Abstract

Removing carbon dioxide from flue gases with subsequent fixation of CO₂ into valuable chemicals is the most effective way of reducing emission of this "greenhouse gas" by thermal power plants. Selecting the direction of CO₂ transformation into chemical compounds is dependent on the technology applied for the purification of flue gases (chemisorption, physical absorption, etc.). In the case of using the method of monoethanolamine chemisorption, there is proposed to carry out the hydrogenation of recovered carbon dioxide to obtain formic acid and methyl formate. When removing CO₂ from flue gases by the method of physical absorption, there is the most appropriate considered the transformation of organic carbon dioxide into organic carbonates (propylene carbonate, glycerol carbonate).

Key words: carbon dioxide utilization, flue gases purification, carbon dioxide hydrogenation, formic acid, methyl formate, propylene carbonate, glycerol carbonate, glycerol, glycerol hydrogenation, propylene glycol

1. INTRODUCTION

Over the last hundred years, mankind has been extensively used fossil fuels (coal, oil, natural gas) as an energy source. On the one hand, burning of fossil fuels releases the energy which has been stored by a biomass in the Earth 200-600 millions years ago. But, on the other hand, this leads to the formation of large amounts of carbon dioxide: during the combustion of one ton of fossil fuels, there are released into the environment about 2.76 CO₂ tons (from coal), 2.28 CO₂ tons (from oil) and 1.62 CO₂ tons (from natural gas) (Avtonomov 2003). Carbon dioxide is an inert chemical: it can be kept unchanged in the atmosphere for about 120 years. As a result, CO₂ emitted by power plants is gradually accumulated in the atmosphere that makes a great contribution to the “greenhouse effect”. At present, there are about 750 billions of CO₂ tons in the Earth atmosphere (Halman & Steinberg 1999); among them, 13 ton’s billions is a result of the human activity relating to the intensive operation of carbon containing fuels. About 30% of all industrial carbon dioxide emissions are the result of the activity of power plants (Gorkov, AV, Mikushevich VM & Chastnov VB 2005).

Over the last century, CO₂ concentration in the atmosphere has increased by 30% (Golub, Rogankov & Saphonov 2005), and the world community is very concerned about this fact. As known, the Kyoto Protocol regulating restrictions on “greenhouse gas” emissions has been recently extended until 2020. Nowadays this document has been ratified by 38 countries (including all countries of the European Union). According to the Kyoto Protocol, thermal power companies should solved the problem of reducing CO₂ emissions with flue gases of power plants.

There are three ways of reducing carbon dioxide emissions by thermal power plants using fossil fuels (table 1). The cheapest method is switching to fuels with a low content of carbon (it means the replacement of coal and fuel oil to natural gas), but this way is limited in a scope and it application is ineffective. Another method is increasing the efficiency of power units (due to the implementation of
new technical solutions or due to the introduction of advanced technologies), but it does not give a significant result either. A radical solution to the problem of carbon dioxide emissions by power plants is a CO₂ accumulation which is removing this “hotbed” gas from flue gases for its subsequent disposal or for its application in the industry. This way, with the purification of power plants flue gases from carbon dioxide, gives the possibility of 80-99% reducing CO₂ emissions into the atmosphere, and the CO₂ accumulation is regarded as an important contribution to the environmental protection. A number of programs for extracting and accumulating CO₂ from gas streams have already been implemented in Norway, Great Britain, Germany, USA, Japan, China (Lagerung 2006; Smith 2002). Today the industry uses less 1% of dismissed carbon dioxide, so CO₂ recovered from the flue gases should be disposed under the ground or under water. It shouldn’t be considered as an enough effective way of carbon dioxide utilization. The matter is that CO₂ is a carbon-containing raw material. Using this very cheap and nontoxic material, instead of natural gas or oil, gives the possibility for the natural resources economy.

