

A Novel CO₂ Capture and Utilization Strategy by Enzyme Catalysis: Preliminary Assessment of Process Layout

Luigi Marra^{a,b}, Hanna Knuutila^c, Maria Elena Russo^{a*}

^a Istituto di Scienze e Tecnologie per l'Energia e la Mobilità Sostenibili– Consiglio Nazionale delle Ricerche, P.le V. Tecchio 80, 80125 Napoli, Italy]

^b Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale – Università degli Studi di Napoli Federico II, P.le V. Tecchio 80, 80125 Napoli – Italy]

^c Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway
 mariaelena.russo@stems.cnr.it

Catalytic conversion of CO₂ into fuels and valuable chemicals has gained large attention in the scientific and industrial research aimed at developing novel Carbon Capture and Utilization (CCU) processes. Among current uses of CO₂, the Kolbe-Smith process allows the production of salicylic acid through carboxylation of phenol using CO₂ at high pressure and temperatures. A biocatalytic route has been proposed and it is based on the enzymatic carboxylation of phenolic substrates (e.g. catechol and resorcinol) into ortho-hydroxybenzoic acids catalyzed by non-oxidative carboxylases. The main advantages of such biocatalytic carboxylation are related to good selectivity of the biocatalyst, absence of co-substrates, and the mild conditions of temperature and pressure typically applied in enzymatic bioconversions. Experimental studies on enzymatic carboxylation of phenols (Pesci et al., 2015; Meyer et al., 2018) provided data on thermodynamics and kinetics of the process in 1.8 – 2 M K₂CO₃ solutions. The present contribution addresses some process design issues related to the development of an enzymatic carboxylation process as a possible CO₂ utilization route. The following points have been considered in the study: the use of phenolic substrates from pyrolytic bio-oils as renewable carbon source; the capture of CO₂ in the form of bicarbonate in aq. solvents to provide the necessary bicarbonate source to carboxylation; the effect of phenolic substrates solubility on the maximum equilibrium conversion into carboxylic acids. These points have been analyzed by simulations with the ASPEN PLUS® software. In the simulations, a CO₂ absorption column operated with K₂CO₃ solution and immobilized carbonic anhydrase as a promoter. The composition of the solvent from the absorption column has been used for equilibrium calculations of enzymatic carboxylation to assess the potential use of this bicarbonate enriched solvent as carbon vector in the enzymatic CCU process.

1. Introduction

The scientific community has turned attention to new technologies to reduce greenhouse gas emissions, especially CO₂. Many efforts are ongoing to capture CO₂ and reuse it as a carbon source. Captured CO₂ can be stored underground or in deep oceans or used for enhanced oil recovery processes. In addition, CO₂ conversion into chemicals, fuels, and materials by Carbon Capture and Utilization (CCU) processed will bring a further benefit providing non-fossil commodities and integrating CO₂ as raw material into the circular economy. Absorption in carbonate and amines solutions has been widely used for acid gas scrubbing from various sources, e.g. natural gas, and has been applied as the first step for CCU technologies (Gondal et al., 2016; Bernhardsen and Knuutila, 2017). Absorption in aq. carbonate solutions yields captured CO₂ in the form of bicarbonate ions. The common configuration includes a closed loop with an absorption unit coupled to a desorption unit, pure gaseous CO₂ is recovered, and the solvent regenerated. The desorption step impacts the overall costs of the process as heat is needed to reverse the absorption reactions during regeneration. This is the major fraction of the energy consumption of the process (Knuutila et al., 2009). To avoid desorption costs, direct utilization of bicarbonate ions has been proposed as an alternative to gaseous CO₂ recovery.

