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Carbon dioxide uptake as ammonia and amine carbamates and their efficient conversion into urea and 1,3-disubstituted ureas

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ABSTRACT

Solid mixtures of ammonium carbamate and bicarbonate originating from the CO_2 capture by NH_3 in water–ethanol solution were converted into urea by heating to 428 K for 60–90 min. The yield of urea was up to 53% on molar basis. An analogous technique was employed to capture CO_2 with 1-aminobutane, 1-amino-2-methylpropane, 2-amino-2-methylpropane, 1-aminooctane, aminocyclohexane and 1,4-diazacyclohexane, in organic solvents as amine carbamates which were separated in the solid state and thermally converted at 423 K for 15–16 h into 1,3-disubstituted ureas with 30–40% yield on molar scale. The formation of 1,3-disubstituted ureas was 100% selective. The rate of the conversion reaction was significantly improved in the presence of copper catalysts. The identification and quantification of the products in the reaction mixtures were obtained by ^{13}C NMR analysis.

1. Introduction

The chemical absorption of CO_2 by aqueous alkanolamines is an efficient methodology for CO_2 separation in ammonia and hydrogen plants, natural gas sweetening and, in general, for CO_2 removing from industrial exhaust streams [1–11]. However, the critical questions facing this technology are the high energy costs of the amine regeneration and the environmental concerns because of the amine loss by thermal and oxidative degradation [12–17]. In comparison with aqueous alkanolamines, ammonia scrubbing process provides the advantage of high CO_2 loading capacity and absorption efficiency with no absorbent degradation [18–25]. However, this technique suffers of serious hurdles due to the ammonia loss and to the costs of NH_3 separation from concentrated CO_2 in the regeneration step.

In our laboratory we are developing a new concept of CO_2 capture technology which combines the CO_2 abatement with the production of commercially valuable products [26,27]. Even if we must admit that the conversion of CO_2 into commercial products does not significantly reduce the anthropogenic CO_2 emissions (billions of metric tons for year), nonetheless turning carbon dioxide into useful chemicals in relatively mild conditions can contribute to reduce the cost of biogas and natural gas cleaning, hydrogen and ammonia production, and of all the processes where the separation of CO_2 from other gases is unavoidable.

In a previous experimental study [28] we reported that the carbon dioxide capture with ammonia in non-aqueous solvents was fast and efficient and produced pure ammonium carbamate that was subsequently converted into urea in the presence of copper(II) promoters. However, this process was unsuitable for a commercial application, due to the low rate of conversion (two–three days heating).

By going on with these studies, we present here our results focused on the fast urea production by heating mixtures of ammonium carbamate and bicarbonate to 438 K for 60–90 min. Besides the advantage of an efficient CO_2 capture, this unconventional process could circumvent the high energy costs of the commercial processes of urea production which is carried out in the gas phase with an excess of ammonia (NH_3/CO_2 molar ratio up to 4) and purified carbon dioxide at 450–500 K and 150–250 bar. Pure CO_2 is obtained by the conventional process of aqueous amine scrubbing and thermal stripping, in turn. In the commercial plants, the yield of the reaction is in the order 30–55% on NH_3 basis and strongly depends on reaction temperature, pressure, time and NH_3/CO_2 ratio.

We also used an analogous concept for the CO_2 uptake by the non-aqueous solutions of some selected amines and for the thermal conversion of the solid amine carbamates into the corresponding substituted 1,3-disubstituted ureas. The 1,3-disubstituted ureas are valuable products with a wide range of application as intermediates in agrochemical, pharmaceutical,

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dye chemicals and recently as precursors of isocyanates and raw materials of polyurethanes [29–34]. Their traditional synthesis required unsafe chemicals such as phosgene or carbon oxide and Au or Pt catalysts [35–38]. In recent years the direct synthesis of substituted ureas has been accomplished with the non toxic and cheap carbon dioxide in the presence of different catalysts and dehydrating agents to increase the yield of reaction [39–42]. Ionic liquids in conjunction with a base (CsOH) or transition metal (Fe, Co, Ni, Cu, Zn) acetates were also employed as reaction medium and catalysts to obtain 1,3-disubstituted ureas in good yield [43–46]. However, most catalysts can be reused no more than 3–4 times. Carbon dioxide has been also reacted with aziridines and ionic liquids as catalysts, affording oxazolidones, which are valuable intermediates in several organic synthesis [47–50].

The unconventional technology we have devised combines the efficient CO_2 uptake from anthropogenic activities by some amines with the thermal conversion of the amine carbamates obtained in the solid state into 1,3-disubstituted ureas without any catalyst, dehydrating agent or external pressure, yet with acceptable yields.

2. Experimental

2.1. General information

All reagents were reagent grade. CuCl, $CuCl_2 \cdot 2H_2O$, ammonium bicarbonate, 1-aminobutane (*n*-butylamine, NBA), 1-amino-2-methylpropane (isobutylamine, IBA), 2-amino-2-methylpropane (*tert*-butylamine, TBA), 1-aminoheptane (*n*-heptylamine, NHA), 1,4-diazacyclohexane (piperazine, PIP), aminocyclohexane (cyclohexylamine, CHA), 1-aminooctane (*n*-octylamine, NOA), bis(2-ethoxyethyl) ether (diethylene glycol diethyl ether, DEGDEE), 2-(2-methoxyethoxy) ethanol (diethylene glycol methyl ether, DEGMME), 2-ethoxyethanol (ethylene glycol monoethyl ether, EGMEE), 3-pentanone (diethyl ketone, DEK), and ethanol (Sigma–Aldrich) were used as received. Standard NH_3 solution 15.2 mol dm^{-3} (Sigma–Aldrich) was used to prepare the ethanol–water–ammonia solutions. Pure CO_2 and N_2 used to simulate flue gas and pure NH_3 were obtained by Rivoira. Flow rates of air, CO_2 and NH_3 were measured with gas mass flow meters (Aalborg) equipped with gas controllers (Cole Parmer). The inlet and outlet CO_2 concentrations in the flue gas mixture were measured with a Varian CP-4900 gas chromatograph calibrated with 10% and 40% (v/v) CO_2/N_2 and 100% CO_2 reference gases (Rivoira).