Table 1: Modern ways of reducing carbon dioxide emissions by thermal power plants using fossil fuels

<table>
<thead>
<tr>
<th>Method</th>
<th>Reduction in CO₂ emissions, %</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replacement of coal and fuel oil to natural gas</td>
<td>30-40</td>
<td>Discussion 2001; Glebov, Medik &amp; Chugaeva 2002; Emissiosfreie kraft 2003</td>
</tr>
<tr>
<td>Implementation of a new technical equipment and advanced technologies</td>
<td>20-30</td>
<td>Curry 2006</td>
</tr>
<tr>
<td>Carbon dioxide accumulation (removing CO₂ from flue gases for its subsequent disposal or its application in the industry)</td>
<td>80-99</td>
<td>Smith 2002; Curry 2006; Lagerung 2006</td>
</tr>
</tbody>
</table>

Nowadays chemists are looking for the ways of an effective transformation of carbon dioxide recovered from flue gases into valuable chemicals (Van Niekerk et al. 2006; Aresta & Dibenedetto 2007). Numerous methods of the CO₂ chemical utilization are offered (Centi & Perathoner 2010; Darensbourg 2010; Shi et al 2012). But selecting the direction of CO₂ transformation into chemical compounds should be dependent on the technology applied for carbon dioxide removing from flue gases of thermal power plants.

2. MODERN METHODS OF REMOVING CARBON DIOXIDE FROM FLUE GASES OF THERMAL POWER PLANTS

There are known various methods of CO₂ removal from flue gases of power plants. Among them, there are membrane separation techniques and a few of sorption technologies (table 2, 3).

Table 2: Technologies of CO₂ removal from flue gases and the efficiency and the cost of the electricity produced by power plants (with capacities 330-340 MW)

<table>
<thead>
<tr>
<th>Technology of CO₂ removal</th>
<th>T, °C</th>
<th>CO₂ capture, %</th>
<th>Energy efficiency, %</th>
<th>Electricity relative cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without CO₂ removal</td>
<td>-</td>
<td>0</td>
<td>47,8</td>
<td>1,0</td>
</tr>
</tbody>
</table>
Chemisorption by aqueous monoethanol amine solution (MEA) &nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&nbsp;&n...
3. CHEMICAL TRANSFORMATION OF CARBON DIOXIDE RECOVERED FROM A FLUE GAS BY THE ABSORPTION WITH AMINE SOLUTIONS

In our view, when removing CO₂ from a gas stream by the absorption with amine solutions, the most expedient way of the carbon dioxide chemical transformation is the CO₂ hydrogenation into formic acid:

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{HCOOH} \quad /1/ \]

This reaction is realized in the presence of an amine (Jessop, Joo & Tai 2004; Behr & Nowakowski 2014). The thermodynamics of the reaction /1/ is unfavorable, but an amine solves this problem by acting as a trap of HCOOH and forming an azeotrope which including 1,5-2,5 formic acid molecules to one nitrogen atom /2/ (Burgemeister, Kastner & Leitner 1993).

\[
(1,5-2,5)\text{HCOOH} + \text{N(C}_2\text{H}_5\text{)}_3 \leftrightarrow (1,5-2,5)\text{HCOOH-N(C}_2\text{H}_5\text{)}_3 \quad /2/ \]

HCOOH acid is easily restored from this azeotrope by heating (Anderson & Hamlin 1994). Formic acid is widely used in pharmaceutical factories, tanneries, in the pulp industry, in the agriculture, in the production of pentaerythritol and various solvents. So, when combining the CO₂ removal from a flue gas with the carbon dioxide hydrogenation, there is a possibility to obtain a valuable oxygen-containing chemical. This kind of the combination is:

**CO₂ absorption in an amine solution → CO₂ hydrogenation → HCOOH desorption**

It should improve the efficiency of the CO₂ capture from a flue gas. The significant increase of the load of the amine absorbent for CO₂ (by almost 10 times) should be expected (table 4). Additional increasing the CO₂ load should been when adding methanol to amine solutions: in methanol solution of an amine, the carbon dioxide conversion into formic acid increases by 2-3 times (Lindner, Keppeler & Wegner 1997; Kolesnichenko et al. 2004; Ng et al. 2004). Combining the carbon dioxide recovery
from the flue gases with followed the CO₂ hydrogenation is especially perspective for combined-cycle plants producing the generating gas which comprises hydrogen.

