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Organocatalytic synthesis of bio-based cyclic carbonates from CO_2 and vegetable oils

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Bio-based cyclic carbonates were synthesized by coupling CO_2 with epoxidized linseed oil using a catalytic platform composed of a bicomponent organocatalyst. A screening of the catalytic activity of a series of organic salts and ionic liquids used in combination with (multi)phenolic or fluorinated hydrogen bond donors was realized before highlighting the synergistic effect between the organocatalyst and the most efficient cocatalysts. These kinetics studies, followed by IR spectroscopy under pressure, enabled to optimize the reaction conditions and to provide quantitative formation of the cyclocarbonated vegetable oil in short reaction time without using any organic solvent.

Introduction

Regarding the economical and environmental issues, finding alternatives to petrochemicals has become one of the most important worldwide challenges. Valorising CO_2 as a C1 feedstock for producing building blocks [1-3] is seducing as it is a free and inexhaustive waste resulting from the human activity. As examples, carbon dioxide can be transformed into added value products such as carboxylic acids[4-8], esters or lactones[9-12], urea[13], carbamates[14-18] or isocyanates [19, 20]. By coupling with epoxides, CO_2 can be converted into cyclic carbonates that find applications as green solvents, electrolytes for lithium batteries or as monomers for the production of polycarbonates and non-isocyanate polyurethanes. However, due to the low reactivity of CO_2 with epoxides, addition of metallic or organic catalysts is necessary, but their use generally suffers from some drawbacks. Indeed, some metal complexes are sensitive to hydrolysis and oxidation or/and are poorly selective. Additionally, some of them are toxic whereas less/non-toxic and eco-friendly organocatalysts such as ionic liquids and halide salts are generally only efficient at high temperature and pressure that favours their degradation[21-25]. In the last years, development of new bicomponent organocatalysts[26] combining the use of organic salt or ionic liquids with hydrogen bond donor activators such as phenolic derivatives[27, 28], (amino)alcohols [29-31], carboxylic acids [32-34], (fluoro)alcohols[35], silanols[36], has been proposed to fasten the coupling of CO_2 with epoxides under mild conditions. The efficiency of these catalytic systems has been mainly investigated for the coupling of CO_2 with model petro-sourced small organic molecules such as propylene oxide or styrene oxide. Besides, the synthesis of bio-based cyclic carbonates from CO_2 and epoxidized vegetables oils is a subject of growing interest that allows the synthesis of fully bio-based chemicals. However, the identification and development of efficient (organo)catalysts for synthesizing cyclic carbonates from bio-based epoxides still remains challenging[37]. At the exception of Rokicki's work[38], coupling of CO_2 with vernonia oil (a naturally epoxy functionalized triglyceride) or epoxidized soybean, linseed or cotton oils was only promoted by tetrabutylammonium bromide (TBABr). At low CO_2 pressure, the reaction was complete within several days at high temperature (110 °C < T < 160 °C)[39-42] and was fastened by using CO_2 under supercritical conditions[43, 44]. Addition of water or $SnCl_4$ was also proposed as alternative to improve the catalytic efficiency of the TBABr promoted CO_2/epoxide coupling at moderate pressure[45, 46]. However, even in the presence of these additives, conversion of the epoxidized vegetables oils into the cyclocarbonated ones was slow (t > 30 h) at high temperature (T = 140°C) and a CO_2 pressure of 1.5 MPa. Therefore, there is a need to develop more efficient (organo)catalysts that are active under milder conditions for the conversion of epoxidized vegetable oils into cyclic carbonates. These cyclocarbonated vegetable oils are indeed attractive synthons for the production of cheap and bio-based non-isocyanate polyurethanes[39, 40, 47-49], the most promising substitutes for conventional polyurethanes used in paints, coatings or biomaterials.

In this contribution, we describe the synthesis of cyclocarbonated linseed oil (CLSO) from epoxydized linseed oil (ELSO) (scheme 1) by developing a catalytic platform composed of bicomponent organocatalysts (Scheme 2) that fasten the reaction under mild experimental conditions. First, a survey of the catalytic activity of a series of organic halide salts or ionic liquids including onium (1), phosphonium (2), imidazolium (3), sulfonium (4), pyrolidinium (5), pyridinium (6),

