

The chemistry of resorcinol carboxylation and its possible application to the CO₂ removal from exhaust gases



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ABSTRACT

The carbon dioxide uptake by resorcinol solutions has been investigated under different operational procedures and experimental conditions. Batch experiments have been carried out in aqueous and glycerol–water solutions of KOH, KHCO₃ or K₂CO₃, and the yield of resorcinol carbonatation has been investigated as a function of the CO₂ partial pressure as well as reaction temperature and time. The β-resorcylic acid (2,4-dihydroxy benzoic acid) has been isolated in the solid state and identified on the basis of its IR spectrum. The ¹³C NMR analysis has been applied to identify and quantify the carbonated species in solution upon CO₂ uptake and after thermal resorcinol regeneration. The maximum yield of resorcinol conversion into β-resorcylic acid was 60% with 1.0 bar of CO₂ and 120 min reaction time at 110 °C. A 34% yield of resorcinol conversion was also obtained with the resorcinol/K₂CO₃ solution in the absence of CO₂. A relationship between the CO₂ absorption capacity and the possible mechanism of CO₂ capture has been proposed. The CO₂ absorption efficiency from a simulated flue gases (15% CO₂ in air) has been measured in continuous cycles of CO₂ absorption–desorption carried out in packed columns and with a glycerol–water solution of resorcinol/KOH/KHCO₃. The maximum absorption efficiency was 82% at absorption–desorption temperatures of 70 °C and, respectively, 170 °C. Oxidative conditions and the presence of H₂S did not affect the yield of β-resorcylic acid and the resorcinol capacity of CO₂ capture. Finally, a simple method for the selective separation of H₂S from CO₂ has been reported.

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1. Introduction

The Kolbe–Schmitt method is still the standard protocol for the preparation of a variety of aromatic carboxylic acids starting from phenol, sodium hydroxide and pressurized CO₂ at high temperatures [1]. With the much more reactive resorcinol (1,3-dihydroxy benzene) the insertion of CO₂ into the aromatic ring has been reported to occur in refluxing aqueous potassium bicarbonate and CO₂ at atmospheric pressure affording the β-resorcylic acid (2,4-dihydroxy benzoic acid) [2]. Moreover, the carboxylation reaction of resorcinol was reported to be reversible [3]. The β-resorcylic acid is a useful intermediate for the industrial production of pharmaceuticals, cosmetic preparations, reprographic materials, dyestuffs and fine chemicals, and experimental studies have been

recently addressed to improve the production of the β-resorcylic acid [4].

The development of processes based on the CO₂ fixation as a C1 building block in organic synthesis, is of paramount importance in view of both environmental and industrial objectives.

Aimed at investigating new protocols for the CO₂ removal from industrial exhaust streams, our previous experimental studies have been addressed to a new approach to the CO₂ capture technique which combines the production of valuable chemicals with an efficient CO₂ abatement [5].

The CO₂ capture by aqueous alkanolamines is considered a feasible technology for CO₂ separation from flue gases [6]. However, the high operating costs associated to the thermal regeneration of the amine-based absorbents [7], the environmental concerns because of the amine loss by evaporation and degradation [8] are the major hurdles to the extensive application of this methodology to large scale CO₂ capture. On the contrary, the conversion of carbon dioxide into useful chemicals should circumvent the environmental problems and the energy intensive processes of amine regeneration, CO₂ compression, transportation and disposal.

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In this paper we report the results of the experimental studies addressed to investigate the chemistry and the efficiency of the CO₂ reaction with resorcinol in different operational conditions. Most of the experiments were performed by using solutions of resorcinol 2.0 mol dm⁻³ and either single KOH, KHCO₃, K₂CO₃ or their mixtures in a mixture of glycerol (1,2,3-propantriol) and water 1:1 (v/v) and CO₂ 100%, 15% or 12% (v/v). The choice of the solvent was dictated by two main constraints: (i) solubility in water of both the reagents and the products, otherwise a mixture of the potassium salts of the carbonated compounds would crystallize; (ii) the high temperatures of the experiments up to 170 °C required the high boiling temperature of glycerol.

We have designed two different experimental procedures: (i) batch experiments of CO₂ absorption as a function of the different experimental conditions in order to investigate the chemistry of resorcinol carbonatation and to maximize the conversion efficiency into β-resorcylic acid; (ii) continuous cycles of simultaneous CO₂ absorption and resorcinol regeneration aimed at exploiting the CO₂ absorption efficiency from a simulated flue gases.

The CO₂/resorcinol equilibria were analyzed by ¹³C NMR spectroscopy which enabled us to identify and quantify the carbonated species in solution originated from resorcinol carbonatation. The capacity of CO₂ uptake by resorcinol upon oxidation and in the presence of H₂S was also investigated.

As a contribution to that way, an ENEA patented process [9] based on the reaction of resorcinol with carbon dioxide in alkaline solution has been recently filed out. Lower vapor pressure, higher flash point and low toxicity respect to the alkanolamines, could make this absorbent system suitable for a safer CO₂ capture.

2. Experimental

2.1. General information

All reagents were reagent grade. Resorcinol, β-resorcylic acid, glycerol, KOH, KHCO₃, K₂CO₃ and Na₂S·9H₂O (Sigma–Aldrich) were used as received without further purification. Pure CO₂, 12% CO₂ in N₂, 15% CO₂ in air and 50 ppm H₂S in air (Rivoira Spa) were used to simulate flue gas. Flow rates of the gases were measured with gas mass flow meters (Aalborg) equipped with gas controllers (Cole Parmer). The inlet and outlet CO₂ concentrations in the flue gas mixtures were measured with a Varian CP-4900 gas chromatograph calibrated with a 10% v/v CO₂/N₂ reference gas (Rivoira Spa).

The batch experiments under pressure were carried out in a stainless steel Parr reactor Mod. 4560 (the volume of the reactor is 0.450 dm³) equipped with a pressure gauge and a thermocouple. The reactor was charged with 0.100 dm³ of water which was degassed with N₂ before the dissolution of KOH and resorcinol. The concentration of resorcinol was fixed at 3.00 mol dm⁻³ with the KOH/resorcinol molar ratio 1.5. After the dissolution was completed, the temperature of the reactor was raised to the set value comprised between 80 and 120 °C and the CO₂ gas (95% in N₂) was continuously injected into the solution at the partial pressure of CO₂ of either 1.0 bar or 3.0 bar. At the end each absorption experiment that lasted between 30 and 140 min, the reaction product was precipitated with hydrochloric acid, separated from the solution by filtration and purified by recrystallization. IR spectroscopy (VARIAN FTIR-1000) was used to identify the species in the reaction mixture.