### Table 4: Carbon dioxide capture from a gas stream by the absorption in amine solutions and CO₂ hydrogenation into formic acid

<table>
<thead>
<tr>
<th>CO₂ utilization way from a flue gas</th>
<th>Conditions</th>
<th>Load for CO₂ removed/ N-amine, mol/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amine</td>
<td>T, °C</td>
</tr>
<tr>
<td>CO₂ absorption by amine solutions:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aqueous solution</td>
<td>Monoethanol amine, methyl diethanol amine, diglycol amine</td>
<td>20-40</td>
</tr>
<tr>
<td>in organic solvents</td>
<td></td>
<td>25-35</td>
</tr>
<tr>
<td>methanol solution</td>
<td></td>
<td>20-30</td>
</tr>
<tr>
<td>CO₂ hydrogenation into formic acid in amine solutions catalyzed by Rh-complexes:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>aqueous solution</td>
<td>Triethyl amine, monoethanol amine</td>
<td>25-35</td>
</tr>
<tr>
<td>in organic solvents (DMSO**)</td>
<td></td>
<td>25-35</td>
</tr>
<tr>
<td>DMSO** + methanol</td>
<td></td>
<td>25-30</td>
</tr>
<tr>
<td>methanol solutions</td>
<td></td>
<td>55</td>
</tr>
</tbody>
</table>

*Carbon dioxide pressure.

**DMSO- dimethyl sulfoxide.

The carbon dioxide hydrogenation into formic acid is catalyzed by rhodium and ruthenium complexes (Lau & Chen 1995; Lindner, Keppeler & Wegner 1997; Jessop, Joo & Tai 2004; Jószai & Joo 2004 ; Kolesnichenko et al. 2004), supported ruthenium systems (Zhang et al. 2004; Hao et al. 2010), immobilized ruthenium systems (Zhang & Zheng 2004; Ma & Xu 2013), scandium oxide (Hwang & Mebel 2004). But among them, the rhodium complexes are the only which leads the reaction /1/ under mild conditions. These reaction conditions (20-35°C) are similar to the conditions of the CO₂ absorption (table 4). Therefore, the systems with rhodium complexes should be used to enhance the efficiency of the utilization of carbon dioxide removed from a flue gas of power plant.

When the carbon dioxide hydrogenation catalyzed by rhodium complexes in the presence of amines, besides formic acid, methyl formate can be obtained (reaction /3/), being as well as in methanol solution and in the absence of the latter (Kolesnichenko et al. 2004).

$$2\text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{HCOOCH}_3 + 2\text{H}_2\text{O} \quad /3/$$

Methyl formate is used in the production of some urethanes, amides, formic acid and other formates. It is also applied to dissolve a fat, minerals, vegetable oils, cellulose esters, fatty acids. It means that methyl formate, as well as formic acid, is a valuable chemical. As methyl formate boils at the lower temperature (31,8°C) than formic acid (100,7°C), it should be much easier to organize the combined process with the production of methyl formate:

$$\text{CO}_2 \text{ absorption} \rightarrow \text{CO}_2 \text{ hydrogenation} \rightarrow \text{HCOOCH}_3 \text{ desorption}$$
But till this time there have not been known investigations devoted to the production of methyl formate by the CO₂ hydrogenation. This is due to the absence of HCOOCH₃ selective catalytic systems.

