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(54) Title: AN IMPROVED PROCESS FOR THE PREPARATION OF DIMETHYL CARBONATE USING IONIC LIQUIDS AS CATALYST

(57) Abstract: The present invention relates to an improved process for the preparation of dimethyl carbonate and methyl-N-methyl carbamate starting from methanol and methyl carbamate catalyzed by ionic liquid catalyst in batch or continuous reactor.



WO 2015/087341 A1

**AN IMPROVED PROCESS FOR THE PREPARATION OF DIMETHYL
CARBONATE USING IONIC LIQUIDS AS CATALYST**

FIELD OF THE INVENTION:

[0001] The present invention relates to an improved process for the preparation of dimethyl carbonate and methyl-N-methyl carbamate catalyzed by ionic liquid catalyst in batch or continuous reactor.

BACKGROUND AND PRIOR ART:

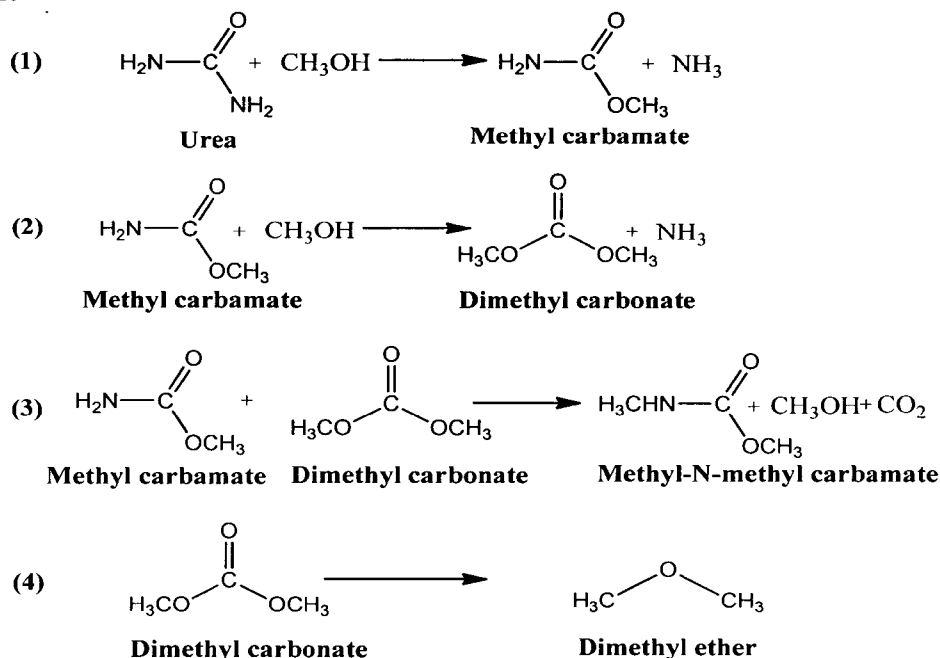
[0002] Dimethyl carbonate (DMC) is an important intermediate and is widely used in industry such as fuel additive, solvents. Owing to its low toxicity, dimethyl carbonate is considered a "green" chemical product with bright development prospects. This increasing focus is mainly due to the bio-degradability, with a low bioaccumulation as well as its low toxicity.

[0003] The ionic liquids are largely made of ions and short-lived ion pairs. An ionic liquid (IL) is a salt. They are commonly known as liquids that are composed entirely of ions with a melting point lower than 373 K (100 °C). The much smaller group of room-temperature ionic liquids (RTILs) exhibit melting points up to 298 K. Often the term ionic liquid and RTILs is used synonymously. These ionic liquid substances are also referred as liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses. Further ammonium, imidazolium-, phosphonium-, pyridinium-, pyrrolidinium-, and sulfonium cation based ionic liquids are widely available in market. Moreover the ionic liquids consist of bulky cations such as 1,3-dialkylimidazolium (or N,N'-dialkylimidazolium) or 1-alkylpyridinium (or N-alkylpyridinium), and anions comprising of Bis(trifluoromethylsulfonyl)imide (NTf₂), Trifluoromethanesulfonate (OTf), Tris(trifluoromethylsulfonyl)methanide (CTf₃), Fluoride (F), Bromine (Br), Iodide (I), Tetrafluoroborate (BF₄), Hexafluorophosphate (PF₆), acetate (CH₃COO), Dicyanamide [N(CN)₂], Trifluoroacetate (CF₃COO), Nitrate (NO₃), Heptachlorodialuminate (Al₂Cl₇), Tetrachloroaluminate [AlCl₄], the anions based mostly on

haloaluminate(III), Chloride (Cl), Tetrafluoroborate (BF₄) and Hexafluorophosphate (PF₆) are highly exploited.

