Carbonation of Vegetable Oils: Influence of Mass Transfer on Reaction Kinetics

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Abstract

The carbonation of epoxydized vegetable oil was studied by using tetra-n-butylammonium bromide (TBAB) as catalyst. Thermal stability of TBAB was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and it was demonstrated that the maximum reaction temperature should not exceed 130°C. Reaction conditions were optimum at 130°C, 50 bar, with 3.5% mol of catalyst. The gas-liquid mass transfer coefficient and solubility of CO_2 were determined by taking into account the non-ideality of the gas phase using Peng-Robinson state equations. At 130°C, the CO_2 solubility was found to be independent from epoxide conversion and equal to 0.57 $mol.L^{-1}$, and the gas liquid mass transfer

coefficient (k_La) decrease with the epoxide conversion, i.e., at 0 % of conversion k_La = 0.0249 s^{-1} and at 94 % of conversion k_La = 0.0021 s^{-1}.

1. Introduction

The control of greenhouse gases, especially carbon dioxide, is one of the most serious challenges that humanity is facing today[1,2]. How the CO_2 molecule should be considered: waste or re-usable raw materials? Due to the difficulty to diminish the CO_2 emissions, the academic and industrial communities tend to recycle this molecule[3] in different ways such as the CO_2 storage, the use of CO_2 as solvent[4] or the use of CO_2 for enhanced oil recovery[5]. The benefit of these methods is the non-transformation of CO_2 but can it be a sustainable solution?

From a chemical viewpoint, carbon dioxide is considered as a C1 building block, i.e., synthesis of new molecules from a single-carbon molecule. Some industrial process exists such as the synthesis of urea or the synthesis of carbonated short-chain molecules. Investigation of direct synthesis of methanol from hydrogen and carbon dioxide is gaining growing interest. Private and public sectors are mobilized to develop the suitable catalyst, efficient chemical reactor and the cheapest non-fossil hydrogen in order to produce inexpensive methanol.

As summarized by Yu et al.[6] and Olajire[7], there are other promising routes of CO_2 valorization into fuels such as formic acid, dimethyl carbonate, methyl formate or into chemicals such as carboxylates, lactones, carbamates, carboxylic acids or polymers.

These existing and potential industrial CO_2 valorization examples have shown the importance of kinetic, thermodynamic and mass transfer data. To be able to propose a sustainable process based on the CO_2 valorization, it is important to gather experimental data for the different routes of valorization.

The use of CO_2 as the raw material in an industrial park can ensure its sustainability. The philosophy of eco-park is to look for some renewable and inexpensive raw materials. The coupling of renewable materials and reusable materials could be of high interest from the viewpoint of economy and energy.

Vegetable oils (VOs) are excellent candidates for the substitution of petroleum-derived products due to their renewability, low toxicity and biodegradability[8,9]. The worldwide production of VOs for industrial use and as biodiesel components has increased in the past decades[10]. The research trend is to investigate different ways to modify VOs, and among them epoxidation and carbonation have received a lot of attention during the recent years[11].

Synthesis of carbonated vegetable oils from epoxidized vegetable oils and carbon dioxide is a very green chemical route. Currently, carbonated vegetable oils are mainly used in the synthesis of nonisocyanate polyurethanes (NIPU), which does not require the use of highly toxic isocyanates compared with conventional methods[12]. They are also good candidates for lubricants to be used at high temperature and pressure[11].

The atom economy of this reaction is close to 100%[1,2]. Indeed, carbon dioxide reacts with the epoxide group to produce cyclic carbonates (Figure 1).

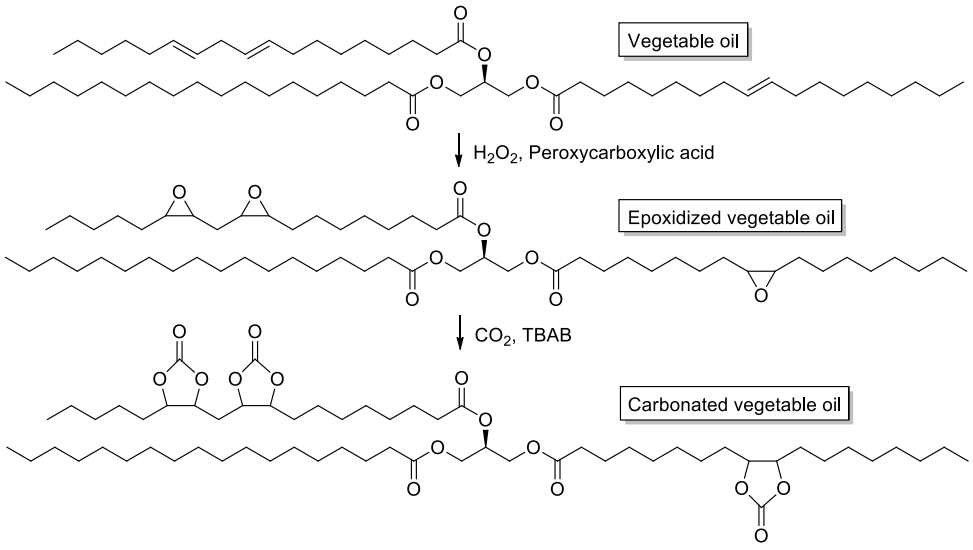

Figure 1. Synthesis of carbonated vegetable oils.

From a process point of view, the production of such compound should include the epoxidation process as illustrated by Figure 1. The epoxidation reaction is performed at atmospheric pressure by the Prileschajew reaction[13]. The carbonation reaction is performed at higher CO_2 pressure (50-70 bar) and temperature (140-150°C). Thus, these two steps cannot be performed in a one-pot synthesis.

Tamami et al.[14] were the first to publish the method of synthesis of carbonated soybean oil by using 5% of tetra-n-butylammonium bromide (TBAB) as catalyst under atmospheric pressure at 110°C. They have reported slow reaction rate and viscosity increased during this reaction. Experiment under same conditions were performed by Javni et al.[15] in 2008, 78% of conversion was achieved in 89 hours of reaction time.

In terms of catalysis, various co-catalysts such as $SnCl_4 \cdot 5H_2O$[16] and $CaCl_2$ [17] have been screened and enhanced the performance of TBAB. Other catalysts such as KI with 18-crown-6 ether (Parzuchowski et al.[18], 2006), silica supported 4-pyrrolidinopyridinium iodide (Bähr et al.[19], 2012), Pt doped $H_3PW_{12}O_{40}/ZrO_2$ (Wang et al.[20], 2012) have been tested, but they were less efficient.

In terms of process intensification, Doll et al.[21] have conducted the synthesis under supercritical CO_2, achieving 94% of conversion, in 20 hours. Mazo et al.[22] have demonstrated that microwave irradiation improves the carbonation kinetics.

Table 1 summarizes the major results obtained for the carbonation of vegetable oils.

Table 1. General result obtained by various groups in carbonation of VOs.

Reference	Oil	Nature of the reactor system	Catalyst
Tamami et al.[14]	ESBO	Flow of CO_2	TBAB, homogeneous
Doll and Erhan[21]	ESBO	Autoclave/scCO_2	TBAB, homogeneous
Parzuchowski et al.[18]	ESBO	Pressure reactor	KI/18-crown-6, homogeneous
Li et al.[16]	ESBO + DMF	Autoclave	TBAB/$SnCl_4$, homogeneous
Javni et al.[15]	ESBO	Pressure reactor	TBAB, homogeneous
Wang et al.[20]	ESBO + DMF	Autoclave	$H_3PW_{12}O_{40}/ZrO_2$, heterogeneous
Bähr and Mülhaupt[19]	ELO	Pressure reactor	TBAB, homogeneous
Bähr and Mülhaupt[19]	ELO	Pressure reactor	(SiO_2–(I)), heterogeneous
Mazo and Rios[22]	ESBO	Microwave irradiation with flow of CO_2	TBAB, homogeneous
Zhang et al.[23]	ECSO	Autoclave	TBAB, homogeneous

* ESBO: Epoxidized soybean oil; ELO: Epoxidized linseed oil; ECSO: Epoxidized cottonseed oil; SiO2–(I):silica-supported 4-pyrrolidinopyridinium iodide

Reference	Temperature [°C]	CO_2 pressure [Bar]	Reaction time [hours]	Conversion [%]
Tamami et al.[14]	110	1.01	70	94
Doll and Erhan[21]	100	103	20	94
Parzuchowski et al.[18]	130	6	48	98.3
Li et al.[16]	120	10	20	89.2
Javni et al.[15]	140	56.5	20	100
Wang et al.[20]	150	10	40	94.3
Bähr and Mülhaupt[19]	140	30	20	100
Bähr and Mülhaupt[19]	140	30	45	100
Mazo and Rios[22]	120	1.01	40	95
Zhang et al.[23]	140	30	24	100

TBAB is the most used catalyst for this reaction, but at higher temperature it can undergo decomposition into various products such as hydrogen bromide[21].