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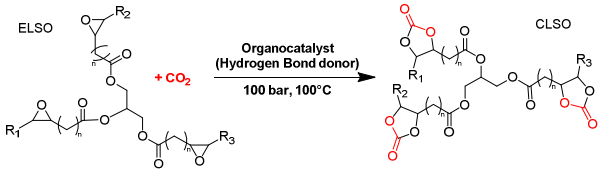
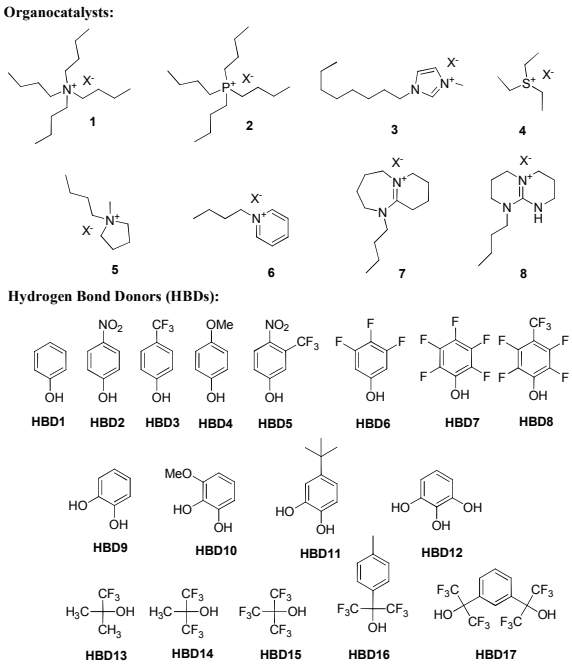
amidinium (7) and guanidinium (8) (Scheme 1) was studied in order to identify the most active organocatalyst.



Scheme 1 Synthesis of CLSO by organocatalytic promoted coupling of CO_2 with ELSO



Scheme 2 Catalytic platform developed for the synthesis of CLSO from ELSO and CO_2

Then, the catalytic efficiency was improved by the addition of different hydrogen bond donors activators (HBD) derived from (multi)phenolic compounds or fluoroalcohols, and the synergistic effects between the catalyst and the most efficient HBDs are highlighted by online kinetic studies using IR spectroscopy.

Experimental

Materials

Epoxidized linseed oil (ELSO) was kindly donated by Vandeputte Oleochemicals (Belgium). Carbon dioxide N45 (purity: 99, 95%) was supplied by Air Liquide. Quaternary ammonium salts, phosphonium halides, 1-bromobutane, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), phenol, 4-nitrophenol, 4-trifluoromethylphenol, 4-methoxyphenol, 3,4,5-trifluorophenol, pentafluorophenol, pyrocatechol, 3-methoxypyrocatechol, 4-tertbutoxycatechol, and pyrogallol were purchased from Sigma-Aldrich. 5-hydroxy-2-nitrobenzotrifluoride, 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene, 2,2,2-trifluoro-*tert*-butanol, 1,1,1,3,3,3-hexafluoro-*tert*-butanol, perfluoro-*tert*-butanol were purchased from Fluorochem. 2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenol, hexafluoro-2-(*p*-toluyl)isopropanol, 1,1,1,3,3,3-hexafluoro-2-propanol were supplied by ABCR. Triethylsulfonium iodide, 1-butyl-1-methylpyrrolidinium iodide, 1-butylpyridinium iodide and 1-methyl-3-octylimidazolium halides were purchased from Ioliditec. All reactants or catalysts were used as received. Amidinium and guanidinium salts, respectively named and 1-butyl-2,3,4,5,7,8,9,10-octahydropyrido[1,2-a][1,3]diazepin-1-ium bromide and 1-butyl-3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidin-1-ium bromide were respectively synthesized by quaternisation of DBU and TBD with 1-bromobutane. In a typical experiment, DBU (1.96 ml, 0.0131 mol) was dissolved in 10 ml CH_2Cl_2 before slow dropwise addition of 1-bromobutane (1.41 ml, 0.0131 mol). Then, the reaction was allowed to stir for 24 h at room temperature. After reaction, the highly viscous sample was simply collected by removal of the solvent and drying under vacuum. The guanidinium salts was synthesized following the same procedure.

1-butyl-2,3,4,5,7,8,9,10-octahydropyrido[1,2-a][1,3]diazepin-1-ium bromide: ^{1}H NMR, 250MHz ($CDCl_3$): δ = 0.85 ppm (t, 3H); δ = 1.27 ppm (m, 2H), δ = 1.52 ppm (m, 2H); δ = 1.71 ppm (broad, 6H); δ = 2.06 ppm (m, 2H); δ = 2.83 ppm (d, 2H); 3.35 ppm < δ < 3.75 ppm (m, 8H).

1-butyl-3,4,6,7,8,9-hexahydro-2H-pyrimido[1,2-a]pyrimidin-1-ium bromide: ^{1}H NMR, 250MHz ($CDCl_3$): δ = 0.85 ppm (t, 3H); δ = 1.37 ppm (m, 2H), δ = 1.54 ppm (m, 2H); δ = 1.96 ppm (broad, 6H); 3.15 < δ < 3.35 ppm (m, 9H).