In the batch experiments carried out at room pressure in a glycerol–water mixture, the absorber was a home-built glass cylinder with a diameter of 56 mm and a height of 300 mm fitted with a sintered gas diffuser (16–40 μm). The absorber was charged with 0.100 dm³ of 2.0 mol dm⁻³ resorcinol solution in a 1/1 (v/v) glycerol/water mixture. KOH, KHCO₃ or K₂CO₃ were used separately with a resorcinol/base molar ratio in the range

1/1–1/2. The absorber temperature was maintained at the appropriate value (90–170 °C) either with a thermostatted bath (Julabo model F33 MC) or a silicone oil bath. Pure CO₂ or a gas mixture containing 12% (v/v) CO₂ in N₂ at 1.0 bar flowed continuously through the gas diffuser at the bottom of the absorber at a flow rate of 14 dm³ h⁻¹. The release of pure CO₂ during the desorption processes was followed using a gastight apparatus which comprises a 0.250 dm³ conical flask containing the CO₂-loaded solutions obtained during the absorption steps. The solution was stirred with a magnetic stirrer to accelerate the CO₂ release and was maintained at 150 °C by means of a silicone oil bath. The conical flask was equipped with two condensers cooled at room temperature and connected to two 0.250 dm³ gas-burettes equipped with pressure-equalising device. Both burettes and pressure-equalising devices are filled with CO₂ saturated water. By means of three way valves, one buret is filled with CO₂ while the other is emptied, thus allowing continuous collection of the gas. The buret internal gas pressure was continuously equilibrated with the external one. The accuracy of the overall volume measurements was ± 5 × 10⁻³ dm³.

In order to test the carboxylation efficiency of the oxidized resorcinol, pure CO₂ and air were alternatively introduced into the alkaline solution heated at 130 °C. Each flux lasted 1 h and was repeated four times.

The apparatus used for continuous absorption-desorption cycles consists of the absorber and the desorber units connected to each other by means of a double head peristaltic pump (Masterflex), which allows the solutions to circulate continuously in a closed loop between the absorber and the desorber at the flow rate of 0.300 dm³ h⁻¹. The absorber is a home-built glass cylinder with the internal diameter of 56 mm and height 400 mm, equipped with a jacket and packed with glass rings (diameter 5 mm). The temperature of the absorber (70–110 °C) was maintained at the appropriate value by circulating a thermostatted liquid (Julabo model F33-MC bath) through the jacket. The absorber was designed to operate in a counter current mode: the regenerated absorbent was introduced from the top of the packed column while the gas mixture was continuously injected at the bottom of the column below the packing. The carbonated absorbent exited at the bottom of the column and sent to the top of the desorber. The desorption of CO₂ and the resorcinol regeneration were performed in a 0.500 dm³ flask where the solution was stirred with a magnetic stirring to accelerate the CO₂ release and was maintained at 170 °C using a thermostatted silicone oil bath. Both absorber and desorber were equipped with a water cooled condenser to reflux the possible overhead vapor. The entire apparatus was charged with 0.400 dm³ of the alkaline resorcinol solution. The gas mixture (15% CO₂ in air) was continuously fed into the bottom of the absorber with a flow rate of 12.2 dm³ h⁻¹ (0.0750 mol of CO₂ at 24 °C). The vent gas exited from the top of the absorber. The outlet gas was purified before being analyzed by the gas chromatograph. A complete cyclic experiment lasted 24–36 h and it was stopped when the reactions of CO₂ capture and resorcinol regeneration were equilibrated to each other. In the experiments aimed at separating H₂S from CO₂, a gas stream containing 50 ppm H₂S was employed. Another set of H₂S capture experiments was carried out with the solution charged with 5.00 g of Na₂S·9H₂O (2.08 × 10⁻² mol). The selective removal of H₂S was accomplished subsequently to the CO₂–H₂S stripping by flowing the gas mixture through a H₂O₂ aqueous solution either 0.10 or 0.65 mol dm⁻³. The precipitation of CaSO₄ was accomplished in a separate vessel with the stoichiometric amount of CaO. The unreacted H₂O₂ solution was recycled to the H₂S absorber. To check the efficiency of H₂S removal, the CO₂ stream exited from the H₂S absorber was bubbled through an aqueous solution of Cu(II). No CuS precipitation was detected in all of the experiments.

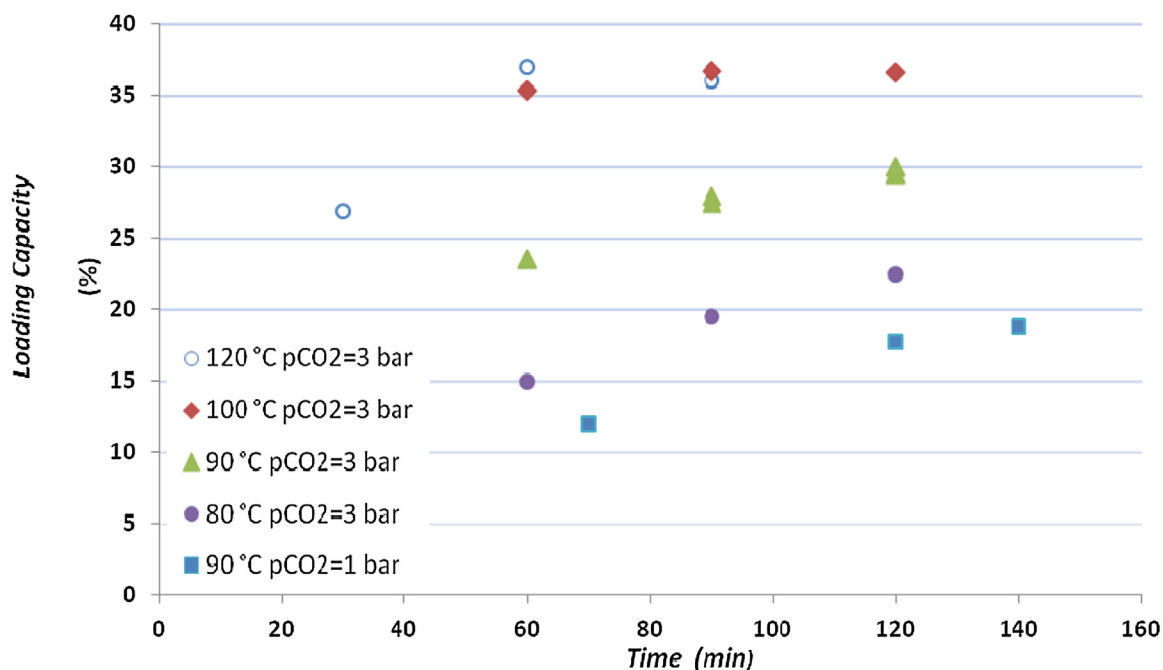


Fig. 1. CO₂ loading capacity of aqueous resorcinol as a function of absorption temperature, time and pressure.

2.2. ¹³C NMR spectroscopy

The ¹³C NMR spectra of the solutions were obtained with a Bruker AvanceIII 400 spectrometer operating at 100.61271 MHz. Chemical shifts are to high frequency relative to tetramethylsilane as external standard at 0.00 ppm. CH₃CN was used as internal reference (CH₃, δ = 1.47). To provide enough signal for deuterium lock, D₂O (Aldrich) contained in a sealed glass capillary was introduced into the NMR tubes containing the resorcinol solutions. The standard pulse sequence with proton decoupling and NOE suppression was used to acquire the ¹³C{¹H} with the following acquisition parameters: pulse angle = 90.0°, at = 1.3632 s, dl = 0 s, data points = 65 K, ns = 500–2 × 10³. Increasing the acquisition time and/or the relaxation delay (up to 60 s) does not produce substantial changes in the relative peak areas of the carbon atoms that contain the same number of attached protons. The ¹³C atoms of –CO₂[–], –COH and –CCO₂[–] functionalities have no attached hydrogen and exhibit much higher relaxation times than those of the –CH– groups, thus resulting in lower intensity resonances. The integration of the carbon resonances of the –CH carbons of aromatic ring is an estimation (5% deviation) of the relative amounts of the two species, resorcinol and deprotonated β-resorcylic acid.

