricsfalussy et al., 1996), UBE (Matsuzaki and Nakamura, 1997) and ENIChem (Tundo and Selva, 2002), the synthesis of DMC utilizing CO_2 is an option worth investigating since it offers direct benefits to the environment while creating valuable products from the emitted and undesired CO_2. In this paper, CO_2 based processes for production of DMC are selected for evaluation and compared according to a set of performance criteria that includes yield, energy consumption and CO_2 emission. For a consistent comparison, the various criteria are evaluated for the same product specification (that is, a fixed purity) and per unit mass of the desired product.

2. DMC production process alternatives

The production of DMC is classified here in terms of two main types, namely conventional processes and CO_2-based processes. Among the conventional processes, the productions of DMC from phosgene, through partial carbonylation of methanol (BAYER process) and from methyl nitrile (UBE process) are well-known. The processes utilizing CO_2 include direct synthesis with methanol and integrated processes involving intermediate compounds such as urea, propylene carbonate and ethylene carbonate, which are derived from CO_2. The involved reactions and associated thermodynamic data are given in Table 1 for the above process routes.

Table 1 – List of reactions found in DMC production.

Process	Reaction		$\Delta G_{r25\,^\circ C}$ (kJ/mol)	$\Delta H_{r25\,^\circ C}$ (kJ/mol)	$K_{25\,^\circ C}$
Phosgene route	$COCl + 2CH_3OH \rightleftharpoons (CHO)CO + 2HCl$	(1)	−305.543	−321.670	0.883
Partial carbonylation	$CO + 1/2O_2 + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O$	(2)	−233.077	−300.399	0.910
Methyl nitrile	$CO + 2CH_3ONO \rightleftharpoons (CH_3O)_2CO + 2NO$	(3)	−115.438	−107.945	0.954
CO_2 direct synthesis	$CO_2 + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O$	(4)	29.583	−15.259	1.012
Urea route	$2NH_3 + CO_2 \rightleftharpoons NH_2CONH_2 + H_2O$	(5)	21.009	−0.042	1.000
	$NH_2CONH_2 + CH_3OH \rightleftharpoons CH_3OCONH_2 + NH_3$	(6)	−13.240	−10.310	1.005
	$CH_3OCONH_2 + CH_3OH \rightleftharpoons (CH_3O)_2CO + NH_3$	(7)	15.390	13.11	0.993
Propylene carbonate route	$C_3H_6O + CO_2 \rightleftharpoons CH_3(C_2H_3O_2)CO$	(8)	−0.054	−0.908	0.999
	$CH_3(C_2H_3O_2)CO + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + C_3H_8O_2$	(9)	35.115	22.854	1.014
Ethylene carbonate route	$C_2H_4O + CO_2 \rightleftharpoons (CH_2O)_2CO$	(10)	−0.025	−0.083	0.999
	$(CH_2O)_2CO + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + (CH_2OH)_2$	(11)	−14.926	27.500	0.993

2.1. *Conventional process*

2.1.1. *Synthesis of DMC from phosgene*

This process employs the traditional (pre-1980) method to produce DMC (Pacheco and Marshall, 1997). Here, phosgene reacts with methanol to form methyl chloroformate (CH_3OCOCl), which further reacts with methanol to form DMC according to Eq. (1) in Table 1. However, phosgene is an extremely hazardous material (Matsuzaki and Nakamura, 1997) and is classified by the US Department of Transportation (DOT) as a class-A poison. Consequently, there is an incentive to phase out phosgene (Matsuzaki and Nakamura, 1997).

2.1.2. *DMC from partial carbonylation (BAYER process)*

This non-phosgene process produces DMC by reacting methanol, carbon monoxide and oxygen in liquid phase, as

Please cite this article in press as: Kongpanna, P., et al., Techno-economic evaluation of different CO_2-based processes for dimethyl carbonate production. Chem. Eng. Res. Des. (2014), http://dx.doi.org/10.1016/j.cherd.2014.07.013