

# PRODUCTION OF CARBONATE FROM $CO_2$ OR DIOLS

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## Abstract

Global warming is one of today's biggest problems with numerous serious short-term and long-term consequences and it has attracted a lot of attention lately. One of the main causes of the greenhouse effect is the carbon dioxide present in the atmosphere. One of the measures taken to minimize the damage from global warming is to capture and use  $CO_2$  as a raw material in the production of value-added chemicals. Hence the growing interest in developing chemical processes and catalysts capable of converting thermodynamically and chemically stable  $CO_2$  at industrial level. Many chemicals can be produced from  $CO_2$ , including carbonates and polycarbonates (PC).

In this work, we use two approaches to convert  $CO_2$  in carbonates. The first one was its direct use to transform styrene oxide and propylene oxide in carbonates and the second approach was the use of urea and diols to produce carbonates and ammonia. The ammonia can be treated with  $CO_2$  to produce urea. In both cases, were used four different catalyst, three ferrite and one C-scorpionate, obtained conversions up to 100%.

**Keywords:** Carbon dioxide, cyclic carbonate, urea, epoxide, C-scorpionate complex, iron catalyst.

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## 1 Introduction

Global warming is one of the biggest problems nowadays with numerous serious short-term and long-term consequences and has attracted more and more attention from the population, governments, companies and other relevant authorities looking for a solution to that problem. One of the main causes of global warming is the carbon dioxide present in the atmosphere. Carbon dioxide, like other greenhouse gases, holds in the atmosphere the radiation reflected by the Earth's coast that is normally returned by space, which results in the raising of global average temperature [1, 2]. The temperature been increasing since the industrial revolution achieving lately threatening rates [3]. One of the measures taken to minimize the damage from global warming is to capture and use  $CO_2$  as a raw material in the production of other value-added chemicals [1, 4]. The use of  $CO_2$  as a raw material has some advantages as it is cheap and is readily available. Hence the growing interest in different chemical processes and catalysts capable of converting the thermodynamically and chemically stable  $CO_2$  to make the different processes sufficiently efficient to be applied at the industrial level. Many chemicals can be made from  $CO_2$ , including carbonates and polycarbonates. With a focus on the production of cyclic carbonates which has several applications including as a monomer in polycarbonate production, two of the various production routes have been tested with different catalysts under different conditions in this wale. One process is based on the direct conversion of  $CO_2$  reaction with epoxide while the second process is the 1,2-diol and urea reaction which produces ammonia as a by-product that can be treated with  $CO_2$  and produces urea which is thus recycled.

The standard process to produce polycarbonate was the phosgene process. This process presents many drawbacks such as phosgene and bisphenol A (BPA) usage, dangerous compounds due to its toxicity, large amount of solvent usage and so on. In 1969, Inoue and co-workers discovered that propylene oxide polymerises in presence of  $CO_2$  and  $ZnEt_2/H_2O$  [5]. After that, a large effort was made all over the world to develop a catalyst and catalysis process that allows the use of  $CO_2$  to produce fine chemicals at an industrial level. Many catalysts were found to form only cyclic carbonate, others to form only PC and others both cyclic carbonate and PC but none of those efforts achieve sufficient reproducibility and high turnovers to be implanted at industrial scale. It wasn't until 2002, that Asahi Kasei corp announced the first successfully non-phosgene

industrial process to produce PC from  $CO_2$  [4, 6, 7].

## 2 Methods

All the products were purchased from providers and used without further purification. Two different methods were used in this work, see Figure 1. To produce cyclic carbonate from direct conversion of  $CO_2$  and epoxide (Method 1), was introduced in the reactor 1.75 mmol of substrate,  $5.25 \times 10^{-2}$  mmol of co-catalyst tetrabutylammonium bromide (TBABr) and the desired amount of catalyst. The  $CO_2$  was introduced in the reactor until the pressure of 4MPa. The reactor was plugged in oil bath at the desired temperature and magnetic stirring for four hours. Regarding the second process used (Method 2), 0.5 mmol of urea, 0.5 mmol of substrate and the intended amount of catalyst was mixed in the reactor with 1 mL of solvent (toluene). The reactor was set in oil bath with magnetic stirring at temperature of 150 °C for six hours.