3. Results and discussion

3.1. Batch experiments of CO₂ absorption in a Parr reactor under pressure

The CO₂ loading capacity of resorcinol (CO_{2(adsorbed)}/resorcinol_(starting) % on molar scale) was initially tested in water solutions under pressure in a Parr reactor. The resorcinol concentration was 3.0 mol dm^{–3} and potassium hydroxide was the base with the KOH/resorcinol molar ratio 1.5.

Before their use, the aqueous solutions were bubbled with nitrogen to remove the oxygen content. The Parr reactor was charged with 0.100 dm³ of each solution and the 95% (v/v) CO₂ in N₂ was continuously injected at a partial pressure of either 3.0 bar or 1.0 bar at a flow rate of 0.200 dm³ min^{–1}. After each CO₂ uptake

was complete (30–140 min), the reaction product was recovered in the solid state with aqueous hydrochloric acid, separated from the solution by filtration and purified by recrystallization. The amount of CO₂ absorbed by resorcinol was evaluated by gravimetry from the weight of the carbonated compound.

The results of CO₂ absorption at different reaction times and temperatures are reported in Fig. 1. In general, the loading capacity at 3.0 bar, comprised between 15% and 37%, increased with temperature and reaction time because of the increased reaction rate that overcome the thermodynamic requirements of the exothermic reaction of CO₂ with resorcinol. At 100 °C the equilibrium of the reaction was reached after 90 min and no appreciable increasing of loading capacity occurred at 120 °C and 120 min. As expected, the loading capacity decreased by decreasing the partial pressure of CO₂ from 3.0 bar to 1.0 bar because of the decreased reaction rate and of the left hand shift of the equilibrium.

IR spectroscopy was used to identify the carbonated species separated from the reaction mixture as the 2,4-dihydroxybenzoic acid (β-resorcylic acid). The IR spectra of authentic β-resorcylic acid and of a sample product recovered from the carbonated resorcinol after acidification are quite similar, as reported in Fig. 2. For a detailed assignment of the peaks, dedicated paper are available [10,11]. Presumably, the short time of reaction and the low temperatures, hindered the formation of the γ-isomer, and the IR spectra show only the β-resorcylic acid signals.

3.2. Batch experiments of CO₂ absorption and desorption in glycerol/water mixtures at room pressure

The experiments of CO₂ capture were performed with a 2.0 mol dm^{–3} solution of resorcinol in a 1/1 (v/v) glycerol/water mixture that combines a high boiling temperature of the absorbent with the solubility of both the reagents and the carbonated species. The bases employed were, separately, KOH, KHCO₃ or K₂CO₃ with a base/resorcinol molar ratio 1, 1.5, 2. The absorbents were maintained at the appropriate temperature with a thermostatted bath. Pure CO₂ at 1.0 bar flowed through a gas diffuser at the

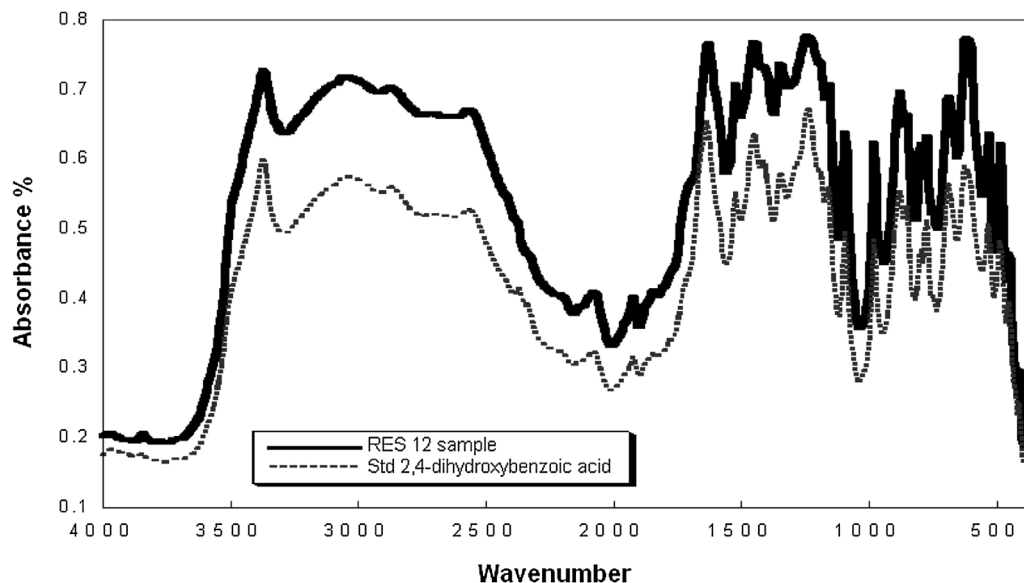
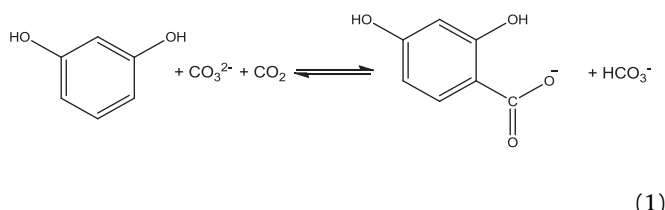


Fig. 2. IR spectrum of a sample (RES 12) of β -resorcylic acid, solid line, and a β -resorcylic acid reference standard, dotted line.

bottom of the absorber charged with 0.100 dm³ of the alkaline resorcinol solution.

The exothermic reaction of resorcinol with CO₂ in alkaline solution [in Eq. (1) the base is K₂CO₃] is slow at room temperature and, consequently, the reactions were performed at temperatures in the range 90–140 °C



The results of the reaction (1) at 90 °C with the different bases as a function of resorcinol/base molar ratio and reaction time are reported in Table 1. For the sake of simplicity, through the text β -resorcylic acid stands for the equilibrating protonated and deprotonated β -resorcylic acid.

The carbonated species in solution were analyzed by means of ¹³C NMR spectroscopy that allowed us to identify and quantify the species in equilibrium at the end of the CO₂ uptake and release. The

Table 1

Yield of resorcinol conversion into β -resorcylic acid in the absorption step (1.0 bar of CO₂; 90 °C) with the different bases; percentage of β -resorcylic acid (Res-CO₂⁻) that was left in solution after desorption (150 °C), as a function of the base/resorcinol ratio and of the reaction time. The resorcinol concentration was 2.0 mol dm⁻³ and the percentages are referred to the starting resorcinol.

Base	Base/Res ^a molar ratio	Convers. % absorption ^b			% Res-CO ₂ ⁻ desorption ^c		
		1 h	2 h	3 h	1 h	2 h	3 h
KOH	1	16	23	29	16	6	4
	1.5	12	24	31	18	14	12
K ₂ CO ₃	1	9	26	38	28	20	17
	1.5	37	50	57	40	33	27
	2	40	49	56	48	43	42
KHCO ₃	1	3.6	8.5	16	16	11	9
	1.5	8	22	35	30	20	16
	2	11	28	41	36	25	21

^a Molar ratio between the base and resorcinol.

^b Percentage of resorcinol conversion at the end of each hour.