[0004] The significant amount of work is being carried out to develop alternative and safer route for the synthesis of DMC. Synthesis of DMC by the reaction of urea and methanol is an attractive alternative route. This will be a GREEN Process, being based on cheap and renewable raw materials. The reaction scheme is presented herein below:

Scheme 1:



[0005] There are several patents as well as publications in recent times on the synthesis of DMC from methanol and urea leading to the development of new and improved catalysts and methodologies for this important reaction. Reaction of urea with methanol gives methyl carbamate (MC) as an intermediate (Scheme 1).

[0006] PCT application No. 2014072803A1 discloses synthesis of methyl carbamate (MC) and dimethyl carbonate (DMC) from methyl carbamate and methanol in presence of stripping inert gas or superheated methanol vapors using packed column reactor and bubble column reactor and optionally the reaction is carried out in

presence of catalyst selected from the group consisting of hydrotalcite and hydrotalcite like compounds, double metal cyanides, cenosphere or ionic liquids.

[0007] CN101671253A discloses a catalytic synthesis method of dimethyl carbonate (DMC), and the method comprises the steps of adding methanol, potassium carbonate or sodium carbonate, ionic liquid and methyl iodide into a microwave digestion tank in sequence. The ionic liquids are the anions, is a chlorine ion, a tetrafluoroborate anion, or hexafluorophosphate anion that these ionic liquids are [Bmim] Cl, [Bmim] BF₄ or [Bmim] PF₆.

[0008] PCT application No. 2014005417A1 discloses a method for preparing dimethyl carbonate by taking an ionic liquid as a promoter of lipase to catalyze wherein the ionic liquids are selected from 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium hexafluorophosphate salt, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate salts. The invention takes the ionic liquid as the promoter of the lipase to catalyze the methyl alcohol and ethylene carbonate or the methyl alcohol and propylene carbonate to perform transesterification reaction to prepare the dimethyl carbonate.

[0009] PCT application No. 2011013880A2 discloses a method for preparing dialkyl carbonate from urea or alkyl carbamate and alkyl alcohol using an ionic liquid comprising a cation, which produces a hydrogen ion, and a hydrophobic anion containing fluorine with high temperature stability in the presence of catalyst containing a metal oxide or hydrotalcite.

[0010] PCT application No. 2009013062A1 discloses a process for the synthesis of non-cyclic carbamate derivatives from amine compounds, alcohols and CO₂ in the presence of ionic liquids and optionally in the presence of a base. Wherein ionic liquids are selected from 1-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-methylimidazolium tetrafluoroborate, 1-hexyl-3-methylimidazolium

chloride, 1-hexyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium tetrafluoroborate etc.

[0011] Article titled "Highly selective synthesis of dimethyl carbonate from urea and methanol catalyzed by ionic liquids" by H Wang *et al.* published in *Fuel Processing Technology*, Volume 90, Issue 10, October 2009, pages 1198–1201 reports direct synthesis of dimethyl carbonate from methanol and urea using ionic liquids, such as $\text{Et}_3\text{NHCl-FeCl}_3$, $\text{Et}_3\text{NHCl-ZnCl}_2$, $\text{Et}_3\text{NHCl-CuCl}_2$, $\text{Et}_3\text{NHCl-SnCl}_2$ and emimBr-ZnCl_2 , as catalysts. Among the ionic liquids, $\text{Et}_3\text{NHCl-ZnCl}_2$ or emimBr-ZnCl_2 exhibited higher activity for the synthetic reaction and surprisingly high selectivity to DMC. The effects of the various reaction conditions, i.e. reaction temperature, molar ratio of methanol to urea, and amount and composition of catalysts, on the synthesis of DMC were discussed in a systematic way.