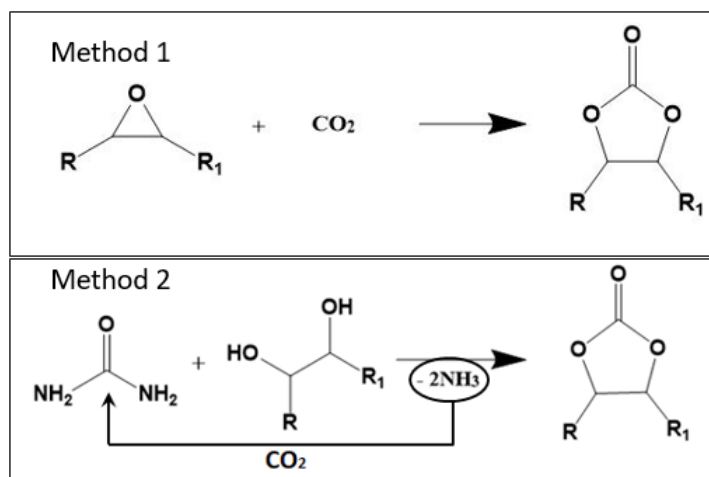


Figure 1: Reactions scheme of both methods.

## 3 Results and Discussion

### 3.1 Catalyst characterisation

#### 3.1.1 Nickel ferrite

##### XRD study

The powder X-ray pattern recorded for the sample of  $NiFe_2O_4$  is shown in Figure 2a. It is consistent with the standard pattern cubic spinel structure of bulk  $NiFe_2O_4$  JCPDS (Card No. 10-0325). The lattice parameter of  $NiFe_2O_4$  is  $a = 8.339 \text{ \AA}$ . Extra reflections are not detected in the X-ray diffraction pattern.

##### FT-IR study

The formation of spinel  $NiFe_2O_4$  structure is further supported by FT-IR spectrum shown in Figure 2b. The bands at  $563 \text{ cm}^{-1}$  and  $474 \text{ cm}^{-1}$  represented tetrahedral and octahedral modes of  $NiFe_2O_4$ , respectively. The band located at  $3399 \text{ cm}^{-1}$  can be attributed to the symmetric vibration of  $-OH$  groups. The bands with peaks observed at  $1045 \text{ cm}^{-1}$  can be assigned to  $O-H$  bending vibration. The peak at  $2333$  is ascribed to  $H-O-H$  bending vibration of the free or absorbed water.