To the best of our knowledge, no mass transfer studies have been performed on this reaction system. Knowing the mass transfer and mixing effects is however essential at the scale-up stage. Furthermore, as the double bond is saturated with steric chemical groups, the viscosity is expected to increase[24]. As described in the article of Campanella et al.[24], epoxidized vegetable oils are non-Newtonian thixotropic fluids.

The main objective of this work was to study the limitation of different factors on the carbonation of epoxidized vegetable oils, and the kinetics of gas-liquid mass transfer by taking into account the non-ideality of the gas. Cottonseed oil was used during this study. The thermal stability of TBAB was investigated to determine its onset temperature of decomposition. A mass transfer study was performed by taking into account the non-ideality of the gas phase. Furthermore, a simple method was proposed to determine the solubility and mass transfer coefficient (k_La) of CO_2 under non-ideal conditions, and the influence of temperature, addition of catalyst and epoxy group conversion was investigated.

2. Experimental part

2.1 Materials.

Cottonseed oil was purchased from Sigma-Aldrich Co., while hydrogen peroxide (33 wt % in water) and formic acid (99 wt %) was purchased from VWR International. Perchloric acid solution (0.1 M) in glacial acetic acid was purchased from Alfa Aesar GmbH. TBAB (99.8 wt %) was purchased from Alfa Aesar and carbon dioxide was purchased from Air Liquide.

2.2 Apparatus and experimental procedures.

Carbonation reaction and solubility measurements were carried out in a 300mL high-pressure stainless steel autoclave (Parr Instrument Company) shown in Figure 2. The reactor was equipped with a temperature control system. A pressure probe and a gas entrainment impeller (diameter 2.5 cm) with a hollow shaft were used. A gas feed system including a CO_2 bottle and a gas reservoir equipped with a pressure probe was connected to the reactor. The uncertainty for the pressure probe is 0.01 bar and for the temperature probe is 0.1°C.

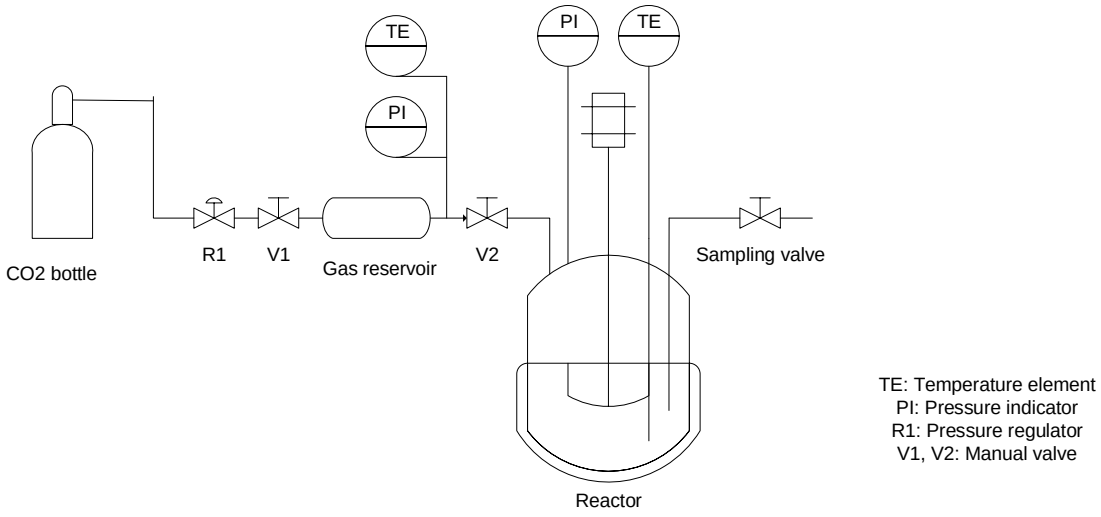

Figure 2. Simplified reactor scheme.

2.2.1 Preparation of epoxidized cottonseed oil.

The epoxidized cottonseed oil (ECSO) was prepared according to the protocol described in our previous article[25]. 180 g of cottonseed oil, 180 g of hydrogen peroxide (33 wt %) and 50g of distillated water was loaded in a 500 mL glass-jacketed reactor and stabilized at 60°C under vigorous agitation, then formic acid was introduced via a dosing pump at a volumetric flow-rate of 2.9 ml/min for 25 minutes. The reaction took one hour after which the agitation was stopped for phase separation. The resulting aqueous phase was removed, and the organic phase was washed with 300 mL of a 10 wt % aqueous solution of Na_2CO_3 in water, and three times with 200 mL of water to remove residual acid. The product was first dried using a rotary evaporator, and then magnesium sulfate was added to further remove water present in the product. The final product was filtered and stored at 3°C under argon to prevent oxidation. The epoxide content was measured by the method of Jay[26], and the conversion of double bounds was characterized by titrating the iodine value using the method of Hanus[27]. The resulting epoxidized cottonseed oil had a conversion exceeding 97% and the selectivity exceeded 81%.

2.2.2 Kinetic study of carbonation reaction.

The epoxidized cottonseed oil and the catalyst (TBAB) were charged into the reactor and heated to the desired temperature under agitation. Then, the agitation was stopped and the atmosphere inside the reactor was purged with CO_2. The output pressure was adjusted via the pressure regulator R1 connected to the CO_2 bottle, then valve V2 was opened and the stirring was started at the desired speed. Samples were withdrawn via the sampling valve during the reaction, and stored at 3°C prior to analysis.

2.2.3 Measurement of CO_2 solubility.

Epoxidized cottonseed oil (with or without catalyst) was charged into the reactor and heated to the desired temperature under agitation, then the agitation was stopped and the atmosphere inside the reactor was purged with CO_2. Using the regulator R1, CO_2 was introduced into the gas reservoir at the desired pressure. After the pressure stabilization, the agitation was switched on. The pressure and temperature in the gas reservoir were monitored in order to obtain the amount of CO_2 dissolved in the liquid phase.

2.3 Analytical methods.

The concentration of the oxirane group was determined by the method of Jay, where oil samples were dissolved in a solution of 10 ml tetra-n-etylammonium bromide (20 w%) and 10 ml of chloroform, then titrated by using a 0.1 N perchloric acid solution in acetic acid[26]. The uncertainty of the titration method is 0.01mol/L. The structure of products was characterized by Fourier transform infrared (FTIR) (Perkin-Elmer), ^{1}H NMR and ^{13}C NMR (Bruker Avance 300 MHz Spectrometer). Studies on the thermal stability of products were carried out using TA Instruments Q1000 Modulated Differential Scanning Calorimeter (DSC) and Q600 thermogravimetric analysis (TGA). For the DSC, temperature and energy calibration were performed using indium (T_{fusion} = 156.6°C et ΔH_{fusion} = 28.45 $J.g^{-1}$). Samples were heated from -90°C to 100°C under nitrogen (50 $mL.min^{-1}$) using a heating rate of 10°C/min. For the TGA, calibration was performed using Alumel and Nickel which Curie points are respectively 163°C and 358°C.

Dynamic viscosity of cottonseed oil (CSO), epoxidized cottonseed oil (ECSO) and carbonated cottonseed oil (CCSO) were measured with the viscometers FUNGILAB.S.A and BROOKFIELD CAP2000+.

3. Results and discussions

3.1 Thermal stability of catalyst

At high temperature, TBAB can readily decompose into volatile and toxic compounds such as Hydrogen Bromide[21] (Figure 3), which is highly reactive with epoxy groups. To prevent he decomposition of TBAB and potential side reactions, the carbonation reaction should be carried out at a temperature lower than the TBAB decomposition temperature. For this purpose, a decomposition study by DSC and TGA analysis was performed.

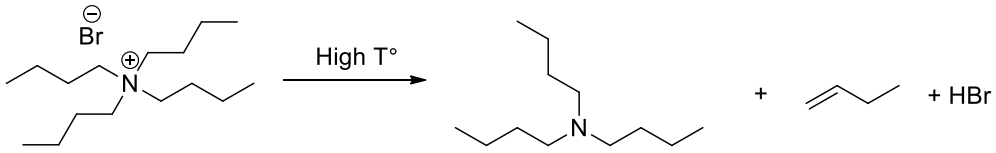

Figure 3. Decomposition of TBAB

Figure 4 shows the TBAB thermogram under dynamic mode from 50°C to 250°C with a temperature ramp of 1°C/min. One can notice the presence of two peaks at 86°C and 116°C, which corresponds respectively to crystalline structure and phase change[28]. The third peak corresponds to the TBAB decomposition, but due to the difficulty of determining the onset temperature under DSC, studies with TGA was carried out.