Hybrid processes based on enzyme and microalgae biocatalysis have been proposed (Dibenedetto et al., 2012; Chi et al., 2011). The present work preliminary develops a new CCU process for the production of carboxylic acids as platform chemicals that may enlarge the spectrum of CO₂-based products other than fuels. The process includes carboxylation of phenolic compounds with bicarbonate ions obtained through CO₂ absorption into a K₂CO₃ solution. The CO₂ reactive absorption is catalysed by carbonic anhydrase (CA) (Russo et al., 2013a). The bicarbonate-rich liquid can react with the phenolic substrates (e.g. catechol, orcinol, resorcinol) and form the corresponding carboxylic acids thanks to the activity of the enzymes hydroxybenzoic acid (de)carboxylase (HBDC) (Glueck et al., 2010). Some studies addressed the recovery of the carboxylic acid through adsorption and precipitation steps (Meyer et al., 2018; Ohde et al., 2021). CO₂ reactive absorption into aqueous solutions is driven by two parallel reactions: hydration reaction and hydroxylation reaction. At pH > 8 hydroxylation rate is higher than hydration rate, but CA is able to catalyze the first reaction. The overall rate of CO₂ absorption is strongly affected by the CA activity and the operating conditions (pH, salts concentration, and temperature) (Russo et al., 2013a; Russo et al., 2018).

In biological equivalent of the Kolbe–Schmitt reaction, a phenolic substrate reacts with a bicarbonate ion and the corresponding phenolic carboxylic acid is formed (Figure 1) (Pesci et al., 2015). HBDC act in the C–C bond-forming direction to provide a more polar and water-soluble carboxylate anion (Brackmann and Fuchs, 1993; Payer et al., 2019) using bicarbonate ion as second substrate.

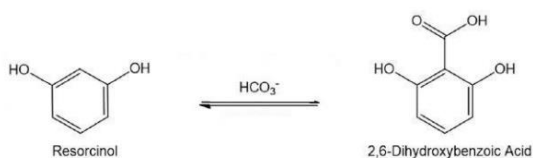


Figure 1: Carboxylation of resorcinol catalysed by 2,6-DHBA decarboxylase from *Rhizobium* sp.

Wuensch et al. [2014] investigated the reaction conditions of resorcinol carboxylation catalyzed by 2,6-dihydroxybenzoic acid (2,6-DHBA) decarboxylases from *Rhizobium* sp. and achieved 50% conversion at optimal conditions. The same enzyme was studied by Pesci et al. [2015] using catechol as substrate, the enzyme mechanism and a kinetic model were proposed. The present theoretical study is aimed at assessing the potential performances of coupled enzymatic process of reactive CO₂ absorption and carboxylation of phenols according to the kinetic models reported in the literature.

2. Theoretical methods

The development of the theoretical model was based on the scheme in Figure 2. Simulation of a pilot unit where CO₂ absorption is promoted by CA was obtained with the software ASPEN PLUS®. The resulting composition of the bicarbonate rich stream, as the outlet of the absorption unit, has been considered as the inlet stream of a carboxylation unit. 1,2-DHB has been considered as substrate for the base case simulation of the carboxylation unit, and 2,6-DHBA decarboxylase as the biocatalyst. The carboxylation unit model has been developed through mass balance equations and equilibrium conditions retrieved from the literature and were solved by WOLFRAM MATHEMATICA® software.

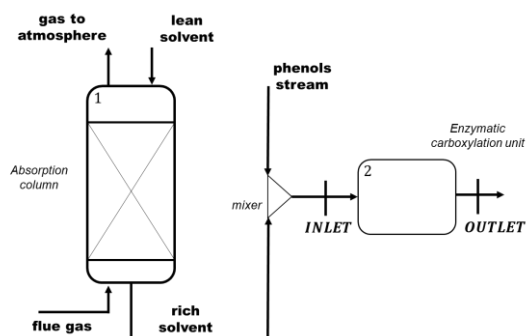


Figure 2: Block diagram of enzymatic CO₂ capture and carboxylation process. 1) Packed column for CO₂ enzymatic absorption; 2) enzymatic carboxylation unit.

The recovery of the product and solvent regeneration is beyond the scope of the study and will be addressed in the future. Further simulations have been obtained for other phenolic substrates (3,5-DHT and 1,3-DHB). The effect of operating conditions on the equilibrium conversion degree has been assessed.