The cyclic absorption–filtration device was quite similar to that previously described [28] and comprised the absorber and the filtration units that are connected to each other by means of a peristaltic pump (Masterflex L/S) that allows the absorbent slurry and the filtered solution to circulate continuously in a closed loop between the absorber and the filtration unit (Fig. 1). The temperature of the absorbent solution was kept constant by a thermostatted water bath (Julabo model F33-MC refrigerated bath).

The NH_3 absorbent solution was made by mixing 0.020 dm^3 of 15.2 mol dm^{-3} aqueous NH_3 with 0.270 dm^3 of ethanol. Both CO_2 (12% v/v in air) and NH_3 were simultaneously and continuously introduced at the bottom of the absorbent solution through two separate gas diffuser. The CO_2/NH_3 flow ratio was 1/1.5 (v/v) with a flow rate of 14 dm^3 h^{-1}. The outlet gas from the top of the absorber was dried by flowing in turn through a condenser cooled at 268 K, a concentrated H_2SO_4 solution and a gas purification tower filled with P_2O_5, before being analysed with a gas chromatograph which measured the percentage of the CO_2 absorbed at intervals of 10 min. At the end of the experiment fixed at eight hours, the solid collected by filtration was washed with CO_2 saturated ethanol and diethyl ether in turn before being dried at room temperature in a stream of pure CO_2 to avoid the decomposition of both ammonium carbamate and bicarbonate.

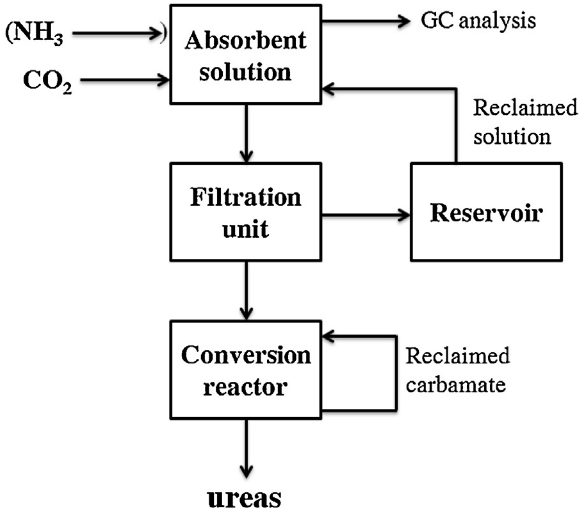


Fig. 1. Simplified flow diagram of the cyclic process configuration. Gaseous ammonia was used in conjunction with CO_2 absorption by water–ethanol NH_3.

Analogous equipment (Fig. 1) and procedure were used to capture CO_2 by non aqueous amines and to collect the corresponding solid amine carbamates. The absorber device was charged with 0.300 dm^3 of 3.0 mol dm^{-3} solutions of the different amines in bis(2-ethoxyethyl) ether (NBA, IBA, TBA), in 2-(2-methoxyethoxy) ethanol (CHA), in 2-ethoxyetanol (PIP), or in 3-pentanone (NOA). The temperature of the absorbent solution was kept constant at 293 K by a thermostatted water bath. The gas mixture containing 15% (v/v) CO_2 in air was continuously fed into the bottom of the absorber with a flow rate of 14 dm^3 h^{-1}. The outlet gas, exited from the top of the absorber, was analysed by the gas chromatograph. A complete experiment lasted 150–660 min and it was stopped when the CO_2 absorption efficiency at the end of the experiment was reduced to about 50% (average absorption efficiency in the range 91–97%). The solid was collected by filtration unit, washed with a 1/1 mixture of ethanol and diethyl ether and pure diethyl ether in turn before being dried at room temperature in a stream of N_2.

The batch experiments aimed at measuring the loading capacities of the different amine solutions were carried out using the same absorber and absorption procedure as above described but pure CO_2 was used and the carbonated products were not separated from the solution by filtration. The absorption was stopped when no more CO_2 was absorbed. The maximum amine loading (CO_2/amine molar ratio) was computed from the weight increase of the CO_2 saturated slurry contained in the absorber.

The conversion of ammonium salts into urea was carried out in a stainless steel reactor (PARR MOD. 4791) with a volume of is 0.025 dm^3 equipped with a thermocouple and pressure gauge. The reactor was heated to the appropriate temperature (438 K) by means of a silicone oil heating bath (IKA HB4). In each experiment, the reactor is charged with 12.0 g of the mixture of ammonium carbamate and bicarbonate in slightly different ratio (67–73% of carbamate, in molar ratio). For comparison purposes, blank experiments were carried with pure ammonium bicarbonate. Each conversion experiment comprised six separate heating times, 30, 45, 60, 75, 90, 105 min, aimed at measuring the urea yield as a function of heating time.

After each heating time was completed, the reactor was water cooled to room temperature and a sample of the mixture recovered from the vessel was dissolved in D_2O and analysed by ^{13}C NMR spectroscopy. Each experiment was repeated ten times showing a sufficient reproducibility of the results with changes in the percentage of each species never higher than 4 units.

The conversion of amine carbamate salts into the corresponding 1,3-disubstituted ureas was carried out in the same PARR reactor by heating 10.0–14.0 g of the salt to 423 K. In some experiments, the amine carbamate and protonated amine ion pairs were mixed with 1% (molar scale) of either CuCl or $CuCl_2\cdot2H_2O$. The reaction mixtures were analysed by ^{13}C NMR technique.

