



(51) International Patent Classification:

C07C 68/01 (2020.01) C07C 41/09 (2006.01)

C07C 69/96 (2006.01) C07C 43/04 (2006.01)

EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(21) International Application Number:

PCT/EP2019/085682

(22) International Filing Date:

17 December 2019 (17.12.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

PA 2018 01042 20 December 2018 (20.12.2018) DK

(71) Applicant: HALDOR TOPSØE A/S [DK/DK]; Haldor Topsøes Allé 1, 2800 Kgs. Lyngby (DK).

(72) Inventor: JOENSEN, Finn; Møllevænget 28, 2970 Hørsholm (DK).

(81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

Declarations under Rule 4.17:

- as to the identity of the inventor (Rule 4.17(i))
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: A PROCESS FOR PREPARING DIMETHYL CARBONATE

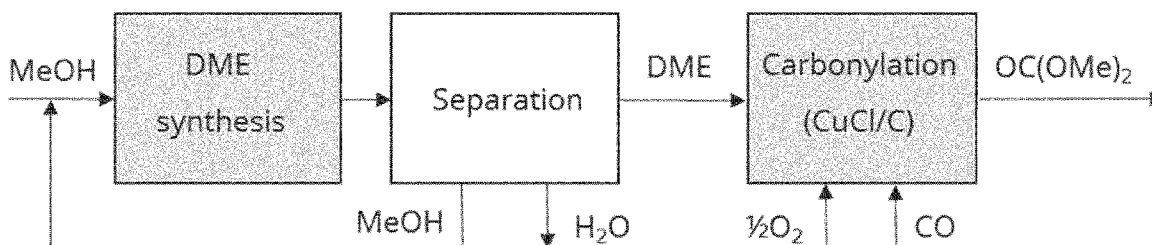


Fig. 1

(57) Abstract: In a process for making dimethyl carbonate (DMC) by direct carbonylation, where dimethyl ether (DME) is used as feed, any formation of water is eliminated completely in the oxidative carbonylation step. The carbonylation of DME into DMC is catalyzed using a supported Cu or Pd-Cu catalyst.

5 **Title: A process for preparing dimethyl carbonate**

The present invention relates to a process for the preparation of dimethyl carbonate (DMC), which is an organic compound with the formula $\text{OC}(\text{OCH}_3)_2$. It is a colorless liquid
10 classified as a carbonate ester.

More specifically, the invention concerns a process for the preparation of dimethyl carbonate (DMC) by direct carbonylation, where dimethyl ether (DME) is used as feed according
15 to the equation



where any formation of water is eliminated completely in
20 the oxidative carbonylation step.

Carbon dioxide is one of the gases contributing heavily to global warming, and its concentration in the atmosphere continues to increase. The use of fossil fuel systems accounts for 33-40% of the CO_2 emission, and much research
25 has recently been focused on how to utilize the waste CO_2 .

CO_2 is a highly oxidized state of carbon, and it is therefore suitable to use it to produce molecules with high oxidation states. As an example of this, organic carbonates
30 can be mentioned, wherein the chemical bonds of the carbonyl carbon are connected to oxygen. Within this group, one interesting chemical is dimethyl carbonate (DMC).

The synthesis of DMC was originally performed using the toxic reagent phosgene (COCl_2), but DMC can in fact be synthesized through many different routes, among which direct synthesis is one that uses carbon dioxide as reactant.

In one of the routes investigated recently, DMC is produced through direct synthesis from methanol and CO_2 according to the equation

10



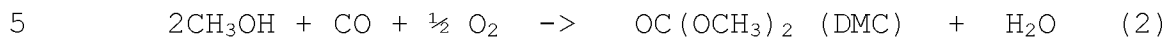
This direct synthesis has been considered promising due to the use of simple, less toxic reactants and the possibility to fixate carbon dioxide by converting it into valuable products. The reaction is exothermic, but under the usual conditions it is not spontaneous. Currently there are no commercial processes using this direct method to produce DMC, but much research has been made on direct synthesis of DMC and on developing effective catalysts (see e.g. US 9,073,849 B2). However, the methanol conversion is quite limited by the thermodynamic equilibrium, and the typical conversions are only 1-2% in the absence of dehydrating agents.