2.1 Modelling of CO₂ absorption unit

Reactive absorption of CO₂ in a K₂CO₃ solution catalyzed by CA has been modelled using ASPEN PLUS® software according to an available base case [Wu et al. 2018]. ASPEN PLUS® settings have been selected to simulate the pilot-scale absorption column: ELECNRTL was used as properties section model, and a rate-based calculation (RADFRAC model) was used in the simulation section. CO₂ hydration and hydroxylation were included in the list of reactions to allow the non-equilibrium calculations of the rate-based simulation. CO₂ hydration was assumed catalyzed by immobilized CA. According to Peirce et al. [2017], the biocatalyst was considered made by CA immobilized on paramagnetic nanoparticles and its kinetics was described by a pseudo-homogeneous model (Eq.s 1-4). The biocatalyst has been assumed confined into the absorption column (e.g. by magnetic field assisted confinement of the biocatalyst particles).

$$r_f = k_f \cdot [CO_2] \quad (1)$$

$$r_b = \frac{k_f}{K_1} \cdot [HCO_3^-] \cdot [H^+] \quad (2)$$

$$k_f = k_E \cdot [CA] \quad (3)$$

$$[CA] = [CA]_{im} \cdot \rho \cdot \varepsilon \quad (4)$$

In the equations [CA]_{im} is the concentration of immobilized CA per unit mass of solid carrier, ε is the solid hold-up in the liquid solvent, ρ is solid density, r_f and r_b are the direct and reverse CO₂ hydration rates, and k_E is the kinetic parameter of immobilized CA according to Peirce et al. (2018). Temperature dependence of the equilibrium constants was described according to ASPEN PLUS® property section. A base case was defined according to the literature (Russo et al., 2013b; Wu et al., 2018). Base case absorption column parameters are listed in Table 1.

Table 1: Selected values of base case parameters.

Flue Gas stream					
Flow Rate	1000	Nm ³ /h	N ₂	0.899	mol/mol
Temperature	60	°C	H ₂ O	0.001	mol/mol
Pressure	1.1	bar	CO ₂	0.1	mol/mol
Lean Solvent stream					
L/G ratio	4	kg/kg	Pressure	1.3	bar
Temperature	25	°C	[K ₂ CO ₃]	3	M
Biocatalyst: immobilized Carbonic Anhydrase					
Solid loading	0.04	kg/kg	Solid hold-up	0.02	
Solid density	5240	kg/m ³	k_E	1460	m ³ /kg s
Column design					
Diameter	0.5	m	Packing Height	10	m
Packing type	MELLAPAK 350Y SULZER		Number of stages	10	

Absorption performances have been calculated as CO₂ removal efficiency from flue gas, bicarbonate concentration in the rich solvent ($[HCO_3^-]_{Rich\ Solvent}$), and fraction of bicarbonate ions formed from CO₂ hydration.

2.2 Modelling of enzymatic carboxylation unit

The carboxylation unit was described assuming an homogeneous system continuously supplied with the liquid solvent from the absorption column (components concentrations $[CO_3^{2-}]_{IN}$, $[HCO_3^-]_{IN}$, $[CO_2]_{IN}$, $[HCO_3^-]_{IN}$, $[K^+]_{IN}$) and the phenolic substrate ($[Ar]_{IN}$). The carboxylation reaction ideally occurs up to the equilibrium conversion (Figure 1). The composition of the outlet liquid from the carboxylation unit has been calculated in terms of the concentrations of the relevant species ($[K^+]_{OUT}$, $[H^+]_{OUT}$, $[OH^-]_{OUT}$, $[HCO_3^-]_{OUT}$, $[A^-]_{OUT}$, $[CO_2]_{OUT}$, $[Ar]_{OUT}$, $[HA]_{OUT}$) according to the following

equations: conservation of the potassium ions condition (Eq. 5); electroneutrality condition among ionic species in the outlet stream (Eq. 6); equilibrium of water dissociation (Eq. 7); equilibrium of first and second carbonic acid dissociations (Eq. 8-9); mass balance of dissolved inorganic carbon (Eq. 10); equilibrium of the carboxylation reaction (Eq. 11) [Pesci et al., 2015]; equilibrium of carboxylic acid dissociation (Eq. 12); stoichiometry of the carboxylation reaction (Eq. 13).