2.2. ^{13}C NMR spectroscopy

The identification of the products was obtained by ^{13}C NMR analysis in either D_2O or $CDCl_3$. The ^{13}C 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. CH_3CN was used as internal reference (CH_3, $\delta = 1.47$ ppm). To obtain quantitative ^{13}C NMR spectra, a pulse sequence with proton decoupling and NOE suppression was used to acquire the $^{13}C\{^1H\}$ with the following acquisition parameters: pulse angle = 90.0°, acquisition time = 1.36 s, delay time = 2–30 s, data points = 64 K, number of scans = 250–500. The data were processed by using Bruker-Biospin Topspin software. 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 CH_3— and —CH_2— carbon atoms that contain the same number of attached protons [51,52]. The carbon atoms of R—CO_2^- and R_2CO with no attached hydrogen atoms, display longer relaxation times and lower intensity resonances compared to CH_3— and —CH_2— carbon atoms. The integration of the signals due to HCO_3^-/CO_3^{2-} ($\delta = 160.22$–163.73 ppm), —$NHCO_2^-$ ($\delta = 163.83$–164.30 ppm), $(NH_2)_2CO$ ($\delta = 161.92$–163.26 ppm), —CH_2— ($\delta = 19.08$–49.06 ppm), CH_3— ($\delta = 13.31$–19.88 ppm) and >C=O (1,3-disubstituted ureas, $\delta = 158.83$–159.27 ppm), allowed us to quantify the molar ratio of the different species. Despite some unavoidable uncertainty in comparing the different integrals, the method provides an estimation of the relative percentage of the different species (estimated error 5%).

While the carbon resonance of the carbonyl group of ureas was not affected by the presence of the Cu(II) catalysts employed in some amine carbamate dehydration, the peaks belonging the C=O groups of amine carbamate are selectively broadened till the signal disappearance. To avoid this unwanted effect of Cu(II) on ^{13}C NMR analysis, after the dehydration experiments were completed, the copper catalyst was precipitated with Na_2S and the reaction mixtures were separated from CuS by extraction either with $CDCl_3$ or D_2O and the solutions analysed by ^{13}C NMR spectroscopy.

3. Results and discussion

3.1. The wet reaction of CO_2 with NH_3 and the conversion of ammonium carbamate and bicarbonate into urea

The urea synthesis from gaseous CO_2 and NH_3 involves the intermediate formation of ammonium carbamate

$$2NH_3 + CO_2 \rightleftarrows NH_2CO_2NH_4 \qquad (1)$$

that is successively dehydrated to form urea

$$NH_2CO_2NH_4 \rightleftarrows (NH_2)_2CO + H_2O \qquad (2)$$

While Reaction (1) is fast and exothermic ($\Delta H^\circ = -151$ kJ mol^{-1}), Reaction (2) is slow and endothermic ($\Delta H^\circ = 32$ kJ mol^{-1}) [53,54]: the latter equilibrium should be right hand shifted and the reaction rate should be substantially increased at high temperature. Moreover, Reaction (2) is an oversimplification of the several equilibria occurring. For example, the carbamate could be hydrolysed by the water produced in Reaction (2) (Reactions (3) and (4))

$$NH_2CO_2NH_4(s) + H_2O(l) \rightleftarrows NH_4HCO_3(s) + NH_3(g) \qquad (3)$$

$$NH_2CO_2NH_4(s) + 2H_2O(l) + CO_2(g) \rightleftarrows 2NH_4HCO_3(s) \qquad (4)$$

Therefore, the final yield of urea is the result of the competition between the conversion reactions of carbamate into urea and its decomposition reactions, mainly, to bicarbonate.

We have accomplished the urea synthesis in two separate steps:

1) The CO_2 capture by NH_3 in aqueous-ethanol at room pressure aimed at obtaining solid mixtures of ammonium carbamate and bicarbonate;
2) The thermal dehydration of the solid ammonium salts into urea.

The fast and efficient carbon dioxide capture by ammonia in water–ethanol solutions has been thoroughly investigated in an our previous experimental study and it will not further discussed [28]. The composition of the solid mixtures of ammonium carbamate and bicarbonate we used in the urea synthesis was identified and quantified by ^{13}C NMR analysis in D_2O solution as already reported [55]. The accurate integration of the signals of the carbon atoms of carbamate ($\delta = 163.83$–164.30 ppm) and of the fast exchanging carbonate and bicarbonate ions ($\delta = 160.22$–163.73 ppm) gave a mixture composition comprised between 67% and 73% (on molar scale) of ammonium carbamate.

The conversion of ammonium bicarbonate into urea (Reaction (5)) is less efficient than that of the ammonium carbamate (Reaction (2)), having a theoretical 50% limit.

$$2NH_4HCO_3 \rightarrow (NH_2)_2CO + CO_2 + 3H_2O \qquad (5)$$

Consequently, the starting ammonium carbamate–bicarbonate mixture must contain at least 50% of carbamate to produce significant yields of urea.

The conversion of ammonium carbamate–bicarbonate mixtures (12 g, 67.1–73.3% carbamate, on molar scale) has been performed in a pressure stainless steel reactor heated to 438 K for 30–105 min. Heating times less than 30 min result into negligible conversion, while heating times greater than 90 min may decrease the urea yield. At the end of each experiment the ^{13}C NMR analysis in D_2O (urea carbon, $\delta = 161.92$–163.26 ppm) allowed us to identify and quantify the composition of the reaction mixtures. Each experiment was repeated ten times. The average results of the experiments are reported in Table 1 and summarized in Fig. 2.