25

According to le Chatelier's principle, water can be removed in order to further increase the production of DMC. This removal can be performed in a separate unit with a recycle or integrated in a sorption-enhanced reactor. Because the equilibrium constant for direct synthesis of DMC is so low, water has to be removed down to small mole fractions.

30

The currently used processes for the synthesis of DMC rely on oxidative carbonylation of methanol (the *EniChem* process):

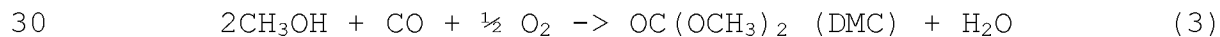


This process, which is described *i.a.* in US 5,536,864 A, is catalyzed by CuCl. It generates equimolar amounts of DMC and water, the latter resulting in a low conversion per
10 pass, azeotrope formation and a strongly corrosive environment.

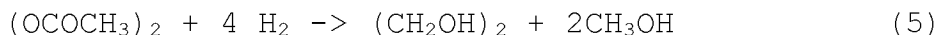
A competing process launched by *Ube Industries* (described in US 5,214,185 A) circumvents some of these drawbacks by
15 avoiding the formation of water in the carbonylation step. This is done by conducting the oxidation of methanol by NO and oxygen (to form methyl nitrite) in a separate step in which a CuCl/Pd catalyst is used.

20 The current processes for the preparation of dimethyl oxalate (DMO), which is a precursor for (mono)ethylene glycol (MEG), and dimethyl carbonate (DMC), both rely on oxidative carbonylation of methanol. The technology is dominated by the direct carbonylation route (the *EniChem* process) for
25 DMC and the *Ube* process, involving methyl nitrite as an intermediate, for both DMC and DMO synthesis.

The DMC process and the DMO process proceed according to

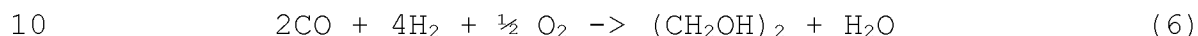


respectively, where the latter may be hydrogenated to form MEG:



5

Thereby, the net process (equations (4) and (5) in combination) becomes an all-syngas based route, in which methanol is merely an intermediate:



10

The *EniChem* process only applies to DMC production, and it suffers from low conversion, azeotrope formation and a very corrosive environment. In the *Ube* process, both for DMC and DMO, these problems are, at least partly, circumvented by avoiding the formation of water in the carbonylation step by conducting the oxidation of methanol by NO and oxygen (to form methyl nitrite) in a separate step. Thus, the advantages of the *Ube* process are, in part, paid for by a more complex synthesis loop.

15

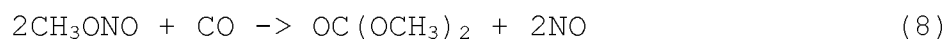
20

The *EniChem* process [(3)-(5)] involves direct oxidative carbonylation by CO in a CuCl (copper(I)chloride) slurry process to produce DMC. The process was commercialized in 1983 with the set-up of a 5500 t/a plant. The overall process suffers from low conversion per pass (approx. 20%) due to water inhibition (max. 3% H₂O), corrosiveness and azeotrope formation. The process is one-pot (120-140°C; 20-30 bar), applying a suspension of CuCl contained in a boiling, self-circulating U-shaped reactor.

25

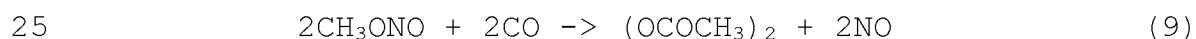
30

Ube Industries developed a vapor phase process [(3), (6), (7), (8)] separating the oxidation and carbonylation steps by first oxidizing methanol by NO and oxygen to form methyl nitrite (7) and subsequently carbonylating methyl nitrite with release of NO (8):



applying a supported $\text{PdCl}_2/\text{CuCl}$ catalyst. The main advantage of the *Ube* process is that it takes place in the gas phase under anhydrous conditions, allowing for close to 100% conversion per pass and, most likely, with much less severe corrosion problems than in the *EniChem* process. It also simplifies separation by avoiding the formation of DMC-MeOH-H₂O azeotrope.