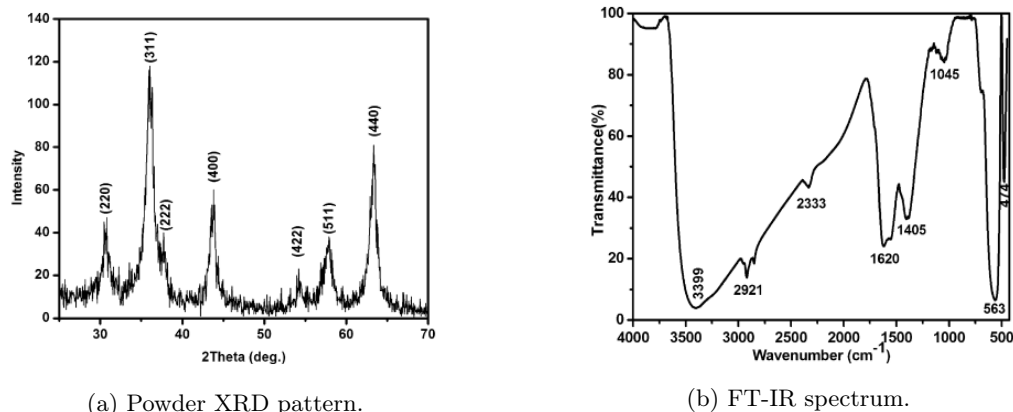


Figure 2: Powder XRD pattern and FT-IR spectrum of the nickel ferrite sample

### 3.1.2 Copper ferrite

#### XRD study

Figure 3a shows the XRD for  $CuFe_2O_4$ . The observed reflection peaks found at  $18^\circ$ ,  $29^\circ$ ,  $34^\circ$ ,  $35^\circ$ ,  $37^\circ$ ,  $41^\circ$ ,  $43^\circ$ ,  $62^\circ$  and  $63^\circ$  were exactly correlated to the inverse spinel tetragonal copper ferrite structure for the entire obtained product. These reflection peaks corresponded to the reflection planes (101), (112), (103), (211), (202), (004), (220), (224) and (400) respectively. The obtained XRD results are in good agreement with the tetragonal copper ferrite (JCPDS card no. 340425).

#### FT-IR study

In the present study, the observed three phonon modes of Raman peaks located at about 278, 393, and 613  $cm^{-1}$  are corresponding to the characteristic peaks of  $CuFe_2O_4$ . The first peak located at 278  $cm^{-1}$  could be attributed to the  $E_{1g}$  mode of phonon vibration for all the prepared samples. The peaks at about 393 and 613  $cm^{-1}$  for all the samples could be attributed to  $F_{2g}$  and  $A_{1g}$  mode of phonon vibrations. The band observed around 393  $cm^{-1}$  attributed to the metal cation vibration in the octahedral site. The last peak observed at 613  $cm^{-1}$  is assigned to the intrinsic stretching vibration of metal cations at the tetrahedral site. The peaks around 480 and 1300  $cm^{-1}$  present in the sample exactly coincided with the characteristic phonon vibration modes of secondary phase hematite which proved the influence of precursor concentration reflects the structural phenomena of the synthesized product, see Figure 3b.

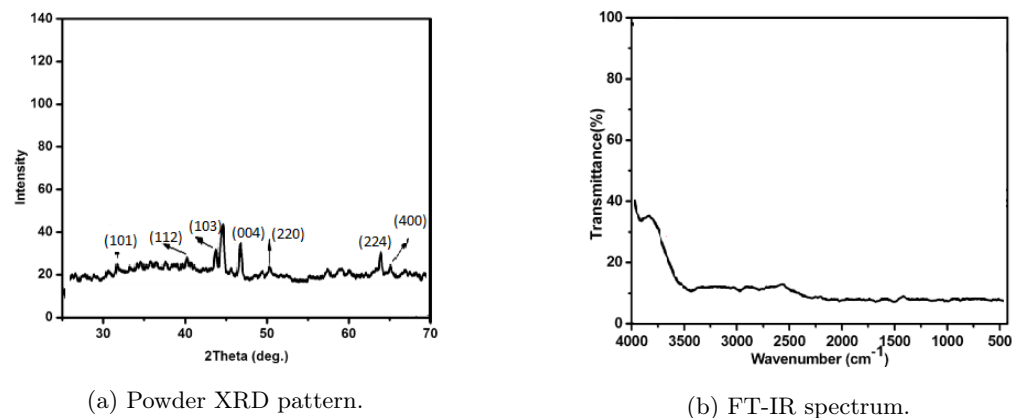


Figure 3: Powder XRD pattern and FT-IR spectrum of the copper ferrite sample

### 3.1.3 Manganese ferrite

#### XRD study

The crystal structure and phase purity of the newly synthesized spinel  $MnFe_2O_4$  were evaluated by X-ray diffraction (XRD). Figure 4 represents the XRD patterns of the sample synthesized. In Figure 4 the diffraction peaks show the reflection planes (111), (202), (311), (222), (400), (333), (404), (440), (533) and (622) which match well with the standard diffraction values of JCPDS file no 74-2403. All these peaks confirm the cubic spinel lattice of  $MnFe_2O_4$ .

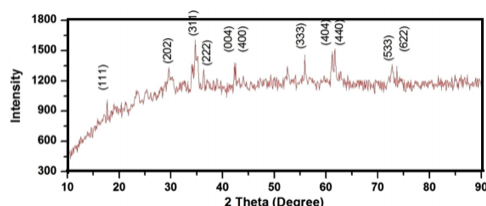


Figure 4: Powder XRD pattern of the manganese ferrite sample.