[0012] Article titled "Performance of ionic liquid as catalysts in the synthesis of dimethyl carbonate from ethylene carbonate and methanol" by HY Ju *et al.* published in *Reaction Kinetics and Catalysis Letters*, February 2007, Volume 90, Issue 1, pages 3-9 reports the synthesis of dimethyl carbonate (DMC) from methanol and ethylene carbonate (EC) without using any solvent in the presence of ionic liquids as catalysts. The conversion of ethylene carbonate was affected by the structure of ionic liquid. For a series of 1-alkyl-3-methylimidazolium ionic liquids, the one with shorter alkyl chain and the one with more nucleophilic anion showed higher reactivity. The conversion of EC also increased with CO_2 pressure and reaction temperature.

[0013] It is thus apparent from the cited documents, IL is used as a solvent along with metal oxide or hydrotalcite as a catalyst for DMC synthesis from urea and alkyl carbamates. Other ionic liquids reported in the art use quaternary ammonium salt along with metal chloride as catalyst, wherein the catalytic activity for this type of catalyst is due to use of metal chloride in combination with IL in 2:1 ratio.

[0014] Therefore, the novel catalyst system for the synthesis of DMC and subsequently other related compounds is desirable. Accordingly the inventors of the present invention employs hitherto unexploited IL catalyst comprising of cations such as imidazolium, pyridinium, phosphonium ions with alkyl groups of different chain length and anions comprising of halides, tetra fluoro borate, hexafluoro phosphate as catalyst to enhance conversion of MC to DMC in batch or continuous reactor for realizing DMC in selectivity.

OBJECTIVE OF INVENTION:

[0015] The main objective of present invention is to provide a cost effective improved process for the preparation of dimethyl carbonate and methyl-N-methyl carbamate starting from methanol and methyl carbamate catalyzed by ionic liquids.

SUMMARY OF THE INVENTION:

[0016] Accordingly, the present invention provides an cost effective, green process for synthesis of dimethyl carbonate and methyl-N-methyl carbamate starting from methanol and methyl carbamate catalyzed by ionic liquids using either batch or continuous reactor.

ABBREVIATIONS:

[0017] (DMC): Dimethyl carbonate

[0018] (MNMC)/(MMC): Methyl-N-methyl carbamate

[0019] (MC): Methyl carbamate

[0020] (IL): Ionic Liquid

DETAILED DESCRIPTION OF THE INVENTION:

[0021] The invention will now be described in detail in connection with certain preferred and optional embodiments, so that various aspects thereof may be more fully understood and appreciated.

[0022] In an embodiment, the present invention provides an efficient process for the synthesis of dimethyl carbonate and Methyl-N-methyl carbamate starting from

methanol and methyl carbamate catalyzed by ionic liquid catalyst in either batch or continuous reactor.

[0023] In another embodiment, the present invention provides an efficient process for the synthesis of dimethyl carbonate (DMC) and further methyl-N-methyl carbamate (MNMC) starting from methanol and methyl carbamate (MC) catalyzed
5 by ionic liquid (IL) catalyst of Formula (I).



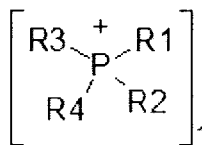
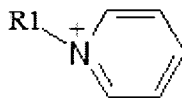
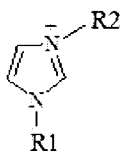
Formula (I)

wherein 'N' is anion selected from the group consisting of
10 Bis(trifluoromethylsulfonyl)imide (NTf₂), Trifluoromethanesulfonate (OTf), Tris(trifluoromethylsulfonyl)methanide (CTf₃), Fluoride (F), Bromine (Br), Iodide (I), Tetrafluoroborate (BF₄), Hexafluorophosphate (PF₆), acetate (CH₃COO), Dicyanamide [N(CN)₂], Trifluoroacetate (CF₃COO), Nitrate (NO₃), Heptachlorodialuminate (Al₂Cl₇), and Tetrachloroaluminate [AlCl₄];

15 **[0024]** More preferably the anions are selected from Chloride (Cl), Tetrafluoroborate (BF₄) and Hexafluorophosphate (PF₆); and

[0025] 'M' is cation selected from the group consisting of quaternary ammonium cation, an imidazolium cation, a pyridium cation, a pyrazolium cation, a pyrrolinium cation, a quaternary phosphonium cation, a thiazolium cation, or a sulfonium cation,
20 where the said cation may have at least one substituent selected from the group consisting of a C₁-C₁₂ alkyl group, C₁-C₁₀ alkoxy group, aryl and aralkyl group;

[0026] More preferably the cation is selected from alkyl substituted quaternary imidazolium cation, phosphonium cation or pyridium cation as depicted herein below.