In a closely related process also developed by *Ube*, a very similar chemistry takes place, in which a (supported) catalyst consisting of Pd(0) only (i.e. comprising no CuCl) is used. This process is promoting double carbonylation at Pd and subsequent C-C coupling to produce DMO:



Other prior art documents within the field include the following:

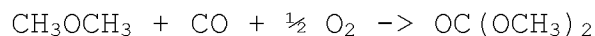
CN 108727194 A describes a method for synthesizing dimethyl carbonate by reacting dimethyl ether (DME) with carbon monoxide and oxygen in a ratio of 2:2:1 at a temperature of

120°C and a pressure of 2 MPa using a Pd-Cu/Ce_{1-x}Zr_xO₂ catalyst. DME is obtained from synthesis gas carrying out the reaction at a temperature of 200-280°C and a pressure of 2-4 MPa using a Cu-Zn-Mn/HZSM-5 catalyst.

5

In JP (H) 1180095 A, a method for synthesizing dimethyl carbonate is described, in which DME is reacted with CO and oxygen in the presence of a copper and a platinum catalyst according to the equation

10



The reaction temperature is 120°C, and the pressure is 30 kg/cm².

15

WO 2014/144099 A1 describes a method for generating DME by dehydration of methanol over a Cu-modified alumina catalyst at a temperature between 50 and 300°C followed by distillation, and in US 2010/0056831 A1 a method for generating DME by dehydration of methanol over an alumina catalyst at a temperature between 300 and 480°C is described.

20

From US 2016/0362355 A1, a method for producing DME from syngas is known, said method using a H₂/CO molar ratio of 0.7-2.5, a reaction temperature of 200-300°C and a reaction pressure of 30-60 atm. And, finally, a method for producing a mixture of DME and methanol from syngas is known from US 2012/0078023 A1, said method using a catalyst which comprises alumina combined with silica-alumina at a pressure of at least 4 MPa and a temperature of 260°C.

25

30

The process according to the present invention involves a direct carbonylation, in which dimethyl ether (DME) is used instead of methanol:



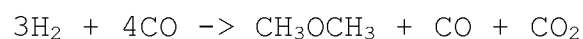
Using this process, the formation of water in the oxidative carbonylation step is eliminated completely, providing the advantages of a high conversion per pass, less or even no
10 corrosion issues and no problems with azeotrope formation.

Studies by Amoco published in 1993, in which the *EniChem* catalyst was employed, concluded that CuCl_2 supported on activated carbon and B-ZSM-5 were both inactive for oxidative carbonylation of DME, but - by changing to a bimodal
15 carbon support, increasing the Cu loading and feeding a mixture of methanol and DME - high levels of conversion, i.e. more than 70%, could be obtained with methylal (dimethoxymethane; $\text{CH}_2(\text{OCH}_3)_2$) as the primary byproduct.

20

A process according to equation (1) warrants essentially the same advantages as the methyl nitrite based DMC process by *Ube* in terms of an anhydrous carbonylation step. Indeed, the *Ube* process is elegant in its chemistry, but it does
25 take a rather complex process to eliminate water in the carbonylation. The simplicity in making DMC from DME instead of methanol would provide a much less complex layout, simply by introducing a MeOH-to-DME synthesis step in front of the DMC synthesis. Thus, in one embodiment of the process of the invention, shown in Fig. 1, the DME feed may be
30 generated by dehydration of methanol, followed by distillative separation of DME.