Recently we have found that it is possible to control the selectivity of the CO₂ hydrogenation by varying the composition of the rhodium precursors and ligands (Kolesnichenko et al. 2006). This research has been carried out with using various oligoaryl phosphonites as ligands for rhodium complexes (table 5, 6). There have been obtained very selective systems either for synthesizing formic acid (RhCl₃ + oligoaryl phosphonite C) or for obtaining methyl formate (RhCl(PPh₃)₃ + oligoaryl phosphonite B) (table 6).

Table 5: Oligoaryl phosphonite ligands for rhodium complexes modification

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Chemical formula</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oligoaryl phosphonite A</td>
<td>![Structure A]</td>
<td>5500</td>
</tr>
<tr>
<td>Oligoaryl phosphonite B</td>
<td>![Structure B]</td>
<td>4600</td>
</tr>
<tr>
<td>Oligoaryl phosphonite C</td>
<td>![Structure C]</td>
<td>3600</td>
</tr>
</tbody>
</table>

Table 6: Carbon dioxide hydrogenation into formic acid and methyl formate catalyzed by rhodium compounds modified with oligoaryl phosphonites

<table>
<thead>
<tr>
<th>Rhodium precursor</th>
<th>Oligoaryl phosphonite ligand</th>
<th>TON</th>
<th>Selectivity, %</th>
<th>Concentration, mol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>HCOOH</td>
<td>HCOOCH₃</td>
</tr>
<tr>
<td>RhCl₃</td>
<td>A</td>
<td>960</td>
<td>88,5</td>
<td>11,5</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>1080</td>
<td>83,3</td>
<td>16,7</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>1210</td>
<td>90,9</td>
<td>9,1</td>
</tr>
<tr>
<td>RhCl(PPh₃)₃</td>
<td>B</td>
<td>1230</td>
<td>20,3</td>
<td>79,7</td>
</tr>
<tr>
<td>Rh₂Cl₂(CO)₄</td>
<td>B</td>
<td>860</td>
<td>12,8</td>
<td>87,2</td>
</tr>
</tbody>
</table>

*Conditions: [Rh]= 1·10⁻³ g-at/l; P/Rh= 9 (mol.); DMSO (dimethyl sulfoxide) as a solvent; [NEt₃]= 20% vol.; 25°C; 3.5 MPa; 20 hrs.
4. CHEMICAL TRANSFORMATION OF CARBON DIOXIDE RECOVERED FROM A FLUE GAS BY THE PHYSICAL ABSORPTION WITH PROPYLENE CARBONATE

When removing CO₂ from flue gases by the method of physical absorption, there is the most appropriate considered the transformation of organic carbon dioxide into organic carbonates. It should be noticed that among not numerous chemical manufactures with applying carbon dioxide, the CO₂ transformation into cyclic organic carbonates is one of the most effective ways of the carbon dioxide chemical utilization. The world requirement of these chemicals is more 80 millions of tons per year that allows to fix more 40 millions of CO₂ tons per year (Li et al. 2007). One of the most valuable cyclic carbonate is propylene carbonate which is not only a nontoxic solvent and an absorbent of carbon dioxide. It is also an important intermediate in the production of some polymers, plasticizers, modifiers, pesticides. Moreover, recently propylene carbonate has been a necessary for several advanced technologies (like the laser and optical engineering).

At present propylene carbonate is produced with the CO₂ participation by several corporations such as Jefferson Chemical, Huntsman, Lyondell Chemical, Respol YPF, Dow Chemical (Fukuoka et al. 2003). These industrial processes are based on the oil feedstock and they include two stages:

\[
\text{propylene} \rightarrow \text{propylene oxide} \rightarrow \text{propylene carbonate},
\]

the last stage being the fixation of carbon dioxide by CO₂ interaction with propylene carbonate /4/:

\[
\begin{array}{ccc}
\text{CH}_3\text{-CH-CH}_2 + \text{CO}_2 & \rightarrow & \text{CH}_3\text{-CH-CH}_2 \text{O} \\
\end{array}
\]