$$[K^+]_{IN} = [K^+]_{OUT} \quad (5)$$

$$[H^+]_{OUT} + [K^+]_{OUT} - [OH^-]_{OUT} - [HCO_3^-]_{OUT} - 2 \cdot [CO_3^{2-}]_{OUT} - [A^-]_{OUT} = 0 \quad (6)$$

$$K_w = [H^+]_{OUT} \cdot [OH^-]_{OUT} \quad (7)$$

$$K_1 = \frac{[HCO_3^-]_{OUT} \cdot [H^+]_{OUT}}{[CO_2]_{OUT}} \quad (8)$$

$$K_2 = \frac{[CO_3^{2-}]_{OUT} \cdot [H^+]_{OUT}}{[HCO_3^-]_{OUT}} \quad (9)$$

$$[CO_3^{2-}]_{IN} + [HCO_3^-]_{IN} + [CO_2]_{IN} = [CO_3^{2-}]_{OUT} + [HCO_3^-]_{OUT} + [CO_2]_{OUT} + [A^-]_{OUT} + [HA]_{OUT} \quad (10)$$

$$K_A = \frac{[A^-]_{OUT} \cdot [H^+]_{OUT}}{[HA]_{OUT}} \quad (11)$$

$$K_{Carboxy} = \frac{[A]_{OUT}}{[Ar]_{OUT} \cdot [HCO_3^-]_{OUT}} \quad (12)$$

$$[Ar]_{IN} = [Ar]_{OUT} + [A^-]_{OUT} + [HA]_{OUT} \quad (13)$$

The inlet stream composition and properties have been fixed according to the results of ASPEN PLUS® simulation of the CO₂ absorption column. Eq.s 5-13 has been solved using WOLFRAM MATHEMATICA® 12 software by setting chemical and physical parameters as in section 2.3., results yielded the concentrations of all the considered species.

2.3 Chemical and physical data

Carboxylation equilibrium constants and the dissociation constant for DHBA have been fixed according to the literature and values are listed in table 4. In the base case simulations, inlet 1,2 DHB concentration was fixed between 0.03 and 0.08 M according to the solubility limits and tests reported in the literature [Pesci et al., 2015]. Sensitivity analysis of phenolic substrates has been performed at 0.05 M 1,2 DHB.

Table 2: Values of equilibrium constants for enzymatic carboxylation of 1,2-DHB, 3,5-DHT and 1,3 DHB and dissociation equilibrium constant of 2,3-dihydroxybenzoic acid.

Equilibrium Constant	Value [mM ⁻¹]	Ref.
$K_{Carboxy,1,2-DHB}$	$1.60 \cdot 10^{-4}$	Pesci et al. 2015
$K_{Carboxy,3,5-DHT}$	$5.00 \cdot 10^{-4}$	Meyer et al. 2018
$K_{Carboxy,1,3-DHB}$	$5.83 \cdot 10^{-4}$	Ohde et al. 2020
$K_{A,DHBA}$	$5.00 \cdot 10^{-2}$	Pesci et al. 2015

3. Results

3.1 Base-case simulations

The base case simulation referred to the use of 1,2 DHB as substrate. Results of the simulations of the CO₂ reactive absorption unit and enzymatic carboxylation unit are reported in Table 3. Sensitivity analysis of the base case was performed by calculation of equilibrium concentrations in the liquid stream after enzymatic carboxylation at three initial catechol concentrations: 0.03, 0.05 and 0.08 M. Results show that inlet 1,2 DHB concentration slightly affects the equilibrium conversion degree in the enzymatic carboxylation unit. Similarly, due to 1:1 stoichiometry and the large bicarbonate excess, also outlet bicarbonate concentration does not change substantially. Since typical concentration of bicarbonate ions in rich solvent streams are large enough to support enzymatic carboxylation, further sensitivity analysis has been considered.