Infrared set-up. The synthesis of bio-based cyclic carbonates was monitored *in situ* by IR spectroscopy using a home-made Ge ATR accessory suitable for high-pressure measurements (up to 5 MPa) and high temperature (up to 150 °C) coupled with a ThermoOptek interferometer (type 6700) equipped with a globar source, a KBr/Ge beamsplitter and a DTGS (Deuterated TriGlycine Sulphate) detector. Single beam spectra recorded in the spectral range (400-4000 cm^{-1}) with a 4 cm^{-1} resolution were obtained after the Fourier transformation of 150 accumulated interferograms. Spectra were recorded every ten minutes for 24 h. The stainless steel cell with a volume of about 3 mL screwed above the Ge crystal provides one port for the inlet of mixture and CO_2. A magnetic stirrer was placed into the cell to ensure good homogenization of the mixture. The ATR cell was heated using cartridge heaters disposed in the periphery of its body. A thermocouple was used and located close to a cartridge heater for the temperature regulation with an accuracy of about 2 °C. The cell was connected directly to the CO_2 tank allowing the pressure to be raised up to 5 MPa.

NMR characterization. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz in the FT mode with a Bruker AN 400 apparatus at 25 °C

Experimental procedure

Catalyst screening. 30g of ELSO were introduced in a 80 ml high pressure cell equipped with a mechanical stirrer using 2.32 10^{-3} mol of catalyst (that correspond to 1 mol% of catalyst compared to ELSO). Then the cell was heated to 100 °C before addition of CO_2 till the pressure is equilibrated to 10 MPa. After 5 h, the pressure was slowly released and the conversion of ELSO into CLSO was determined by 1H NMR spectroscopy. The same procedure was applied for all the halide salts or ionic liquids tested in this study while keeping the amount of catalyst constant to 2.32 10^{-3} mol.

Catalyst optimisation. 30 g of ELSO were introduced in a 80ml high pressure cell equipped with a mechanical stirrer in presence of 1 mol% of TBABr (0.75 g, 2.32 10^{-3} mol) and 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene (0.573 ml, 2.32 10^{-3} mol). Then the cell was heated to 100°C before addition of CO_2 till the pressure is equilibrated to 100 bar. After 5 h, the pressure was slowly released and the conversion of ELSO into CLSO was determined by 1H NMR spectroscopy. The same procedure was applied for all HBDs tested in this study.

Kinetic studies. In a typical experiment, a mixture composed of epoxydized linseed oil (500 µL) and the catalyst (5.95 10^{-5} mol, 2.2 mol%, 32mg TBABr) and the pyrocatechol (11 mg, 5.95 10^{-5} mol, 2.2 mol%) was introduced in the ATR reactor at ambient temperature. Then, the cell was heated up to the desired temperature (60 - 120 °C) before addition of CO_2 (0.5 - 5 MPa). The infrared spectra were collected online every 10 min. At the end of the reaction, in order to determine the conversion of ELSO into CLSO, the ATR spectrum of the reaction mixture was compared with the corresponding spectrum of the neat carbonate. The absorbance of the carbonate peak at 1808 cm^{-1} corresponding to the ν (C=O) stretching mode was normalized using the peak corresponding to a ν (C-H) stretching mode at 2955 cm^{-1} which does not evolve during the reaction. The yield for the entire kinetic was deduced by proportionality using the Beer-Lambert law according to Equation 1.

$$Yield\ (\%) = \frac{\left[\frac{A_{C=O}}{A_{C-H}}\right]_{Reaction\ mixture}}{\left[\frac{A_{C=O}}{A_{C-H}}\right]_{Neat\ carbonate}} \qquad [1]$$

The same experimental protocol was applied when pyrogallol, perfluoro-*tert*-butanol, hexafluoro-(*p*-toluyl)-isopropanol and 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene were used as HBDs. All these syntheses were conducted at least twice in order to check the reproducibility of the obtained yields and kinetics.

Solubility of CO_2 into ELSO. 2.3 mL of ELSO were introduced in a high pressure transmission cell with a pathlengh of 0.49 cm and heated up at the desired temperature (from 40 to 100 °C). At a fixed temperature, carbon dioxide was added from 0 to 20 MPa. After thermodynamic equilibration (within a few minutes), an infrared spectrum of the liquid phase was collected. The amount of CO_2 solubilized into ELSO was deduced from the height of the combination peak $\nu_1+2\nu_2+\nu_3$ at 4950 cm^{-1} which is characteristic of CO_2. In addition, the concentration of the ELSO can be followed from the peak at 5712 cm^{-1}. The mass fraction of CO_2 dissolved in ELSO can be obtained from Equation 2.[50]

$$X_{CO_2} = \frac{[CO_2]}{[CO_2]+[ELSO]} \qquad [2]$$

Results and discussion

Catalyst screening for the synthesis of carbonated linseed oil.