^c Percentage of β -resorcylic acid at each desorption step.

¹³C NMR spectra are simple displaying resonances in the range 172–105 ppm easily ascribed to the carbon atoms of the aromatic ring of both resorcinol and β -resorcylic acid. The low-intensity resonance at about 176 ppm was assigned to the fast exchanging –CO₂⁻/CO₂H. of both protonated and deprotonated β -resorcylic acid that are fast exchanging on NMR scale. To complete the ¹³C NMR picture the two resonances at 72.09 and 63.53 ppm were ascribed to the carbon atoms of glycerol backbone and the resonance in the range 161–165 ppm to the fast exchanging CO₃²⁻/HCO₃⁻. No other product was detected in the NMR spectra, and no appreciable amount of either γ -resorcylic acid (2,6-dihydroxy benzoic acid) or glycerol carbonate was found. In particular, the R-OCO₂⁻ resonance of the glycerol carbonate expected at 159 ppm [12] was not detected. As an example, the spectrum of CO₂ saturated solution of 1.5 K₂CO₃/resorcinol is reported in Fig. 3.

The relative amounts of unreacted resorcinol and β -resorcylic acid have been confidently determined by careful integration of the C(3) corresponding signals (see inset of Fig. 3 for carbon numbering) in the range 130–132 ppm. These carbon atoms have the same number of hydrogen directly attached and similar chemical environmental, so that they likely exhibit similar T₁ relaxation times [13].

Although some uncertainty in comparing the different integrals is unavoidable (estimated error 5%), nonetheless the method is certainly reliable and provides an estimation of the concentration changes of the carbonated species in solution. This method has been previously and successfully applied to the speciation of aqueous and non-aqueous carbonated amines [14]. The efficiency of the resorcinol carboxylation increased in the order K₂CO₃ > KHCO₃ ≈ KOH, with increasing the base/resorcinol ratio and reaction time. The decarboxylation reaction was carried out at 150 °C and its efficiency had an opposite feature with respect to that of the forward reaction (1) (except with time, obviously). As an example, the K₂CO₃/resorcinol molar ratio 1.5 and 2 gave a similar concentration of β -resorcylic acid but the decarboxylation of the solution with 2 ratio is neatly less efficient as the increased base/resorcinol ratio sets an unavoidable limit to the decarboxylation equilibrium (see Section 3.3). Some experiments of resorcinol carboxylation were performed with K₂CO₃/resorcinol molar ratio greater than 2 (up to 6), but it was necessary to reduce the resorcinol concentration to 1.0 mol dm⁻³ (molar ratio 3) and 0.50 mol dm⁻³ (molar ratio 6), to avoid the formation of solid KHCO₃ during the CO₂ uptake. In spite of the lower resorcinol concentration, the K₂CO₃/resorcinol molar ratio 6 gave a 75%

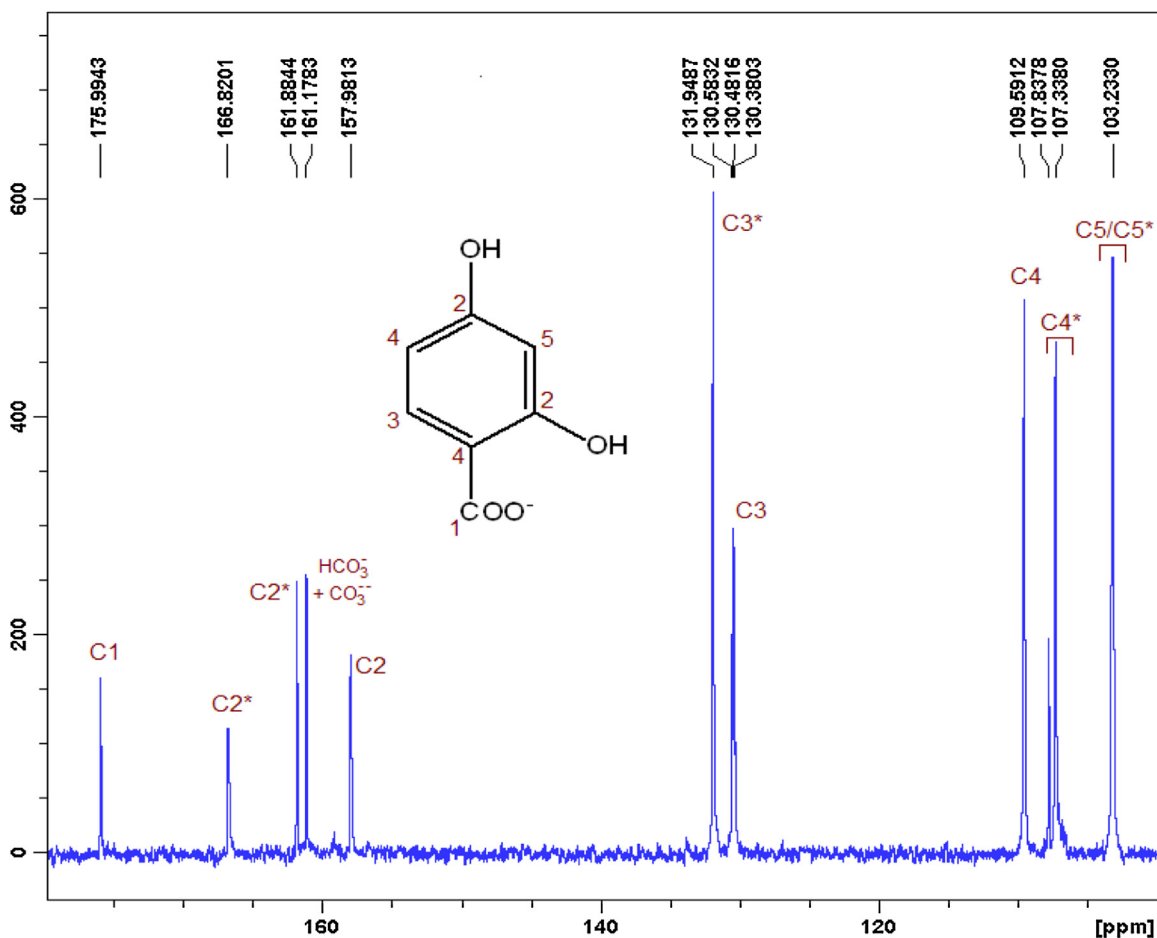


Fig. 3. ¹³C NMR spectrum of the CO₂ saturated (3 h) solution of resorcinol/K₂CO₃ 1/1.5 molar ratio. The asterisks denote the chemical shifts of the ring carbons of the fast exchanging protonated and deprotonated β-resorcylic acid. The assignment refers to the arbitrary numbering of the ring carbon atoms in the inset. HCO₃⁻ + CO₃²⁻ indicates the resonance of the carbon atoms the two fast exchanging species; the resonances of the carbon atoms of glycerol backbone were omitted.

conversion after 3 h of CO₂ uptake at 130 °C, but at the cost of a lower amount of β-resorcylic acid.

The efficiency of resorcinol carboxylation as a function of temperature in the range 90–140 °C with the decarboxylation carried out at 150 °C was measured in the systems K₂CO₃/

Table 2

Percentages of resorcinol conversion into β-resorcylic acid formed in the absorption step (90–140 °C; 1.0 bar of CO₂) and of residual β-resorcylic acid (Res-CO₂⁻) after desorption (150 °C) as a function of the absorption temperature and the reaction time. The resorcinol concentration was 2.0 mol dm⁻³ and the base/resorcinol molar ratio was fixed at 1.5.