Table 3: Simulation results for CO₂ enzymatic absorption and 1,2 DHB enzymatic carboxylation according to methods reported in section 2.

CO ₂ enzymatic absorption unit			
Mass of captured CO ₂	129.8	kg/hr	
CO ₂ removal efficiency	74.2	%	
HCO ₃ ⁻ Rich Solvent	1.643	M	
Fraction of bicarbonate from CO ₂	49	%	
pH Rich Solvent	9.75		
Enzymatic carboxylation unit			
	Initial 1,2-DHB concentration, M		
	0.03	0.05	0.08
1,2 DHB conversion degree, %	20.8	20.8	20.7
[A ⁻] _{OUT} , M	0.0062	0.0104	0.0165
[HA] _{OUT} , M	7.6 10 ⁻¹²	1.3 10 ⁻¹¹	2.0 10 ⁻¹¹
[HCO ₃ ⁻] _{OUT} , M	1.641	1.637	1.630

3.2 Sensitivity analysis of reactants concentrations.

Bicarbonate concentration can affect the equilibrium conversion of the enzymatic carboxylation. Results of simulations carried out at bicarbonate concentrations between 0.5 and 3 M are reported in Figure 3 in terms of phenols conversion degree for each considered substrate.

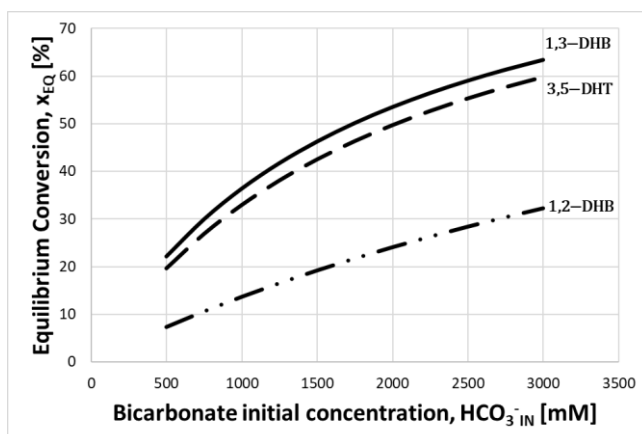


Figure 3: Equilibrium conversion degree against bicarbonate inlet concentration calculated according to eq. 17-18 and equilibrium constants in table 2. Phenols inlet concentrations set at 50 mM.

Results show that 3,5-DHT and 1,3-DHB achieved the largest equilibrium conversion due to the higher carboxylation equilibrium constants. Further sensitivity analysis of phenolics inlet concentration provided negligible effect on the equilibrium conversion in agreement with the results of the base case simulations (not reported).

4. Conclusions

A novel potential carbon capture and utilization process has been investigated. Preliminary process layout assessment has shown the opportunity of coupling CO₂ absorption by K₂CO₃ solutions with enzymatic carboxylation of phenols to carboxylic acids. Two major issues have been pointed out by simulation results. Bicarbonate concentration larger than 1.8 M is required to boost the carboxylation conversion towards the desired products, to this purpose the absorption unit should be designed to meet the bicarbonate demand in the rich stream. According to carboxylation equilibrium, 1,2-DHB shows the lower theoretical conversion among the selected substrates, while 1,3-DHB reaches more than 50% equilibrium conversion when

bicarbonate concentration is 2 M. Phenols concentration does not affect noticeably equilibrium conversion but fixes the amount of CO₂ converted into organic acids. For this reason, the solubility limit is the second key issue to improve carbon utilization and make it feasible along this biocatalytic route. Further investigations are envisaged to overcome phenols concentration limit (e.g. solvent composition, *in situ* acid separation) as well as *ad hoc* designed continuous carboxylation reactors configuration to maximize phenols conversion. The latter point asks for careful development of biocatalyst made by immobilized carboxylases.

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