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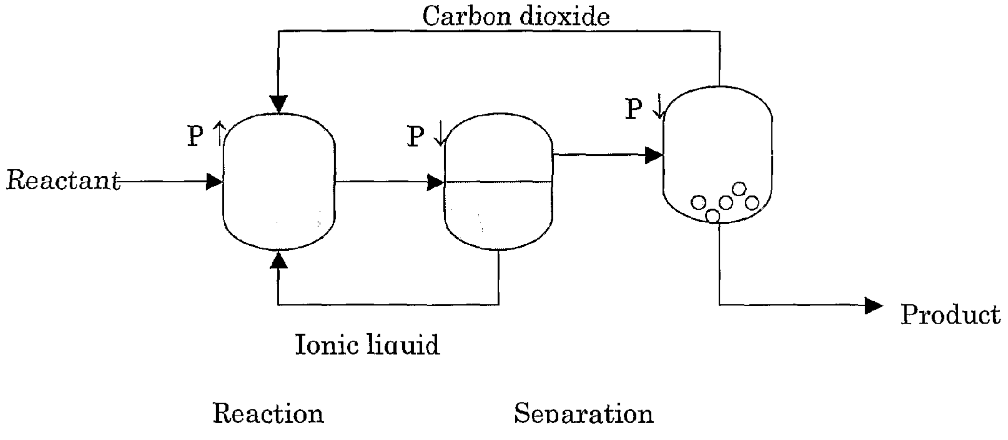
(54) Title: PROCESS FOR CARRYING OUT A CHEMICAL REACTION WITH IONIC LIQUID AND CARBON DIOXIDE UNDER PRESSURE



(57) Abstract: The invention is directed to a process for carrying out a chemical reaction in an ionic liquid as solvent and CO2 as cosolvent, in which process reactants are reacted in a homogeneous phase at selected pressure and temperature to generate a reaction product at least containing an end-product of the reaction, and upon completion of the reaction a multiphase system is obtained by change of conditions, wherein at least one of the phases is the ionic liquid and at least one other phase is a carbon dioxide phase at least containing the end-product, which carbon dioxide phase is substantially free of ionic liquid, separating the carbon and recovering the end-product.

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Title:
PROCESS FOR CARRYING OU A CHEMICAL REACION WITH IONIC LIQUID AND CARBON DIOXIDE UNDER PRESSURE

The invention is in the area of chemical reactions, more in particular chemical reactions followed by separation of the various components from reaction mixtures after completion of the reaction. The present invention especially aims at reactions producing minimal waste and ultra pure products.

The chemical industry is under considerable pressure to replace many existing processes by new technology with preferably zero or at least much less generation of chemical waste and impact on the environment as well. In particular, this holds for the fine chemical and pharmaceutical industries, which industries by definition generate per kg net product the highest amount of chemical waste. The occurrence of excessive amounts of chemical waste is mainly caused by insufficient atom-efficiency of the reactions performed, while the use of volatile organic solvents (VOS), both as reaction media and as product extraction solvents, are released in too large amounts into the environment.

A further important aspect of chemical reactions is the reaction rate and reaction selectivity. These factors are often negatively influenced when the reaction is done in a heterogeneous system.

The separation of the intended end product from the reaction mixtures often requires high costs and/or results in serious loss of product, especially in case the starting materials and the end product have comparable properties in conventional separation techniques such as distillation or extraction, for example with supercritical carbon dioxide. In addition thereto, the end-product is often contaminated with remaining solvent, which has to be removed there from in separate purification steps.

It has been described that it is possible to use ionic liquids as solvent for chemical reactions.

Room temperature ionic liquids are organic salts with melting points under 100 degrees, often even lower than room temperature. Recently they are employed more and more as substitute for the traditional organic solvents in chemical reactions. The most common ones are imidazolium, pyridinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolium, thiazolium, oxazolium and triazolium derivatives, but also phosphonium or tetralkylammonium compounds can be used for this purpose. As anion various anions may be used, provided the room-temperature ionic liquid character is not lost.