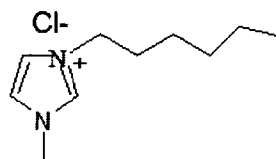
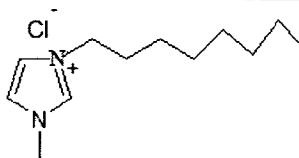
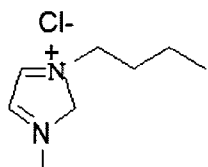
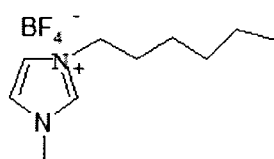
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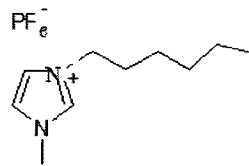
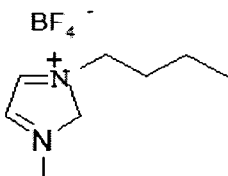
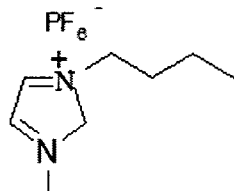
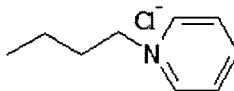
wherein, R1, R2, R3 and R4 are similar or different and independently selected from the group consisting of branched or linear (C₁-C₁₀) alkyl, aryl, aralkyl.

[0027] In preferred embodiment, the ionic liquids used in the instant process having Formula (I) are selected from the group enlisted in Table 1:

5

Table: 1

ILs	Abbreviations	Structure
tetra(C ₁ -C ₁₀) alkyl phosphonium chloride	----	$\left[\begin{array}{c} \text{R3}^+ \text{R1} \\ \text{P} \\ \text{R4} \text{R2} \end{array} \right]_1$ where, R₁-R₄=(C₁-C₁₀)alkyl
1-hexyl- 3-methyl imidazolium chloride	(C ₆ MImCl)	
1-octyl-3-methyl imidazolium chloride	(C ₈ MImCl)	
1-butyl-3-methyl imidazolium chloride	(C ₄ MImCl)	
1-hexyl 3-methyl imidazolium tetra fluoro borate	(C ₆ MImBF ₄)	

1-hexyl 3-methyl imidazolium hexa fluoro phosphate	(C ₆ MImPF ₆)	
1-butyl 3-methyl imidazolium tetra fluoro borate	(C ₄ MImBF ₄)	
1-butyl 3-methyl imidazolium hexa fluoro phosphate	(C ₄ MImPF ₆)	
N-butyl pyridinium chloride	----	

[0028] The amount of ionic liquid used as a catalyst may be 0.1 to 30 % mol/mol based on weight of the methyl carbamate as a main raw material for the preparation of dimethyl carbonate. Moreover, the molar ratio of methanol to methyl carbamate may be 5:1 to 35:1. The less amount of methanol (less than 4), reduces the yield of dimethyl carbonate, or the amount exceeds 35, will increase the energy required for the recycling of methanol. Therefore, the molar ratio of methanol to alkyl carbamate may be maintained within the above range, preferably 10:1 to 25:1.

[0029] The reaction is carried out in a high pressure stirred batch reactor at a temperature in the range of 150°-230°C with slow stirring and continued for 6-10 hrs. Ammonia formed during the reaction is removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. After 6-10 hrs of reaction the reactor is cooled to room temperature. The

reaction mixture is analyzed by known chromatographic techniques such as gas chromatography, HPLC, mass spectroscopy, TLC.

[0030] The invention furnishes use of IL of Formula (I) as catalyst to enhance conversion of MC to DMC in batch or continuous reactor.

5 **[0031]** In yet another embodiment, the present invention provides an improved process for the preparation of dimethyl carbonate and methyl-N-methyl carbamate comprising charging methyl carbamate and methanol in the ratio ranging from 1:5 to 1:20 with ionic liquid catalyst in a high pressure reactor followed by heating at temperature in the range of 160-200°C with stirring for period in the range of 2-8
10 hours with continuously removing ammonia from the reactor to obtain dimethyl carbonate.

