The reaction between carbon dioxide and epoxides using a non-metallic catalytic system can produce cyclic carbonates with excellent yields. The activation of the chemical system can occur in two ways: activation of epoxide or activation of carbon dioxide at the first step. A kinetic investigation of epichlorohydrin carbonate synthesis from epichlorohydrin and carbon dioxide was performed. The mass transfer, the kinetic of reaction and the activation of the chemical system was included in the analysis. A kinetic model was developed based on the reaction mechanism and the mass transfer phenomena. The quasi steady state assumption was considered on intermediate species and its results were compared with the detailed model. The optimization of the kinetic parameters estimated was performed by using a genetic algorithm in the model, the results obtained were in agreement with the experimental data.

Introduction

Influence of atmospheric concentration of carbon dioxide in global warming is now well-established and is caused by an increase of greenhouse effect according to an acceleration of fossil energy consumption. Several ways are being implemented in the mitigation of carbon dioxide emissions like pre-combustion capture, oxyfuel combustion and post-combustion capture. These technologies are not at the same level of maturity but they can only be acceptable for a transition period. At present, only the long-term storage of carbon dioxide captured has been considered in the large scale. However the capture and storage of carbon dioxide have been questioned on the last years due to economics and environmental problems, which are associated with the energy consumed in the process and the stability of the stored gases. About 20-30% of energy in a power station is required to store carbon dioxide (Metcalfe et al. 2010).

During the transition period valorization of CO₂ should be developed. The objective is to consider carbon dioxide as a starting material needed by the chemical industry. In this way, carbon dioxide transformation would avoid the costs of carbon capture and storage associated (Metcalfe, North, and Villuendas 2013). Several chemical process for carbon dioxide valorization have been studied, the most common processes include the synthesis of urea, urethane derivatives, carboxylic acid, dimethyl carbonate, polycarbonates, cyclic carbonates and the catalytic hydrogenation of carbon dioxide (Olajire 2013).

Chemical valorization of carbon dioxide

Carbon dioxide transformation is not simple due to its high thermodynamic stability and low reactivity (Sakakura, Choi, and Yasuda 2007). In most cases high input energy is required to convert carbon dioxide or the use of complex catalytic systems is necessary to reduce the activation energy of the reaction. There are some exothermic systems which can be used for the chemical valorization of carbon dioxide such as epoxides, hydrogen, acetylene, amines, etc. Epoxides seem potential candidates for converting carbon dioxide into high value products.

The reaction between carbon dioxide and epoxides in presence of a catalyst (Figure 1) can produce two types of products: cyclic carbonates and polycarbonates. Typically, the formation of polycarbonates is less thermodynamically favorable than the synthesis of cyclic carbonates, but it requires lower activation energy. Therefore, the formation of any of these products will depend on the selectivity of catalytic systems, substrate used (type of epoxide) and conditions of the reaction. Cyclic carbonates has attracted much attention in the...
chemical industry due to the large number of applications (Pescarmona and Taherimehr 2012).

Cyclic carbonates are mainly used as intermediates in the synthesis of fine or bulk chemicals (polymers), polar aprotic green solvents and as electrolyte solvents for lithium-ion batteries. The commercial production of organic carbonates mostly relies on the use of phosgene, which is toxic and dangerous (Abbas-Alli G. Shaikh 1996). Only minor amounts are produced by other pathways as oxidative carbonylation or by using epoxides and carbon dioxide (Aresta 2003). The last option requires high temperatures, above 150°C and high carbon dioxide pressures between 50 - 80 bar (Metcalfe et al. 2010).

Different types of homogeneous and heterogeneous catalytic systems have been suggested for the synthesis of cyclic carbonates. The recent works are focusing on new catalytic systems to avoid the use of large amounts of energy in the reaction between epoxides and carbon dioxide (Pescarmona and Taherimehr 2012).

In this work the kinetic of a non-metallic catalytic system was investigated using epichlorohydrin and carbon dioxide under mild conditions of pressure and temperature. Since the reaction is biphasic, the mass transfer and the reaction mechanism should be studied in order to model the system. The kinetic model was developed considering the reaction mechanism and the mass transfer in a stirred tank reactor. The modeling of system using the approach of quasi steady state was considered and compared with the complex model.