Room temperature ionic liquids consist solely of ions. However, unlike conventional molten salts (for example, molten sodium chloride), these materials often melt below 100° C. This is achieved by incorporating a bulky asymmetric cation into the structure to stop the ions packing easily. Since the melting points are low, ionic liquids can act as solvents in which reactions can be performed, and because the liquid is made of ions rather than molecules, such reactions often give distinct selectivities and reactivity when compared with conventional organic solvents. Much effort has been put in developing processes using ionic liquids as solvents for chemical reactions. However, all approaches that have been developed prior to the invention, were based on heterogeneous systems.

It is an object of the present invention to provide a novel principle for performing chemical reactions in ionic liquids in a homogeneous system and the subsequent separation of the reaction mixture, more in particular the recovery of the end-product from the reaction mixture, which reactions are very atom efficient, while at the same time having a good (enantio)-selectivity and reaction rate.

These and other objects of the invention are obtained through the process of the invention, as will become clear from the subsequent description thereof.

The invention is based thereon that when using an ionic liquid as solvent for the reaction, in combination with CO_2 as co-solvent, the reaction can be performed in a homogeneous phase by selection of suitable pressure, temperature and CO_2 concentration. After completion of the reaction, adaptation of the conditions result in a multi-phase system, wherein one of the phases is an ionic liquid and at least one of the other phases is a carbon dioxide rich phase, substantially free of ionic liquid.

The invention is based on the phenomenon, that at certain temperature, pressure and CO_2 concentration, CO_2 is always able to transform a heterogeneous system based on ionic liquid as solvent, into a homogeneous phase. On the one hand this phenomenon creates an operating window wherein reactants are dissolved in the homogeneous ionic liquid/CO_2 phase, whereas on the other hand, by change of conditions, more in particular CO_2 amount and/or pressure and/or temperature, the homogeneous phase system breaks down into two or more phases, one of them being an ionic liquid rich phase and another being a carbon dioxide rich phase containing at least some of the components of the reaction mixture including the intended end-product.

Since ionic liquids do not have a detectable own vapor pressure, which is a characteristic and very important feature of ionic liquids with respect to this novel process, the product can be selectively extracted from this heterogeneous system without contaminating the product(s) with the solvent.

Very often the reactant / product phase, liquid or solid, is poorly soluble in the ionic liquid phase. The inhomogeneity of this two-phase system results in relatively low reaction rates. Therefore, it is important to create and maintain a homogeneous liquid phase during reaction. For that purpose, the so-called phenomenon of miscibility switch can be applied.

In any ternary inhomogeneous system of the nature CO_2 + liquid (1) + liquid (2) (or solid), with both condensed phases (partly) miscible, pressurization of the system with CO_2 will force the heterogeneous two-phase system to form a homogeneous one-liquid phase system, along with, of course, a gaseous phase mainly containing CO_2. In reverse, at pressure relief the homogeneous liquid phase will phase split again into a liquid-liquid or a liquid-solid two-phase system. This means that the homogeneity of the reacting phase is fully controlled by varying the CO_2 pressure.

Since the occurrence of a miscibility switch in ternary CO_2 systems (and in multi-component systems as well) has been recognized as a very general phenomenon, it forms the basis of controlling homogeneity / inhomogeneity of the fluid system simply by varying the CO_2 pressure of the reacting system and of the system from which the product has to be extracted by supercritical CO_2.