#### FT-IR study

From the FT-IR spectra, it is found that high frequency bands at  $875\text{ cm}^{-1}$  is associated to the tetrahedral site while the low frequency band at  $629\text{ cm}^{-1}$  is associated to the octahedral site. The sharpness of these bands is correlated to the high degree of crystallinity of  $MnFe_2O_4$  nanostructures. A broad vibration band at  $3449$  and  $3421\text{ cm}^{-1}$  are associated with the O–H stretching vibration of the adsorbed water molecules indicating a higher amount of surface OH. A small band at  $1383\text{ cm}^{-1}$  is assigned to the stretching vibrations of the COO group. A band at  $1441$  and  $1449\text{ cm}^{-1}$  are assigned to C–H bending modes. The peaks at  $1116$  and  $1110\text{ cm}^{-1}$  may be due to (C–O–C) symmetric vibration and dehydration of OH group from the polymers. The absence of peaks in the range of  $2000\text{--}3000\text{ cm}^{-1}$  in the sample confirms the absence of O–H mode, C–O mode and C–H stretching mode, see Figure 5.

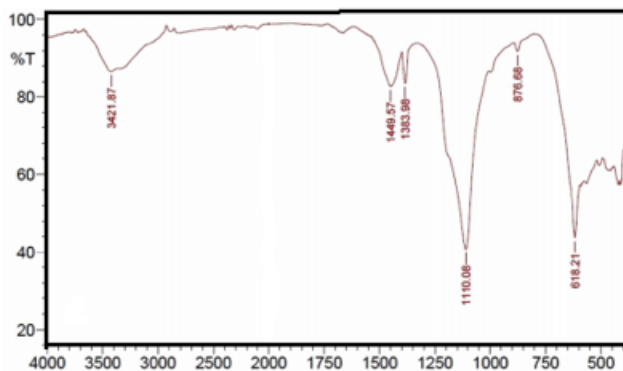


Figure 5: FT-IR spectrum of the manganese ferrite sample.

## 3.2 Method 1 - Reaction of $CO_2$ and Epoxide

The method 1 came to replace the phosgene process used before. This process phosgene free, beside greener is also cheaper. The process uses epoxide that helps to overcome the thermodynamic stability since they are highly energetic compounds and there is an atom economy since there is no side product been formed. The drawback of this process is that the epoxides are generally produced by the oxidation of olefins using

hazardous hydroperoxide and reactive epoxide is difficult to hand. There are reported a large number and types of catalysts to use in this process [8–15]. The direct transformation of  $CO_2$  and epoxide to produce cyclic carbonate is one of the most promising routes to use  $CO_2$  as a start material and there are a remarkable number of catalysts developed to perform the reaction with success. Nevertheless, a large number of those catalysts suffer from high costs, low activity, high pressure and temperature required or need of co-solvents usage. So, it's still a challenge to design a highly efficient heterogeneous catalyst to function at low  $CO_2$  pressure, low temperature and easily separated catalyst to realise the process. In this method, styrene oxide (SO) and propylene oxide (PO) were used as substrates, see Figure 6. These two are widely used in this reaction process with different catalysts and presenting very high yields with some catalysts [9, 16].



Figure 6: Substrates used in the reactions with  $CO_2$  at different conditions.

Different results were observed, and the yields of each reaction at different conditions presented in the following Table 1. The catalyst turnover number (TON) and turnover frequency (TOF) was calculated from each reaction.

$$TON = \frac{Yield(\%) * mol\ of\ reactant}{100 * mol\ of\ catalyst} \quad (1)$$

$$TOF = \frac{TON}{reactoin\ time} \quad (2)$$

Table 1: Reaction of  $CO_2$  with epoxide and  $8.75 * 10^{-3}$  mmol of catalyst at temperature of 40 °C.