Base	T _{abs} (°C)	T _{des} (°C)	Convers. % absorption ^a			% Res-CO ₂ ⁻ desorption ^b		
			1 h	2 h	3 h	1 h	2 h	3 h
K ₂ CO ₃	90	150	37	50	57	40	33	27
	100	150	37	49	58	50	37	32
	110	150	54	60	61	46	37	35
	120	150	57	58	60	48	37	31
	130	150	58	60	59	39	27	24
	140	150	57	56	57	37	29	26
KHCO ₃	90	150	8	22	35	30	20	16
	100	150	12	34	44	24	19	15
	110	150	26	43	45	27	19	15
	120	150	35	43	45	27	18	14
	130	150	40	40	40	28	19	15
	140	150	41	42	40	27	18	15

^a Percentage of resorcinol conversion at each one hour step.

^b Percentage of residual β-resorcylic acid at each desorption step.

resorcinol and KHCO₃/resorcinol 1.5. The results are reported in Table 2. Once again, the carboxylation efficiency in the presence of K₂CO₃ is higher than that of KHCO₃, for any reaction time and temperature.

The increasing yield of β-resorcylic acid with reaction temperature and time indicates that the kinetic constraints of reaction (1) prevail over the thermodynamic ones at temperatures up to 120–130 °C. In this connection, 58% of β-resorcylic acid was obtained by flowing CO₂ into the resorcinol/K₂CO₃ solution either at 100 °C for 3 h or at 130 °C for 1 h. The reaction rate at 140 °C was sufficient to reach the equilibrium in one hour and the percentage of the carboxylic acid did not substantially change with reaction time.

The decreased carboxylation efficiency of resorcinol/K₂CO₃ from 61% to 57% after 3 h by increasing the temperature from 110 to 140 °C, was due to the decreasing equilibrium constant of the exothermic reaction (1). The results referred to the resorcinol/K₂CO₃ solution are reported in Fig. 4. The figure clearly shows the kinetic constraints of the carboxylation reaction at the lower temperatures (90 and 100 °C) that required more time to attain nearly the same efficiency of the reactions performed at higher temperatures.

For comparison purposes with the above mentioned results obtained with 100% CO, the carboxylation efficiency was also investigated either with CO₂ 12% (N₂ for balance) or in the absence of CO₂. The experiments were performed with resorcinol 2.0 mol dm⁻³, base/resorcinol molar ratio 1.5 (base, K₂CO₃ or KHCO₃). The absorption temperature was set at 90, 130 and 170 °C

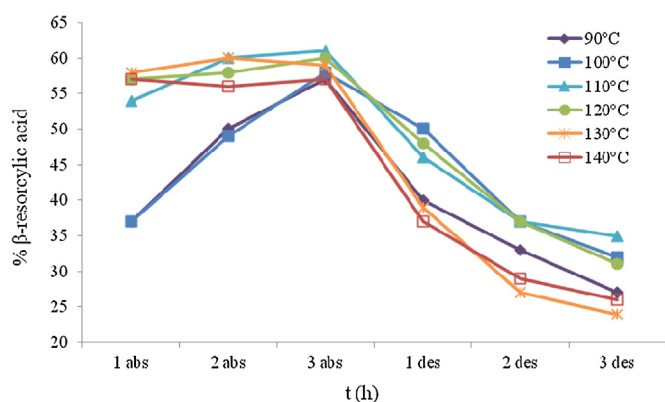


Fig. 4. Yield of resorcinol conversion into β -resorcylic acid (percentage in mol) at each absorption step (abs; 90–140 °C; 1.0 bar of CO₂) and percentage of residual β -resorcylic acid in the desorption steps (des) at 150 °C. Absorption and desorption steps are in hours. The resorcinol concentration was 2.0 mol dm⁻³ and the K₂CO₃/resorcinol molar ratio was 1.5.

and reaction time 1–5 h. The results are reported in Tables 3 and 4 and Figs 5 and 6.

As expected, the carboxylation efficiency increased with the increased CO₂ concentration (Table 3), but the β -resorcylic acid was obtained even in the absence of CO₂. Experiments in the absence of CO₂ were carried out at a fixed temperature as a function of heating time (Table 4) and at a fixed time as a function of the temperature.

The carboxylation efficiency at 90 °C increased with time (Fig. 5) because of the low reaction rate that required more than 3 h for the equilibrium to be reached. At 130 °C the reaction is fast and the equilibrium was reached within 1 h. By further increasing the reaction time, the decarboxylation overcomes the carboxylation and the yield of β -resorcylic acid progressively decreased by emitting CO₂. The results of the carboxylation experiments in the absence of CO₂ with increasing the temperature, the heating time being fixed at 1 h, are reported in Fig. 6. Between 90 and 130 °C the increased rate of carboxylation reaction prevailed over the exothermic equilibrium. At temperatures over 130 °C the equilibrium became increasingly left hand shifted, the percentage of β -resorcylic acid decreased and CO₂ was evolved. Notwithstanding, it should be noticed that about 27% of β -resorcylic acid occurred in the resorcinol/K₂CO₃ solution heated at 170 °C.

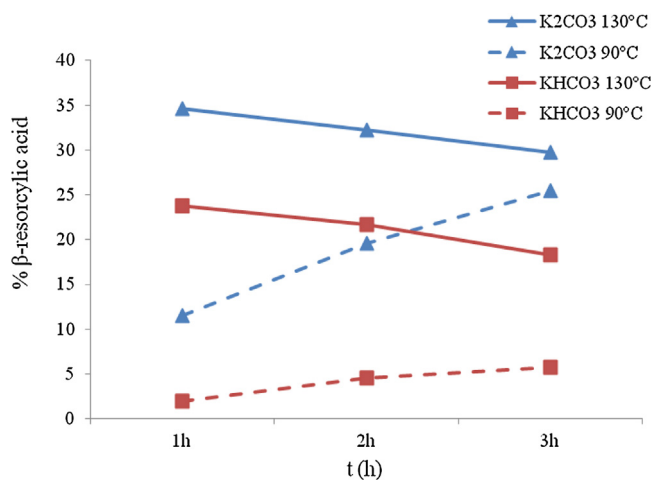


Fig. 5. Resorcinol conversion into β -resorcylic acid (percentage in mol) as a function of heating time at 90 and 130 °C in the absence of CO₂. Resorcinol concentration 2.0 mol dm⁻³, K₂CO₃/resorcinol and KHCO₃ resorcinol molar ratio 1.5.

Table 3

Carboxylation efficiency at 130 °C (3 h heating) as a function of CO₂ concentration. Base/resorcinol 1/1.5.

Base	% CO ₂		
	100 ^a	12	0
	Conversion %		
K ₂ CO ₃	59	45	29
KHCO ₃	40	34	20

^a Values from Table 2.

Table 4

Carboxylation efficiency at 130 °C as a function of the heating time in the absence of CO₂. Base/resorcinol 1/1.5.