Experimental Set-up

The experiments between carbon dioxide and epoxides were carried out in a stirred tank reactor at several temperatures (50°C – 90°C) and pressures (P < 5 bar). The reactor is composed of a jacket which keeps constant the temperature inside of the vessel by using a heat carrier fluid. The vessel (Tr) and jacket (Tj) temperatures are regulated to an accuracy of ±0.1°C. A calorimetric approach is possible by using a heater installed in the system that quantifies the amount of energy released or absorbed by the mixture. In order to obtain a heat balance in the reactor, a calibration is conducted to determine global heat coefficient (U W/m²/K) and heat capacity for the mixture (C J/kg/K). A stirrer in the reactor allows keeping the homogeneity in the liquid phase and it improves the gas transfer to the liquid. A gas inlet is available in the reactor which is linked to a gas chamber where the pressure and temperature of gas are measured as a function of time. The gas feeding is controlled from the regulation of pressure inside of the reactor. The scheme of the reactor is shown in Figure 2.

In a typical reaction sequence, the vacuum is established in the reactor, followed by the catalyst (99%) and epichlorohydrin (99%) introduction and then stirring of the mixture. The catalyst concentration used is lower than 7.0% mol. The reactor is heated to the desired temperature which is kept constant throughout the reaction. Carbon dioxide is introduced continuously to assure a constant pressure inside of the reactor. At specific time intervals, samples are withdrawn for further analysis. The samples are analyzed by gas chromatography (GC) and infrared spectroscopy (FTIR).
Results

The substrate used was a mixture of epichlorohydrin with non-metallic catalyst. Effects of stirring, catalyst concentration and temperature were studied for modeling of the system.

Effect of stirring

The mass transfer limitation should be studied in order to correlate the kinetic parameters. The interaction between carbon dioxide and epichlorohydrin was studied at several stirring speeds and temperatures. In the absence of catalyst, carbon dioxide and epichlorohydrin present a low reactivity, therefore the effect of the mass transfer phenomena can be observed. We assumed that at low concentrations of catalyst, the physical properties of epichlorohydrin do not have a meaningful influence, thus the effect of stirring in the physical system can be extrapolated to the chemical system. The results indicate that the mass transfer is increased by stirring enhancement which is reflected on the mass transfer coefficient of the liquid phase (Figure 3). The mass transfer coefficient increases with temperature, first by a decrease of liquid viscosity and second by an increase of gas diffusion into the liquid film. Since the mass transfer phenomena in our case was faster than the rate of reaction, the reaction regime is directly controlled by the chemical kinetic but the hydrodynamic of the system must be considered in the model.

![Figure 3 – Effect of temperature and stirring on the mass transfer coefficient of carbon dioxide into epoxides](image)

Effect of temperature and catalyst concentration

The reactions were carried out under solvent-free conditions with epichlorohydrin as substrate and using 2.5% mol to 7% mol of non-metallic catalyst at temperatures between 50°C and 90°C. It was noticed that the reactions carried out at low concentrations of catalyst have an induction period (Figure 4-a) at the beginning of the process, though this was not apparent in reactions carried out at 7% mol of non-metallic catalyst. Additionally, at high temperatures the induction period was not observed even at low concentration of catalyst (Figure 4-b). Apparently at low temperatures and low catalyst concentrations, the activity of catalyst and its interaction rate in the system is slowest and we suppose according to the experimental data that the catalyst can be involved in the mechanism in a different form.

The conversion of epichlorohydrin was up to 90% at 70°C and 90°C after 480 min and 240 min of reaction respectively and the yields achieved were higher than 85%. The results suggest that one part of epichlorohydrin is converted into another product different from the cyclic carbonate. This aspect can have an impact in the modeling, and it must be considered.