The figures 1-4 demonstrate the experimentally determined miscibility switch phenomenon for a model ternary system (CO_2 + [hmim]BF_4 + isopropanol) where [hmim]BF_4 is an ionic liquid [1-hexyl-3-methylimidazolium], and isopropanol an arbitrarily chosen organic. In all pictures both liquids have the same mixing ratio, while from left to right the mole fraction of CO_2 slightly increases from 0.5209 up to 0.6023. Going from left to right, the first picture shows that the homogeneous liquid phase region L is surrounded by three two-phase regions: two $L_1 + L_2$ regions and one region $L_1 + V$. Also two narrow three-phase regions $L_1 + L_2 + V$ are present. As can be seen from the second picture, a slight increase of the mole fraction of CO_2 causes that the two two-phase regions are approaching each other, which means a narrowing of the temperature window for the occurrence of a homogeneous one-phase region L. This shift continues with increasing CO_2 mole fraction in the third picture, and as shown in this picture the homogeneous L region is completely surrounded by the two-phase region $L_1 + L_2$, while at the same time the homogeneous L region also shifts rapidly to higher pressures. The fourth picture shows that in the given temperature and pressure window, there is no homogeneous one-phase region at all.

In our previous studies we found that a homogeneous one-phase region always has to be present in ternary or even multi-component CO_2 systems, though its exact location in terms of temperature and pressure depends on the nature of the molecules present in the system and the composition of the mixture.

The sequence of figures also makes clear that the homogeneous one-phase region easily can be missed since its location is rather sensitive to the CO_2 mole fraction. This undoubtedly also explains that in earlier emphasis to combine reactions and separations, using ionic liquids and supercritical CO_2, this new approach remained limited to biphasic systems. The latter conclusion becomes even more apparent because higher concentrations of CO_2 are preferred because of the more favorable transport properties at higher CO_2 concentrations. Therefore, the low-concentration region of CO_2 is avoided because of less favorable transport properties of the system and unsuitable conditions for the product extraction step after the reaction.

In all, it can be concluded that the existence of the miscibility switch phenomenon makes it possible to develop numerous novel processes that are characterized by significantly reduced waste generations and without applying VOS's.

The most common ionic liquids to be used in the invention are imidazolium, pyridinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolium, thiazolium, oxazolium and triazolium derivatives, but also phosphonium or tetralkylammonium compounds can be used for this purpose. As anion various anions may be used, provided the room-temperature ionic liquid character is not lost. Suitable anions are tetrafluoroborate, BF_4^-, PF_6^-, $CF_3SO_3^-$, $CF_3CO_2^-$, $N(CF_3SO_2)_2^-$, $N(CN)_2^-$, $Al_2Cl_7^-$, $AlCl_4^-$, Cl^- and the like.

The present invention is applicable to all kinds of chemical reactions, more in particular reactions involving organic materials, both reactions between components which are generally liquid or solid, but it is also possible to use reactants which are gaseous under normal conditions, such as hydrogen and oxygen. All reactants will form a homogeneous phase with the ionic liquid in combination with pressurized CO_2. Suitable reactions to be used in conjunction with the present invention are hydrogenation reactions, oxidation reactions, addition reactions, alkylation reactions, acylation reactions, hydroformylation reactions and nucleophilic substitution reactions. As the invention makes it possible to carry out enantioselective reactions with great selectivity towards the specific enantiomer.

The invention is especially suitable for reactions requiring the presence of homogeneous catalysts that have ionic character, such as the various reactions involving phosphine-type precious metal catalysts. Example thereof are $[RuCl_2(S)\text{-}BINAP]_2NEt_3$ and (-)-1,2-bis(92R,5R)-2,5-dimethylphospholano)benzene(cyclo-octadiene)rhodium(I) tetrafluoroborate, and other catalysts of the same category.

Since these catalysts also have ionic liquid features, no catalyst will be extracted either by the supercritical CO_2, i.e. a highly pure product will be obtained. Further the catalyst is easily recycled in the ionic liquid rich phase.

Depending on the nature of the reaction this will be carried out in a continuous or in a discontinuous manner.

There are various ways to proceed after the reaction has been completed, whereby the actual way in which this is done will strongly depend on the nature of the reaction, the properties of the reactants, end and by products and the solubility thereof in the ionic liquid and in carbon dioxide, as well as the change of these properties with temperature and pressure.