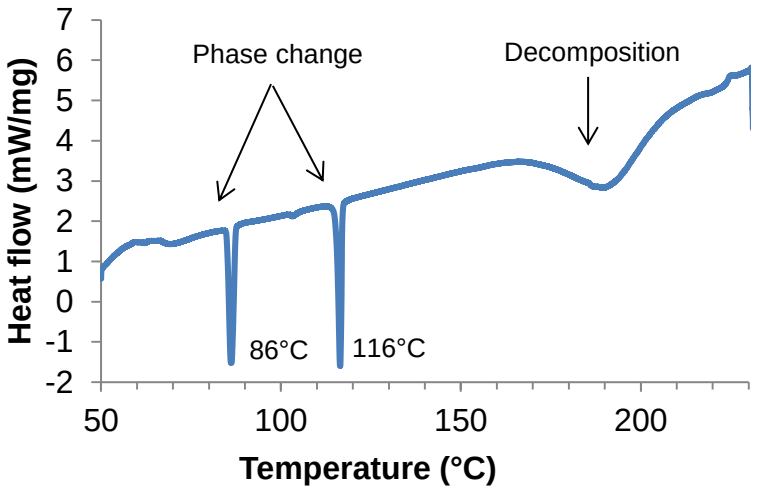

Figure 4. Dynamic thermal analysis of TBAB by DSC under dynamic mode with a heating ramp of 1°C/min.

Sample was heated under dynamic mode from 50°C to 300°C with a temperature ramp of 2°C/min. Starting of the mass drop was observed at ca.130°C (Figure 5).

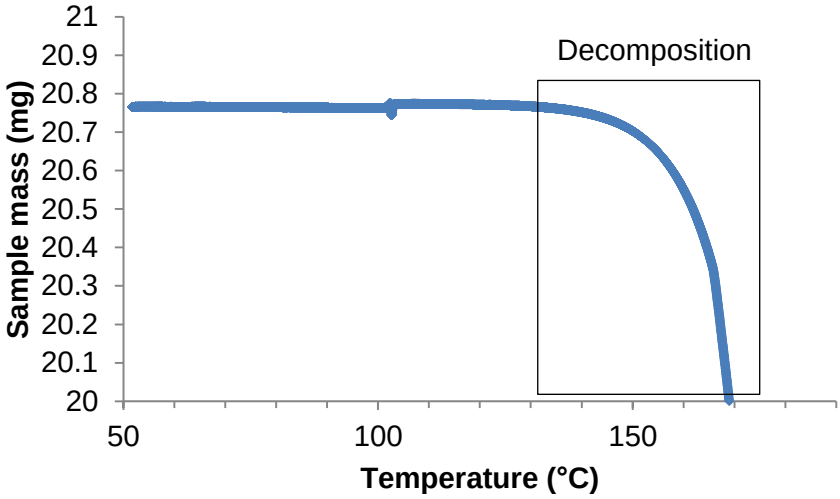

Figure 5. Dynamic thermal analysis of TBAB by TGA under dynamic mode with a heating ramp of 2°C/min.

To verify the stability of TBAB on a long reaction time, TGA experiments under isothermal mode at 120°C, 130°C, 140°C and 150°C were conducted for 10 hours (Figure 6).

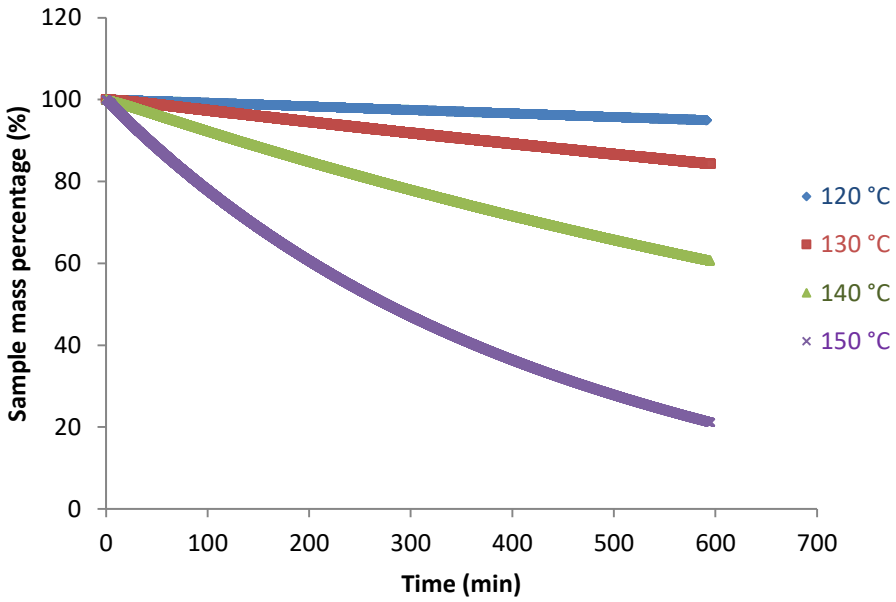

Figure 6. Study of TBAB thermal stability under isothermal mode by TGA.

It can be noticed that at 140°C and 150°C, the mass loss of TBAB is significantly faster and higher than at 120°C and 130°C. Thus, carbonation experiments should be performed at reaction temperature lower than 130°C to prevent catalyst loss.

One should also keep in mind that experiments carried out in DSC or TGA were not performed in similar condition as the one in the autoclave. Indeed, during the micro-calorimetry experiments, there was not epoxidized cottonseed oil and CO_2 atmosphere, which could interfere slightly with the onset temperature.

3.2 Influence of rotation speed.

To check the influence of the agitation velocity on the reaction kinetics, experiments were carried out at different rotating speeds (300-900 rpm), at 130°C, 50 bar of CO_2 pressure and with 3.5 mol% of TBAB with respect to epoxy groups (Figure 7). One can distinguish two different behaviors: low rotating speed, i.e. < 300 rpm and high rotating speed, i.e., > 500 rpm. Rate of ECSO conversion is lower for experiments carried out at 300 rpm during 400 minutes of reaction time, which can be linked to a

slow gas-liquid mass transfer rate. Experiments carried out at 500, 700 or 900 rpm show similar kinetics. Thus, to optimize the rate of ECSO conversion, experiments were carried out at 500 rpm.

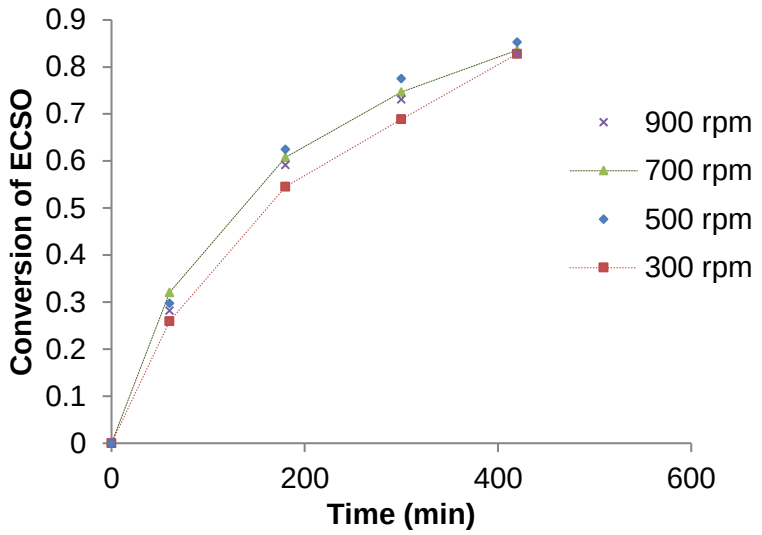

Figure 7. Influence of rotation speed on ECSO conversion at 130°C.

3.3 Influence of catalyst loading.

The carbonation reaction was studied with 1.4, 3.5, 5 and 10 mol% of TBAB with respect to the epoxide groups (Figure 8). As there is no significant kinetic increase from 3.5% to 5% of catalyst and 10% was impractical in real situations, 3.5% TBAB have been chosen for the rest of this work.

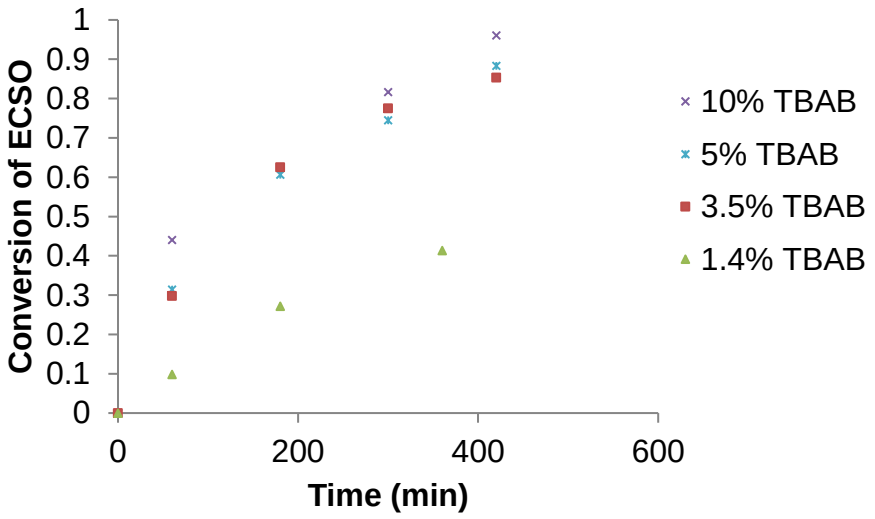

Figure 8. Influence of catalyst amount on reaction kinetics at 130°C, 50 bar and 500 rpm.