To identify the most efficient organocatalyst for converting neat ELSO into CLSO, a screening of the catalytic activity of a series of iodide salts was first realized at 100 °C and 10 MPa. From the results reported in Table 1, onium, phosphonium and imidazolium salts were found to exhibit the highest catalytic activity with a 25% conversion of ELSO into CSBO after 5h (entries 1, 4, 7), whereas pyrrolidinium, pyridinium or triethylsulfonium salts were less efficient or even ineffective as evidenced by a conversion of 19, 12 and 0 % respectively. These very low activities are explained by the poor solubility of these salts in the CO_2/linseed oil biphasic mixture. Then, the influence of the halide counter anion on the CO_2/ESLO coupling was investigated for the most efficient onium, phosphonium or imidazolium organocatalysts. Coupling of CO_2 with ESLO was slowed down by using the less nucleophilic chloride counter ion (Table 1, entries 3, 6, 9) as evidenced by a conversion of the epoxide into cyclic carbonate close to 20 %. In contrast, substitution of iodine by bromine counter-anion slightly increased the reaction rate (Table 1, entries 2, 5, 8). In view of these results, the bromide counter ion offers the best compromise in terms of reactivity and steric hindrance/size even if it is less nucleophilic than iodide. It is supposed that its higher catalytic activity arises from its smaller size that favours its faster diffusion towards the internal epoxide groups of the fatty chains of the highly viscous vegetable oil. Finally, the coupling of CO_2 with ELSO was carried out in the presence of guanidinium and amidinium salts as organocatalysts (catalysts 7 and 8, Scheme 1). If the amidinium salt showed a similar activity than the previously tested organocatalysts (Table 1, entry 13), the conversion of ELSO into CLSO was increased by 20 % in the presence of the guanidinium salt (Table 1, entry 14). These results are consistent with those reported by Foltran et al. who demonstrated that the coupling of CO_2 with propylene oxide was improved by replacing tetrabutylammonium bromide by 1,5,7-triaza-bicyclo[4.4.0]dec-5-enium bromide[51, 52]. However, even at high temperature and pressure, the conversion of ELSO into CLSO still remains low compared to results reported for the coupling of CO_2 with model epoxides. These observations are not surprising because the ring-opening of di-substituted epoxides is more difficult than the ring-opening of terminal/monosubstituted epoxides, as the result of increased steric hindrance. In an effort to boost the reaction and to improve the conversion yield, some activators are added to the reaction medium. The organocatalytic system is therefore composed by the organocatalyst, TBABr, and an activator that is expected to interact with the oxygen of the epoxide ring through hydrogen bonding and to activate it for the ring-opening. The potential activators that are tested are commercially available phenolic

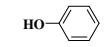
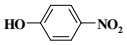
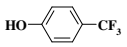
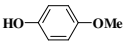
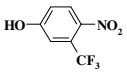
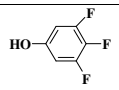
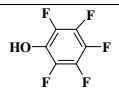
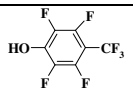
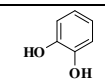
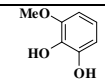
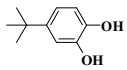
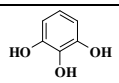
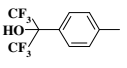
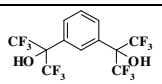
Table 1 Catalyst screening for the synthesis of CLSO by coupling of CO_2 with ELSO. Conditions: P = 10 MPa, T = 100 °C, catalyst = 2.32 10^{-3} mol, t = 5 h, ELSO = 30 g, volume of the cell = 80 ml

Entry	Catalyst	Halide counter anion	Conv (%)*
1		I^-	26
2	1	Br^-	30
3		Cl^-	17
4		I^-	21
5	2	Br^-	28
6		Cl^-	19
7		I^-	25
8	3	Br^-	30
9		Cl^-	20
10	4	I^-	/
11	5	I^-	19
12	6	I^-	12
13	7	Br^-	28
14	8	Br^-	36