However, there are some basic methods within which most of the recovery methods fall.

In general the homogeneous phase is turned into a multiphase (two or more phases) by change of operational conditions. This may entail increasing the amount of carbon dioxide at substantially the same pressure, with the result that a separate carbon dioxide rich phase is obtained, into which the organics are extracted. An alternative is to decrease the pressure, whereby a separate carbon dioxide phase is generated containing the organics. A third method is based thereon that the temperature is changed, resulting in a multiphase system.

Due to the negligibly low vapour pressure of ionic liquids, the carbon dioxide phase, and consequently also the product, is substantially free of ionic liquid. The ionic liquid phase may contain some organic material, but as this can be recycled, this does not constitute a problem.

The carbon dioxide rich phase will subsequently be freed from the organic material, preferably by decrease of pressure, resulting in a precipitation of the organic material from the carbon dioxide.

The reaction and separation may take place physically in the same vessel. To make a proper design, various parameters should be known such as characteristics of the reaction, of the phase boundaries and fusion temperature of the various substances involved in the process, their vapour pressures, solubilities in the ionic liquid phase, heat and mass transfer properties should be determined and put into a predictive model. From this model not only static conditions, but also the dynamics, and measurement and control should be calculated. The equipment should be able to deal with gases and liquid at pressures up to say 20 MPa, preferably operating full continuously.

In figure 5 the principle of one embodiment of the present invention has been elucidated schematically. In the first reactor, reactants, ionic liquid and carbon dioxide are introduced. The conditions (P, T and CO_2 concentration) in the reactor are such, that a homogeneous phase exists therein. The contents of the reactor is continuously or discontinuously introduced in the second vessel, with decrease of pressure. In that vessel, a two phase system is formed, one being rich in ionic liquid (at the lower part) and one being rich in carbon dioxide (in the upper part). The ionic liquid rich phase in recycled to the first reactor and the carbon dioxide rich phase, containing the reactants and end product (organic material), is introduced into a third vessel, under further decrease of pressure. The organic material precipitates form the carbon dioxide rich phase and is separated off, while the carbon dioxide rich phase is recycled to the first reactor.

In figure 6 the process of the invention is elucidated in a slightly different manner. The reaction and extraction are done in the section denoted Reaction & extraction. The ionic liquid rich phase, also containing catalyst, is recycled over the section with addition of fresh reactants. The carbon dioxide rich phase is decreased in pressure and the precipitated product is removed there from in liquid or solid form. The CO_2 vapour is recycled with increase in pressure to the value required in the reaction section.

The pressures and temperatures to be used in the invention can vary considerably, depending on the nature of the reaction and the properties of the various chemicals involved. Carbon dioxide pressures and the temperature can be such that the system is supercritical, near-critical or subcritical.

The advantage of working under supercritical conditions is, that supercritical CO_2 is known to be a very good extractant. This makes the extraction of the end-product easier.

The CO_2 pressure at which the end-product is precipitated from the carbon dioxide rich phase is generally a compromise between effectivity of the precipitation and the energy required for recompressing the carbon dioxide to the reaction pressure. It is not necessary to remove the end product completely from the carbon dioxide rich phase, as it is recycled to the reactor.

A serious criterion for the applicability of the process is the presence of any traces ionic liquid and / or catalyst in the extracted product. Within the detection limits of the analytical facilities, not any ionic liquid and / or catalyst could be detected.

The present invention is now elucidated on the basis of the asymmetric hydrogenation of methyl-(Z)-α-acetamido cinnamate, yielding N-acetyl-(S)-phenylalanine methyl ester.