Entry	Epoxide	Catalyst	Yields (%)	TON	TOF(h <sup>-1</sup> )
1	SO	$NiFe_2O_4$	9.9	19.5	3.9
2		$CuFe_2O_4$	3.8	7.7	1.5
3		$MnFe_2O_4$	3.8	7.4	1.5
4		$[FeCl_2(Tpm)]$	19.4	38.5	7.7
5	PO	$NiFe_2O_4$	7.4	14.6	2.9
6		$CuFe_2O_4$	0.1	0.2	0.0
7		$MnFe_2O_4$	9.1	18.3	3.7
8		$[FeCl_2(Tpm)]$	13.0	25.9	5.2

Reaction conditions: Epoxide (1.75 mmol); TBABr ( $5.25 * 10^{-2}$  mmol); Pressure 4 MPa; Reaction time (5 h).

Catalysts are very important parameters in a chemical process, since its allows the reaction the process to take a different path energetically favourable usually by decreasing the activation energy. This leads to an increase in the reaction velocity allowing to save time and reduce energy usage. It also increases the selectivity and reduce the amount of waste produced in the process by increasing the velocity of formation of the desired product. Temperature is another parameter very important in a chemical process once the reactions happen

when the molecules/particles collide with enough energy to overcome the activation energy and the increase of temperature results in a faster movement of the particles what increases the frequency of collisions and the amount of energy generated. The temperature affects the reaction rate constant exponentially according to the Arrhenius law, and the reaction rate is proportional to the reaction rate constant. So it is important to test the effects of those parameters in the reaction. First was studied the effects of catalyst concentration by increasing twice the amount of catalyst while maintaining the temperature constant, and the results presented, see Table 2. Then the temperature effect also by increasing twice the temperature value while maintaining the amount of catalyst equal to the initial values of Table 1. The results are presented in Table 3.

Table 2: Reaction of  $CO_2$  with epoxide and  $1.75 * 10^{-2}$  mmol of catalyst at temperature of 40 °C.

Entry	Epoxide	Catalyst	Yields (%)	TON	TOF( $h^{-1}$ )
1		$NiFe_2O_4$	6.5	6.4	1.3
2	SO	$CuFe_2O_4$	2.9	2.8	0.6
3		$MnFe_2O_4$	5.7	5.6	1.1
4		$[FeCl_2(Tpm)]$	5.7	5.5	1.1
5		$NiFe_2O_4$	13.0	12.8	2.6
6	PO	$CuFe_2O_4$	18.7	18.2	3.6
7		$MnFe_2O_4$	15.3	15.4	3.1
8		$[FeCl_2(Tpm)]$	23.7	23.1	4.6

Reaction conditions: Epoxide (1.75 mmol); TBABr ( $5.25 * 10^{-2}$  mmol); Pressure 4 MPa; Reaction time (5 h).

From the Table 1 it can be observed that the higher yields are obtained from the reaction with SO in the presence of C-scorpionate iron(II) complex, Table 1 entry 4. From the Table 2 the higher yields is observed at the reaction with PO with  $[FeCl_2(Tpm)]$  catalyst, Table 2 entry 8. It can be observed that for the reactions with PO the yields, as expected, increase from with the increase of catalyst concentration. Nevertheless, for the reactions with SO the yields decrease. This behaviour must be related to the fact of PO is more reactive than SO.

Table 3: Reaction of  $CO_2$  with epoxide and  $8.75 * 10^{-3}$  mmol of catalyst at temperature of 80 °C, during five hours.

Entry	Epoxide	Catalyst	Yields (%)	TON	TOF( $h^{-1}$ )
1		$NiFe_2O_4$	49.2	92.6	18.5
2	SO	$CuFe_2O_4$	67.5	128.5	25.7
3		$MnFe_2O_4$	54.8	110.5	22.1
4		$[FeCl_2(Tpm)]$	78.6	156.4	31.3
5		$NiFe_2O_4$	18.0	35.5	7.1
6	PO	$CuFe_2O_4$	23.7	45.0	9.0
7		$MnFe_2O_4$	28.1	51.5	10.3
8		$[FeCl_2(Tpm)]$	67.5	125.9	25.2

Reaction conditions: Epoxide (1.75 mmol); TBABr ( $5.25 * 10^{-2}$  mmol); Pressure 4 MPa; Reaction time (5 h).

From the Table 3 it is observed that the higher yield is from the reaction with SO in presence of  $[FeCl_2(Tpm)]$  catalyst, Table 3 entry 4. The yields of all the reactions increased in comparison with the Table 1, as it was expected since the temperature increased.