[0032] According to the invention the synthesized ILs are screened for DMC and MMC synthesis, wherein ILs with PF₆ anion with 1-butyl-3-methyl imidazole as cation are water immiscible or poorly miscible shows higher DMC selectivity [more
15 than 30%]. By changing the anion such as halides Cl⁻ exhibit better MMC selectivity at temperature 190°C. The process according to the present invention provides a selectivity of methyl-N-methyl carbamate in the range of 1-25% and the selectivity of dimethyl carbonate in the range of 5-30 %. Interestingly the said ionic liquids with different anions show tunable Lewis acidity depending on the molar ratio of cation to
20 anion.

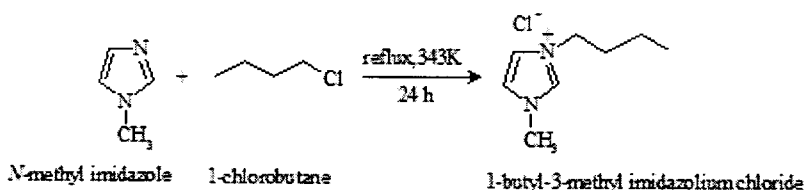
[0033] The following examples, which include preferred embodiments, will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purpose of illustrative discussion of preferred embodiments of the invention.

25 **EXAMPLES:**

Example 1: Synthesis of (1-butyl-3-methyl imidazolium) chloride (C4MImCl):

[0034] In a typical synthesis a solution of 1-chlorobutane (108 mmol) and N-methyl imidazole (108 mmol) was refluxed in round bottom flask at 343K for 24 h under

inert atmosphere. After 24 h the reaction mixture showed two distinct layers. The upper layer containing unreacted starting material was decanted and bottom layer was extracted with ethyl acetate. IL showed slightly yellow appearance and crystallizes at room temperature.



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Example 2: Synthesis of DMC in the presence of (C₄MImCl):

[0035] Methyl carbamate (MC) 7.5 g (100 mmol) and methanol 64 g (2000 mmol) were charged to a 300 ml reactor with 1g of IL (C₄MImCl). The contents were heated to 190°C with slow stirring. After attaining the temperature stirring speed was increased to 1000 rpm and the time was noted as zero time. The reaction was continued for 8 hours. Ammonia formed during the reaction was removed using cooled high pressure condenser (condenser was cooled to 15°C) fitted above the gas outlet valve of the reactor. Ammonia was removed at the interval of 1 hour during the course of the reaction. After 8 h reaction the reactor was cooled to room temperature. Reaction mixture was analyzed by Gas Chromatography. 15.1% of conversion of MC was observed with 19.5% selectivity towards dimethyl carbonate (DMC) and 22.7% selectivity towards MMC (Table 2).

Similarly other ionic liquids were screened for the synthesis of DMC using the procedure described in the Example 2 and the results are presented in Table 2.

20

Table 2:

Sr. No	MC Conv%	DMC sel(%)	MMC Sel(%)	Catalyst
1	17.4	12.1	8.9	C ₈ MImCl

2	19.9	13.5	11.3	C ₆ MImCl
3	15.1	19.5	22.7	C ₄ MImCl
4	17.9	30.1	7.6	C ₄ MImPF ₆
5	1.5	46.2	14.2	C ₄ MImBF ₄
6	14.1	7	1.02	Butyl pyridinium chloride
Reaction Conditions: 190°C, 300ml Parr reactor intermittent NH ₃ removal, 8h.				