Nevertheless, there is a possibility to obtain propylene carbonate with CO₂ participation without an oil feedstock. This new way is based on carbon dioxide and glycerol which is a byproduct of a modern process of biodiesel production. This technology also includes two stages:

\[
\text{glycerol} \rightarrow \text{propylene glycol} \rightarrow \text{propylene carbonate},
\]

accordingly to the reaction of glycerol hydrogenation /5/ and the reaction of propylene glycol carboxylation /6/.

\[
\begin{array}{ccc}
\text{HOCH}_2\text{-CH(OH)-CH}_2\text{OH} + \text{H}_2 & \rightarrow & \text{CH}_3\text{-CH(OH)-CH}_2\text{OH} + \text{H}_2\text{O} \\
\text{CH}_3\text{-CH(OH)-CH}_2\text{OH} + \text{CO}_2 & \rightarrow & \text{CH}_3\text{-CH-CH}_2 \text{O} + \text{H}_2\text{O} \\
\end{array}
\]

Recently the reactions of hydrogenation of glycerol (or its derivatives) have been actively explored (Casale & Gomez 1993; Casale & Gomez 1994; Chaminand et al. 2004; Kusunoki et al. 2005; Martina et al. 2013; Lahr & Shanks 2005; Dasari 2006). There have been found catalysts for ensuring 90-100% conversion of glycerol to propylene glycol (table 7).

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Catalyst</th>
<th>T, °C</th>
<th>P(H₂), MPa</th>
<th>τ, hrs</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>Ru/C</td>
<td>270</td>
<td>10,0-15,0</td>
<td>2</td>
<td>42</td>
</tr>
<tr>
<td>(Kusunoki et al. 2005; Lahr &amp; Shanks 2005; Martina et al. 2013)</td>
<td>CuO-ZnO/Al₂O₃</td>
<td>240-270</td>
<td>10,0-15,0</td>
<td>2</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Cu-Cr-Mn-Ba</td>
<td>180</td>
<td>1,4</td>
<td>24</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Cu-Co-Mn-Mo-P</td>
<td>250</td>
<td>25,0</td>
<td>6</td>
<td>92-96</td>
</tr>
</tbody>
</table>

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Glycidol (Ezhova et al. 2010) | Ru(Pd, Rh)/Al2O3 | 100 | 5,0 | 6 | 100
---|---|---|---|---|---
Acetol (Dasari 2006) | Ru/C | 185 | 1,4 | 24 | 100
Cu-Cr-Mn-Ba | 185 | 1,4 | 24 | 95

At present there are searching catalysts and conditions for the effective implementation of the propylene glycol carboxylation into propylene carbonate (Chen, Zhao & Wang 2005; Du et al. 2005; Huang et al. 2008; Ma et al. 2010). The encouraging results have been obtained with mineral and organic bases as catalysts (table 8).

Table 8: Catalytic reactions of organic carbonate synthesis

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>T, °C</th>
<th>P, MPa</th>
<th>τ, hrs</th>
<th>Conversion, %</th>
<th>Carbonate yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K2CO3 (Chen, Zhao &amp; Wang 2005)</td>
<td>Acetonitrile</td>
<td>150</td>
<td>2,0</td>
<td>12</td>
<td>24</td>
<td>13</td>
</tr>
<tr>
<td>TBD* (Huang et al. 2008; Ma et al. 2010)</td>
<td>Acetonitrile</td>
<td>175</td>
<td>10,0</td>
<td>15</td>
<td>37</td>
<td>23</td>
</tr>
<tr>
<td>Chitozan (Kolesnichenko et al. 2013)</td>
<td>Propylene carbonate</td>
<td>140</td>
<td>0,1</td>
<td>20</td>
<td>56</td>
<td>56</td>
</tr>
<tr>
<td>RhCl3 + chitozan (Kolesnichenko et al. 2013)</td>
<td>Propylene carbonate</td>
<td>140</td>
<td>0,1</td>
<td>20</td>
<td>61</td>
<td>47</td>
</tr>
<tr>
<td>RhCl3 + chitozan (Kolesnichenko et al. 2013)</td>
<td>Methanol</td>
<td>140</td>
<td>0,1</td>
<td>20</td>
<td>82</td>
<td>82</td>
</tr>
</tbody>
</table>

*TBD= 1,5,7-triazabicyclo[4.4.0]dec-5-ene.