### 3.3 Method 2 - Reaction of Urea and Diols

In 1991, Su and Speranza were the first ones to announce this alternative process [17]. Although low conversion and decomposition of urea were reported, it was the beginning of the search for a new catalyst to perform this reaction more efficiently. The new procedure uses as a start material urea and 1,2-diols and produces cyclic carbonate and ammonia as a side product. Although this process does not use direct  $CO_2$  as raw material it produces ammonia as a side product and the ammonia produced can be treated with  $CO_2$  to produce the initial start material, urea. This process has the advantages of using urea and diols that are cheap and readily available compounds, also diols are generally bioavailable from a renewable resource, the ammonia produced is easily separable from the product, very low risk of explosions or poisons. Since then, there were reported catalysts to successfully perform this reaction with remarkable results [18–22]. In this method was used three substrates, 3-mercapto-1,2-propanediol (MP), *cis*-1,2-cyclohexanediol (CCH) and *trans*-1,2-cyclohexanediol (TCH), see Figure 7. The results of the reactions are presented in the Table 4.

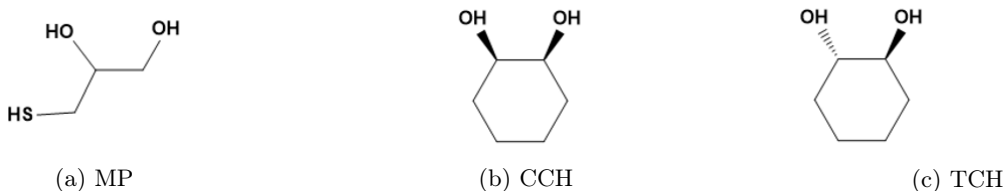


Figure 7: Substrates used in the reactions with urea at different conditions.

Table 4: Reaction of urea, diol and 0.02 mmol of catalyst at temperature of 150 °C.

Entry	Diol	Catalyst	Yields (%)	TON	TOF ( $h^{-1}$ )
1	MP	$NiFe_2O_4$	1.2	0.3	0.1
2		$CuFe_2O_4$	2.9	0.7	0.1
3		$MnFe_2O_4$	1.3	0.3	0.1
4		$[FeCl_2(Tpm)]$	5.1	1.2	0.2
5	CCH	$NiFe_2O_4$	9.1	2.2	0.4
6		$CuFe_2O_4$	30.1	7.5	1.2
7		$MnFe_2O_4$	9.9	2.5	0.4
8		$[FeCl_2(Tpm)]$	14.5	3.5	0.6
9	TCH	$NiFe_2O_4$	25.4	6.3	1.0
10		$CuFe_2O_4$	10.7	2.7	0.4
11		$MnFe_2O_4$	3.6	0.9	0.1
12		$[FeCl_2(Tpm)]$	13.8	3.3	0.6

Reaction conditions: Urea (0.05 mmol); Diol (0.05 mmol); Pressure 1 atm; Reaction time (5 h)

## 4 Green metric

Green chemistry metrics measure aspects of a chemical process relating to the principles of green chemistry. These metrics quantify the efficiency or environmental performance of chemical processes, and allow changes in performance to be measured. The motivation for using these metrics is the expectation that quantifying technical and environmental improvements can make the benefits of new technologies more tangible and understandable and more likely to be used at industrial level. Numerous metrics have been formulated over time, such as: i) Carbon efficiency that measures how much carbon from the reagents ends up in the useful

products [23]; ii) Environmental (E) factor was the first metrics developed and it relate the waste produced to the desired product, still one of the most popular and flexible metric [23, 24]; iii) The Eco-Scale gives a score from 0 to 100 and takes into account cost, safety, technical set-up, energy and purification aspects [24]. In this work, two metrics were calculated, the Effective mass yield and the Atom economy.