* determined by ^{1}H NMR spectroscopy by comparison of the relative intensities of the peaks characteristic of the CH groups of the epoxide (2.8 ppm < δ < 3.25 ppm) and the cyclic carbonate (4.6 ppm < δ < 4.9 ppm)

compounds and fluoroalcohols (Scheme 2). Some of them have been demonstrated to fasten the coupling of CO_2 with model epoxides but were not tested on hindered epoxidized vegetable oils. The coupling of CO_2 with ELSO was therefore investigated at 100 °C and 10 MPa using 2.2 mol% of TBABr compared to ELSO and a TBABr/HBD molar ratio of 1 (Table 2). As reported by Kleij, phenol (HBD 1) had no cocatalytic activity[28] and a similar trend was observed for the coupling of ELSO with CO_2 using 4-methoxyphenol (HBD 4). Substitution of the hydrogen atom in para position by a trifluoromethyl- or a nitro- electron-withdrawing group clearly improved the cocatalytic efficiency of phenol. Indeed the conversion was increased from 30 to 47 % in the presence of 4-nitrophenol (HBD 2), and from 30 to 58 % in the presence of 4-trifluoromethylphenol (HBD 3). The latter was therefore doubling the productivity in cyclocarbonated vegetable oils. Finally, a phenolic derivative combining two different electron-withdrawing groups in meta (CF_3) and para (NO_2) positions

Table 2 Hydrogen bond donors screening for the TBABr promoted coupling of CO_2 with ELSO. Conditions: P = 10 MPa, T = 100 °C, catalyst = 2.32 10^{-3} mol (1 mol% compared to ELSO), [TBABr]/[HBD] = 1, t = 5 h, ELSO = 30 g, volume of the cell = 80 ml

Entry	HBD	Reference	Conv (%)*
1	/	/	30
2		HBD 1	32
3		HBD 2	47
4		HBD 3	58
5		HBD 4	31
6		HBD 5	42
7		HBD 6	41
8		HBD 7	45
9		HBD 8	38
10		HBD 9	63
11		HBD 10	55
12		HBD 11	57
13		HBD 12	56
14		HBD 13	42
15		HBD 14	58
16		HBD 15	63
17		HBD 16	55
18		HDB 17	58

* determined by ^{1}H NMR spectroscopy by comparison of the relative intensities of the peaks characteristic of the CH groups of the epoxide (2.8 ppm < δ < 3.25 ppm) and the cyclic carbonate (4.6 ppm < δ < 4.9 ppm)

(HBD 5) or partially/fully fluorinated HBDs (HBDs 6 - 8) were poor activators with a weak increase of the epoxide conversion by 20 to 30%. Coupling of CO_2 with ELSO was also studied using multiphenolic activators derived from catechol (HBDs 9 - 11) and pyrogallol (HBD 12) or fluoroalcohols. (HBDs 13 - 17). At the exception of HBD 13, all these HBDs exhibited the highest cocatalytic activity as evidenced by a 1.85 to 2-fold increase of the conversion of ELSO into CLSO.

Detailed kinetic study of the TBABr/HBD promoted ELSO/CO_2 coupling.

After this first organocatalyst and activator screening, a detailed kinetic study of the synthesis of CLSO using the catalytic platform was realized by online IR spectroscopy under pressure and the influence of various experimental parameters, such as CO_2 pressure, catalyst content and the temperature, on the conversion of ELSO into CLSO was investigated. Formation of CLSO was monitored by following the evolution with time of the signal at 1808 cm^{-1} reflecting the ν(C=O) stretching mode of CLSO (Figure 1). The presence of CO_2 dissolved in the ELSO rich phase was also highlighted by the presence of a very narrow peak at 2350 cm^{-1} corresponding to the antisymmetric stretch ν_3 of CO_2 that is superimposed over a broad doublet profile that is due to atmospheric CO_2. The yield of reaction was deduced from the comparison of the intensity of the peak at 1808 cm^{1} and the peak at 2955 cm^{-1} corresponding to the ν(C-H) stretching modes of the linseed oil that does not evolve during the reaction. Coupling of CO_2 with ELSO was catalysed by TBABr (2.2 mol%) at 80 °C and 2 MPa using HBDs 9, 12, 15, 16 and 17 ([TBABr]/[HBD] = 1) that were selected as representative activators as they showed the highest cocatalytic activity for the synthesis of CLSO (Figure 2). In the absence of HBD, the TBABr promoted reaction was slow as evidenced by a conversion of the epoxides into the corresponding cyclic carbonates of 45% after 1200 min.