Alternatively, a direct synthesis of DME from a coal gas having a H₂/CO ratio of about 0.8, leaving essentially over one mole of CO for downstream carbonylation, would make the DMC synthesis virtually self-sustaining. Thus, in another embodiment, shown in Fig. 2, DME and CO may be generated directly from synthesis gas by making use of a combined methanol/DME synthesis. In this case it is particularly advantageous to apply a synthesis gas having a H₂/CO ratio of about 0.8, whereby the DME synthesis takes place essentially according to the equation



This way, a feed is obtained, which consists of approximately equimolar amounts of DME and CO for the oxidative carbonylation step plus CO₂, which serves as a diluent and heat sink in the exothermic DMC synthesis. As opposed to the *Ube* process, CO purity is not an issue in the direct carbonylation. In fact, in 1982, *EniChem* specifically patented the use of synthesis gas in the carbonylation reaction (US 4,318,862). Therefore, the layout shown in Fig. 2 may entail a significant cost reduction by eliminating the need for a separate CO generation and purification.

DME may be synthesized by dehydration of methanol over an acidic catalyst, typically an alumina-based acidic catalyst, at temperatures between 280 and 360°C.

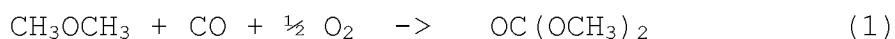
In the alternative embodiment according to the present invention, the combined synthesis of methanol/DME from synthesis gas typically takes place at about 200-350°C at a pressure of 20 to 60 bar over catalysts comprising mixtures

of alumina, silica/alumina and/or zeolites and Cu/Zn/Al₂O₃-based catalysts.

5 The carbonylation of DME into DMC is catalyzed using a supported Cu or Pd/Cu catalyst at a temperature between 90 and 200°C under a pressure, which is preferably between 5 and 40 bar.

Claims:

1. A process for preparing dimethyl carbonate (DMC) by
5 direct carbonylation, where dimethyl ether (DME) is used as
feed according to the equation



- 10 where any formation of water is eliminated completely in
the oxidative carbonylation step.

2. Process according to claim 1, wherein the carbonyl-
15 ation of DME into DMC is catalyzed using a supported Cu or
Pd-Cu catalyst at a temperature between 90 and 200°C under
a pressure between 5 and 40 bar.

- 20 3. Process according to claim 2, wherein the DME feed
is generated by dehydration of methanol followed by distil-
lative separation of DME.

- 25 4. Process according to claim 3, wherein the dehydra-
tion of methanol is carried out over an acidic catalyst at
a temperature between 280 and 360°C.

- 30 5. Process according to claim 4, wherein the catalyst
is an alumina-based catalyst.

6. Process according to claim 1, wherein DME and CO are generated directly from synthesis gas by using a combined methanol/DME synthesis.

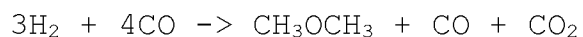
5

7. Process according to claim 6, wherein the combined synthesis of methanol/DME from synthesis gas takes place at about 200-350°C under a pressure of 20 to 60 bar using a catalyst comprising mixtures of alumina, silica/alumina and/or zeolites and Cu/Zn/Al₂O₃-based catalysts.

10

8. Process according to claim 7, wherein a synthesis gas, in which the H₂/CO ratio is approximately 0.8, is used whereby the DME synthesis proceeds essentially according to the reaction

15



leading to a feed of approximately equimolar amounts of DME and CO for the oxidative carbonylation step.