After 90 min heating to 438 K, the average yield of urea was 48.9% (percentage in mol) respect to the amount of carbamate and bicarbonate mixture (maximum yield 51.8%). The pressure generated in situ by the mixture decomposition and by the excess of CO_2 (Reactions (5) and (6)) was at most 38 bar at 438 K. The comparative analysis based on ^{13}C NMR spectra has shown that more than 80% of the bicarbonate contained in the reacting mixture was converted into urea and into carbamate (Reactions (5) and (6)).

$$2NH_4HCO_3 \rightarrow NH_2CO_2NH_4 + CO_2 + 2H_2O \qquad (6)$$

Because of the contribution of Reactions (5) and (6), there is not a clear relationship between the urea yield and the composition of the starting reactants that what is more comprised no less than 70% of carbamate (on molar scale) in most experiments. No other species was detected in the ^{13}C NMR spectra, in particular no trace of biuret ($\delta = 158.08$ ppm) was found. Presumably, dimerization of

Table 1
Average yields of the conversion of ammonium carbamate/bicarbonate mixtures into urea as a function of heating time.

Time (min)	P max (bar)	Reagents (%)[a]		Products (%)[b]		
		HCO_3^-	$NH_2CO_2^-$	Urea	HCO_3^-	$NH_2CO_2^-$
30	38	32.9 ± 2.5	67.1	13.5 ± 0.8	32.2 ± 1.6	54.3
45	35	26.7 ± 2.8	73.3	37.5 ± 2.2	11.1 ± 2.9	51.3
60	35	28.5 ± 1.3	71.5	46.7 ± 2.1	6.8 ± 1.2	46.6
75	36	29.3 ± 3.3	70.7	47.9 ± 2.1	6.5 ± 1.1	45.7
90	36	30.1 ± 1.3	69.9	48.9 ± 1.8	6.3 ± 1.1	44.7
105	38	28.0 ± 1.0	72.0	46.2 ± 0.4	7.6 ± 0.2	46.2

[a] Average values (percentage, molar scale) in the reagent mixtures.
[b] Average values (percentage, molar scale) in the urea mixtures.

urea to biuret requires more time and/or higher pressure than those of our experiments.

As the yield of urea increased with heating time and temperature, it is worth of noting that the conversion shows an initial delay of about 30 min, this being the time taken by the mixture inside the reactor to reach 413–423 K and to start the dehydration process at a sufficient rate. On the contrary, increasing the heating times over 90 min did not increase the urea yield (Table 1 and Fig. 2) as a prolonged heating time has the opposite effect, probably due to secondary reactions of urea, for instance due to guanidine formation.

$$NH_2CONH_2 + NH_3 \rightleftarrows (NH_2)_2CNH + H_2O \qquad (7)$$

The best compromise between the maximum urea yield and the minimum heating time (i.e., the minimum energy consumption), is the 46.7% (average value, ±2.1) yield after 60 min heating. At the end of each reaction, ^{13}C NMR analysis in D_2O showed no other product besides urea, unreacted carbamate and bicarbonate/carbonate mixture. Pure urea can be easily recovered by heating the reaction mixtures (333 K) to constant weight. After the gaseous H_2O, NH_3 and CO_2 were completely removed, the purity of urea was checked by ^{13}C NMR spectroscopy as already reported [28]. Blank experiments carried out with pure ammonium bicarbonate gave no more than 10% urea, irrespective of heating times in the range 60–120 min.

The yield of urea from ammonium carbamate and bicarbonate mixtures here reported is comparable to that obtained from pure carbamate and copper promoters previously reported [28], but it has been now obtained in much less heating time (60–90 min, instead of 2–3 days) and in the absence of any catalyst. This quite surprising result was presumably due to the much greater pressure (38 bar instead of 14 bar) in the reactor, produced by the thermal decomposition of bicarbonate (Reactions (5) and (6)).

3.2. The CO_2 capture by amines in non-aqueous solvents and the formation of amine carbamates

The experiments of CO_2 capture by non-aqueous amines were performed with 3.0 mol dm^{-3} solutions of 1-aminobutane (*n*-butylamine NBA), 1-amino-2-methylpropane (isobutylamine IBA), 2-amino-2-methylpropane (*tert*-butylamine TBA) in bis(2-ethoxyethyl) ether (diethylene glycol diethyl ether, DEGDEE), aminocyclohexane (cyclohexylamine, CHA) in 2-(2-methoxyethoxy) ethanol (diethylene glycol methyl ether, DEGMME), 1,4-diazacyclohexane (piperazine, PIP) in 2-ethoxyetanol (ethylene glycol monoethyl ether, EGMEE) and 1-aminooctane (*n*-octylamine, NOA) in 3-pentanone (diethyl ketone, DEK). The choice of the diluents was due to fulfil the main requirement of the insolubility of the carbonated compounds, but the absence of foaming problems as well as of immiscible liquid phases was also appreciable advantages. In order to measure the maximum loading capacity of the amine (CO_2/amine molar ratio) and to recover the amine carbamates used for urea synthesis in reasonable reaction times, each amine solution was saturated with pure CO_2 in batch experiments.

A gas mixture containing 15% CO_2 in air (pressure of the gas mixture 1 bar) was used to measure the efficiency of CO_2 capture in flow experiments. Either pure CO_2 or the gas mixture were flowed at the rate of 12 dm^3 h^{-1} (0.50 and, respectively, 0.0748 mol h^{-1} of CO_2 at 293 K) through a gas diffuser at the bottom of the absorber charged with 0.300 dm^3 of the absorbent at the temperature of 293 K kept constant with a thermostatted bath.