Time (h)	Conversion %				
	1	2	3	4	5
	Conversion %				
K ₂ CO ₃	34	32	30	28	25
KHCO ₃	24	22	19	16	14

3.3. The proposed mechanism of resorcinol carboxylation by K₂CO₃ in the absence of CO₂

On the basis of the results previously reported, in particular those obtained with K₂CO₃ in the absence of CO₂, the following pathway of resorcinol carboxylation seems the most plausible, and was reinforced by further experiments (see later).

The CO₂ introduction into the aromatic ring was initiated by the resorcinol deprotonation [in Eq. (2) Res stands for the neutral resorcinol]



At 90–130 °C the decomposition of HCO₃⁻ occurred

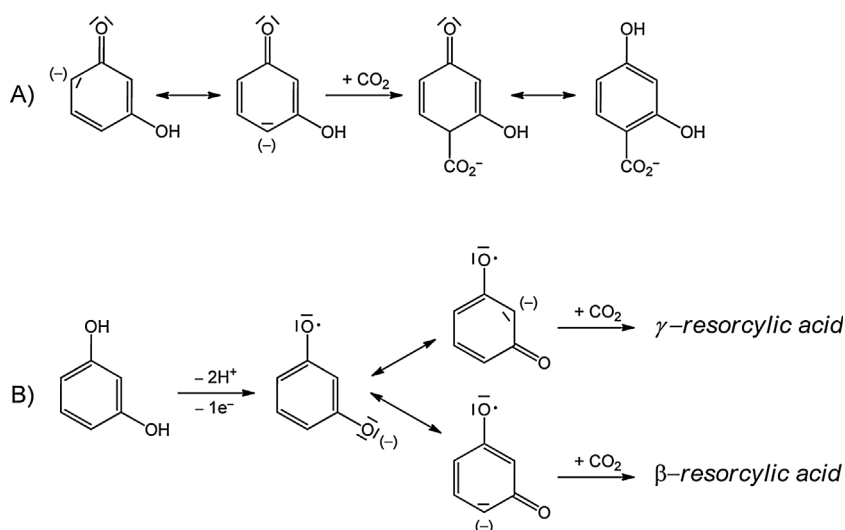


Once formed, CO₂ (at least in part) reacted with deprotonated resorcinol



The reaction (3) is endothermic and is favored by the increasing temperature that has an opposite effect on the exothermic equilibrium (4), even if its rate is increased. When the amount of CO₂ formed by reaction (3) overcomes that consumed by the carboxylation reaction (4), the unreacted CO₂ exited from the solution. The overall efficiency of resorcinol carboxylation is a subtle balance of the temperature as high as possible to produce both the maximum amount of CO₂ from the reaction (3) and to enhance the rate of the reaction (4), and the reaction equilibrium (4) which becomes increasingly left hand shifted with increasing the temperature. The heating time too gives an important contribution to the carboxylation yield, mainly at the lower temperatures investigated. In summary, the best compromise between the thermodynamic and kinetic constraints accounts for the maximum efficiency of resorcinol carboxylation. According to proposed pathway, the reacting species is CO₂ produced *in situ* by reaction (3) by means of an electrophilic attack to the carbon(-) of the deprotonated resorcinol (Scheme 1A).

This mechanism explains the lower carboxylation efficiency of resorcinol/KOH with respect to resorcinol/K₂CO₃ in the presence of CO₂ (Table 1), despite KOH is much more basic than K₂CO₃. In this experiment, resorcinol was deprotonated by KOH, no CO₂ was produced *in situ* and the gaseous CO₂ introduced into the solution has to be dissolved before to react. Noteworthy, the efficiency of



Scheme 1. (A) The CO₂ insertion into deprotonated resorcinol in alkaline solution and the formation of β-resorcylic acid. (B) The CO₂ insertion into deprotonated (−2H⁺) and oxidized (−1e⁻) resorcinol in alkaline solution and the formation of the corresponding forms of both β-resorcylic and γ-resorcylic. The hydrogen atoms of the ring are omitted.

KOH under 3.0 bar of CO₂ (30%, 90 °C, 120 min, Fig. 1) is much lower than that of K₂CO₃ under 1.0 bar of CO₂ (50%, 90 °C, 120 min, Table 1). Obviously, a higher carboxylation was obtained if the gaseous CO₂ was added to the carbonating HCO₃⁻ [Eq. (3) and Table 3].

The crucial role of the *in situ* formation of CO₂ was verified by further experiments in the absence of CO₂. A solution of resorcinol/K₂CO₃/KOH in 1/1/2 molar ratio was heated at 110 °C for 5 h and neither HCO₃⁻ nor CO₂ could be formed *in situ*: the ¹³C NMR analysis of the solution did not reveal the formation of the β-resorcylic acid because resorcinol deprotonated by the more basic KOH cannot be carboxylated by CO₃²⁻. If K₂CO₃ is replaced by KHCO₃, it was expected that the solution of resorcinol/KHCO₃/KOH would display analogous features of the resorcinol/K₂CO₃. This hypothesis was indeed verified in the cyclic systems of absorption-desorption (Section 4).

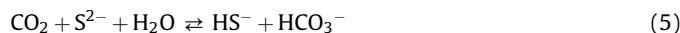
3.4. Carboxylation of resorcinol under oxidative conditions and in the presence of H₂S

In these experiments, fluxes of 12.0 dm³ h⁻¹ of pure CO₂ and air were alternatively introduced into the standard solutions of 2.0 mol dm⁻³ resorcinol and K₂CO₃ in 1/1.5 molar ratio at 130 °C (see Section 2). The experiments lasted 4 h and the species in solution were identified and quantified by ¹³C NMR analysis. The carboxylation efficiency was in the range 57–60% and did not

change appreciably before and after the solution oxidation. The ¹³C NMR spectra allowed us to identify the β-resorcylic acid (C(3), δ = 132.37 ppm) and a small amount (3–5%) of the γ-resorcylic acid (C(3), δ = 134.36 ppm) that slightly increased with the time of the CO₂ absorption (Fig. 7).

Analogous experiments were also performed either with gaseous mixtures of H₂S (50 ppm) in air or with a resorcinol/K₂CO₃ solution also containing 30 mg of Na₂S·9H₂O (1.25 × 10⁻⁴ mol). The results did not differ substantially from those obtained without hydrogen or sodium sulfide. In summary, either the resorcinol oxidation or the presence of variable amount of sulfide in solution did not significantly affect the efficiency of resorcinol carboxylation by CO₂. These results can be explained by the peculiar electronic features of oxidized resorcinol that are substantially different from those of the two comparable isomers, namely pyrocatechol (1,2-dihydroxy benzene) and hydroquinone (1,4-dihydroxy benzene). The oxidation of both pyrocatechol and hydroquinone in alkaline solution yields the corresponding *ortho*-benzoquinone and *para*-benzoquinone featuring localized π bonds, whereas the resonance with other electronic structures with separate charges yields electrophilic carbon atoms that are unable to react with CO₂. On the contrary, a corresponding *meta*-benzoquinone cannot be formulated upon resorcinol oxidation. The oxidation of resorcinol in alkaline solution can produce a mononegative species (−2H⁺/−1e⁻) with one delocalized electron over the entire molecular system and a nucleophilic carbon atom well suited to react with CO₂ affording a paramagnetic form of β-resorcylic or γ-resorcylic acid, as shown in the Scheme 1B. Besides the aforesaid formulae, we can formulate different electronic structures with different arrangements of π electrons that produce either neutral unreactive species or electrophilic monopositive carbon atoms. The oxidized paramagnetic species (−2H⁺/−1e⁻) with an unpaired electron delocalized over the entire system did not substantially affect the broadness of the NMR signals.