EXAMPLE

The asymmetric hydrogenation of methyl-(Z)-α-acetamido cinnamate, yielding N-acetyl-(S)-phenylalanine methyl ester is catalysed by (-)-

1,2-bis(92R,5R)-2,5-dimethylphospholano)benzene(cyclo-octadiene)rhodium(I) tetrafluoroborate and an important step in the industrial manufacture of levodopa, an antiparkinsonian drug.

The reactant (72 g/l) and catalyst (0.20 g/l) were dissolved in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate. When carbon dioxide was added to the reaction mixture (51 mole%, 150 bar, 50 °C), the solubility of the reactant was increased. The pH_2 was 20 bar and the reaction took place at high rate in a homogeneous phase. After completion of the reaction the pressure was lowered to 120 bar and a carbon dioxide phase was formed, containing the product (solubility of product in CO_2 is 1.78 g/kg) without any ionic liquid contamination, because the ionic liquid has negligible vapour pressure.

When the pressure of the carbon dioxide was decreased to 80 bar(solubility of product in CO_2 is 0.14 g/kg), the product precipitated out and was easily obtained. The carbon dioxide was compressed and recycled. The conversion of the methyl-(Z)-α-acetamido cinnamate was 100% with 99% selectivity towards the S-enantiomer.

Claims

1. Process for carrying out a chemical reaction in an ionic liquid as solvent and CO_2 as cosolvent, in which process reactants are reacted in a homogeneous phase at selected pressure and temperature to generate a reaction product at least containing an end-product of the reaction, and upon completion of the reaction a multiphase system is obtained by change of conditions, wherein at least one of the phases is the ionic liquid and at least one other phase is a carbon dioxide phase at least containing the end-product, which carbon dioxide phase is substantially free of ionic liquid, separating the carbon and recovering the end-product.

2. Process according to claim 1, wherein said change of conditions includes change of pressure, change of amount of carbon dioxide and/or change of temperature.

3. Process according to claim 2, where the amount of carbon dioxide is increased by adding carbon dioxide at substantially the same pressure, thereby creating at least one ionic liquid phase and at least one carbon dioxide phase containing at least the end product and which carbon dioxide phase is substantially free of ionic liquid..

4. Process according to claim 2, wherein the pressure is decreased to create at least one ionic liquid phase and at least one carbon dioxide phase containing at least the end product and which carbon dioxide phase is substantially free of ionic liquid.

5. Process according to claim 1-4, wherein the end product is recovered from the carbon dioxide phase by decrease of pressure of the carbon dioxide phase.

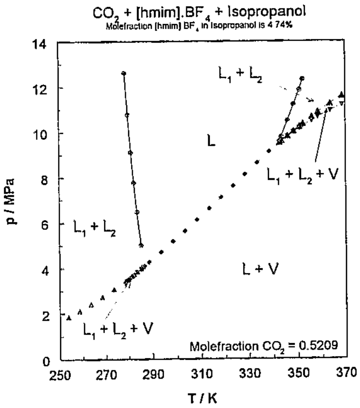
6. Process according to claim 1, 2 or 5, wherein the multiphase system is obtained by increase or decrease of the temperature.

7. Process according to claim 1-6, wherein the chemical reaction is a reaction involving at least one organic reactant.

8. Process according to claim 1-7, wherein the chemical reaction is selected from hydrogenation reactions, oxidation reactions, addition reactions, alkylation reactions, acylation reactions, hydroformylation reactions and nucleophilic substitution reactions.

9. Process according to claim 1-8, wherein a catalyst is used in the reaction, such as a precious metal based homogeneous catalyst.

10. Process according to claim 1-9, wherein the ionic liquid is based on a cation from the group of imidazolium, pyridinium, pyridazinium, pyrimidinium, pyrazinium, pyrazolium, thiazolium, oxazolium, triazolium, phosphonium and tetralkylammonium based ions.