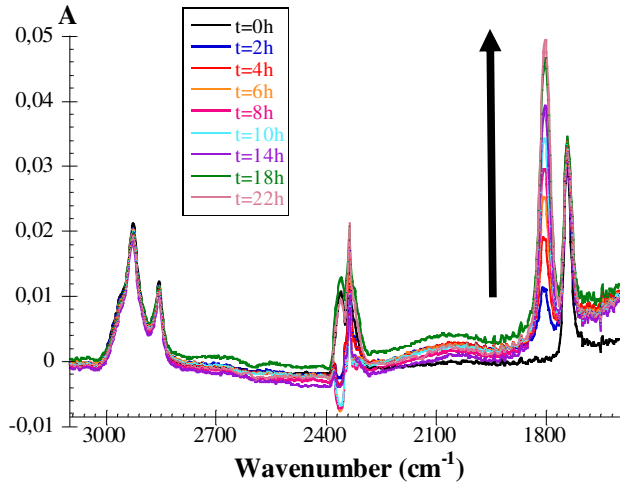


Figure 1 Evolution with time of the ATR-IR spectra for the TBABr/HBD 15 promoted ELSO/CO_2 coupling. Conditions: T = 80 °C, P = 2 MPa, TBABr = 2.2 mol%, [TBABr]/[HBD 15] = 1

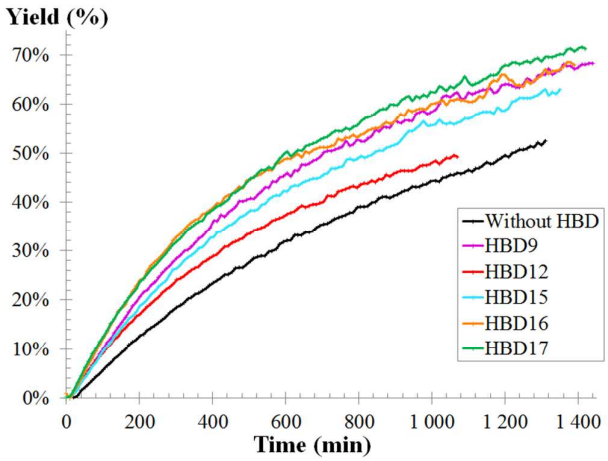


Figure 2 Kinetic study of the TBABr/HBD promoted coupling of CO_2 with ELSO: effect of the HBDs. Conditions: T = 80 °C, P = 2 MPa, TBABr = 2.2 mol%, [TBABr]/[HBD] = 1

Synergistic effects between TBABr and the cocatalysts are highlighted by an increase of the conversion of ELSO into CLSO after addition of the HBDs. Figure 2 suggests that HBD 17 is slightly more efficient than the others HBDs as evidenced by an increase after 1200 min of the ELSO conversion from 45% to 66% compared to 64% for HBDs 9 and 16, 60% for HBD 15 and about 50% for HBD 12. The slightly higher cocatalytic activity of HBD 17 could be explained by the formation of 3 hydrogen bonds between the oxygen atom of ELSO and both protons of the alcohol functions and the aromatic proton in para position of both hexafluoroisopropyl alcohol of HBD 17, which favor the activation of the epoxide groups. This assumption is supported by previous DFT calculations and NMR titration of epoxydodecane with HBD 17 [28]. The influence of the temperature on the kinetics and the yield of the ELSO/CO_2 coupling was studied from 60 to 120°C at 2 MPa using 2.2 mol% of catalyst (TBABr) in combination with 2.2 mol% of perfluoro-*tert*-butanol (HBD 15) as a model hydrogen bond donor activator. The resulting kinetic profiles, illustrated in Figure 3, show that the reaction rate was strongly affected by the temperature. At 120°C, ELSO was quantitatively converted into CLSO in 1000 min whereas the conversion only reached 25% at 60°C. Therefore, although the temperature increase (at constant CO_2 pressure) induced a slight decrease of the CO_2 concentration in the ELSO phase (Figure 4 and 5), the CO_2/epoxide coupling was favored at higher temperature. Moreover raising the temperature decreased the viscosity of ELSO and was consequently expected to improve the diffusion of the catalytic species in the reaction medium. Thermodynamic considerations show that the concentration of CO_2 dissolved in the oil phase is increased at higher CO_2 pressure as evidenced by an increase of the intensity of the peak at 4950 cm^{-1} (Figure 4). At 2 MPa and 80°C, the CO_2 molar fraction is low ($X_{CO2} < 0.05$) but doubled by increasing the pressure to 5 MPa ($X_{CO2} \approx 0.1$) (Figure 5). Therefore, the impact of the pressure on the synthesis of CLSO from ELSO and CO_2 was also investigated. Reaction was performed in the presence of 2.2 mol% TBABr and 2.2 mol% of HDB15 at 80°C in a pressure range of 0.5 to 5 MPa (Figure 6).