20

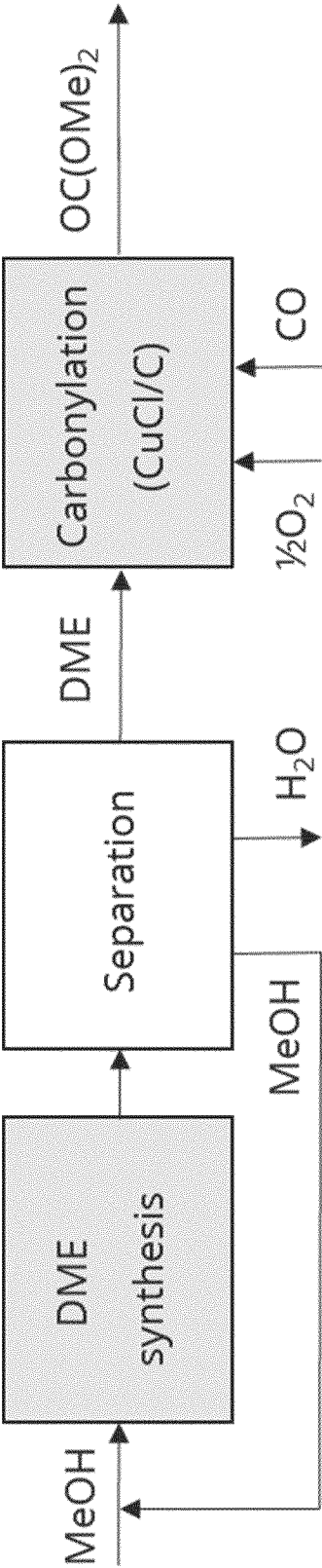


Fig. 1

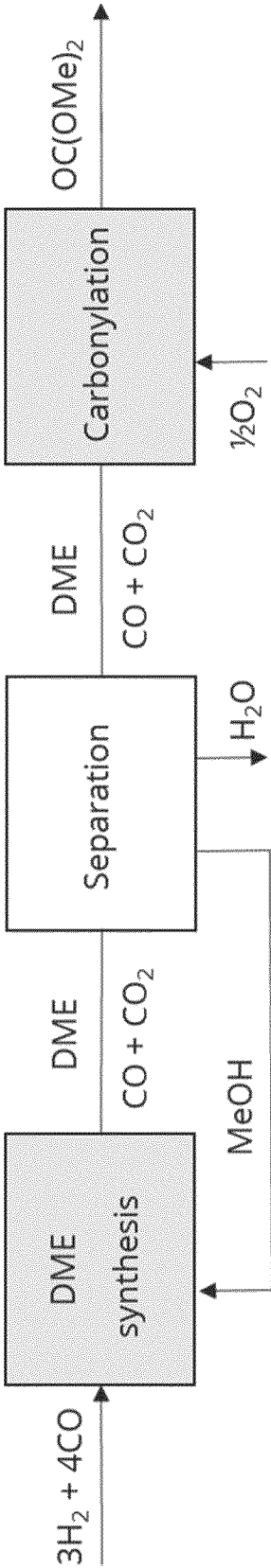


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/085682

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C68/01 C07C69/96 C07C41/09 C07C43/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 108 727 194 A (QINGDAO INST BIOENERGY & BIOPROCESS TECH CAS) 2 November 2018 (2018-11-02) cited in the application	1,2
Y	paragraph [0037] - paragraph [0044]; example 3	3-8
X	----- JP H11 80095 A (NIPPON KOKAN KK) 23 March 1999 (1999-03-23) cited in the application	1,2
Y	paragraph [0019]; claim ----- WO 2004/074228 A1 (KOREA RES INST CHEM TECH [KR]; JUN KI-WON [KR] ET AL.) 2 September 2004 (2004-09-02) claims; examples ----- -/-	3-5



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

28 February 2020

Date of mailing of the international search report

06/03/2020

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Zervas, Brigitte

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/085682

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 481 305 A (JORN ERNEST [DK] ET AL) 6 November 1984 (1984-11-06) claims -----	6-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/085682

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
CN 108727194	A	02-11-2018	NONE	

JP H1180095	A	23-03-1999	JP 3372196 B2	27-01-2003
			JP H1180095 A	23-03-1999

WO 2004074228	A1	02-09-2004	AU 2003235494 A1	09-09-2004
			CN 1741980 A	01-03-2006
			EP 1597225 A1	23-11-2005
			JP 4364126 B2	11-11-2009
			JP 2006514085 A	27-04-2006
			KR 20040074519 A	25-08-2004
			US 2006135823 A1	22-06-2006
			WO 2004074228 A1	02-09-2004

US 4481305	A	06-11-1984	AU 562487 B2	11-06-1987
			CA 1211760 A	23-09-1986
			DE 3332314 A1	08-03-1984
			DK 399082 A	08-03-1984
			IN 158403 B	08-11-1986
			IT 1194387 B	22-09-1988
			SE 455091 B	20-06-1988
			US 4481305 A	06-11-1984
			ZA 8306345 B	25-04-1984