CO$_2$ + [hmim].BF$_4$ + Isopropanol
Molefraction [hmim] BF$_4$ in Isopropanol is 4 74%
p / MPa
T / K
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6
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270
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L$_1$ + L$_2$
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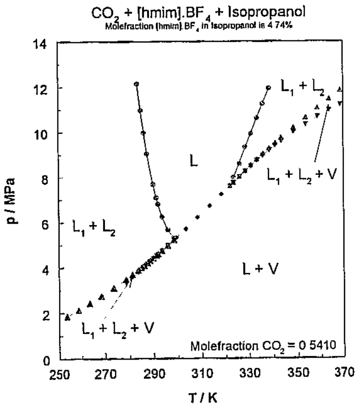
L$_1$ + L$_2$
L$_1$ + L$_2$ + V
L + V
L$_1$ + L$_2$ + V
Molefraction CO$_2$ = 0.5209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L$_1$ + L$_2$
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L$_1$ + L$_2$ + V
L$_1$ + L$_2$
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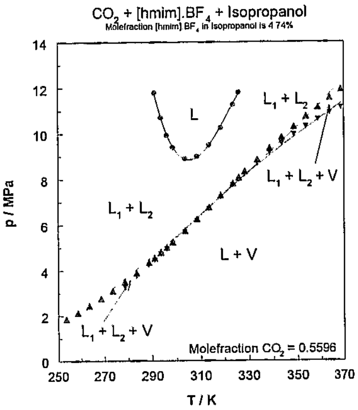
Molefraction CO$_2$ = 0 5410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L$_1$ + L$_2$
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L$_1$ + L$_2$ + V
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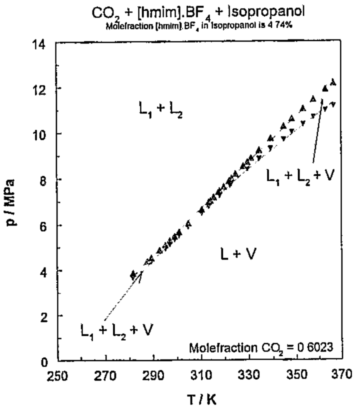
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Molefraction [hmim] BF$_4$ in Isopropanol is 4 74%
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L$_1$ + L$_2$
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L + V
L$_1$ + L$_2$ + V
Molefraction CO$_2$ = 0 6023