#### 4.1 Effective mass yield

Hudlicky et al. [25] proposed a metric known as effective mass yield that is defined ‘as the percentage of the mass of desired product relative to the mass of all non-benign materials used in its synthesis.’ Or, stated mathematically: This metric attempts to define yield in terms of what proportion of the final mass, i.e., the mass of the product, that is made from non-toxic materials. The introduction of reagent and reactant toxicity is an extremely important consideration that is frequently absent from discussions about yield. Values for effective mass yield are showed in Table 5. The values of effective mass yield are higher for the more efficient reaction, which means that the processes are more green than harmful for the environment.

$$\text{Effective mass yield} = \frac{\text{Mass of products}}{\text{Mass of non benign reagents}} \quad (3)$$

#### 4.2 Atom economy

When developing chemical processes, chemists for obvious reasons focus mainly on maximizing selectivity and yield. In recent years, another variable some chemists have been considering is the atom economy. This term, first introduced by Barry Trost, [26] was an attempt to prompt synthetic organic chemists to pursue ‘greener chemistry’. Simply stated, the atom economy is a calculation of how much of the reactants remain in the final product. The final product in this context applies to a single chemical transformation, a series of chemical transformations in a single stage of a multistage synthetic route, or the entire route to a final product. The method for calculating the atom economy is kept deliberately simple by making certain key assumptions, ignoring reaction yield and molar excesses of reactants. It also does not account for solvents and reagents.

$$\text{Atom economy} = \frac{\text{Molecular weight of products}}{\text{Molecular weight of reagents}} \quad (4)$$

The calculation considers only the reactants used and ignores the intermediates that are made in one stage and consumed in the next. Because of this, it is not possible to multiply the atom economy of each stage to give an overall process atom economy. The atom economy for the cyclic carbonate of  $CO_2$  and epoxides and the cyclic carbonate from urea and 1,2-diols reactions are presented in Table 5 All results have to be between 0 and 1, and it is important that some of the metrics are close to the maximum value. It is an indication that both the methods follow a green chemistry approach.

## 5 Conclusion and future work

Both methods are very simple to use and complex equipment is not needed. In the first method, it is a little more difficult, since the  $CO_2$  usage is required which due to the pressure imposed on the system requires little more care.

It is been reported process in similar conditions with those performed in this work. For instance, Castro et al (2016) reported reactions of PO and SO with  $CO_2$  and TBABr as co-catalyst in presence of several catalysts with yields up to 72% and 84% respectively [9]. Clegg et al (2010) reported reactions of SO with



Table 5: Effective mass yield and atom economy for the reactions studied in this thesis.

Reagents	Product	Green metric	Atom economy
3-mercapto-1,2-propanediol + urea	3-mercapto-1,2-propylene carbonate	1.3	0.7
<i>cis</i> -1,2-ciclohexandiol + urea	1,2-cyclohexylene carbonate	0.7	0.8
<i>trans</i> -1,2-ciclohexandiol + urea	1,2-cyclohexylene carbonate	0.7	0.8
styrene oxide + $CO_2$	styrene carbonate	1.0	1.0
propylene oxide + $CO_2$	propylene carbonate	1.8	1.0

$CO_2$  in the presence of metal salts catalyst and presented yields up to 57% [16]. In comparison with the best yields obtained in this work, it is observed that  $[FeCl_2(Tpm)]$  is a very promising catalyst to convert  $CO_2$  with epoxide. Related to the second process used, Peña et al (2016) reported reactions using iron bromide ( $FeBr_2$ ) as a catalyst to perform the transformation of urea and CCH with yields of 75% [20]. Others reported reactions of urea with different substrates and catalyst with yield up to 100% [19, 22]. It is observed that the catalyst used presented values way too low in comparison with others works developed.

It is part of the future work to test other substrates, catalysts and solvents as well as to determine ideal conditions for the realisation of reactions such as temperature and concentration of different species. Studying reaction kinetics, understanding the mechanism and catalyst recovery are other important matter to consider.

Exploration of a variety of metrics has revealed the following:

1- Pursuing a metric such as yield, a ubiquitous metric chemists utilise to evaluate reaction efficiency, will not by itself drive a business towards sustainable practices. However, from an economic standpoint, the yield remains a very good metric, especially for high value added materials such as pharmaceuticals; 2- Atom economy may be useful as an organising concept or in combination with other metrics, but at this time it is not considered to be useful as a stand-alone metric.

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