3.4 Influence of temperature and CO_2 pressure.

The kinetic study was studied within the temperature range of 110-130°C for the sake of catalyst stability and within the CO_2 pressure range of 30-50 bar (Figures 9-10).

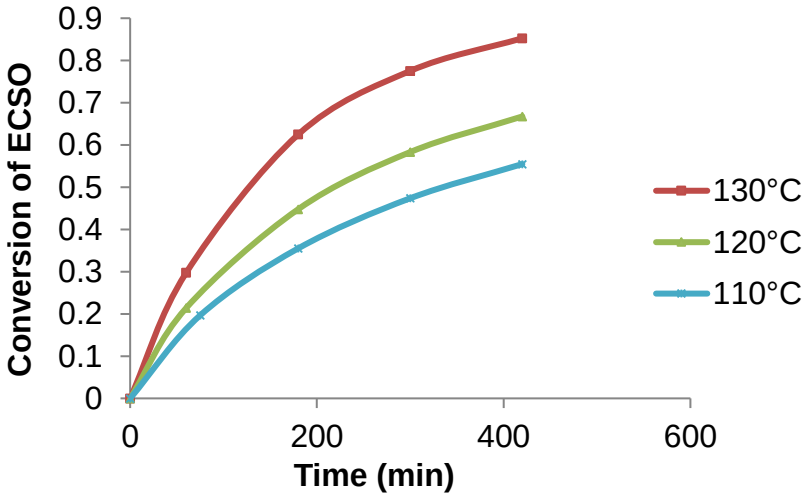

Figure 9. Influence of temperature on reaction kinetics at 50 bar and with 3.5 mol% TBAB at 500 rpm.

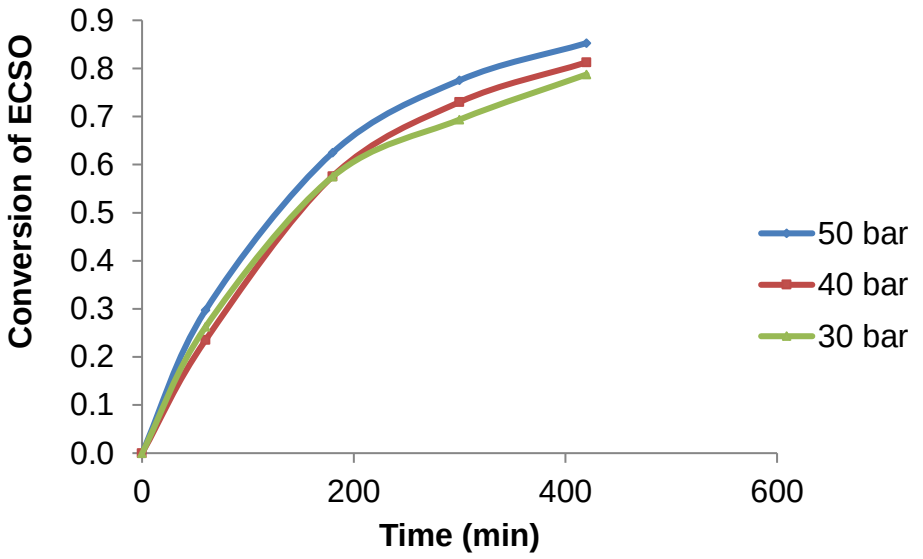

Figure 10. Influence of CO_2 pressure on reaction kinetics at 130°C, with 3.5 mol% TBAB at 500 rpm.

Figure 9 shows that as the reaction temperature increases, the initial rate of ESCO conversion increase. The increase of reaction temperature leads to the increase of carbonation reaction kinetics with Arrhenius law and the increase of mass transfer kinetics which is proportional to the temperature[29].

From Figure 10, it can be noticed that initial kinetics between 30 and 50 bar of CO_2 was not significantly different. One could have expected that by increasing the CO_2 pressure, carbonation reaction kinetic could have been higher due to a faster mass transfer linked to a higher CO_2 gradient. In this system, there is slight benefit to increase the CO_2 pressure on reaction temperature within reaction pressure of 30-50 bar. Bähr and Mülhaupt[19] have noticed that the conversion of epoxidized linseed oil a 140°C have a stronger influence on reaction kinetics between 1 atm and 10 bar than between 10 and 30 bar.

Based on the thermal study of the catalyst, the influence of the catalyst amount and CO_2 pressure, it can be stated that the optimal experimental conditions were 130°C, 50 bar of CO_2 and 3.5 mol % of TBAB.

3.5 Product characterization.

Samples withdrawn at different reaction times during the reaction were analyzed by ^{1}H NMR, ^{13}C NMR and FTIR. Figure 11 clearly reveals the formation of carbonyl groups on the band 1800 cm^{-1} and the consumption of oxirane groups in the wavenumber range of 820-840 cm^{-1}.

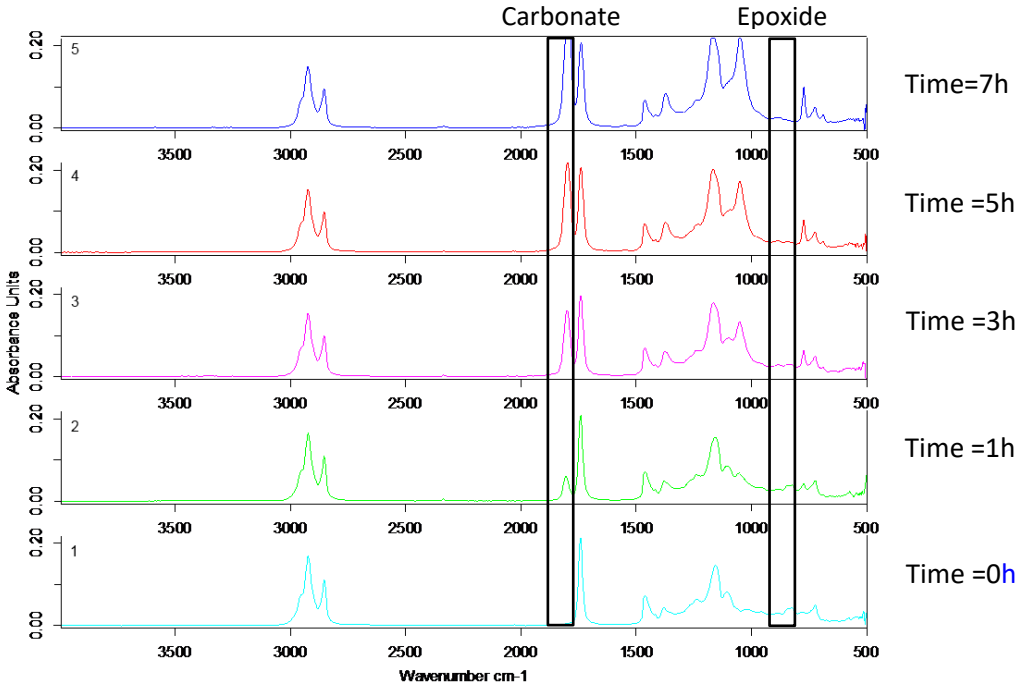

Figure 11. FTIR spectra for samples at different reaction times at 130°C, 50 bar and 3.5 mol% of TBAB under 500 rpm.

Figure 12 shows the ^{1}H NMR spectra of the same sample as on FTIR. Epoxy groups towards 2.8-3.1 ppm decreased during the reaction and carbonates at 4.3-4.9 ppm were formed. By taking the group at 4.09-4.15 ppm as reference (two protons from

glycerol), the integration can be normalized and the selectivity of the reaction can be calculated by

$$S\,(\%) = \frac{C-2}{A-B} = \frac{8.11-2}{6.55-0.21} = 0.96$$

where A is the integration of signal of sample 1 from 2.8 to 3.1 ppm (initial amount of epoxide), B the integration of signal of sample 5 from 2.8 to 3.1 ppm (final amount of epoxide), and C the integration of signal of sample 5 from 4.2 to 4.9 ppm (signal of carbonates with 2 protons from glycerol). The final value obtained for these conditions is 96%.