This perspective way of propylene carbonate production, including glycerol hydrogenolysis /5/ and propylene carbonate carboxylation /6/, has a distinct advantage over the industrial process (through propylene oxide interaction with CO2). It is the application of the waste of biodiesel production (glycerol) instead of any oil feedstock. However, this progressive method has also a few deficiencies. One of them is using hydrogen which is rather expensive chemical. Another one is operating the rather high temperatures and pressures which is an obstacle to combine this process of carbon dioxide fixation with the removal of CO2 from a flue gas.

In order to overcome these shortcomings, we propose to add the stage of the transesterification of propylene carbonate with glycerol (reaction /7/). Methods and catalytic systems for this reaction are described in our paper (Kolesnichenko et al. 2013). As seen from the data of table 8, this catalytic reaction has been realized under atmospheric pressure in the medium of propylene carbonate. That means that, unlike the reactions of CO2 interaction with propylene glycol /6/ or with propylene oxide /4/, the reaction of propylene carbonate transesterification with glycerol may be combined with the
process of removing CO₂ from a flue gas by the physical absorption with propylene carbonate (on the desorption stage) (table 9).

In this combined process, the transesterification reaction /7/ should be the first one which producing glycerol carbonate and propylene glycol. Then, propylene glycol should interact with carbon dioxide to fix CO₂ and to restore propylene carbonate /6/. This kind of process may be realized without a participation of expensive hydrogen. The major product is glycerol carbonate. Unlike propylene carbonate, glycerol carbonate is a new valuable chemical, but it has been already started to apply in the production of plasticizers, harmless solvents, medicines, varnishes, dyes.

\[
\text{CH}_3\text{-CH-CH}_2\text{+HOCH}_2\text{-CH(OH)-CH}_2\text{OH} \rightarrow \text{HOCH}_2\text{-CH-CH}_2\text{+CH}_3\text{-CH(OH)-CH}_2\text{(OH)} \quad /7/ \\
\text{CH}_3\text{-CH(OH)-CH}_2\text{OH} + \text{CO}_2 \rightarrow \text{CH}_3\text{-CH-CH}_2\text{ + H}_2\text{O} \quad /6/
\]

Table 9: Conditions of removing carbon dioxide from a flue gas and CO₂ transformations into organic carbonates

<table>
<thead>
<tr>
<th>Processes</th>
<th>T, °C</th>
<th>P, MPa</th>
</tr>
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<tbody>
<tr>
<td>Removing carbon dioxide from a flue gas by the physical absorption with propylene carbonate</td>
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<tr>
<td>CO₂ absorption</td>
<td>20-30</td>
<td>2,7-14,0</td>
</tr>
<tr>
<td>CO₂ desorption</td>
<td>20-30</td>
<td>0,1-0,2</td>
</tr>
<tr>
<td>Carbon dioxide transformations into propylene carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂ interaction with propylene oxide (the industrial process) /4/</td>
<td>150-200</td>
<td>10,5</td>
</tr>
<tr>
<td>CO₂ interaction with propylene glycol /6/</td>
<td>150-175</td>
<td>2,0-10,0</td>
</tr>
<tr>
<td>The carbon dioxide transformation into glycerol carbonate</td>
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<tr>
<td>The transesterification of propylene carbonate with glycerol into propylene carbonate /7/</td>
<td>140</td>
<td>0,1</td>
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