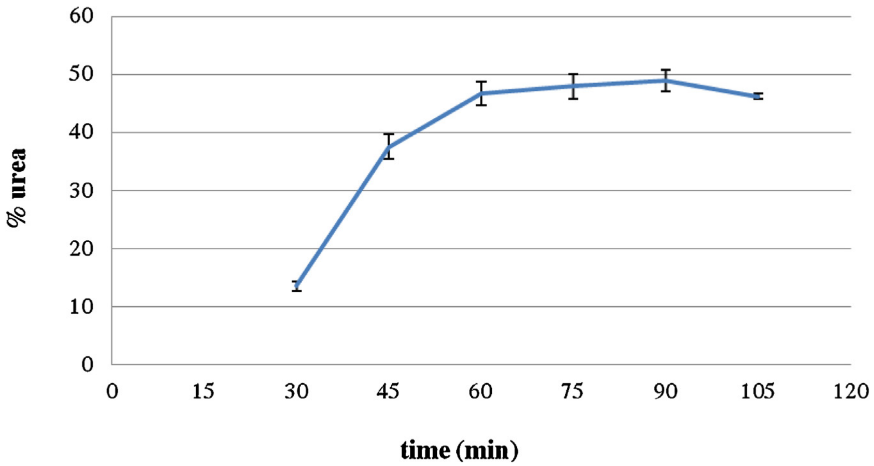


Fig. 2. Percentage of urea formation as a function of heating time.

Table 2
CO_2 loading capacity and average absorption rate of the different amines at 293 K.

Amine	Solvent	Absorption			Loading[c]
		t (min)	mol CO_2[a]	Rate[b] (mol min^{-1})	
NBA	DEGDEE	40	0.49	0.012	0.54
IBA	DEGDEE	70	0.52	0.0074	0.58
TBA	DEGDEE	100	0.24	0.0024	0.27
NOA	DEK	40	0.43	0.011	0.48
CHA	DEGMME	150	0.38	0.0025	0.42
PIP	EGMEE	120	0.86	0.0072	0.96

[a] mol CO_2 absorbed.
[b] Average rate of CO_2 absorption.
[c] mol CO_2/mol amine.

In anhydrous solvents, CO_2 reacts with an excess of the primary amines NBA, IBA, TBA, CHA and NOA, forming the corresponding carbamates (in Eq. (8) AmH denotes the amine)

$$2AmH + CO_2 \rightarrow AmCO_2^- + AmH_2^+ \tag{8}$$

with a theoretical loading capacity of 0.5.

The loading capacity measured by gravimetry (see Section 2) ranges between 0.48 of NOA and 0.58 of IBA (Table 2), near to the expected theoretical value. The experimental values slightly greater than 0.5 may be ascribed to a small physical absorption by the organic solvents. The much lower loading of TBA, 0.27, was likewise due to the steric hindrance of the *tert*-butyl group at the amine function that is disadvantageous to the insertion of CO_2 and to the carbamate stability [56], thus disfavouring the reaction rate and the carbonatation equilibrium; the same occurs, but at a lower extent, to CHA featuring a 0.42 loading. The considerably greater value of 0.96 loading of PIP was ascribed to the two secondary amine groups which promoted a different reaction mechanism (see later).

The ^{13}C NMR spectra of the different carbamates of the primary amines dissolved in $CDCl_3$, display couples of resonances ascribed to the same carbon atoms of amine carbamates and protonated amines in the range 13.31–49.06 ppm. The low intensity resonance of the carboxylated group, $—CO_2^-$, was found in the range 162.28–164.30 ppm. As an example, we report here the ^{13}C NMR spectrum of the NBA carbamate compared to that of pure amine (Fig. 3A and B). As shown in Fig. 3B, the couple of resonances at 12.96 and 13.19 ppm ($—CH_3$), 19.37 and 19.53 ppm, 29.81 and 32.27 ppm, 38.64 and 40.88 ppm ($—CH_2$) are ascribable to the carbon atom of both carbamate and protonated *n*-butylamine. The low intensity resonance at 163.05 ppm is readily assigned to the carbon atom of the $—CO_2^-$ group.

The average rate of carbonatation reaction of the different amines decrease in the order NBA ≈ NOA > IBA > CHA > TBA (Table 2) in the same order of the increasing steric hindrance at the amine functionality. The rate of carbonatation of PIP cannot be compared because of the different mechanism of amine carbonatation.

The secondary amine 1,4-diazacyclohexane (piperazine, PIP) contains two basic nitrogen atoms ($pK_b(1) = 5.35$; $pK_b(2) = 9.73$ at 298 K) and, consequently, it may give rise to more equilibria by the reaction with CO_2 (AmN_2H_2 stands for piperazine in Eqs. (9)–(11))

$$2AmN_2H_2 + CO_2 \rightarrow [AmN_2H(CO_2^-)] + [AmN_2H_3^+] \text{ loading 0.5} \tag{9}$$

$$3AmN_2H_2 + 2CO_2 \rightarrow [AmN_2(CO_2^-)_2] + 2[AmN_2H_3^+] \text{ loading 0.67} \tag{10}$$

$$AmN_2H_2 + CO_2 \rightarrow [AmN_2H(CO_2H)] \text{ loading 1} \tag{11}$$

The formation of diprotonated PIP ($AmN_2H_4^{2+}$) should be negligible, on account of the weak acidity of CO_2 ($pK_a = 6.4$) as well as of the weak basicity of monoprotonated PIP ($pK_b(2) = 9.73$). The experimental value of CO_2 loading, 0.96, can be accounted for on the basis of Reaction (11), with a much minor contribution of Reactions (9) and (10) (overall, less than 10%).

The formation of carbamic acid by the reaction of an amine and an excess of CO_2 is quite uncommon, but it has been previously reported in the absence of water [57]. The ^{13}C NMR spectrum in D_2O of the carbonated PIP with an excess of pure CO_2 is reported in Fig. 4.