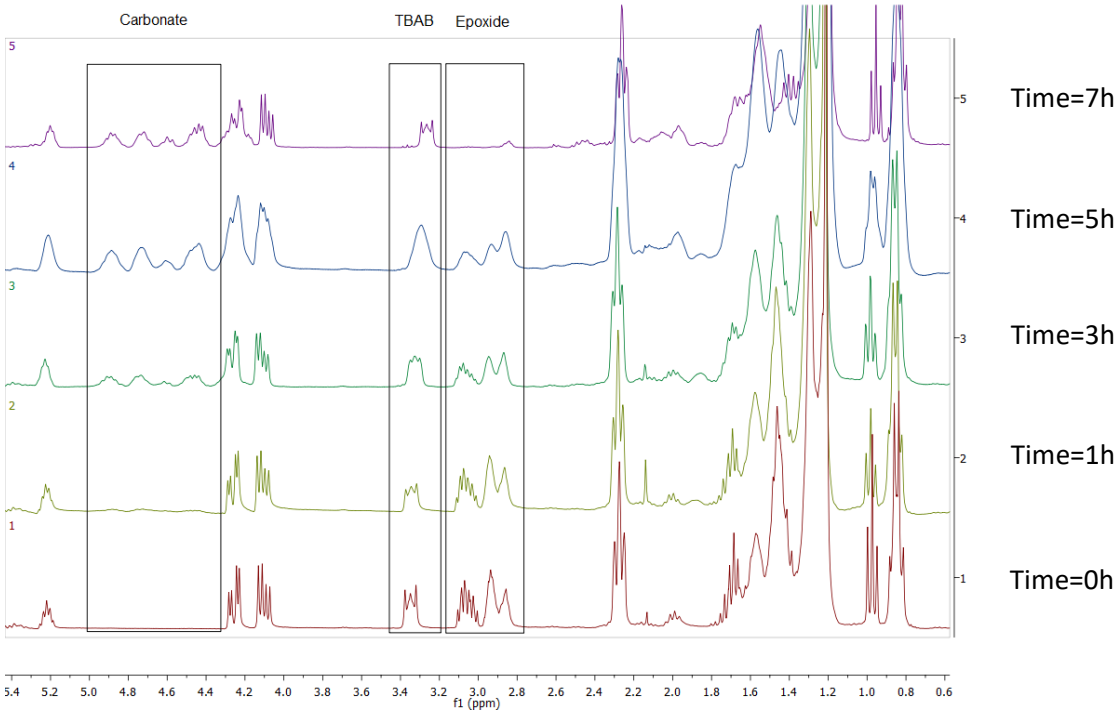

Figure 12. ^{1}H NMR spectra for samples at different intervals of reaction. T= 130°C, P=50bar, 3.5% TBAB.

Furthermore, ^{13}C NMR spectra were obtained for the initial (1) and final (2) products. The signals of oxirane groups are located at 54.4, 56.8, 57.1, 57.3 ppm, and signals of carbonates are located at 77.8, 79.5, 82.1 and 153.9 ppm (Figure 13).

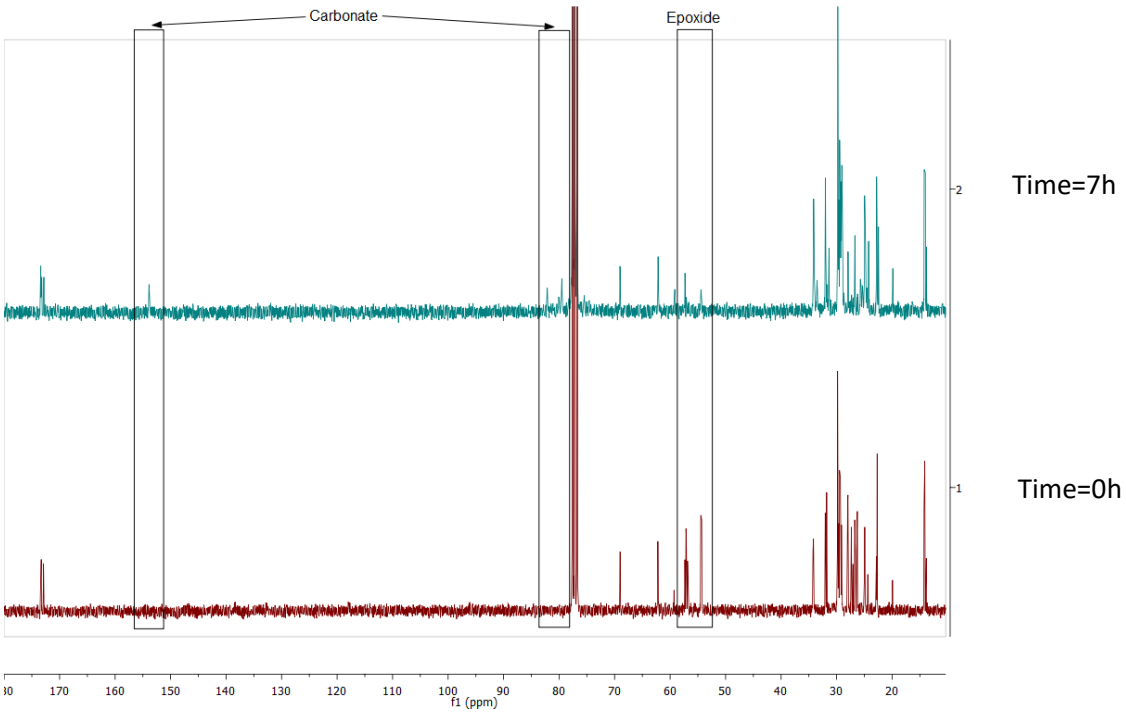

Figure 13. ^{13}C NMR spectra for samples at the beginning (1) and the end (2) of reaction. T= 130°C, P=50bar, 3.5% TBAB.

3.6 Measurement of CO_2 solubility.

The concentration of CO_2 present in the liquid phase is an important factor affecting the reaction kinetics. For this reason, the evolution of this factor with the conversion of ECSO and the influence of the electrolyte TBAB was investigated. Indeed, Henry's coefficient and mass transfer parameters might change with the reactant conversion due to the increase of the liquid viscosity. Figure 14 illustrates this evolution.

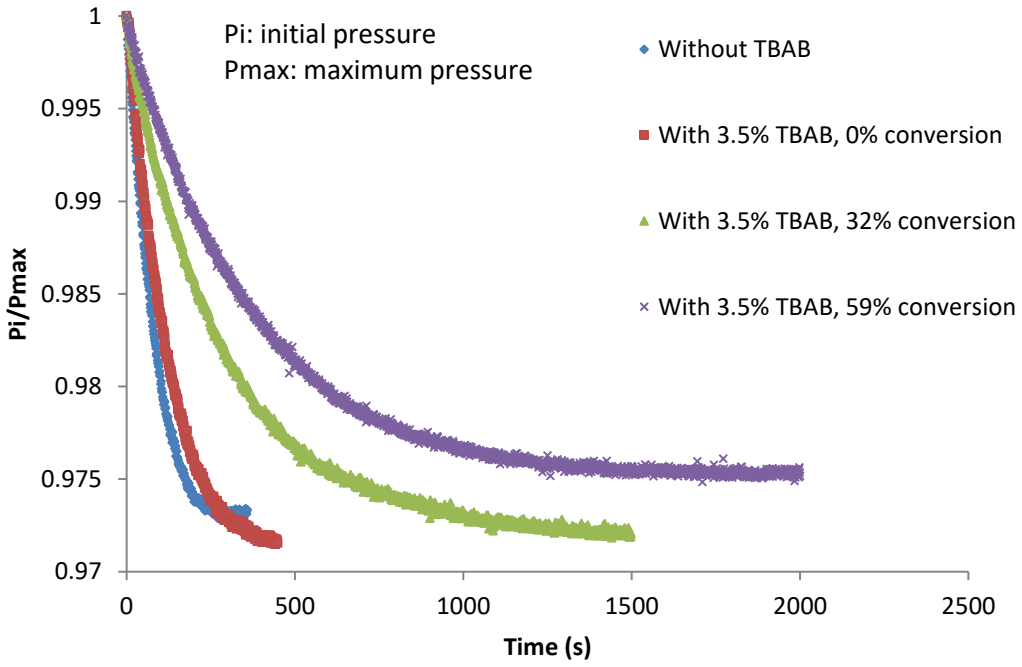

Figure 14. Normalized pressure drop rate at 100°C, with and without catalyst and at different ECSO conversions.

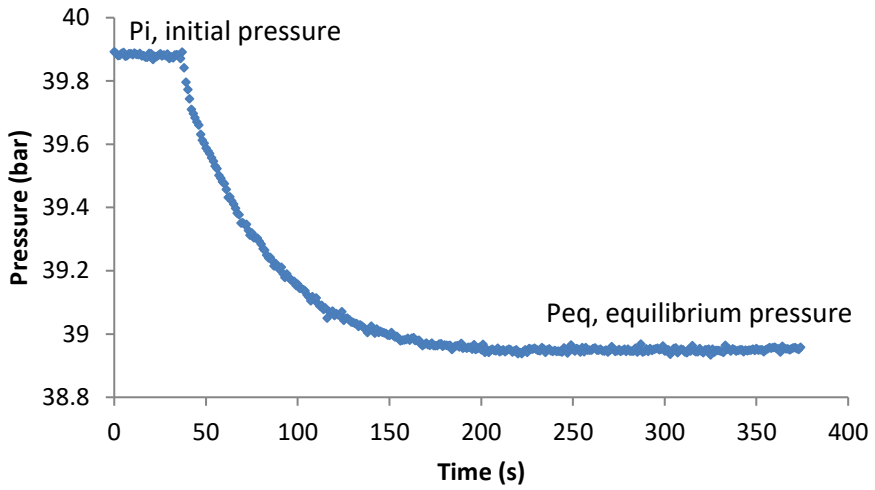

Figure 15. Pressure drop in the gas reservoir at 120°C in absence of TBAB.