On the other hand, we notice that the temperature has an accelerator role in the reaction and is more important than catalyst concentration. At high temperature the catalyst concentration does not have a meaningful impact in the consumption rate of epichlorohydrin.
Figure 4 – Decrease in epichlorohydrin concentration with time at various concentration of non-metallic catalyst
(a) 70°C (b) 90°C

Analysis of reaction mechanism

Organic cations can be used as catalyst for the reaction of carbon dioxide with epoxides. The most common reaction mechanism involves a nucleophilic attack of the catalyst which open the epoxide ring followed by the insertion of carbon dioxide to form the cyclic carbonate (Figure 5-a). In other way if the catalyst molecule is bulky, the attack can occur on carbon dioxide molecule followed by the interaction with epoxide and finally the formation of cyclic carbonate (Figure 5-b). In order to analyze the impact of reaction mechanism in the modeling, we compared the results obtained with both ways.

Figure 5 – Reaction mechanism between CO₂ and epoxides, with CO₂ activation at the first step (A) or with epoxides activation at the first step (B) (Pescarmona and Taherimehr 2012)

Kinetic modeling

The main reactions leading to the formation of cyclic carbonates, such as carbon dioxide absorption, interaction between catalyst and carbon dioxide or catalyst and epoxide and the subsequent formation of cyclic carbonate are presented considering the two possible ways:

<table>
<thead>
<tr>
<th>Way A: Catalyst/CO₂</th>
<th>Way B: Catalyst/Epoxide</th>
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<tbody>
<tr>
<td>Step 1: ( CO_2(g) \leftrightarrow CO_2(l) )</td>
<td>Step 1: ( CO_2(g) \leftrightarrow CO_2(l) )</td>
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<tr>
<td>Step 2: ( CO_2(l) + CAT \rightarrow I_1 )</td>
<td>Step 2: ( EPOX + CAT \rightarrow I_1 )</td>
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<tr>
<td>Step 3: ( I_1 + EPOX \rightarrow I_2 )</td>
<td>Step 3: ( I_1 + CO_2 \rightarrow I_2 )</td>
</tr>
<tr>
<td>Step 4: ( I_2 \rightarrow CAT + Carbonate )</td>
<td>Step 4: ( I_2 \rightarrow CAT + Carbonate )</td>
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</tbody>
</table>

We mentioned above that the steps 1 and 2 in the ways A and B change according to the interaction with the catalyst system, but the structure of mathematical model is the same. Thus, we present below the detailed mathematical model for the way A. Regardless of the way considered for the analysis the first order for each species was observed.
According to the elementary reactions, the rate of formation of epichlorohydrin carbonate and intermediates and the rate of consumption of epichlorohydrin in a batch reactor with continuous feeding of carbon dioxide can be written as follows:

\[
\frac{d[C{O}_2]}{dt} = a_1k_1E \left( \frac{P_i}{n_e} - [C{O}_2]_t \right) - k_1[C{A}T][C{O}_2]_t
\]

(1)

\[
\frac{d[C{A}T]}{dt} = -k_1[C{A}T][C{O}_2]_t + k_3[I_2]
\]

(2)

\[
\frac{d[I_1]}{dt} = k_1[C{A}T][C{O}_2]_t - k_2[I_1][EPOX]
\]

(3)

\[
\frac{d[EPOX]}{dt} = -k_2[I_1][EPOX]
\]

(4)

\[
\frac{d[I_2]}{dt} = k_2[I_1][EPOX] - k_3[I_2]
\]

(5)

\[
\frac{d[Carbonate]}{dt} = k_3[I_2]
\]

(6)

Figure 6 shows the profiles of concentration for every species involving in the detailed reaction mechanism which consider the catalyst interaction with carbon dioxide at the first step (Way A). Two cases are presented with and without the induction period at low (70°C) and high (90°C) temperature respectively.

We notice that the amount of epichlorohydrin carbonate increased gradually as the reaction proceeds. The attainment of equilibrium is produced after 480 min at 70°C and 300 min at 90°C. The results suggest that at low temperature, carbon dioxide saturates the liquid phase during the induction period. Then its concentration decreases once the acceleration phase begins. At high temperature this phenomena is present but is less observable because the reaction rate is faster than at low temperature. The intermediates concentrations are present in a small proportion to promote the reaction, we suppose that catalyst remains active along the reaction and only when the system is in the equilibrium the catalyst is recuperated.