The spectrum displays four resonances of CH_2 carbon atoms of PIP backbone in the range 40.68–43.79 ppm and two much less intense signals at 160.13 ppm and 161.75 ppm. The latter is due to the carbon atom of the fast exchanging $—CO_2^-/—CO_2H$ pair and the signal at 160.13 ppm should be ascribed to HCO_3^- species [55,58] originating from the hydrolysis of the carbamate in D_2O, as already found for other amine carbamates in aqueous solutions [59]. The two signals at 40.68 and 42.86 ppm (integrated signals in 1/1 molar ratio) are assigned to the two couples of CH_2 carbon atoms of the neutral carbamic acid $[AmN_2H(CO_2H)]$ (Eq. (11)), presumably fast exchanging with the zwitterionic form $[AmN_2H_2^+(CO_2^-)]$. The resonance at 43.79 ppm is assigned to the CH_2 carbon atoms of a small amount (about 7%) of the symmetrically substituted bis-carbamate of piperazine. To complete the NMR analysis, the signal at 42.06 ppm is assigned to the carbon atoms of the protonated piperazine. The carbonated PIP was not soluble in the common deuterated organic solvents and, consequently, it was not possible to prevent its hydrolysis in D_2O in the ^{13}C NMR analysis.

The absorption efficiency of the amines was measured with the 15% CO_2 mixture in air and the cyclic absorption–filtration device (Fig. 1) which allowed the carbonated slurry to be continuously transferred from the absorber to the filtration unit and the filtered liquid to be reclaimed to the absorber. During the experiments of CO_2 absorption no new amine was added to the absorbent solution. Most of the experiments lasted 150–360 min (660 min with the diamine piperazine) and were stopped when no more than 50% of CO_2 was still absorbed by the residual amines in excess with respect to flowed CO_2. The average CO_2 removal efficiency by the different amines in the entire experiment was comprised between 91 and 97% (Table 3). At the end of each absorption experiment, the solid recovered by filtration was washed and dried before being analysed by ^{13}C NMR spectroscopy that confirmed the formation of the amine carbamates.

The noticeable different absorption times in comparison with similar absorption efficiencies are inversely correlated to the amount of absorbed CO_2 that decreased in the order PIP >> NBA > NOA > CHA > IBA > TBA. As the average rate of CO_2 absorption by the different amines was the same (0.0011–0.0012 mol min^{-1}), the different amount of absorbed CO_2 was a consequence of Reaction (8) equilibrium of the different amines. In this respect, NBA exhibits the most favourable equilibrium as the formation of the amine carbamate, computed from the amount of absorbed CO_2, was nearly quantitative with respect to starting amine (Table 3). As a matter of fact, when the reaction was stopped, 0.431 mol of CO_2 were absorbed by 0.900 mol of NBA: based on the stoichiometry of Reaction (8), 95.8% of the amine was converted into the corresponding carbamate. As expected, the least favourable equilibrium occurred with TBA which gave a 37.6% of amine carbamate.

3.3. The conversion of amine carbamate into 1,3-disubstituted ureas

In order to circumvent the disadvantages of the conventional syntheses of 1,3-disubstituted ureas which use toxic reactants