As shown in Figure 15, the pressure drop was monitored, the initial pressure (P_i) and equilibrium pressure (P_{eq}) was used to calculate the amount of CO_2 dissolved in the oil. In the presence of the catalyst, the carbonation reaction occurs simultaneously with CO_2 absorption and increases the pressure drop in the reactor. In order to surmount this problem, the pressure was interpolated to determine the corresponding equilibrium pressure.

The reactor and gas reservoir were considered as two individual parts stabilized at the same pressure at different temperatures T_r and T_{res}, respectively. Due to the non-ideality of CO_2 at high pressure, the Peng-Robinson state equation was used to calculate the compressibility factor Z[30]:

$$P = \frac{RT}{\frac{V}{n_{CO_2}} - b} - \frac{a(\omega, T_r)}{\frac{V}{n_{CO_2}}\left(\frac{V}{n_{CO_2}} + b\right) + b\left(\frac{V}{n_{CO_2}} - b\right)} \quad (1)$$

with

$a(\omega, T_r) = a_c \alpha(\omega, Tr)$, where ω is the acentric factor and Tr is the reduced temperature defined as T/Tc;

$a_c = \frac{0.45724 R^2 T_c^2}{P_c}$, where Tc and Pc are temperature and pressure at CO_2 critical point respectively,

$\alpha(\omega, T_r) = \left(1 + \kappa\left(1 - \sqrt{T_r}\right)\right)^2$,

$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$

$b = \frac{0.07780 RT_c}{P_c}$.

Equation (1) can be put in polynomial form as:

$$Z^3 - (1 - B).Z^2 + \left(A - 2.B - 3.B^2\right).Z - \left(A.B - B^2 - B^3\right) = 0 \quad (2)$$

with:

$A = \frac{a.\alpha.P}{R^2 T^2}$,

$B = \frac{b.P}{R\ T}$,

$Z = \frac{P.V}{n_{CO_2} R.T}$.

The cubic equation (2) was solved by Newton-Raphson method in order to obtain the compressibility factor Z.

Thus the quantity of CO_2 at the beginning and at equilibrium can be calculated by the following equations:

$$n_{g,i} = n_{r,i} + n_{res,i} = \frac{P_i(V_r - V_L)}{Z_r R T_r} + \frac{P_i V_{res}}{Z_{res} R T_{res}} \quad (3)$$

$$n_{g,eq} = n_{r,eq} + n_{res,eq} = \frac{P_{eq}(V_r - V_L)}{Z_r R T_r} + \frac{P_{eq} V_{res}}{Z_{res} R T_{res}} \quad (4)$$

Table 2 presents some values of Z_r and Z_{res}. In the reservoir the value of the compressibility factor is close to 0.7, and in the reactor the compressibility factor is ca. 0.9. These values are lower than 1 showing the non-ideality of the gas phase.

The concentration of CO_2 in the oil at T_r and P_{eq} can be expressed as

$$C_{CO2} = \frac{n_i - n_{eq}}{V_{oil}} \quad (5)$$

The Henry's constant can be calculated from

$$k_{H,CO2} = \frac{P_{eq}}{C_{CO2}} \quad (6)$$

Table 2 shows the solubility data within the temperature range 100-130°C. The solubility of CO_2 in the epoxidized or carbonated cottonseed oil is similar and there are no significant changes in solubility by the addition of TBAB. The CO_2 solubility decrease when temperature increases, which is a classical behavior.

3.7 Measurement of mass transfer coefficients.

To measure mass transfer coefficient, we have followed the variation of pressure as in the work of Laugier[31], Frikha[32] and Hichri[33]**.** The mass transfer coefficient (k_La) is defined by the following equation:

$$-\frac{dn_g}{dt} = V_L k_L a (C_L^* - C_L) \quad (7)$$

By assuming that the liquid phase volume is constant, Eq. (7) becomes

$$-\frac{dn_g}{dt} = V_L k_L a \left(\frac{n_{CO2,L,eq}}{V_L} - \frac{n_{CO2,L}}{V_L}\right) \quad (8)$$

$$= k_L a[(n_{g,i} - n_{g,eq}) - (n_{g,i} - n_{g,t})]$$

Where $n_{g,t}$ represents the amount of CO_2 molecules at time t, $n_{g,i}$ the initial amount of CO_2 molecules and $n_{g,eq}$ the amount of molecules at the equilibrium.

Integration of Eq. (8) gives

$$\int_{n_{g,i}}^{n_{g,t}} \frac{dn_{g,t}}{n_{g,eq}-n_{g,t}} = k_L a \cdot \int_{t_0}^{t} dt \quad (9)$$

which is equivalent to

$$\ln\left(\frac{n_{g,eq}-n_{g,t}}{n_{g,eq}-n_{g,i}}\right) = k_L a \cdot (t - t_0) \quad (10)$$

By plotting $\ln\left(\frac{n_{g,f}-n_{g,t}}{n_{g,f}-n_{g,i}}\right)$ along the time t, $k_L a$ can be estimated. Measurements were performed in the temperature range of 100-130°C and graphical results are displayed in Figures 16-19.

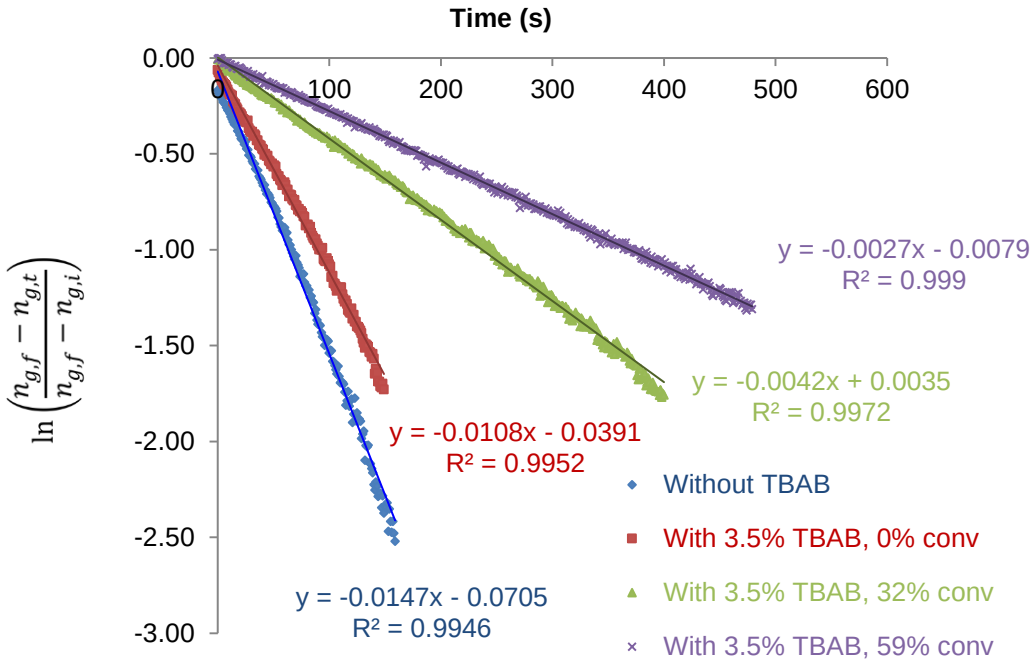

Figure 16. Mass transfer coefficient plot at 100°C.

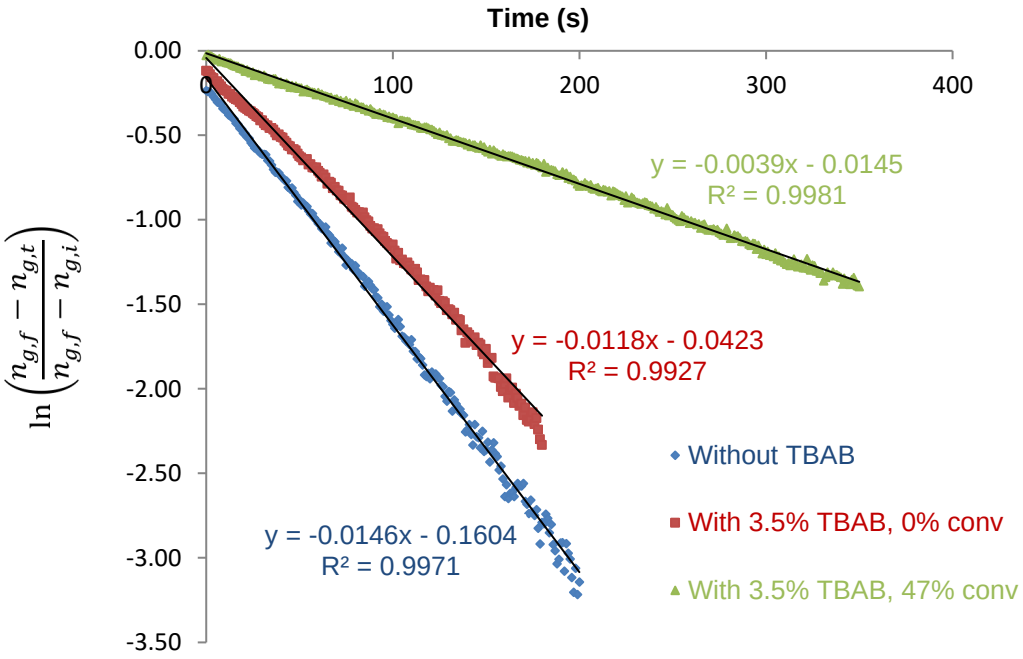

Figure 17. Mass transfer coefficient plot at 110°C.