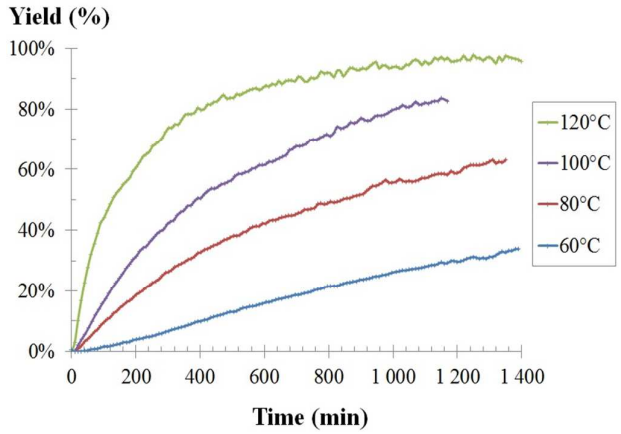


Figure 3 Kinetic study of the TBABr/HBD 15 promoted coupling of CO_2 with ELSO: effect of the temperature. Conditions: P = 2 MPa, TBABr = 2.2 mol%, [TBABr]/[HBD 15] = 1

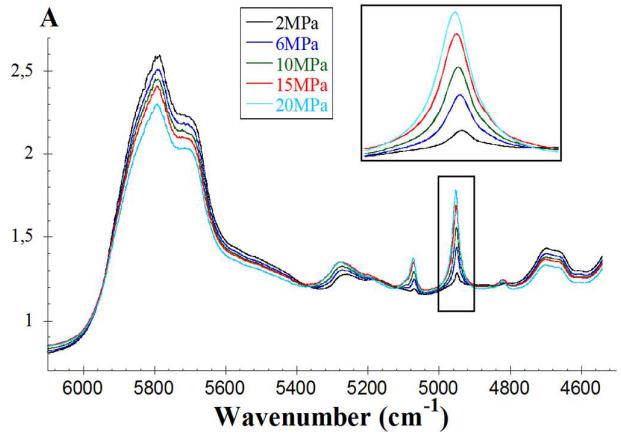


Figure 4 IR absorption spectra of the ELSO rich phase of the ELSO/CO_2 mixture at T = 100 °C for different CO_2 pressures.

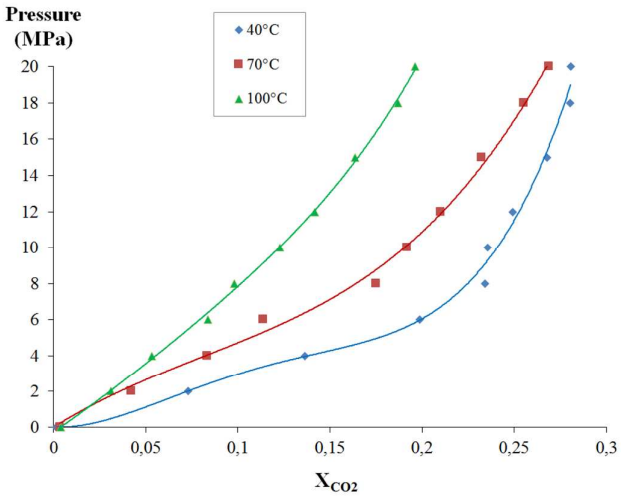


Figure 5 Molar fraction of CO_2 in the ELSO rich phase as a function of pressure and temperature.

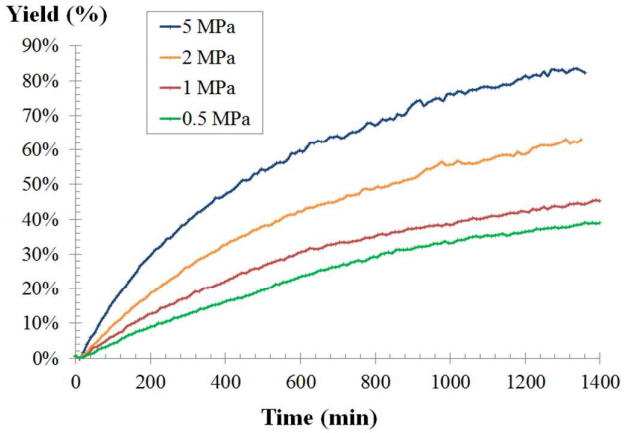


Figure 6 Kinetic study of the TBABr/HBD 15 promoted coupling of CO_2 with ELSO: Pressure effect. Conditions: T = 80 °C, TBABr = 2.2 mol%, [TBABr]/[HBD 15] = 1

For low CO_2 pressures of 0.5 and 1 MPa, the reaction was slow and the yield reached a plateau between 40 and 50% after 1400 min. At such low pressure, the amount of CO_2 dissolved in the epoxide rich phase is insufficient (X_{CO2}<0.02) to completely convert ELSO into CLSO. Increasing the pressure had a positive impact on both the solubility of CO_2 into ELSO and the kinetics. At 2 MPa, the molar fraction of CO_2 dissolved in the epoxidized vegetable soybean oil was increased to 0.035, and the ELSO conversion into CLSO reached 60% after 1400 minutes whereas at 5 MPa, it was almost quantitative (90%) after the same period of time. This last result is the consequence of the highest concentration of CO_2 dissolved in the oil (X_{CO2}~0.1).