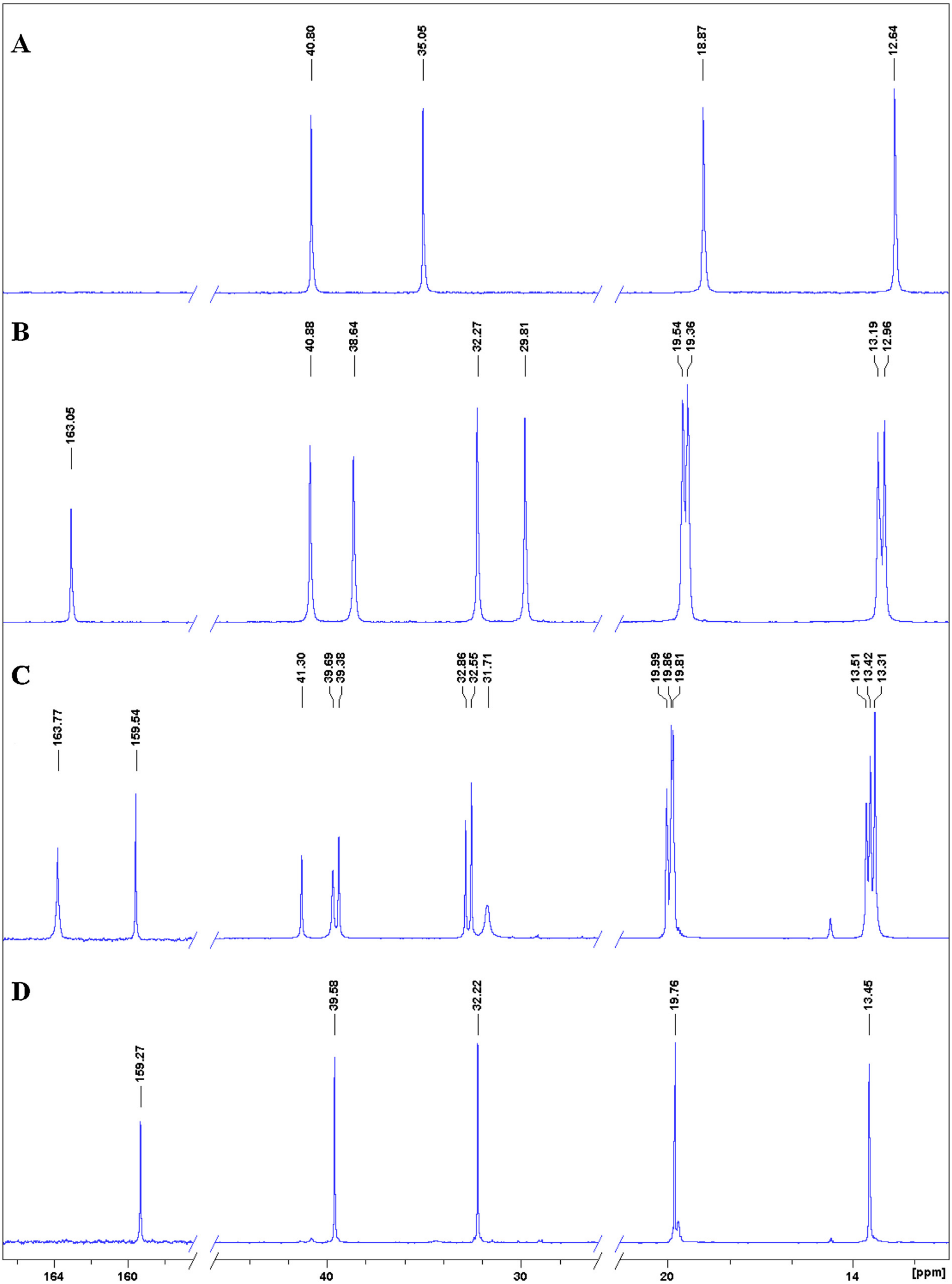


Fig. 3. ^{13}C NMR spectra of: (A) pure NBA; (B) NBA carbamate; (C) reaction mixture (in D_2O) obtained by heating NBA carbamate for 16 h at 423 K; (D) 1,3-dibutylurea recovered from the reaction mixture by extraction with $CHCl_3$. The intensity of the signals at about 160 ppm are not in scale.

such as phosgene or carbon oxide as well as expensive catalysts and dehydrating agents, we looked for the possibility to obtain substituted ureas by the thermal dehydration of amine carbamates with a procedure quite similar to that successfully used for the conversion of ammonium carbamate into urea. To this purpose, 10.0–14.0 g of each amine carbamate and protonated amine ion

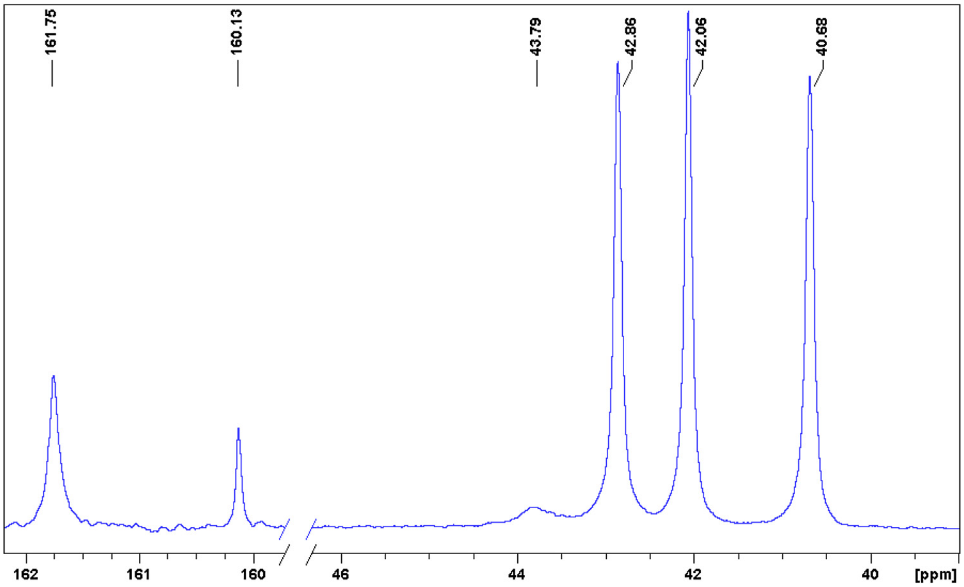


Fig. 4. ^{13}C NMR spectrum in D_2O of the solid recovered by the PIP carbonatation with an excess of pure CO_2. The intensity of the signals at 160–161 ppm are not in scale.

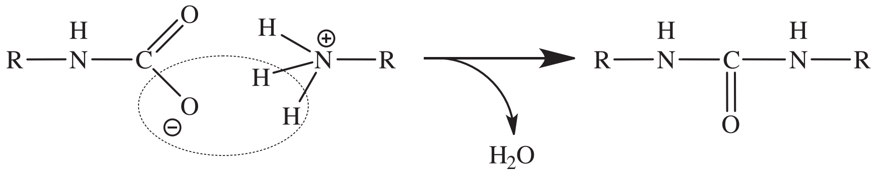
Table 3
CO_2 absorption efficiency of the different amines and percentage of carbamate formation.

Amine	Absorption efficiency[a]		CO_2 abs[b] (mol)	Carbamate[c] (%)
	t (min)	abs%		
NBA	360	95.8	0.431	95.8
IBA	210	94.9	0.248	55.1
TBA	150	90.5	0.169	37.6
NOA	300	95.6	0.358	79.6
CHA	260	96.0	0.311	69.2
PIP	660	97.1	0.799	88.8

[a] Average absorption efficiency of CO_2 and experiment time.
[b] mol of CO_2 absorbed.
[c] Yield of carbamate with respect to the 0.90 mol of starting amine.

pair was heated to 423 K for 5–16 h in a stainless steel sealed reactor equipped with a pressure gauge and a thermocouple. The pressure generated in situ by the dehydration (in Scheme 1, R stands for an aliphatic group) and/or decarboxylation of the reagents (Reactions inverse to (9)–(11)) was in the range 34–40 bar (Table 4).