Figure 6 – Concentration profiles of species involving in the reaction of carbon dioxide with epoxides for detailed reaction mechanism – 3 bar of CO₂, 5% mol of non-metallic catalyst (a) 70°C (b) 90°C
Parameter estimation
The numerical parameter estimation was based on the kinetic experiments where temperature and pressure were maintained constant. The model describing the reaction is composed of six differential equations where the kinetic rate constants should be estimated. During reactions, the intermediates concentrations were not observed neither quantified due to their low stability in the reactive system. In order to simplify the solution of the model, we have supposed that the production rate of intermediates is lower than the consumption rate. Otherwise a quasi-steady state (QSSA) could be assumed for the intermediates.

However the quasi steady state does not be applied on two intermediates. Since the system present an induction period, the intermediate formed in the first step with catalyst has an important role during the reaction and its concentration along time should be consider. This intermediate depends on the activation of carbon dioxide or epichlorohydrin (step 1). Therefore the quasi steady state can be only applied on intermediate 2.

In the quasi steady state the concentration of intermediate 2 is written in the form of an algebraic equation (Eq. 7):

\[ I_2 = \frac{k_2 [I_1] [EPOX]}{k_3} \]  

(7)

The number of differential equations describing the system is reduced to five with an algebraic equation. The model predictions of the kinetic parameters were obtained by solving the ordinary differential equations (Eqs. 1-6) which describe the mass balance. A prediction of the components was obtained by applying a numerical differentiation method using the software Matlab ®. A genetic algorithm was used as optimization method to minimize the normalized root mean square error (NRMSE - Eq. 8):

\[ NRMSE = \sqrt{\frac{\sum (Y_{\text{exp}} - Y_{\text{calc}})^2}{N \cdot (Y_{\text{exp,max}} - Y_{\text{exp,min}})}} \]  

(8)

Experimental concentrations \( Y_{\text{exp}} \) were obtained from measurements and estimated concentrations \( Y_{\text{calc}} \) were obtained from the models. N is the number of experimental points for each experiment and \( Y_{\text{exp,max}} \) and \( Y_{\text{exp,min}} \) are the maximal and minimal experimental concentration value respectively.

The curves of epoxide concentration as a function of time for the experimental points and estimated values from the model by using QSSA and the detailed model (way A) are presented in Figure 7. We compared the two simplified ways of catalyst activation, with the experimental data. It can be noticed that at low temperature only the detailed model can predict the induction period, but it presents some deviations at the equilibrium at high temperature (90°C). As we mentioned before, the kinetic results shown that one part of epichlorohydrin was not used to produce cyclic carbonate, therefore a secondary reaction can take place in the system modifying the equilibrium. The estimated values for the activation energy and the pre exponential factor are summarized in table 1.

<table>
<thead>
<tr>
<th>Table 1. Kinetic parameters estimated</th>
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<tbody>
<tr>
<td>Reaction</td>
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<tr>
<td><strong>Detailed method Way A</strong></td>
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<tr>
<td><strong>QSSA Way A</strong></td>
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<td></td>
</tr>
<tr>
<td><strong>QSSA Way B</strong></td>
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</table>
CONCLUSION
The kinetics of synthesis of epichlorohydrin carbonate from carbon dioxide and epichlorohydrin in presence of a non-metallic catalyst was studied in the temperature range 50°C-90°C. Mass transfer effect was observed with the stirring speed, therefore the system depends on the hydrodynamic of the reactor. The temperature has an important role in the reaction rate, in agreement with the Arrhenius correlation. A kinetic model taking into account the mass transfer and the kinetic of the reaction was developed for the two activation ways. A simplification was introduced by using the quasi steady state on the intermediate 2. The detailed model describes accurately the induction period at low temperature. At high temperatures the models of the way A and the way B and the detailed model presents a similar behavior, however a deviation from the equilibrium is observed at the end of the reaction. We suppose that some phenomena in the equilibrium have not been taken into account in the model. Next work will consist in improving the modeling including the effect of the equilibria concentrations.

REFERENCES