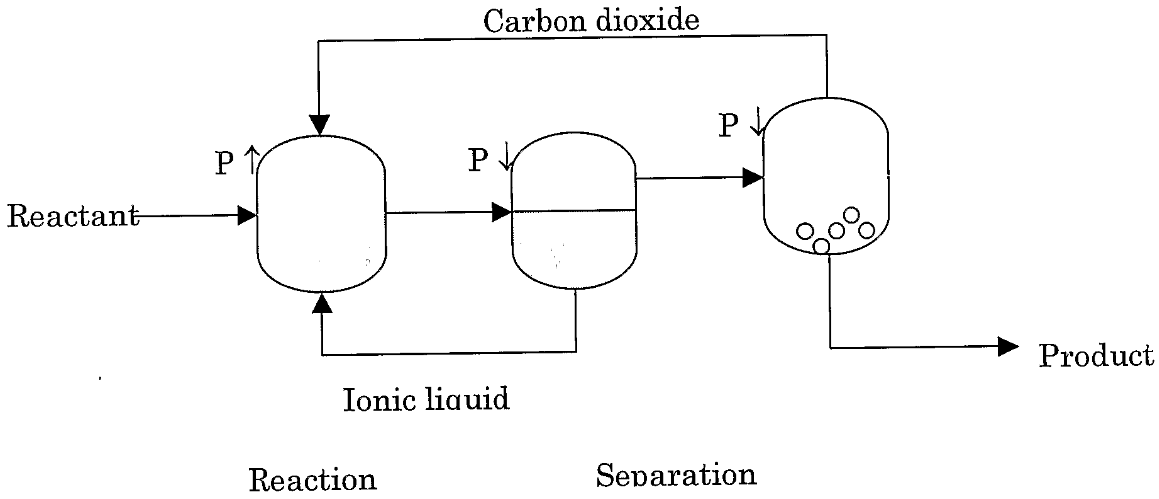

Figure 5

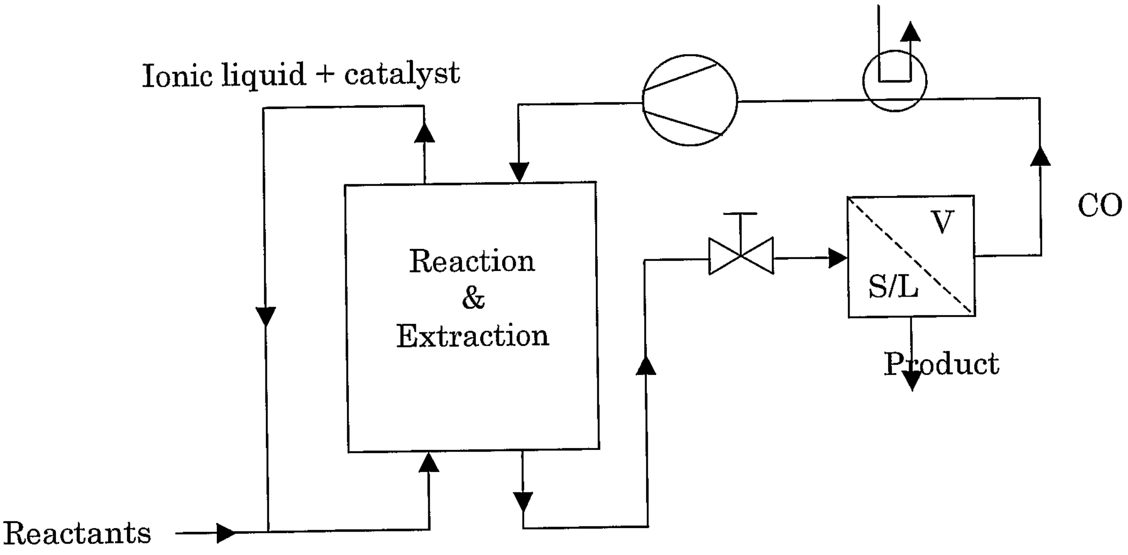

Figure 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL2005/000122

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J3/00

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)
IPC 7 B01J

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/02218 A (THE UNIVERSITY COURT OF THE UNIVERSITY OF ST. ANDREWS; COLE-HAMILTON,) 10 January 2002 (2002-01-10) abstract; claims; figures; examples page 1, line 4 - line 7 page 1, line 22 - page 2, line 4 page 2, line 20 - line 24 page 3, line 8 - line 22 page 4, line 24 - line 27 page 5, line 1 - line 5 page 5, line 10 - line 14 page 6, line 1 - line 12 page 6, line 25 - page 7, line 12 page 7, line 16 - line 19 page 7, line 28 - page 8, line 13 page 8, line 21 - line 32 page 11, line 5 - page 12, line 24 ----- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

Date of the actual completion of the international search 27 October 2005	Date of mailing of the international search report 04/11/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Lapeyrere, J

International Application No
PCT/NL2005/000122

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WASSERSCHEID P ET AL: "IONIC LIQUIDS-NEW SOLUTIONS FRO TRANSITION METAL CATALYSIS" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, WILEY VCH VERLAG, WEINHEIM, DE, vol. 39, no. 21, 3 November 2000 (2000-11-03), pages 3773-3789, XP000967912 ISSN: 1433-7851 page 12, paragraph 4.6	1,2,6-10
A	DE 101 23 467 A1 (STUDIENGESELLSCHAFT KOHLE MBH) 21 November 2002 (2002-11-21) abstract; claims; figures; examples paragraph ‘0008! - paragraph ‘0011! paragraph ‘0015!	1-10
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/NL2005/000122

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