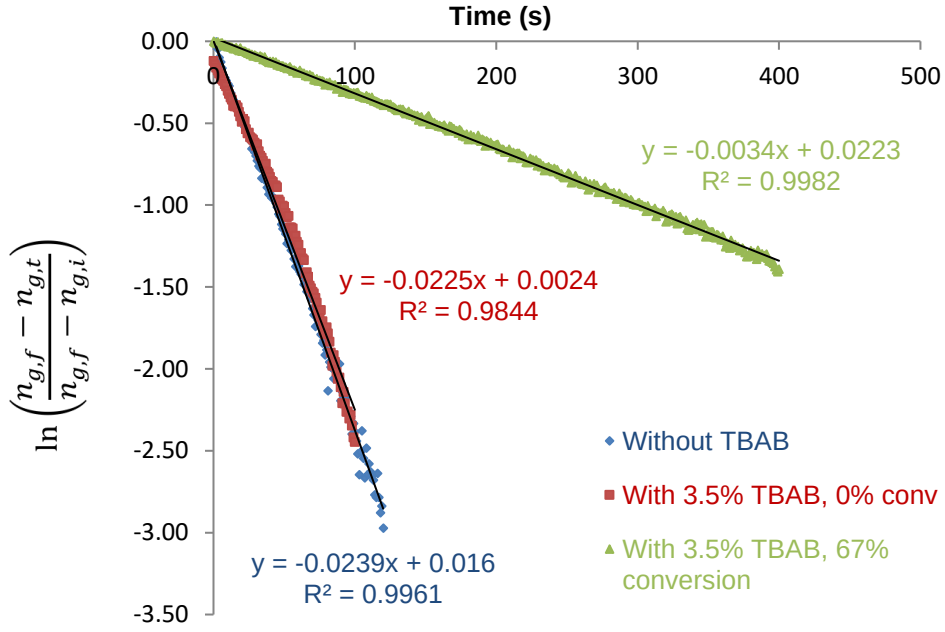

Figure 18. Mass transfer coefficient plot at 120°C.

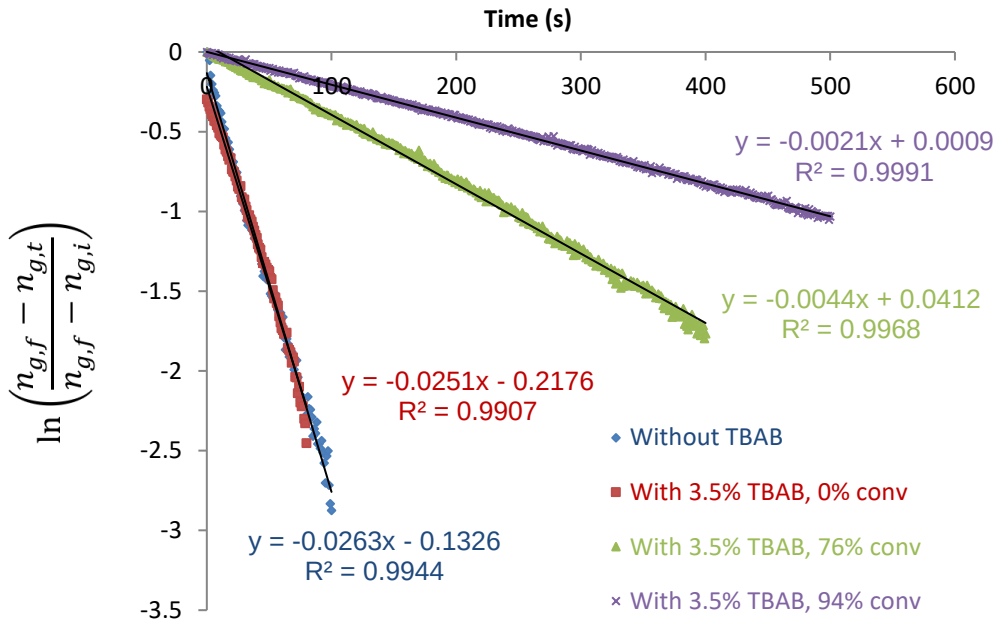

Figure 19. Mass transfer coefficient plot at 130°C.

The correlation developed by Kawase and Moo-Young[34] relates the mass transfer coefficient to liquid viscosity:

$$k_{\mathrm{Liq}}.a = \frac{2}{\sqrt{\pi}}\sqrt{D_{CO_2/Liq}\left(\frac{\xi.\rho^{Liq}}{\mu^{Liq}}\right)^{1/4}}.a \qquad (11)$$

Carbonated cottonseed oil (CCSO) has a higher viscosity than the epoxidized cottonseed oil[24]. From Eq. (11), as the conversion of ECSO increases, then the volumetric mass transfer coefficient decreases. This tendency was observed with the experimental data (Figure 20).

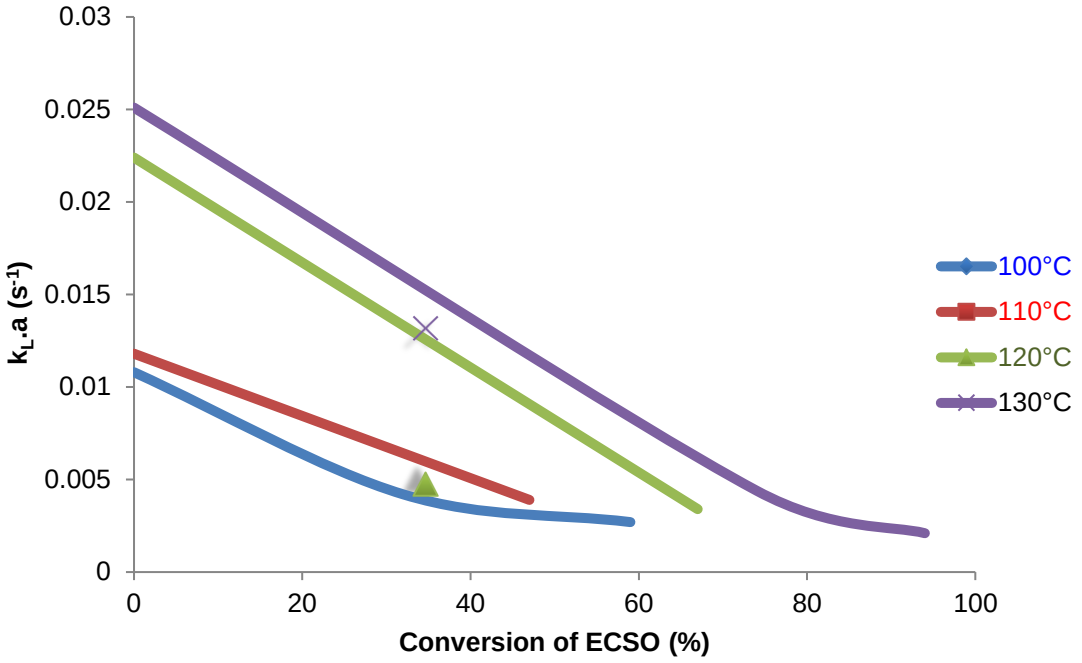

Figure 20. Mass transfer coefficients with ECSO conversion with 3.5 mol% of TBAB at different reaction temperature.

It can be noticed that as the reaction temperature increases, the volumetric mass transfer coefficient increases (Figure 20).

From Table 2, the addition of TBAB decreased k_La by about ¼ at 110°C and below, but this phenomenon is not as evident at 120°C and 130°C. This is possibly due to the phase change of TBAB at 116°C, observed on the DSC graph (Figure 4). Table 2 summarizes the CO_2 solubility data and the values of the volumetric mass transfer coefficient, k_La.

Table 2. Solubility of CO_2 and gas-liquid mass transfer coefficients under various conditions.

T_r (°C)	Pressure (bar)	[TBAB] (mol%)	Epoxide conversion (%)	Z_{res}	Z_r	CO_2 solubility ($mol \cdot L^{-1}$)	k_La (s^{-1})	$k_{H,CO2}$ ($L \cdot bar \cdot mol^{-1}$)
100	39.89	-	0	0.70	0.89	0.66	0.0147	60.44
100	40.05	3.5	0	0.70	0.89	0.65	0.0108	61.62
100	41.62	3.5	32	0.69	0.89	0.66	0.0043	63.06
100	40.04	3.5	59	0.69	0.89	0.67	0.0027	59.76
110	40.10	-	0	0.70	0.90	0.59	0.0145	67.97
110	40.08	3.5	0	0.70	0.90	0.61	0.0117	65.70
110	41.65	3.5	47	0.69	0.90	0.64	0.0040	65.08
120	39.65	-	0	0.70	0.91	0.53	0.0238	74.81
120	39.95	3.5	0	0.70	0.91	0.60	0.0224	66.58
120	42.35	3.5	67	0.68	0.91	0.51	0.0036	83.04
130	41.88	-	0	0.68	0.92	0.57	0.0262	73.47
130	41.00	3.5	0	0.68	0.92	0.55	0.0249	74.55
130	42.05	3.5	74	0.68	0.92	0.57	0.0046	73.77
130	44.30	3.5	94	0.67	0.91	0.59	0.0021	75.08

3.8 Measurement of viscosity

We have measured the viscosity of cottonseed oil, epoxidized cottonseed oil and carbonated cottonseed oil (Figure 21). One can notice that the viscosity of carbonated cottonseed oil (CCSO) is higher than the epoxidized (ECSO) and vegetable oil (CSO). However, as the temperature increase, the difference of viscosity between these different species is less pronounced.