The identification of the species recovered at the end of each reaction was accomplished by ^{13}C NMR analysis. As an example, the ^{13}C NMR spectrum in D_2O of the reaction mixture obtained by heating NBA carbamate for 16 h to 423 K is reported in Fig. 3C. Besides the resonances assigned to the unreacted amine carbamate and protonated amine quite similar to those of the pure compound (Fig. 3B), four distinct signals due to the carbon backbone of the 1,3-dibutyl substituted urea were found at 39.69 ppm, 31.71 ppm, 19.99 ppm ($—CH_2—$) and 13.51 ppm ($—CH_3$). The less intense signal at 159.54 ppm is easily assigned to the carbonyl group ($>C{=}O$) of substituted urea. Pure 1,3-dibutylurea was recovered from the reaction mixture by extraction with $CHCl_3$, as confirmed by the ^{13}C NMR spectrum in $CDCl_3$ (Fig. 3D). To evaluate the relative percentage of the unreacted carbamate and of the substituted urea at the end of the dehydration experiments on the basis of ^{13}C NMR analysis, we carefully integrated the quaternary carbon resonances falling in the range 163.30–164.28 ppm ($R—CO_2^-$) and 158.66–159.54 ppm ($R_2C{=}O$). The percentage of carbamate conversion into the corresponding substituted ureas decreases in the order NBA > NOA ≈ IBA. (Table 4). Noticeably, the selectivity of the conversion reaction was 100% as no by-product could be detected



Scheme 1. Scheme of the amine carbamate dehydration into the corresponding 1,3-disubstituted urea.

Table 4
Average yields of the amine carbamate conversion into the corresponding 1,3-disubstituted urea.

Carbamate of amine	Dehydration reaction			Catalysed dehydration reaction			
	t (h)	*P* (bar)	Urea (%)	*t* (h)	*P* (bar)	Urea (%) CuCl	Urea (%) $CuCl_2$ hydr
NBA	16	34	39	5	40		42
IBA	15	42	30	5	40	37	
NOA	16	36	31	5	42	44	

from the ^{13}C NMR spectra, besides 1,3-disubstituted ureas and unreacted carbamates. Pure 1,3-disubstituted ureas, as checked by ^{13}C NMR analysis in $CDCl_3$, were recovered from the dehydration mixtures by extraction with $CHCl_3$ and solvent evaporation.

The dehydration of the TBA and CHA carbamates gave products not sufficiently soluble in the common deuterated solvents to be identified by the ^{13}C NMR analysis. Presumably, the steric hindrance at the amino functionality of TBA disfavours the stability of both carbamate and substituted urea and a different reaction could have occurred. No corresponding 1,3-disubstituted urea was recovered from the piperazine carbamate that remained substantially unchanged after 16 h heating at 423 K. The reaction of two molecules of the neutral carbamic acid of piperazine should entail a much greater activation energy than the reaction between one carbamate and one protonated amine depicted in Scheme 1. Presumably, a higher temperature and/or heating time should be necessary to increase the rate of conversion of carbamic acid of piperazine.

In our previous study we reported that the thermal conversion of pure ammonium carbamate into urea at relatively low pressure (14 bar at most) was improved by copper(II) catalysts [28]. Therefore, we exploited the feasibility of the thermal conversion of the NBA, NOA and IBA carbamates in the presence of CuCl or $CuCl_2 \cdot 2H_2O$ catalysts. The catalyst (1% on molar scale) substantially decreased the heating time from 15–16 h to 4–5 h, yet attaining a significant increase of the conversion yield (Table 4). Each 1,3-disubstituted urea can be easily separated from the catalysed reaction mixture by extraction with a common organic solvent whereas the mixture of unreacted carbamate and the catalysts, after water evaporation and the addition of new carbamate, is ready to be recycled.

4. Conclusions

We have devised a non-conventional concept of CO_2 capture that combines the absorption efficiency of either ammonia or amines with the production of valuable commodity chemicals such as urea and 1,3-disubtituded ureas. The main goal of the experimental work here reported was to provide a technique that should have the potential of circumventing the main disadvantages of traditional CO_2 absorption processes based on either aqueous amines or ammonia. The high-energy consumption of amine regeneration and the costs associated to avoid the ammonia loss and its separation from CO_2 in the regeneration step, make these traditional scrubbing processes highly questionable. Here we have reported the efficient absorption of CO_2 by some non-aqueous amines and confirmed the efficiency of water–ethanol ammonia in terms of CO_2 loading capacity and removal efficiency [28]. These experiments were addressed to recover the captured CO_2 as solid mixtures of either ammonium carbamate and bicarbonate or carbamates of the protonated amines. By heating the solid ammonium carbonate and bicarbonate mixtures or the amine carbamates in a closed reactor, we obtained their conversion into urea and, respectively, 1,3-disubstituted ureas with reasonable yields (30–50%). This procedure could offer potential advantages in terms of energy saving in urea manufacture as it avoids the energy penalty of the high pressure (150–250 bar) and temperature (450–500 K) reactions, and of CO_2 purification by amine scrubbing affecting the conventional processes of urea production. The thermal conversion of amine carbamates into 1,3-disubstituted ureas is a milder and greener route to the synthesis of these valuable intermediates as it avoids the use of unsafe chemicals or expensive catalysts of the conventional syntheses. Quite interestingly, the use of inexpensive copper catalysts increased the rate of the thermal dehydration of the amine carbamates. Pure 1,3-disubstituted ureas can be easily separated from the unreacted carbamates which can be entirely recycled.

As a final consideration, we are well aware that a complete life cycle assessment and pilot plant experiments should be necessary to verify whether the techniques here described can be successfully scale up to commercial plants. Finally, the experimental study we carried out confirmed the feasibility of ^{13}C NMR analysis to identify and quantify the carbonated species in solution.

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