Finally, the impact of the HBD15 concentration on the ELSO/CO_2 coupling was studied under optimized experimental conditions, i.e. a temperature of 120°C and a pressure of 5 MPa using 2.2 mol% of TBABr as catalyst. HBD 15 was chosen as it was the cheapest HBD that showed one of the most efficient cocatalytic activity. In the main text, we added that HDB15 is chosen as a model activator Figure 7 shows the typical kinetic curves for a cocatalyst loading ranging from 0 to 3.7 mol%. If the addition of 0.5 equivalent of HBD15 only slightly improved the TBABr promoted coupling of CO_2 with

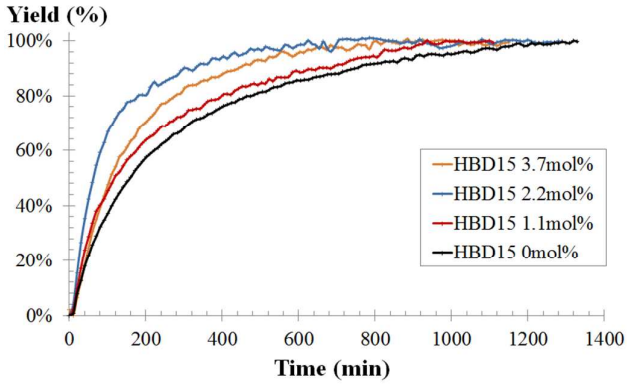


Figure 7 Kinetic study of the TBABr/HBD15 promoted coupling of CO2 with ELSO: effect of HBD content. Conditions: T = 120 °C, P = 5 MPa, TBABr = 2.2 mol%.

ELSO, the kinetic was doubled when TBABr and HBD15 were used in equimolar amount and the reaction was complete within 600 minutes instead of 1200 minutes without HBD15. However, addition of an excess of HBD15 (1.5 equivalent) compared to TBABr, had a detrimental effect on the kinetic as evidenced by a decrease of the rate constant compared to experiment conducted using an equimolar amount. This observation was related to the acidity of the proton of perfluoro-*tert*-butanol that decreased the nucleophilicity of the halide anion by strong solvation[53].

Conclusions

Cyclocarbonated linseed oil was synthesized by coupling CO_2 with epoxidized linseed oil (ELSO) using a catalytic platform composed of an organic halide salt or ionic liquid as organo-catalyst, and an hydrogen bond donor as activator. We first screened the catalytic activity of various organo-catalysts and found that guanidinium salt showed the best catalytic efficiency. The improvement of the CO_2/epoxidized vegetable oil coupling reaction was then investigated by adding various activators to the reaction medium containing TBABr as organocatalyst. Amongst all tested activators, 1,3-bis(2-hydroxyhexafluoroisopropyl)benzene, hexafluoro-2-(*p*-toluyl)isopropanol, perfluoro-*tert*-butanol and pyrocatechol are the most efficient with a doubling of the conversion of epoxide groups into cyclic carbonates compared to the same reaction carried out without the activator. The coupling of CO_2 with ELSO was optimized through detailed kinetic studies highlighting the positive impact of the pressure, the amount of CO_2 dissolved in ELSO, the temperature and the cocatalyst content on the reaction rate. Optimal conditions deduced from kinetic studies (TBABr/activator = 1, 2.2 mol% TBABr, 120 °C, 5 MPa) provides quantitative conversion of ELSO into CLSO in about 600 min without using any organic solvent. Therefore, when comparing the reaction conditions and kinetics previously reported[46] (> 30 h, 140°C, 15 bar) with our optimized conditions (10h, 120°C, 50 bar), we emphasize that the organocatalytic system composed of TBABr and hydrogen bond donor activator is particularly suitable to speed up the production of cyclocarbonated vegetable oils. However, the thermodynamic conditions still remain rather harsh and further research efforts are needed in order to develop more efficient catalysts that are active under mild conditions for the production of cyclocarbonated vegetable oils.

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Optimal conditions deduced from in situ FTIR kinetic studies provide quantitative conversion of epoxidized linseed oil into carbonated linseed oil using a bi-component organocatalyst.