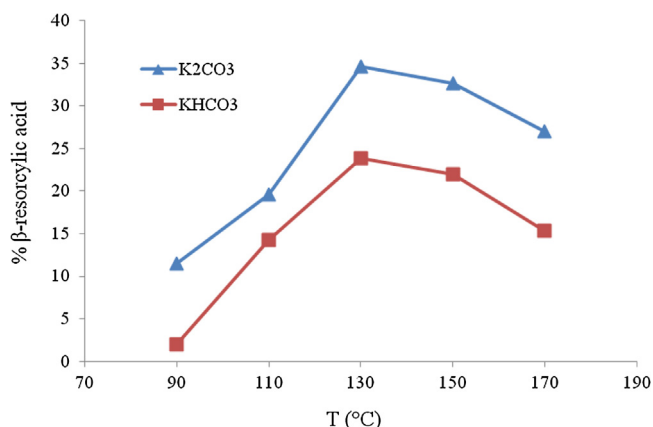
Concerning the sulfur effect, the sulfide of Na₂S reacts with the acidic CO₂



whereas H₂S reacts with the base CO₃²⁻



Fig. 6. Resorcinol conversion into β-resorcylic acid (percentage in mol) as a function of the heating temperature in the absence of CO₂. Heating time fixed at 1 h.



Both the reactions did not affect the efficiency of resorcinol carboxylation, but the thermal decomposition of the solution at

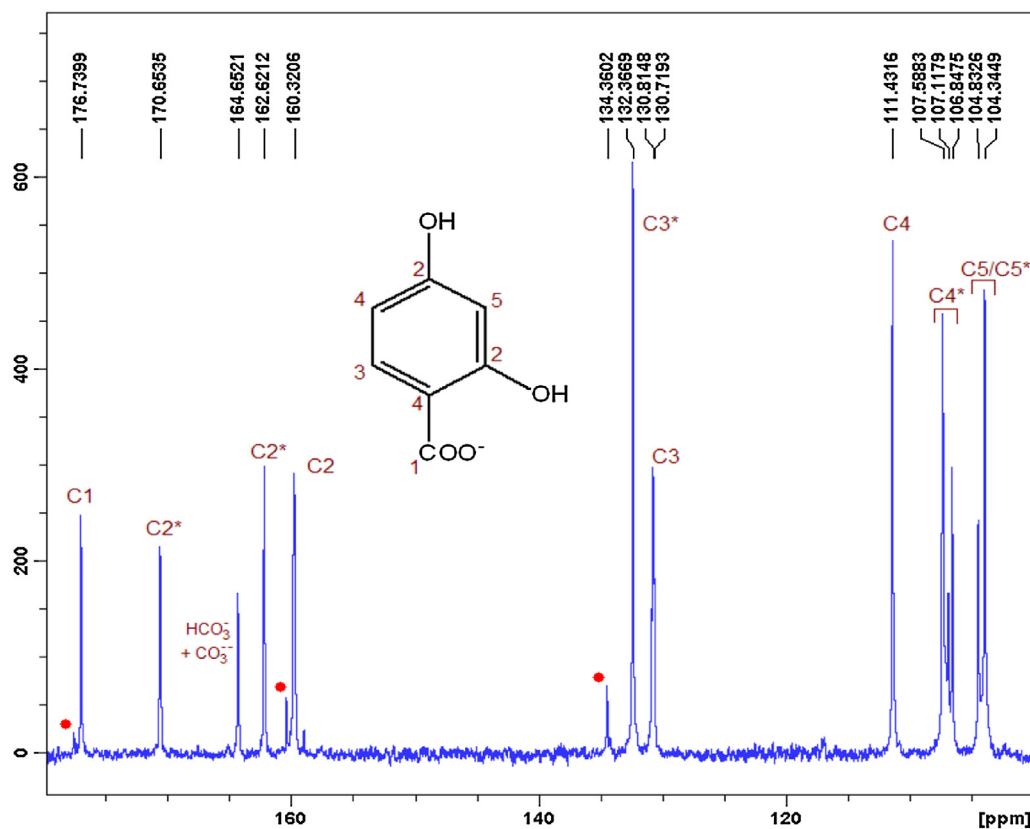


Fig. 7. ¹³C NMR spectrum of the CO₂ saturated solution of oxidized K₂CO₃/resorcinol, 1.5 molar ratio. The chemical shift assignment of the carbon atoms is the same of Fig. 3. The red asterisk denotes the chemical shifts of the carbon atoms of γ -resorcylic acid. The C4 and C5 chemical shifts are masked by the more intense signals of β -resorcylic acid.

high temperature produces H₂S that must be separated from CO₂ before its disposal.

4. Continuous cycles of CO₂ absorption–desorption

As the batch experiments carried out with a gas mixture of 12% CO₂ gave a 45% yield of resorcinol carboxylation, we decided to check whether the alkaline solutions of resorcinol could be feasible absorbents for CO₂ separation and removal from a simulated exhaust gas. To this purpose, we designed lab-scale experiments based on continuous cycles of CO₂ absorption and resorcinol regeneration as previously described for alkanolamines [12,14]. In these experiments, the CO₂ loaded and the regenerated resorcinol solutions were continuously circulating at the same rate of 0.300 dm³ h⁻¹ in a closed cycle between the absorber and the desorber. The absorber is a home-built glass cylinder equipped with a jacket and packed with glass rings (diameter 5 mm); its temperature was maintained at the appropriate value (70–110 °C) by circulating a thermostatted liquid through the jacket. The desorption of CO₂ and the resorcinol regeneration were performed

in a flask maintained at 170 °C by a thermostatted silicone oil bath. The experiments were performed with resorcinol concentration 2.0 mol dm⁻³ and the base/resorcinol 1.5 molar ratio that combines good carboxylation and decarboxylation efficiency. A summary of the operating conditions is reported in Table 5.

The gas mixture of 15% CO₂ (v/v, air for balance) was continuously feeding into the base of the absorber where comes in contact with the liquid getting down off the top. The gas exited from the absorber was dried and purified before being GC-analyzed. Every experiment lasted up to 36 h and was stopped when the steady state was reached and the absorption efficiency did not change with time. In these experiments the stripped CO₂ was not recovered. A small amount (0.5 × 10⁻³ dm³) of the solution was withdrawn from the absorber and checked by ¹³C NMR spectroscopy.

The results of the closed-cycle experiments with different bases and absorption temperatures are reported in Table 6. The maximum absorption efficiency was 82% at 70 °C in the presence of the 1/1 mixture of KHCO₃/KOH, and, in general, the CO₂ absorption efficiency decreased on going from 90 °C to 110 °C. The percentages of β -resorcylic acid contained in the absorber solutions was in the range 33–40% (average values of four tests), well below those obtained in the batch experiments. The results of these closed-cycle experiments were mainly determined by the low rate of resorcinol carboxylation, as the continuous circulation of the liquid between the absorber and the desorber did not allow the reactions to reach their equilibria.