Example 3: Synthesis of DMC in the presence of (C₄MImCl) in continuous set up:

[0036] Methyl carbamate (MC) 25 g (333 mmol) and methanol 200 g (6250 mmol) with 3.3 g of C₄MImCl were charged to a 2000 ml reactor connected to a nitrogen reservoir from gas inlet valve. The reservoir is fitted to reactor through constant pressure regulator which is set at 400 psi. A back pressure regulator was fitted to reactor at gas outlet valve. Back pressure regulator is set at 390 psi. The pressure difference of 10 psi was maintained between constant pressure regulator and back pressure regulator to ensure positive flow of nitrogen. This will help in stripping of CH₃OH along with NH₃ that is formed during reaction. The reactor was then pressurized with nitrogen atmosphere at 400 psi and 25 ml methanol was added to the reactor prior to heating. The inlet valve was closed at this point keeping outlet valve open. The contents were heated to 180°C under very slow stirring condition. After attaining the temperature the inlet valve was opened. The reaction was continued 2 h. During this period methanol along with NH₃ was expelled due to the set positive pressure of nitrogen. This methanol along with dissolved NH₃ was collected in a trap (cooled with ice and salt mixture) connected to BPR outlet. After completion of reaction the reactor was cooled to room temperature. Reaction mixture from bomb as well as from trap was analyzed by Gas Chromatography. From GC

analysis 3% conversion of methyl carbamate and 19.5% selectivity to DMC and 2.7% selectivity to MNMC was observed in the reaction.

Table 3. Catalyst Screening on 2 litre and 300 ml continuous set up						
Sr. No.	Catalyst	MC:MeOH ratio	Time (h)	MC Conv (%)	DMC Sel (%)	MMC Sel(%)
Homogeneous catalyst (2 litre parr reactor, 7ml/min MeOH feeding, 180°C)						
6	C ₄ MImCl	1:5	2	3.0	19.5	2.7
7	C ₄ MImCl ^s	1:20	4	15	19	1
8	C ₄ MImCl*	1:5	2	16.2	12.9	1.4
9	C ₄ MImPF ₆ *	1:5	2	14.3	5.1	1
Reaction Conditions: Temperature: 180°C , 2 litre set up, 7ml/min MeOH feeding, Catalyst 3.3g , *Temperature 190°C						
^s Reaction Conditions: Temperature:190°C ,1:20 MC: MeOH, Time:2h, 300 ml set up, 3ml/min MeOH feeding, Catalyst 1g						

5 [0037] ADVANTAGES OF INVENTION:

- 1) Eliminates use of metal salt
- 2) Better conversion of raw material
- 3) Cost effective process

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WE CLAIM

1. An improved process for the preparation of dimethyl carbonate and methyl-N-methyl carbamate comprising charging methyl carbamate and methanol in
5 the ratio ranging from 1:5 to 1:20 with ionic liquid catalyst in a high pressure reactor followed by heating at temperature in the range of 160-200°C with stirring for period in the range of 2-8 hours with continuously removing ammonia from the reactor to obtain dimethyl carbonate.
2. The process according to claim 1, wherein selectivity of methyl-N-methyl
10 carbamate is in the range of 1-25%.
3. The process according to claim 1, wherein selectivity of dimethyl carbonate is in the range of 5-30%.
4. The process according to claim 1, wherein the ionic liquid catalysts are
15 selected from tetra alkyl (C₁-C₁₀) phosphonium chloride, 1-hexyl- 3-methyl imidazolium chloride, 1-octyl-3-methyl imidazolium chloride, 1-butyl-3-methyl imidazolium chloride, 1-hexyl-3-methyl imidazolium tetrafluoroborate, 1-hexyl-3-methyl imidazolium hexafluorophosphate, 1-butyl-3-methyl imidazolium tetrafluoroborate, 1-butyl-3-methyl imidazolium hexafluorophosphate, N-butyl pyridinium chloride.
- 20 5. The process according to claim 1, wherein high pressure reactors are selected from parr reactors.
6. The process according to claim 1, wherein the process is batch or continuous.

25

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2014/000752

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C68/00 C07C269/04 C07C69/96 C07C271/12
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, WPI Data, 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	WO 2012/144856 A2 (RES INST IND SCIENCE & TECH [KR]; BAIK JOON HYUN [KR]; KOH JAE CHEON []) 26 October 2012 (2012-10-26) examples 7,8 -----	1-6
X	US 5 534 649 A (CHO TSURAHIDE [JP] ET AL) 9 July 1996 (1996-07-09) examples 7,8,11,15 -----	1-6
X	WO 2011/013880 A2 (KOREA RES INST CHEM TECH [KR]; KOH JAE CHEON [KR]; KIM CHUL UNG [KR];) 3 February 2011 (2011-02-03) cited in the application examples 1,1-1,2-15,18-34 -----	1-6



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

11 March 2015

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

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