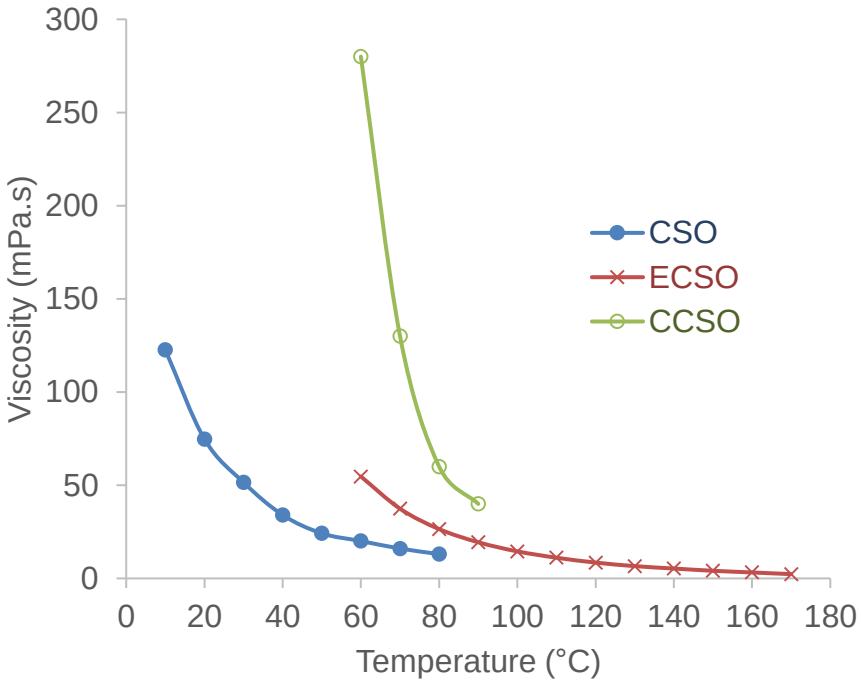

Figure 21. Dynamic viscosity of the different vegetable oils.

Zhang et al.[23] have measured the kinetic viscosity at different conversion of ECSO at 40 and 100°C. To compare their results with our results, we have assumed that densities of CSO, ECSO and CCSO are similar and equal to 1000 $kg.m^{-3}$. Figure 22 shows the evolution of dynamic viscosity with the conversion of ECSO. One can notice that at 100°C, the dynamic viscosity of ECSO and CCSO is respectively, 14.3 mPa.s and 64.7 mPa.s. As the viscosity increases during the reaction, gas-liquid mass transfer coefficient (Eq. (11)) decreases.

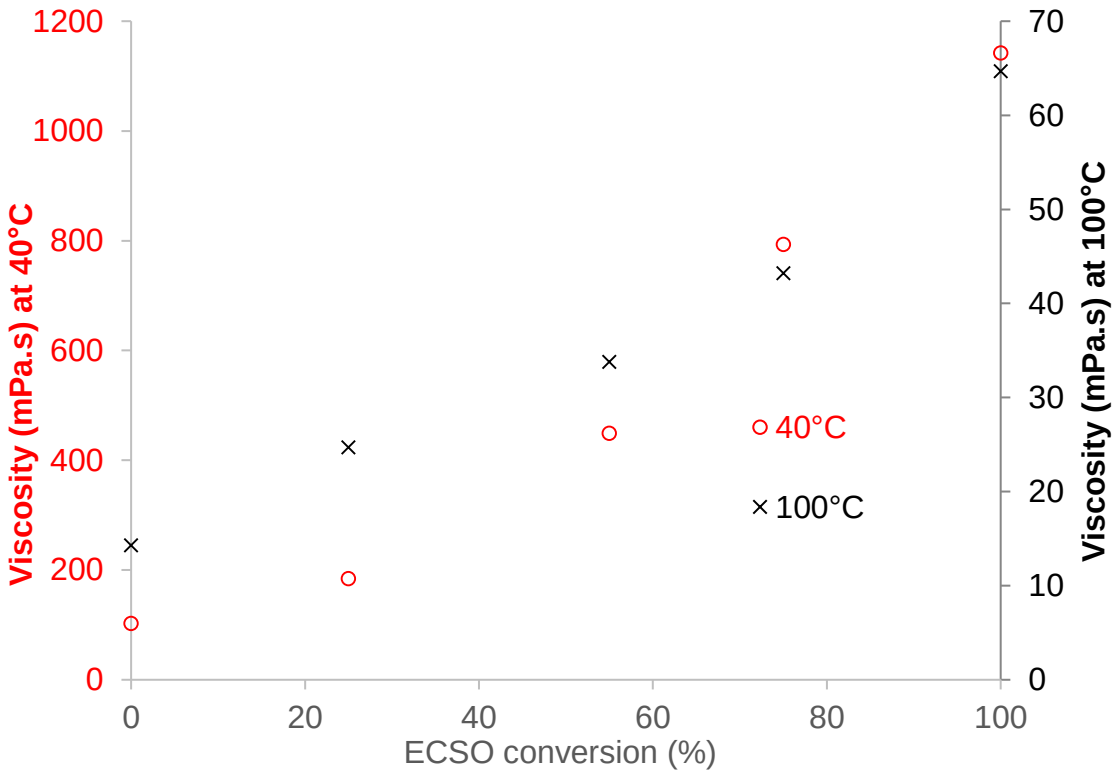

Figure 22. Evolution dynamic viscosity with ECSO conversion at 40 and 100°C.

4 Conclusions

The carbonation of epoxidized cottonseed oil using TBAB as the catalyst has been studied in the temperature range of 110-130°C, and in the pressure range of 30-50 bars. NMR and FTIR analytic techniques were used to determine the presence of carbonated cottonseed oil.

The catalyst onset temperature was found to be at ca. 130°C. The optimal reaction condition was determined to be 130°C and 50 bar of CO_2 pressure. The conversion and selectivity were 85 % and 96 %, respectively for seven hours of reaction.

Mass transfer coefficient of CO_2 was found to decrease with the epoxide conversion due to an increase of viscosity. For example, at 130°C, mass transfer coefficient was measured to 0.0249 s^{-1} at 0% of epoxide conversion and to 0.0021 s^{-1} at 96 % of epoxide conversion.

Solubility of CO_2 was independent of epoxide conversion and decrease with increasing reaction temperature. For example, at 100°C the solubility was calculated to 0.65 $mol.L^{-1}$ and at 130°C the solubility was 0.55 $mol.L^{-1}$.

Nomenclature

T_r (°C)	Reactor temperature
T_a (°C)	Ambient temperature
P_i (bar)	Initial pressure
P_{eq} (bar)	Equilibrium pressure
V_r (L)	Volume of reactor
V_{res} (L)	Volume of gas reservoir
V_L (L)	Volume of liquid phase
$n_{g,I}$ (mol)	Total initial molar molar quantity of CO_2 in the gas phase
$n_{g,eq}$ (mol)	Total molar molar quantity of CO_2 in the gas phase at equilibrium
$n_{r,I}$ (mol)	Initial molar molar quantity of CO_2 in the reactor
$n_{r,eq}$ (mol)	Molar molar quantity of CO_2 in the reactor at equilibrium
$n_{res,I}$ (mol)	Initial molar molar quantity of CO_2 in the gas reservoir
$n_{res,eq}$ (mol)	Molar molar quantity of CO_2 in the gas reservoir at equilibrium
Z_r	Compressibility factor of CO_2 in the reactor
Z_{res}	Compressibility factor of CO_2 in the gas reservoir
$k_L{\cdot}a$ (s^{-1})	Gas-liquid mass transfer coefficient
$k_{H,CO2}$ ($L{\cdot}bar{\cdot}mol^{-1}$)	Henry's constant
C_L^*($mol{\cdot}L^{-1}$)	Concentration of CO_2 in the liquid phase at equilibrium
C_L ($mol{\cdot}L^{-1}$)	Concentration of CO_2 in the liquid phase at time t
$D_{CO2/Liq}$ ($m^2{\cdot}s^{-1}$)	Diffusion coefficient of CO_2 in the liquid phase
ξ ($W{\cdot}kg^{-1}$)	Energy dissipation rate per unit mass
μ_L (Pa·s)	Liquid viscosity

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