Moreover, we should also bear in mind the reaction (3) that adds CO₂ to the 15% CO₂ introduced into the absorbent. Therefore, the lower CO₂ absorption efficiency and the reduced amount of β -resorcylic acid at 110 °C were the consequence of the increasing CO₂ evolution according to the reaction (3) and, respectively, of the reaction equilibrium (4) that was disfavored by higher

Table 5
Operating conditions in the continuous cycles of absorption–desorption.

Resorcinol concentration	2.0 mol dm ⁻³
Base/resorcinol	1.5 on molar scale
Base	K ₂ CO ₃ ; KHCO ₃ /KOH 1/1; KHCO ₃ /K ₂ CO ₃ 1.5/1 molar ratio
Solvent	Glycerol/water 1/1 (v/v)
Volume solution	0.400 dm ³
Gas mixture	15% CO ₂ (v/v) in air
Absorption temperature	70–110 °C
Desorption temperature	170 °C
Liquid flow rate	0.300 dm ³ h ⁻¹
Gas flow rate	12.2 dm ³ h ⁻¹

Table 6

CO₂ absorption efficiency and percentage of β-resorcylic acid in the absorber solution as a function of absorption temperature ($T_{des} = 170\text{ }^{\circ}\text{C}$). Overall base/resorcinol molar ratio 1.5.

Base (molar ratio)	T_{abs}	Abs % ^a	% ^b Res-CO ₂ ⁻
K ₂ CO ₃	70	74	40
	90	78	37
	110	38	35
KHCO ₃ /KOH (1/1)	70	82	33
	90	79	33
	110	50	26
KHCO ₃ /K ₂ CO ₃ (1.5/1)	70	80	37
	90	80	39
	110	73	27

^a CO₂ absorption efficiency.

^b Average values of four experiments.

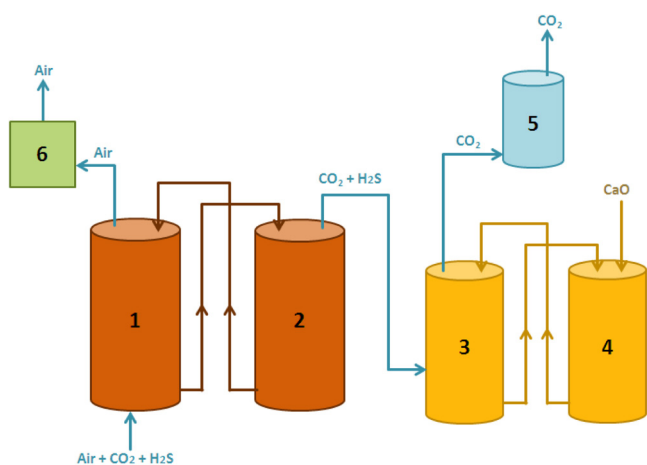
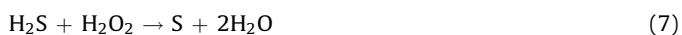


Fig. 8. Simplified flow diagram of the cyclic absorber–desorber configuration for CO₂ and H₂S capture. (1) CO₂ and H₂S absorption; (2) CO₂ and H₂S desorption and resorcinol regeneration; (3) H₂S capture as SO₄²⁻; (4) CaSO₄ precipitation; (5) aqueous CuCl₂ trap; (6) GC analysis.

temperatures. If the amount of CO₂ evolved by reaction (3) becomes greater than CO₂ captured by the reaction (4), the absorption efficiency becomes *negative* and CO₂ was emitted in the absorption step instead of to be captured. The lower absorption efficiency of resorcinol/K₂CO₃ compared to resorcinol/KHCO₃/KOH and resorcinol/KHCO₃/K₂CO₃ was, presumably, due to the rather inefficient decarboxylation of β-resorcylic acid in the presence of K₂CO₃ even at 170 °C. As a matter of fact, the resorcinol/K₂CO₃ solution once heated at 170 °C in the absence of CO₂ yet contained 27% of β-resorcylic acid (Fig. 4).

5. Selective capture of H₂S and its sequestration

Both H₂S and CO₂ are weak acid and consequently their separation requires a selective capture of H₂S and its conversion into a harmless product. The capture of H₂S was performed with an aqueous solution of H₂O₂ sequentially to the desorption step at 170 °C (Fig. 8). The experiments were performed by using the gas mixture of 15% CO₂ in air and 50 ppm of H₂S or by adding 5.0 g of Na₂S·9H₂O (0.021 mol) to the resorcinol/base solution. The reaction of H₂S with a dilute solution of H₂O₂ is

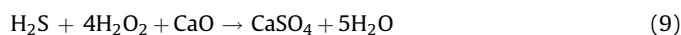


The oxidation is complete and no H₂S escaped from the H₂O₂ solution as confirmed by an aqueous solution of Cu(II) that washed the gas mixture before being introduced in the atmosphere: no CuS

was formed. Owing to the small amount of the expected elemental sulfur (no more than 22 mg at the end of the experiment), the aqueous H₂O₂ became pale yellow due to the formation colloidal sulfur. When the resorcinol solution contained a greater amount of sulfide (0.021 mol), a more concentrated aqueous H₂O₂ was used (0.65 mol dm⁻³) that was three times in excess with respect to the sulfide. The solution of sulfate obtained by the sulfide oxidation



was separated from the solution as calcium sulfate. The complete reaction was



6. Conclusions

We have investigated the chemistry of the CO₂ uptake by resorcinol (1,3-dihydroxy benzene) in alkaline aqueous and water/glycerol solutions under different experimental conditions with the purpose of unveil the reaction mechanism and of maximizing the resorcinol conversion into β-resorcylic acid (2,4-dihydroxybenzoic acid). The ¹³C NMR analysis was successfully applied to identify and quantify the carbonated species in solution, and the β-resorcylic acid (mainly, in the deprotonated form) was the sole product of resorcinol carbonation in alkaline solution. K₂CO₃ was found to be the most efficient base because of a reaction mechanism bringing on the formation *in situ* of CO₂ that is more reactive than the gaseous CO₂ introduced into the solution. Noteworthy, the aerial oxidation of resorcinol and the presence of the sulfide ion in solution did not influence the yield of the β-resorcylic acid formation. IR spectroscopy was used to identify the carbonated species separated from the reaction mixture as the β-resorcylic acid.

The batch experiments of CO₂ capture from a 12% gas mixture with the formation of 34% β-resorcylic acid, could be a promising new technique that combines the CO₂ separation from industrial gas mixtures with the production of useful chemicals.

A different approach to CO₂ capture and separation from exhaust gases was the CO₂ absorption and simultaneous thermal resorcinol regeneration carried out in closed cycles. The results of the batch experiments were the prerequisite to find the operational conditions affording the highest efficiency of CO₂ capture. The best result (82% of CO₂ capture) was obtained with the resorcinol/KHCO₃/KOH solution, absorption temperature at 70 °C and desorption at 170 °C. The H₂S possibly contained in the CO₂ gas mixture was selectively oxidized with aqueous H₂O₂ and separated from CO₂ as harmless elemental sulfur or with aqueous and captured as CaSO₄. Even if the regenerative CO₂ capture requires higher temperatures (90–170 °C) and attains a lower efficiency (82%) compared to those reported for alkanolamines (40–120 °C and 90% efficiency), the resorcinol-based absorbent could avoid some crucial drawbacks of the amine-based technology, namely the thermal and oxidative decomposition of the amines, amine loss by evaporation, corrosion and foaming problems.

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